

Recent Progress of Remediating Heavy Metal Contaminated Soil Using Layered Double Hydroxides as Super-Stable Mineralizer

Tong Lin^{a§}, Haoran Wang^{a§}, Tianyang Shen^a, Zhuoqun Deng^a, Ruifa Chai^a, Xinyuan Sun^a, Dongyuan Cui^a, Sai An^{*ab}, Wei Chen^{*ab}, and Yu-Fei Song^{*ab}

Abstract: Heavy metal contamination in soil, which is harmful to both ecosystem and mankind, has attracted worldwide attention from the academic and industrial communities. However, the most-widely used remediation technologies such as electrochemistry, elution, and phytoremediation, suffer from either secondary pollution, long cycle time or high cost. In contrast, *in situ* mineralization technology shows great potential due to its universality, durability and economical efficiency. As such, the development of mineralizers with both high efficiency and low-cost is the core of *in situ* mineralization. In 2021, the concept of ‘Super-Stable Mineralization’ was proposed for the first time by Kong *et al.*^[1] The layered double hydroxides (denoted as LDHs), with the unique host–guest intercalated structure and multiple interactions between the host laminate and the guest anions, are considered as an ideal class of materials for super-stable mineralization. In this review, we systematically summarize the application of LDHs in the treatment of heavy metal contaminated soil from the view of: 1) the structure–activity relationship of LDHs in *in situ* mineralization, 2) the advantages of LDHs in mineralizing heavy metals, 3) the scale-up preparation of LDHs-based mineralizers and 4) the practical application of LDHs in treating contaminated soil. At last, we highlight the challenges and opportunities for the rational design of LDH-based mineralizer in the future.

Keywords: Heavy metals · Large-scale preparation · LDHs · Soil remediation · Super-stable mineralization

1. Introduction

Soil security, the bottom line of food security, plays a critical role in maintaining ecosystem health and sustainability.^[2] However, most soil is facing severe contamination and degradation due to anthropogenic activities. In 2018, Pérez *et al.* expressed their concern about the 2.8 million sites of soil in EU which were potentially contaminated.^[3] According to the reports of the US Natural Resources Conservation Service, toxic pollutants (heavy metals, microplastics, pesticides, and antibiotic resistance genes, *etc.*) are the main cause of soil pollution worldwide.^[4] Among them, the heavy metal ions (such as Cr⁶⁺, Cu²⁺, Cd²⁺, Hg²⁺, Pb²⁺, As⁵⁺) are the major threat due to their toxicity, ubiquity and non-biodegradability. In other words, heavy metals cannot be decomposed by bacteria or natural organisms, and as a result, the total concentration of the metals can persist for a long time in soils.^[5] In China, the total heavy metal pollution of soil is 16.1% over the standard rate, which is mainly consisted of inorganic heavy metal (82.8%), in which the pollution of Cd²⁺ and Hg²⁺ accounts for more than 8% and 6%, respectively.^[6]

Agriculture activities, industrial waste, and mining operations are the main anthropogenic sources of heavy metal pollution in soil (Fig. 1). Meanwhile, *via* the pathway of atmospheric deposition, heavy metals in dusts and aerosols that are released during industrial production will eventually enter the soil, leading to an additional surge of heavy metal contamination in soil.^[8] Moreover, heavy metals absorbed by plants will not only reduce crop production yield, but also can be eventually transferred to the human body.^[9] Although some heavy elements such as Cu, Zn, Fe and Mn are essential micronutrients for plant and animal growth,

excess concentrations of these heavy metals are harmful to human beings.^[10] Moreover, Cd²⁺, Hg²⁺ and As³⁺ ions are toxic to organisms.^[11] Pb²⁺ can accumulate in the human body and damage the nervous system.^[12] Ingesting water/food contaminated with Cd²⁺ can damage irreversibly the cardiovascular system.^[13] Under such circumstances, various methods including replacement,^[14] passivation,^[1] elution,^[15] electrochemistry^[9] and phytoremediation^[16] have been adopted to remediate different types of heavy metal-contaminated soil. However, the soil replacement and electrochemistry technologies (Fig. 2b) are only feasible for small volumes of heavily polluted shallow soil.^[17] The elution of soil (Fig. 2a) commonly requires large amounts of chelating agents and the resultant secondary pollution is hard to avoid.^[9] The phytoremediation (Fig. 2c) method normally takes long operation times.^[16b,17] Among the existing technologies, *in situ* mineralization (Fig. 2d), which adsorbs or precipitates the heavy metal ions by mineralizers, shows great promise for large-scale applications due to its universality, durability and economical efficiency.^[18]

It is well known that the toxicity of heavy metals polluted soil is mainly caused by the free state of the heavy metals.^[19] Therefore it would be significant to change the occurrence state of heavy metals from the free state to a mineralized state. Thus, development of highly efficient super-stable mineralizers of polluting heavy metals is the key.^[20] The fabrication of a highly efficient and stable mineralizer towards the heavy metal pollution is of great importance.

Layered double hydroxides (LDHs) are a class of anionic clays with a two-dimensional (2D) structure, which are formed by a host laminate and guest anions (Fig. 3). The general formula

*Correspondence: Prof. Y.-F. Song^{ab}, E-mail address: songyf@mail.buct.edu.cn; Dr. S. An, E-Mail: ansai@mail.buct.edu.cn; Dr. W. Chen, E-Mail: chenW@mail.buct.edu.cn

^aState Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China; ^bQuzhou Institute for Innovation in Resource Chemical Engineering, Quzhou, Zhejiang Province, 324000 P. R. China. [§]Authors contributed equally to this work.

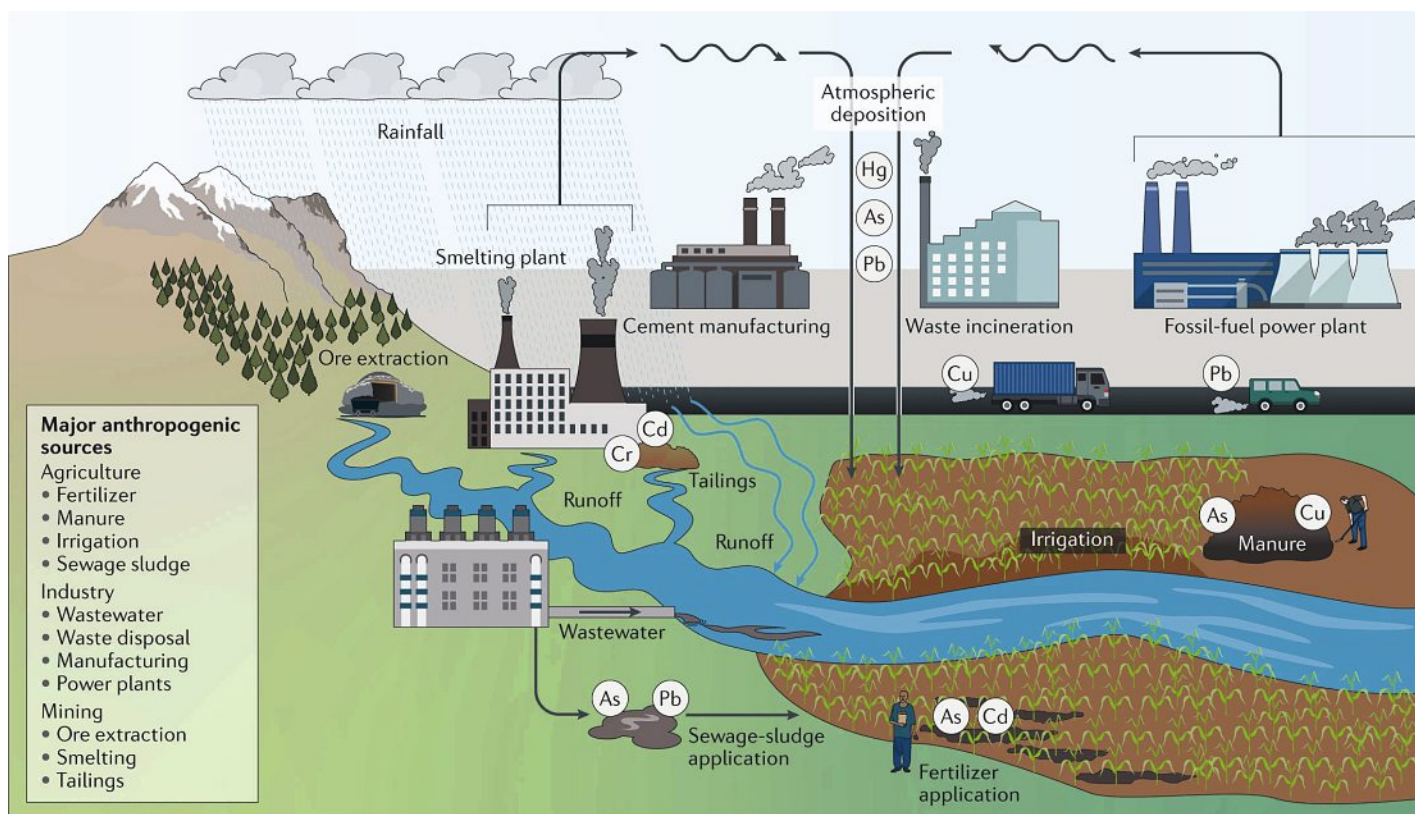


Fig. 1. Sources of heavy metal pollution in agricultural soil.^[7] Reproduced with permission from Springer Nature.

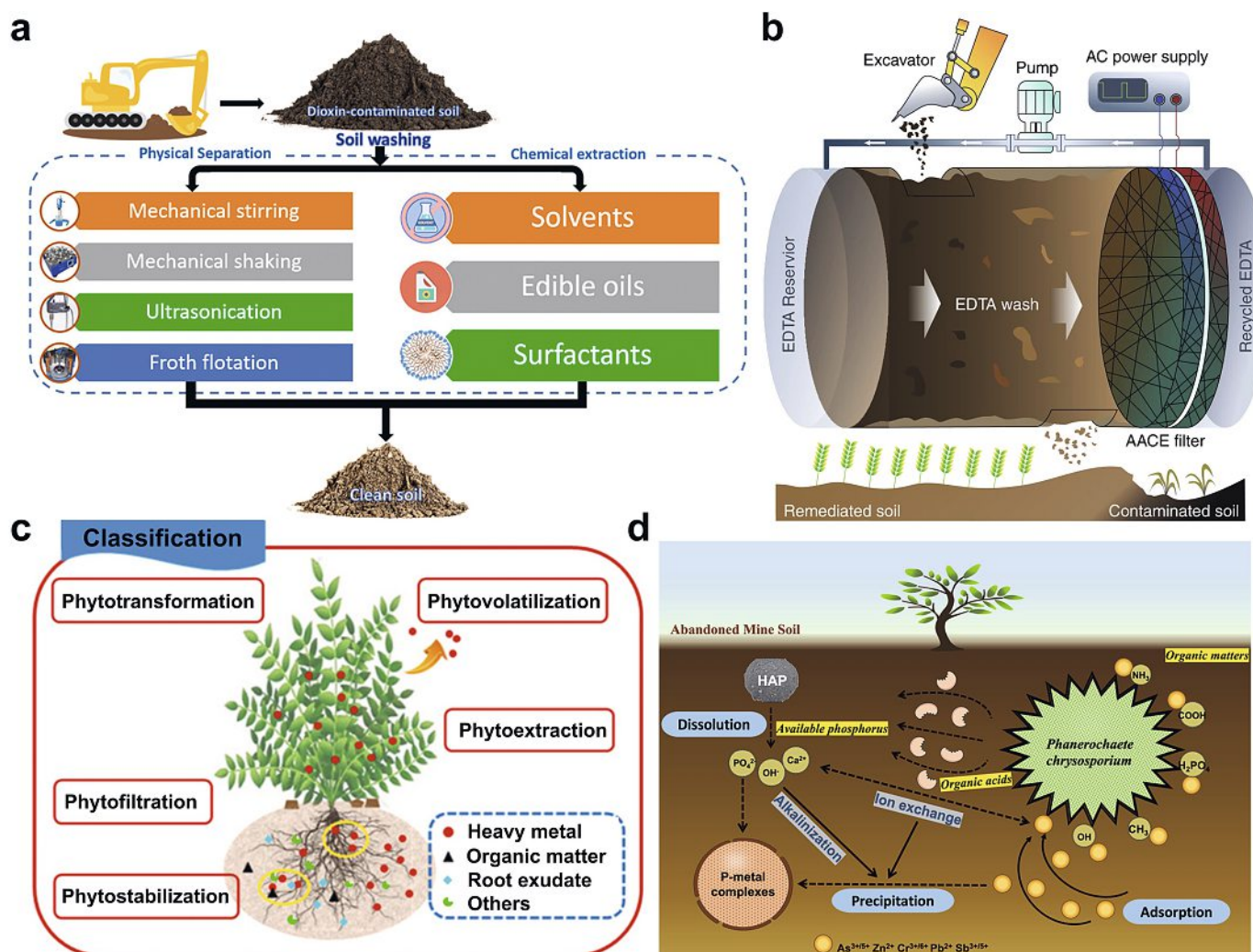


Fig. 2. Different technologies for soil remediation. a) Elution;^[15] b) Electrochemistry;^[9] c) Phytoremediation;^[16a] d) *In situ* mineralization.^[1,48] Figures 2a, c and d reprinted with permission from Elsevier.

of LDHs is $[M^{2+}_x M^{3+}_y (OH)_z](A^{n-})_{x/n} \cdot mH_2O$ (M^{2+}, M^{3+} represents $Zn^{2+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+}$ etc., while A^{n-} corresponds to the interlayer anion, e.g. $CO_3^{2-}, NO_3^-, SO_4^{2-}$ and HPO_4^{2-} etc.). The divalent M^{2+} and trivalent M^{3+} cations (M^{2+} and M^{3+}) are located at the center of each octahedral unit.^[21] Due to the unique layered structure of LDHs, there are multiple interactions between the host laminate and the guest anions of LDHs.^[22] Therefore, over the past decades, LDHs have been widely used for air filtration,^[23] oil–water separation,^[24] infrared invisibility,^[25] seawater desalination,^[26] for example. LDHs have made great progress as a class of adsorbents for a variety of contaminants.

In 1997, the adsorption of CrO_4^{2-} by using LDHs was studied for the first time, in which the CrO_4^{2-} ion can be exchanged into the interlayer of LDHs.^[27] Since then, studies on adsorbing various pollutants by LDHs have been carried out. In 2004 and 2006, Duan *et al.*^[28] found that various anions ($F^-, Cl^-, Br^-, Cr_2O_7^{2-}, S_2O_3^{2-}$) and metal cations ($Ni^{2+}, Pb^{2+}, Co^{2+}, Ce^{3+}$ and Pr^{3+}) can be adsorbed by LDHs. Meanwhile, LDHs were also demonstrated to be capable of adsorbing different kinds of organic compounds such as thiophene, pyrrole, nitrobenzene, and trichlorophenol.^[29] In 2021, Duan *et al.* proposed the concept of ‘Super-Stable Mineralization’ for the first time during application of CaAl-LDHs for Cd^{2+} removal in both wastewater and soil.^[1] Such mineralizer presents a fast adsorption rate and a high removal efficiency (96.9%) towards Cd^{2+} in soil.

In this review, we firstly introduce the sources of heavy metal contamination in soil and the corresponding remediation technol-

ogies. Secondly, we discuss the mineralization mechanism and summarize the advantages of using LDHs as heavy metal mineralizers. And then, we review the scale-up production of LDHs and the application in soil remediation.

2. Structure–Activity Relationship of LDHs in Super-Stable Mineralization

2.1 The Multiple Interactions of LDHs

As shown in Fig. 3a, there are multiple interactions between the host laminate and the guest anions of LDHs, including electrostatic attraction, hydrogen bonding, covalent bonding and intermolecular forces *etc.*^[22] Compared with $Mg(OH)_2$, the MgAl-LDHs possess additional Al^{3+} cations, generating a positively charged laminate. To make the charge balance, various anions ($Cl^-, CO_3^{2-}, NO_3^-, SO_4^{2-}$ and HPO_4^{2-} , for example.) can be intercalated between LDHs laminates, resulting in a unique host–guest intercalation structure. As a result, the excessive electrostatic interactions and intermolecular interactions can be formed between the positively charged laminate and negatively charged intercalated anions (Fig. 3b). Meanwhile, compared to the Mg atoms, Al atoms possess a weaker metallicity, leading to a stronger Al–O covalent bond than Mg–O bond. Additionally, the MgAl-LDHs show lower lattice energy than that of the corresponding $Mg(OH)_2$, indicating the superior structural stability of the LDHs. These multiple interactions make the LDHs a suitable material for *in situ* mineralization.

2.2 The Super-Stable Mineralization of LDHs

Given the above-mentioned multiple interactions in the host–guest structure, the LDHs exhibit lower solubility product constants ($K_{sp} = 10^{-30} \sim 10^{-60}$) than the corresponding hydroxides and carbonates ($K_{sp} = 10^{-10}$) as shown in Table 1. Such low K_{sp} enable LDHs to be an ideal super-stable mineralizer towards various heavy metals. In a typical super-stable mineralization process, the Ca^{2+} and Mg^{2+} in LDH laminates can be isomorphically substituted by the heavy metals (e.g. $Cd^{2+}, Cu^{2+}, Ni^{2+}$).^[21] The resultant CdAl-LDH, CuAl-LDH and NiAl-LDH possess a low K_{sp} value ($\sim 10^{-50}$, Table 1), making the heavy metals hard to dissolve thus avoiding the secondary pollution.

In 2021, Duan *et al.*^[22] proposed the concept of super-stable mineralization of LDHs towards heavy metals for the first time. The as-prepared CaAl-LDHs can mineralize Cd^{2+} through isomorphic substitution at both laboratory scale and practical soil remediation. Such CaAl-LDHs exhibited high removal capacity of 592 mg/g to Cd^{2+} , and the mineralization products showed long-term

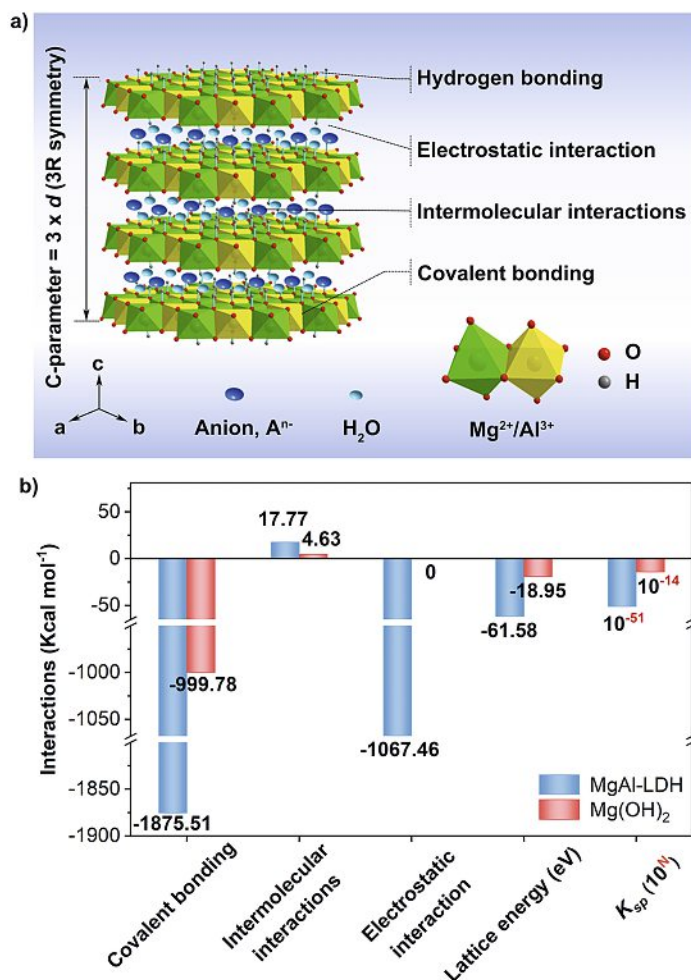


Fig. 3. a) The multiple interactions in MgAl-LDHs.^[21] b) The calculated values of the covalent bonding interaction, intermolecular interactions, electrostatic interaction, and lattice energy for MgAl-LDH and $Mg(OH)_2$, respectively.^[22]

Table 1. K_{sp} of various precipitation substances.^[1,22]

Existing form	K_{sp} (10 ^{*N})	Existing form	K_{sp} (10 ^{*N})
$NiCO_3$	-8.18	$CdCO_3$	-11.28
$Ni(OH)_2$	-14.04	$Cd(OH)_2$	-13.6
$Fe_2Al(OH)_6Cl$	-62.75	$Zn_2Al(OH)_6(CO_3)_{0.5}$	-56.84
$Fe_2(Al(OH)_6(CO_3)_{0.5})$	-62.05	$Cd_2Al(OH)_6Cl$	-53.86
$Cu_2Al(OH)_6Cl$	-60.11	$Cd_2Al(OH)_6(CO_3)_{0.5}$	-53.14
$Cu_2(Al(OH)_6(CO_3)_{0.5})$	-59.35	$Mg_2Al(OH)_6NO_3$	-51.43
$Co_2Al(OH)_6Cl$	-57.69	$Ca_2Al(OH)_6F$	-48.26
$Ni_2Al(OH)_6Cl$	-57.52	$Ca_2Al(OH)_6Cl$	-47.55
$Zn_2Al(OH)_6Cl$	-57.48	$Li_2Al_2(OH)_6Cl$	-47.37
$Mg_2(Al(OH)_6(CO_3)_{0.5})$	-57.11	$Ca_2Al(OH)_6(CO_3)_{0.5}$	-47.25
$Mg_2Al(OH)_6Cl$	-57.04	$Li_2Al_2(OH)_6(CO_3)_{0.5}$	-46.60
$Co_2(Al(OH)_6(CO_3)_{0.5})$	-57.03	$Ca_2Al(OH)_6NO_3$	-45.30

stability in soil for more than five years. DFT calculations (Fig. 4) clearly revealed the isomorphous substitution process of Cd^{2+} by CaAl-LDHs as follows: $\text{Ca}_{12}\text{Al}_6(\text{OH})_{36}(\text{CO}_3)_3 + 12\text{Cd}^{2+}(\text{aq}) \rightarrow \text{Ca}_{11}\text{CdAl}_6(\text{OH})_{36}(\text{CO}_3)_3 + 11\text{Cd}^{2+}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) \rightarrow \dots \rightarrow \text{Cd}_{12}\text{Al}_6(\text{OH})_{36}(\text{CO}_3)_3 + 12\text{Ca}^{2+}(\text{aq})$. In addition, each step of the isomorphous substitution process was energetically favorable with $\Delta G < 0$, confirming that the process was spontaneous from a thermodynamic point of view.

Since the concept of super-stable mineralization was proposed in 2021, systematic investigations of LDHs on the super-stable mineralization of heavy metals have been carried out.^[30] To understand the effect of guest anions in LDHs on mineralization mechanism, Song *et al.*^[31] synthesized MgAl-CO_3 and MgAl-NO_3 to investigate the mineralized progress for Cd^{2+} ions in water. The results showed that in a 300 mg/L Cd^{2+} solution, MgAl-NO_3 can reach the high mineralization capacity of 760.5 mg/g, while the mineralization capacity for MgAl-CO_3 was only 127.3 mg/g. In order to better understand the origin of different mineralization capacity between MgAl-CO_3 and MgAl-NO_3 , *quasi in situ* X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) characterizations were performed. For MgAl-NO_3 , Cd^{2+} can be mineralized in the LDH laminates by isomorphous substitution, while for MgAl-CO_3 , Cd^{2+} was immobilized as CdCO_3 by precipitation. Meanwhile, DFT calculation results proved that the isomorphous substitution of MgAl-NO_3 to the corresponding CdAl-

LDHs was spontaneous. Such results showed that the different types of the interlayer anions can have a profound effect on the mineralization mechanism of heavy metals (Fig. 5). This discovery provided a more thorough and microscopic-level understanding of the adsorption mechanism of heavy metals by LDHs.

Moreover, in terms of environmental protection and resource utilization perspectives, the recycling of mineralization products was essential. As shown in Fig. 6, Song *et al.*^[32] used CaFe-LDHs as stabilizers to mineralize Ni^{2+} , which exhibited a high removal capacity of 321 mg g^{-1} within 5 mins in water. The isomorphous substitution process was carefully investigated by XAFS, and it was found that the Ni-O and Ni-M shell (Fig. 6b and c) gradually increased with increasing mineralization time, indicating that Ni^{2+} can be mineralized into the laminates of LDHs through the isomorphous substitution process. Furthermore, the mineralization products NiCaFe-LDHs and NiFe-LDHs can be applied as efficient catalysts in both the photocatalytic CO_2 reduction reaction (CO_2PR) and the oxygen evolution reaction (OER), respectively. For the OER, the NiCaFe-LDHs possessed a lower overpotential (248 mV) than that of RuO_2 (287 mV) at 10 mA cm^{-1} (Fig. 6d). When applied for CO_2PR , the NiCaFe-LDHs showed a selectivity of 31.7% for CH_4 and 40.5% for CO under visible light irradiation (Fig. 6e).

In addition to the isomorphous substitution, the mineralization of heavy metals by LDHs can be summarized as surface adsorp-

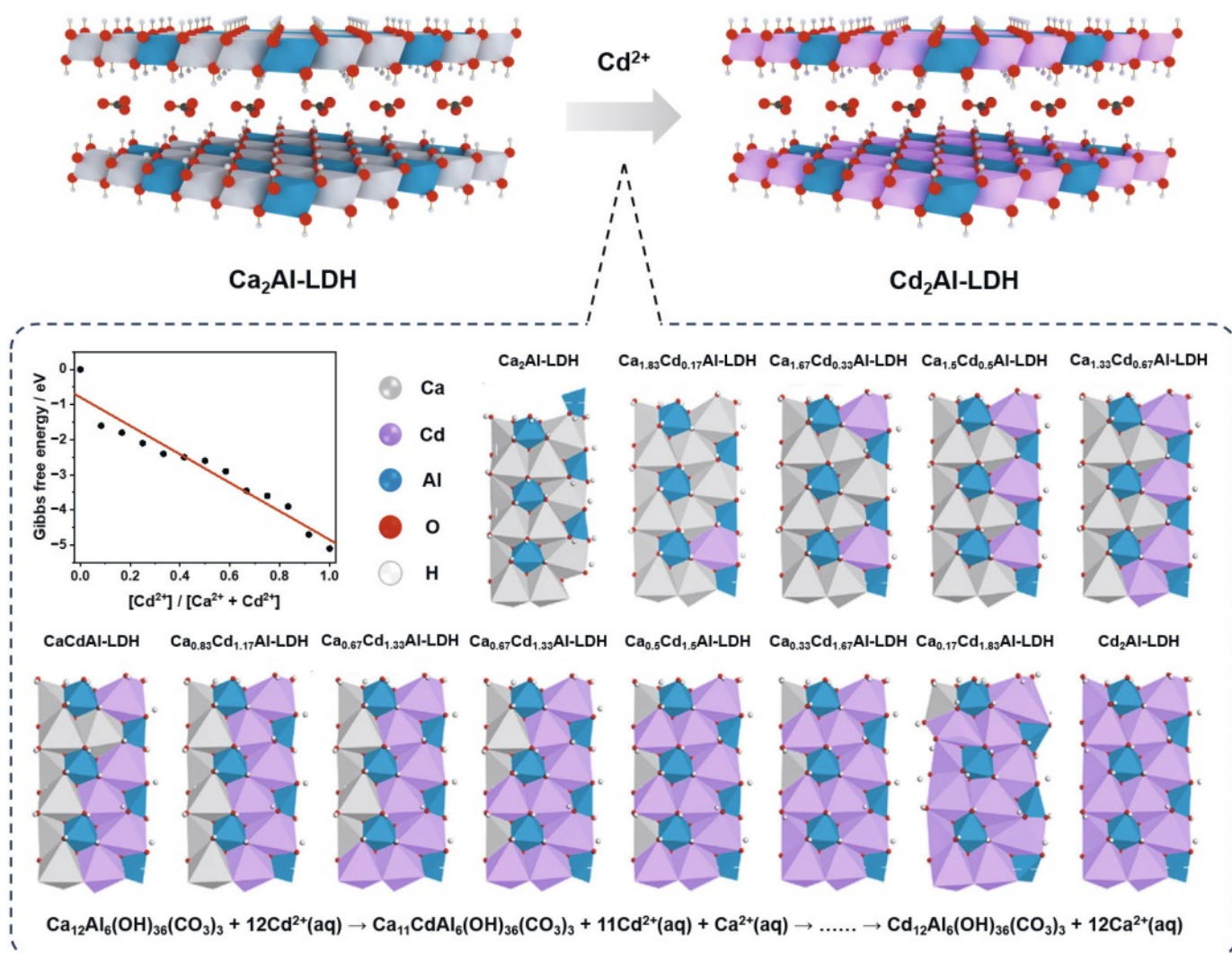


Fig. 4. The relationship between the Gibbs free energy and Cd content during the isomorphous substitution of Ca^{2+} by Cd^{2+} in CaAl-LDH as well as the optimized geometries of $\text{Ca}_2\text{Al-LDH}$, $\text{Cd}_2\text{Al-LDH}$, and corresponding reaction intermediates.^[22] Reprinted with permission from Elsevier.

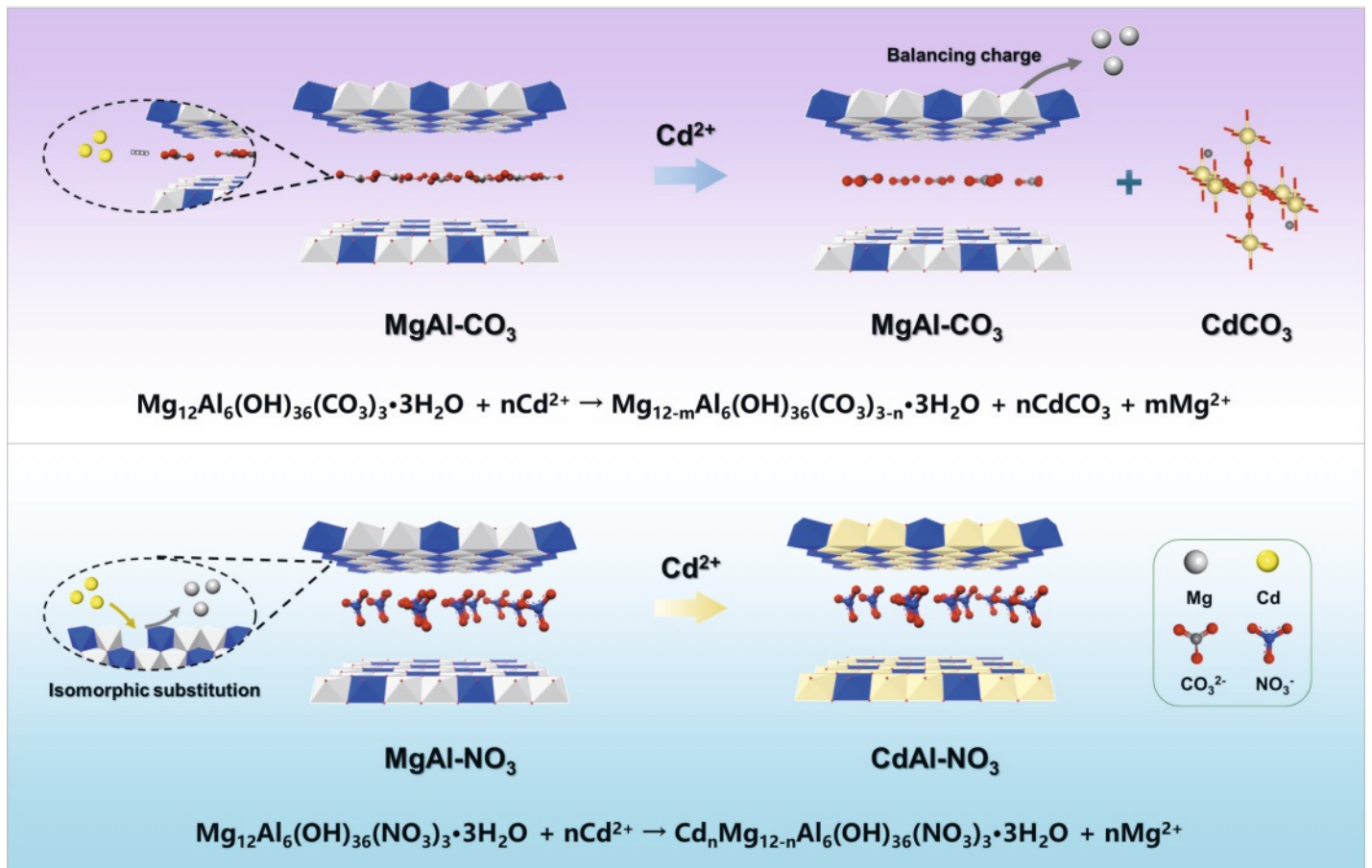


Fig. 5. Schematic diagrams of different adsorption mechanism of Cd²⁺ by MgAl-CO₃ and MgAl-NO₃ in water, respectively.^[31]

tion,^[33] anion exchange^[34] and coordination.^[35] There are three pathways for heavy metal removal using LDHs as adsorbents: Firstly, heavy metals can be chelated by the LDHs laminates^[30b,36] or interlayers.^[37] Secondly, the heavy metals with suitable ionic radius can be mineralized by the isomorphic substitution, and then entered into LDHs laminate.^[30b,32] Thirdly, removal of heavy metals can be achieved by anion exchange in the interlayers of LDHs.^[34a,38]

2.3 Seven Advantages of Using LDHs as Super-Stable Mineralizer

As shown in Fig. 7, the use of LDH for super-stable mineralization to remediate heavy metal contaminated soils has the following seven advantages: 1) high removal capacity, 2) fast mineralization rate, 3) excellent stability, 4) targeted fertilization effect, 5) good acid resistance, 6) high selectivity (menu-style customization) and 7) low cost.

The 1st advantage is high removal capacity. Kong *et al.*^[11] reported that CaAl-LDH was an effective stabilizer for *in situ* mineralization of Cd²⁺, and CaAl-LDH can remove Cd²⁺ with a adsorption capacity of 592 mg/g and a removal efficiency of 96.9%, which was far more than the adsorption capacity of Ca(OH)₂ and hydroxyapatite (Fig. 8a). Song *et al.*^[32] synthesized CaFe-LDHs to recover Ni²⁺ from high concentration Ni-containing electroplating solution, which exhibited a maximum saturated removal capacity of 321 mg/g. Lei *et al.*^[39] prepared CaAl-LDH with excellent performance which exhibited the high removal capacity of 502.4, 315.2 and 600.0 mg/g, for Cu, Zn and Pb, respectively. When applied for soil remediation, the immobilization efficiency of available Cu, Zn and Pb can reach 84.62% and 98.66% and 70.27% respectively. The above results indicated that super-stable mineralization based on LDHs

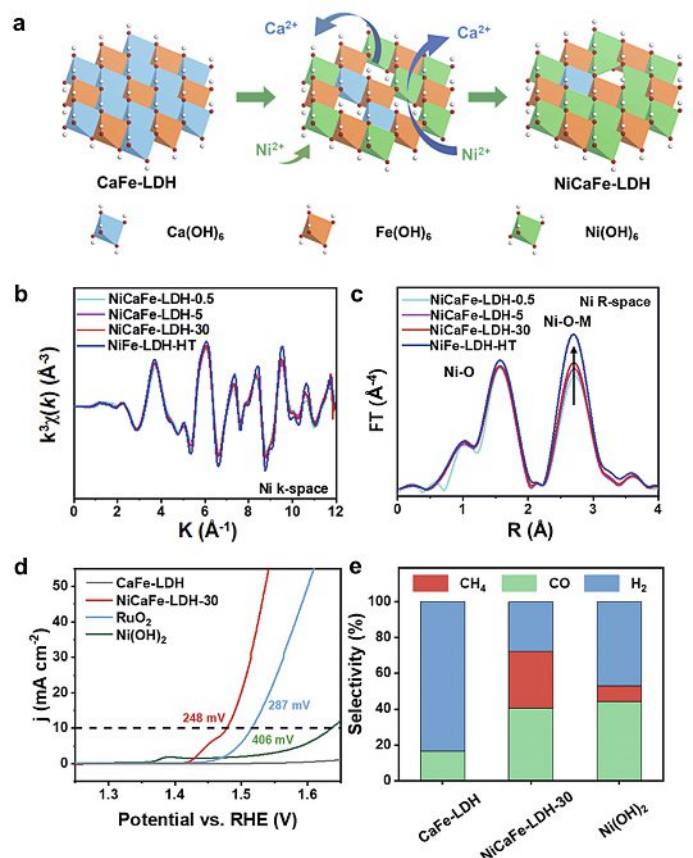


Fig. 6. a) Schematic diagram of adsorption mechanism of Ni²⁺ by CaFe-LDHs; b,c) k-space EXAFS oscillation functions k₃χ of Ni and magnitude of k₄-weighted FT of R-space EXAFS spectra of the Ni; d,e) Resource utilization of mineralized products, OER and CO₂PR, respectively.^[32]



Fig. 7. The seven advantages of super-stable mineralization by using LDHs.

showed an high removal capacity for various kinds of heavy metals.

The 2nd advantage is fast mineralization rate. Kong *et al.*^[11] demonstrated that CaAl-LDH was an efficient stabilizer for removing Cd²⁺, which can adsorb Cd²⁺ ($C_0 = 15, 30$ and 60 mg/L, respectively) with a high removal efficiency exceeding 99%. When applied for agricultural soil, LDHs can mineralize more than 97% of Cd²⁺ in only 7 days (Fig. 8b). The CaFe-LDHs exhibited a removal efficiency of 97% of Ni²⁺ in 5 min.^[32] Moreover, the monolayer MgAl-LDH (denoted as m-MgAl-LDH),^[30b] showed a fast mineralization rate of Cu²⁺, and the Cu²⁺ concentration can be reduced from 100 ppm to 0.016 ppm with a removal efficiency of 99.98% in only 1 min.

The 3rd advantage is good acid resistance. Since there were abundant -OH groups on the laminate of LDHs, it can effectively resist acidic environments. For example, the mineralization product of CdAl-LDH can remain stable in a solution of pH = 5, whereas the Cd(OH)₂ can be completely dissolved under such conditions (Fig. 8c).^[11] The mineralization product of CaFe-LDH can remove 99% of Ni²⁺ when the pH of the solution was 4.^[32] Zhao *et al.* reported that in the range of pH = 3–6, the change of acidity had a negligible effect on the ability of MgFe-LDH to adsorb Cu²⁺.^[40] When pH = 4.5–6 (the typical pH range of soil in south of China), the adsorption products CuFe-LDH was very stable, and the leaching rate of Cu²⁺ was much lower than that of other adsorption materials. Zhao *et al.* reported that the MgFe-mixed metal oxides (MgFe-MMO) through calcination of MgFe-Cl showed a strong removal ability of Pb²⁺ in the range of pH = 3–5 solution.^[12]

The 4th advantage is excellent stability. Since the K_{sp} of mineralized products from conventional mineralizers were not low enough, there was risk of secondary pollution such as from Ca(OH)₂. Therefore, in the practical remediation process, it was necessary to use a large amount or multiple applications of mineralizers to ensure that the treated soil can meet with the national standards. The concept of ‘Super-stable mineralization’ was first proposed by Kong *et al.*^[11] in 2021, in which LDHs showed high adsorption capacity for Cd²⁺ in both wastewater and soil. Most importantly, the scientific explanation for such super-stable mineralization was based on the very low K_{sp} of LDHs when compared with the corresponding carbonate (CdCO₃) or the hydroxides (Cd(OH)₂). From 2016, they treated 10 ha. of Cd²⁺ polluted soil in Jiangsu Province. At the end of 2016, the average Cd²⁺ concentration in wheat grains dropped to 0.08 mg/kg, which was lower than the national standard for agricultural soil (0.1 mg/kg

GB 2762-2017). In 2018, a further check showed that the extractable (active state) Cd²⁺ concentration in the soil had declined to 0.007 mg/kg. In 2022, the Cd²⁺ concentration was still below the national standard limit. These results indicated that the Cd²⁺ ions were *in situ* mineralized through the formation of super-stable mineralization structure in agricultural soil and the long-term stability of LDHs. By combining the advantages of the super-stable mineralization of LDH and the porous structure of attapulgite, the remediation demonstration was implemented successfully in the heavy metal contaminated soil of Dongdagou, Gansu Province in 2019. After 3 years of remediation, the contents of Pb²⁺ and Cd²⁺ were reduced by 73.9% and 75%, respectively (Fig. 8d).^[20a]

The 5th advantage is selectivity (menu-style-customization). According to previous studies, LDHs showed a high selectivity for heavy metal removal, and LDHs with different compositions and structures can be suitable for removal of different types of heavy metals. For example, CaAl-LDH, MgAl-LDH, CaFe-LDH and MgFe-LDH showed the removal capacity of 382, 67, 233 and 83 mg/g for Ni²⁺, among which the CaAl-LDH was the best adsorbent (Fig. 8e).^[32] Zhao *et al.*^[12] reported that the removal capacities of MgAl-LDH, MgFe-LDH, CaAl-LDH and CaFe-LDH for Pb²⁺ can be 1667.5, 1439.5, 917.75 and 785 mg/g, respectively. Wang *et al.*^[35a] synthesized a three-dimensional sulfide intercalation NiFe-LDH (NFL-S) for the selective removal of heavy metals. The embedding of sulfide groups in LDH nanosheets makes NFL-S a selective heavy metal ion filter, and the selective sequence of NFL-S for heavy metals was Pb²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺ > Mn²⁺.

The 6th advantage is low cost. It is well known that Ca(OH)₂ is a commonly used adsorbent for large-scale soil/wastewater treatment. Despite their low price, the final mineralized products tend to form the corresponding hydroxides, which can cause the secondary pollution in a few months. In contrast, LDHs are considered economical, long-lasting, and stable soil remediation materials in the long run (more than 3 years). LDHs offer the advantages of low production cost, large mineralization capacity and long-term stability, which make them cost-effective for practical use. According to our data based on one-time restoration and five-year continuous efficacy, the cost of restoring one mu (1 mu = 666.67 m²) of heavy metal contaminated soil was about 200 yuan per year (Fig. 8f). If the LDHs continued to be effective for longer times, the actual cost can be further reduced.

The 7th advantage is targeted fertilization effect. LDHs can be used as fertilizers to promote plant growth when it is added to soil for super-stable mineralization. When the free Cd²⁺ ions were mineralized into the MgAl-LDH and/or CaAl-LDH lattice to form CdAl-LDHs by isomorphous substitution, the Mg²⁺ and Ca²⁺ ions in the original LDHs were released from the LDH laminate and entered the soil. Soil is often deficient in Mg²⁺ and Ca²⁺ ions, particularly in the south of China. As such, the use of LDH as super-stable mineralization materials can act as fertilizer to promote the growth of crop roots (Fig. 8g).^[40] Previous work showed that slow-release fertilizers by using MgAl-LDHs and sodium alginate (SA) can provide better nutrient management for crop growth.^[41]

3. Industrial Production of LDHs and their Application in Soil Remediation

At present, the large-scale production of LDHs is done in industry. Among numerous methods used to fabricate LDHs, the most practical method for industrial production is ‘Separate Nucleation and Aging Steps’,^[42] which was proposed by Duan *et al.* in 2002. Typically, such technology can avoid the problem of uneven particle sizes of LDHs caused by the long-time mixing. This method was successfully applied to pilot lines in Shandong Province for the industrial-scale synthesis of LDHs materials with production capacity of 3000 ton/a. The production technology can synthesize a wide range of high-quality LDHs using large-capacity hydrothermal kettles in proportionally scaled-up raw

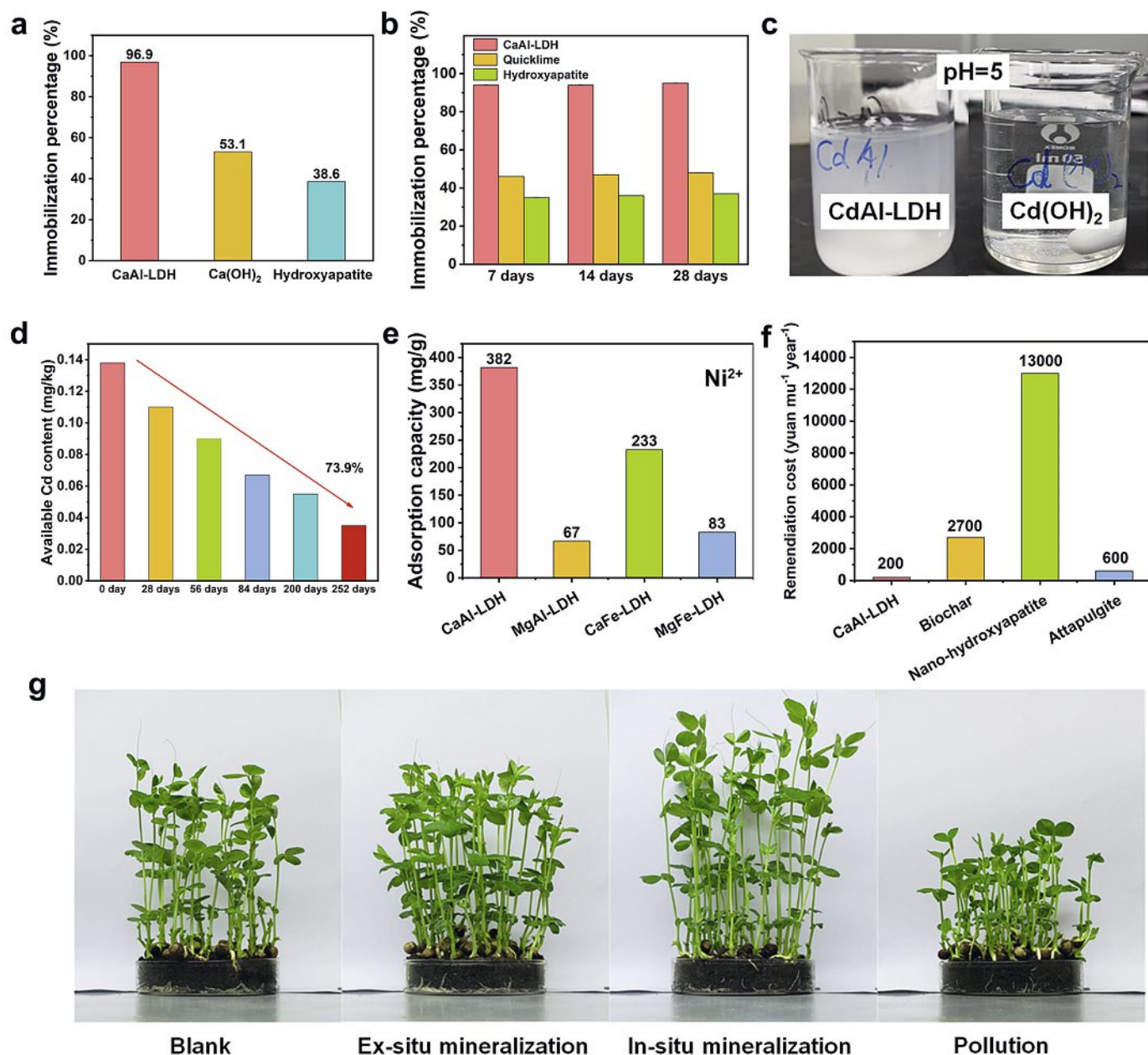


Fig. 8. a) The immobilization of Cd^{2+} ions in soil after remediation by CaAl-LDH, quicklime and hydroxyapatite, respectively. b) The immobilization of Cd^{2+} ions in soil after remediation by CaAl-LDH, quicklime and hydroxyapatite in different days.^[11] c) Comparison of CdAl-LDH and $\text{Cd}(\text{OH})_2$ in pH = 5 solution. d) Changes of available Cd content in soils contaminated by heavy metals after remediation in Dongdagou, Baiyin.^[20a] e) Comparison of adsorption capacity of MgAl-LDH, MgFe-LDH, CaAl-LDH, and CaFe-LDH for Ni^{2+} .^[32] f) Comparison of soil remediation costs of CaAl-LDH, biochar, Nano-hydroxyapatite and attapulgite. g) Photographs of plants in soil remediation experiments.^[40]

material input. Based on the method of Separate Nucleation and Aging Steps, Roy and partners^[19] prepared MgAl-LDHs from the method of using MgO and Al_2O_3 as raw materials instead of nitrates, which can achieve the atomic economy of 100%. In 2019, a LDH production line in Jiangsu Province, was rebuilt with an annual output of 10,000 tons, and the product obtained the Soil Conditioner Registration Certificate of the Ministry of Agriculture and Rural Affairs of China. In 2022, using the abundant Mg and Ca resources in Qinghai Salt Lake as raw materials, a super-stable mineralized material production line with a yield of 20,000 tons/a was built in Delingha, Qinghai Province.^[43]

The large-scale production of LDHs was demonstrated to be efficient in treating the heavy metals contaminated soil.^[1,44] In Dongdagou, Gansu Province, Lei *et al.*^[45] reported that CaAl-LDH can significantly reduce the contents of Cu, Zn, Cd and Pb in large-scale agriculture soil remediation with the immobilization efficiency of 30.15%, 67.30%, 57.80% and 38.71%, respec-

tively. Meanwhile, the Cd contamination of agricultural soils in Kunshan, Jiangsu Province became a serious threat to rice and wheat (crops) safety. Therefore, in 2016, CaAl-LDHs were applied to the contaminated soil, and the Cd concentration was monitored for extended periods of time. Till the end of 2022, the Cd concentration of the rice (from 0.33 to 0.15 mg/kg) and that of wheat (from 0.22 to 0.06 mg/kg) produced in this area were much lower than the national limit of China (GB2762-2017, 0.2 mg/kg for rice and 0.1 mg/kg for wheat, respectively) (Fig. 9b). At the same time, owing to the composite soil contamination of Pb and Cd in Nujiang, Yunnan Province, Ca/Mg-based LDHs were used to treat the co-existing heavy metal contamination. The content of both Cd and Pb in the produced crops were reduced to 0.007 mg/kg and 0.04 mg/kg, respectively, showing the remarkable mineralization results. In 2020, in cooperation with Hunan Agricultural University, 20 mu of demonstration fields were restored in Liuyang and Hengyang Experimental Bases in Hunan

Province.^[46] Such practice in Hunan Province showed a remarkable decline of Cd²⁺ content after treating the rice field with LDHs. (Decline percent = 79.7%, before remediation, Cd content = 0.546 mg/kg; after remediation, Cd content = 0.111 mg/kg).

In 2021, a large scale restoration work was carried out in Heshan National Grain Base in Hunan Province, and the Pb content in the early rice produced in the restored area declined to just 0.006 mg/kg, whereas the As content in rice also decreased significantly to 0.02 mg/kg. Since 2021, the Cd restoration practice of LDHs-based super-stable mineralized materials was carried out in Shimen Village, Hainan Province. Soil remediation results showed that the Cd content in the remediated area was reduced to 0.2 mg/kg (before remediation, Cd = 0.6–1.0 mg/kg).^[47] In summary, the above practical results illustrate that LDHs exhibit a super-stable mineralization effect on the removal of Cd, Pb and As, which can be considered as a potential remediation mineralizer for various heavy metals contaminated soil.^[1]

4. Conclusion and Outlook

To summarize, we reported the origin of multiple interactions in the host–guest structure of LDHs, and discussed structure–activity relationships of LDHs in the super-stable mineralization of heavy metals, in which the low K_{sp} value of LDHs played an essential role for the formation of SSMS. Based on this, we highlighted the seven advantages of using LDHs-based super-stable mineralization materials. Moreover, industrial scale-up production line of LDHs-based super-stable mineralization materials were achieved in Shandong Province (3000 t/a), Jiangsu Province (10000 t/a) and Qinghai Province (20000 t/a). So far 10,000 mu heavy metal-contaminated soil have been remediated successfully by using super-stable mineralization materials of LDHs. Although great progress has been made, there still exist several challenges:

1) How to further improve the acid resistance of LDHs-based mineralizer. The addition of hydroxides to increase the pH of soil is very necessary and further application of super-stable mineralization materials of LDHs can be effective.

2) How to mineralize multiple heavy metals at the same time. Multiple heavy metals often coexist in the actual contaminated

soil. Therefore, it is important to develop super-stable mineralized materials that can mineralize multiple heavy metals synchronously.

This review opens a new pathway for remediation of heavy metal-contaminated soil and may provide certain useful guidance for rational design of advanced functional materials for *in situ* mineralization of heavy metals.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (22178019, 22208013, 22288102) and the Fundamental Research Funds for the Central Universities (XK1802-6, XK1803-05, XK1902).

Received: September 15, 2023

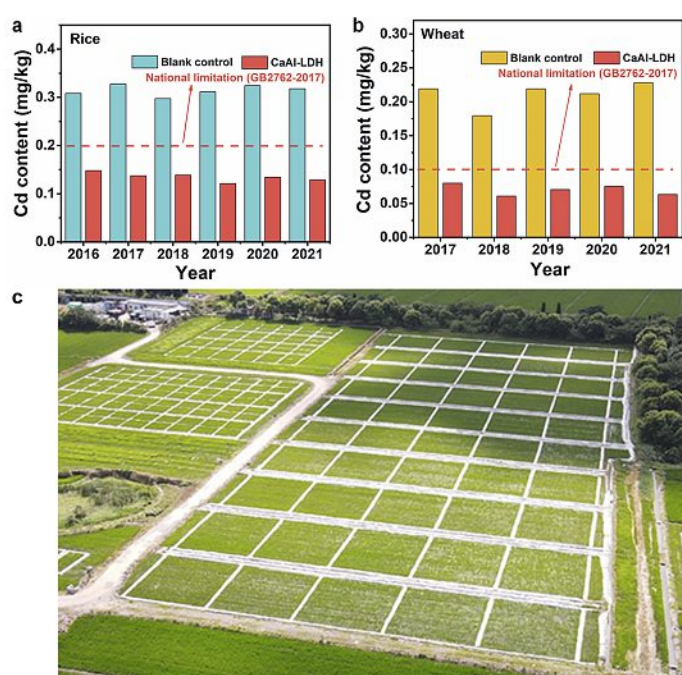


Fig. 9. After 6 years of LDHs remediation of Cd-contaminated fields, the remaining Cd content in crops, a) rice, and b) wheat, respectively, c) photograph of paddy fields after remediation with LDHs in Kunshan, Jiangsu Province.

- [1] X. Kong, R. Ge, T. Liu, S. Xu, P. Hao, X. Zhao, Z. Li, X. Lei, H. Duan, *Chem. Eng. J.* **2021**, *407*, 127178, <https://doi.org/10.1016/j.cej.2020.127178>.
- [2] Y.-R. Liu, M. G. A. v. d. Heijden, J. Riedo, C. Sanz-Lazaro, D. J. Eldridge, F. Bastida, E. Moreno-Jiménez, X.-Q. Zhou, H.-W. Hu, J.-Z. He, J. L. Moreno, S. Abades, F. Alfaro, A. R. Bamigboye, M. Berdugo, J. L. Blanco-Pastor, A. d. L. Ríos, J. Duran, T. Grebenc, J. G. Illán, T. P. Makhalyane, M. A. Molina-Montenegro, T. U. Nahberger, G. F. Peñaloza-Bojacá, C. Plaza, A. Rey, A. Rodríguez, C. Siebe, A. L. Teixido, N. Casado-Coy, P. Trivedi, C. Torres-Díaz, J. P. Verma, A. Mukherjee, X.-M. Zeng, L. Wang, J. Wang, E. Zaady, X. Zhou, Q. Huang, W. Tan, Y.-G. Zhu, M. C. Rillig, M. Delgado-Baquerizo, *Nat. Commun.* **2023**, *14*, <https://doi.org/10.1038/s41467-023-37428-6>.
- [3] A. P. Pérez, N. R. Eugenio, 'Status of local soil contamination in Europe', **2018**.
- [4] G. B. Muckel, 'Using Soil Survey to Identify Areas With Risks and Hazards to Human Life and Property', **2004**.
- [5] N. Bolan, A. Kunhikrishnan, R. Thangarajan, J. Kumpiene, J. Park, T. Makino, M. B. Kirkham, K. Scheckel, *J. Hazard. Mater.* **2014**, *266*, 141, <https://doi.org/10.1016/j.jhazmat.2013.12.018>.
- [6] Q. Yang, Z. Li, X. Lu, Q. Duan, L. Huang, J. Bi, *Sci. Total. Environ.* **2018**, *642*, 690, <https://doi.org/10.1016/j.scitotenv.2018.06.068>.
- [7] D. Hou, D. O'Connor, A. D. Igalavithana, D. C. W. Tsang, D. L. Sparks, Y. S. Ok, *Nat. Rev. Earth Env.* **2020**, *1*, 366, <https://doi.org/10.1038/s43017-020-0061-y>.
- [8] J. Briffa, E. Sinagra, R. Blundell, *Heliyon* **2020**, e04691, <https://doi.org/10.1016/j.heliyon.2020.e04691>.
- [9] J. Xu, C. Liu, P.-C. Hsu, J. Zhao, T. Wu, J. Tang, K. Liu, Y. Cui, *Nat. Commun.* **2019**, *10*, 2440, <https://doi.org/10.1038/s41467-019-10472-x>.
- [10] S. Cheng, *Environ. Sci. Pollut. R.* **2003**, *10*, 256, <https://doi.org/10.1065/espr2002.11.141.2>.
- [11] D. O'Connor, D. Hou, Y. S. Ok, B. P. Lanphear, *Nat. Sustain.* **2020**, *3*, 77, <https://doi.org/10.11766/trxb201912170575>.
- [12] C. Li, Z. Li, J. Wang, W. Xiong, H. Yan, Y. Bai, D. O'Hare, Y. Zhao, *Chem. Eng. J.* **2023**, *462*, <https://doi.org/10.1016/j.cej.2023.141926>.
- [13] K. Vikrant, V. Kumar, K. Vellingiri, K.-H. Kim, *Nano Res.* **2019**, *12*, 1489, <https://doi.org/10.1007/s12274-019-2309-8>.
- [14] Z. Xu, L. S. d. Muchangos, L. Ito, A. Tokai, *J. Clean. Prod.* **2023**, *397*, <https://doi.org/10.1016/j.jclepro.2023.136503>.
- [15] T. Zhao, K. Zhang, J. Chen, X. Shi, X. Li, Y. Ma, S. Xu, *J. Hazard. Mater.* **2019**, *368*, 459, <https://doi.org/10.1016/j.jhazmat.2019.01.061>.
- [16] a) X. Shen, M. Dai, J. Yang, L. Sun, X. Tan, C. Peng, I. Ali, I. Naz, *Chemosphere* **2022**, *291*, 132979, <https://doi.org/10.1016/j.chemosphere.2021.132979>; b) D. E. Salt, R. D. Smith, I. Raskin, *Annu. Rev. Plant Physiol. Plant Mol. Bio.* **1998**, *49*, 643.
- [17] Y. Gong, D. Zhao, Q. Wang, *Water Res.* **2018**, *147*, 440, <https://doi.org/10.1016/j.watres.2018.10.024>.
- [18] S. Zhao, M. Zhao, X. Fan, Z. Meng, Q. Zhang, F. Lv, *Chem. Eng. J.* **2023**, *454*, 139965, <https://doi.org/10.1016/j.cej.2022.139965>.
- [19] F. Mao, P. Hao, Y. Zhu, X. Kong, X. Duan, *Chin. J. Chem. Eng.* **2022**, *41*, 42, <https://doi.org/10.1016/j.cjche.2021.09.023>.
- [20] a) Z. Sun, Y. Wang, T. Liu, X. Kong, T. Pan, F. Zhang, X. Lei, X. Duan, *J. Hazard. Mater.* **2023**, *447*, 130723, <https://doi.org/10.1016/j.jhazmat.2023.130723>; b) H. Zhao, LiyuDu, Y. Wu, X. Wu, W. Han, *Sci. Total. Environ.* **2021**, *779*, <https://doi.org/10.1016/j.scitotenv.2021.146485>.
- [21] T. He, Q. Li, T. Lin, J. Li, S. Bai, S. An, X. Kong, Y.-F. Song, *Chem. Eng. J.* **2023**, *462*, <https://doi.org/10.1016/j.cej.2023.142041>.
- [22] X.-J. Zhao, S.-M. Xu, P. Yin, J.-Y. Guo, W. Zhang, Y. Jie, H. Yan, *Chem. Eng. J.* **2023**, *451*, 138500, <https://doi.org/10.1016/j.cej.2022.138500>.

- [23] Y. Cheng, L. Li, W. He, W. Chen, G. Deng, Y.-F. Song, *Appl. Catal. B* **2020**, 263, 118312, <https://doi.org/10.1016/j.apcatb.2019.118312>.
- [24] W. He, T. Lin, Z. Song, Y. Cheng, R. Zheng, W. Chen, H. N. Miras, Y.-F. Song, *ACS Appl. Mater. Interfaces* **2023**, 15, 4755, <https://doi.org/10.1021/acsami.2c19015>.
- [25] R. Zheng, Y. Cheng, X. Jiang, T. Lin, W. Chen, G. Deng, H. N. Miras, Y.-F. Song, *ACS Appl. Mater. Interfaces* **2022**, 14, 27214, <https://doi.org/10.1021/acsami.2c05906>.
- [26] R. Zheng, T. Lin, W.-L. Zhao, R. Yin, H. Li, Z. Deng, W. Chen, Y.-F. Song, *Chem. Eng. J.* **2023**, 470, 144103, <https://doi.org/10.1016/j.cej.2023.144103>.
- [27] S. W. Rhee, M. J. Kang, H. Kim, C. H. Moon, *Environ. Technol.* **1997**, 18, 231, <https://doi.org/10.1080/09593331808616532>.
- [28] a) C. Li, G. Wang, D. G. Evans, X. Duan, *J. Solid. State. Chem.* **2004**, 177, 4569, <https://doi.org/10.1016/j.jssc.2004.09.005>; b) L. Lv, J. He, M. Wei, X. Duan, *Ind. Eng. Chem. Res.* **2006**, 45, 8623, <https://doi.org/10.1021/ie050363d>
- [29] Q. Zhao, Z. Chang, X. Lei, X. Sun, *Ind. Eng. Chem. Res.* **2011**, 50, 10253, <https://doi.org/10.1021/ie201021k>.
- [30] a) J. Li, T. Shen, H. Wang, S. Li, J. Wang, G. R. Williams, Y. Zhao, X. Kong, L. Zheng, Y.-F. Song, *ACS Appl. Mater. Interfaces* **2022**, 14, 37823, <https://doi.org/10.1021/acsami.2c10298>; b) T. Lai, J. Wang, W. Xiong, H. Wang, M. Yang, T. Li, X. Kong, X. Zou, Y. Zhao, D. O'Hare, Y.-F. Song, *Chem. Eng. Sci.* **2022**, 257, <https://doi.org/10.1016/j.ces.2022.117704>.
- [31] Q. Li, Z. Wu, S. Bai, Y. Liu, J. Li, Y.-F. Song, *Chem. Eur. J.* **2023**, 29, e202300050, <https://doi.org/10.1002/chem.202300050>.
- [32] H. Chi, J. Wang, H. Wang, S. Li, M. Yang, S. Bai, C. Li, X. Sun, Y. Zhao, Y.-F. Song, *Adv. Funct. Mater.* **2022**, 32, 2106645, <https://doi.org/10.1002/adfm.202106645>.
- [33] a) J. Liu, P. Wu, S. Li, M. Chen, W. Cai, D. Zou, N. Zhu, Z. Dang, *Chemosphere* **2019**, 225, 115, <https://doi.org/10.1016/j.chemosphere.2019.03.009>; b) H. Asiabia, Y. Yaminia, M. Shamsayeia, K. Molaiea, M. Shamsipur, *J. Hazard. Mater.* **2018**, 357, 217, <https://doi.org/10.1016/j.jhazmat.2018.05.055>.
- [34] a) L. Ma, S. M. Islam, C. Xiao, J. Zhao, H. Liu, M. Yuan, G. Sun, H. Li, S. Ma, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, 139, 12745, <https://doi.org/10.1021/jacs.7b07123>; b) T. Liu, M. Zheng, K. Ji, X. Xue, J. Yang, M. Shao, H. Duan, X. Kong, *Mater. Adv.* **2023**, 4, 2494, <https://doi.org/10.1039/D3MA00140G>; c) T. Liu, M. Zheng, P. Hao, K. Ji, M. Shao, H. Duan, X. Kong, *J. Environ. Chem. Eng.* **2023**, 11, 109233, <https://doi.org/10.1016/j.jece.2022.109233>.
- [35] a) J. Wang, L. Zhang, T. Zhang, T. Du, T. Li, T. Yue, Z. Li, J. Wang, *J. Mater. Sci. Technol.* **2019**, 35, 1809, <https://doi.org/10.1016/j.jmst.2019.04.016>; b) L. Ma, Q. Wang, S. M. Islam, Y. Liu, S. Ma, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2016**, 138, 2858, <https://doi.org/10.1021/jacs.6b00110>; c) A. Celik, D. R. Baker, Z. Arslan, X. Zhu, A. Blanton, J. Nie, S. Yang, S. Ma, F. X. Han, S. M. Islam, *Chem. Eng. J.* **2021**, 426, 131696, <https://doi.org/10.1016/j.cej.2021.131696>.
- [36] L. Li, G. Qi, B. Wang, D. Yue, Y. Wang, T. Sato, *J. Hazard. Mater.* **2018**, 343, 19, <https://doi.org/10.1016/j.jhazmat.2017.09.006>.
- [37] a) C. T. Gore, S. Omwoma, W. Chen, Y.-F. Song, *Chem. Eng. J.* **2016**, 284, 794, <https://doi.org/10.1016/j.cej.2015.09.056>; b) S. Zhu, Y. Chen, M. A. Khan, H. Xu, F. Wang, M. Xia, *ACS Appl. Mater. Interfaces* **2022**, 14, 7450, <https://doi.org/10.1021/acsami.1c22035>.
- [38] a) C. Tian, J. Tu, P. Qiu, S. Wang, H. Song, Y. Xu, X. Yan, Z. Lin, L. Chai, *Environ. Sci. Technol.* **2020**, 55, 930, <https://doi.org/10.1021/acs.est.0c03775>; b) N. Chubar, *J. Mater. Chem. A* **2014**, 2, 15995, <https://doi.org/10.1039/c4ta03463e>.
- [39] Z. Sun, J. Ge, C. Li, Y. Wang, F. Zhang, X. Lei, *Chemosphere* **2022**, 300, 134543, <https://doi.org/10.1016/j.chemosphere.2022.134543>.
- [40] J. Wang, X. Kong, M. Yang, W. Xiong, Z. Li, H. Zhou, G. I. N. Waterhouse, S.-M. Xu, H. Yan, Y.-F. Song, H. Duan, Y. Zhao, *Ind. Eng. Chem. Res.* **2022**, 62, 365, <https://doi.org/10.1021/acs.iecr.2c03082>.
- [41] C. T. Vu, T. Wu, *J. Clean. Prod.* **2022**, 379, 134508, <https://doi.org/10.1016/j.jclepro.2022.134508>.
- [42] Y. Zhao, F. Li, R. Zhang, D. G. Evans, X. Duan, *Chem. Mater.* **2002**, 14, 4286, <https://doi.org/10.1021/cm020370h>.
- [43] H. Li, The project of 'Development and demonstration of key technologies for industrialization of super-stable mineralized soil remediation materials with an annual output of 20,000 tons' of Western Magnesium Industry was successfully put into operation, <https://cdm.qinghai.gov.cn/system/2022/04/27/010407782.shtml>.
- [44] X. Kong, P. Hao, H. Duan, *Exploration* **2021**, 1, 20210052, <https://doi.org/10.1002/exp.20210052>.
- [45] Z. Sun, Y. Wang, T. Liu, X. Kong, T. Pan, F. Zhang, X. Lei, X. Duan, *J. Hazard. Mater.* **2023**, 447, <https://doi.org/10.1016/j.jhazmat.2023.130723>.
- [46] H. Yang, 'Research and development of Mg-based super-stable mineralization soil remediation materials in Qinghai has yielded fruitful results', <https://finance.sina.com.cn/jjxw/2023-01-06/doc-imxzfiqm8952328.shtml>.
- [47] 'Development and demonstration of key technologies for industrialization of Mg-based super-stable mineralized soil remediation materials' passed through project evaluation by Department of Science and Technology, Qinghai Province, <https://news.buct.edu.cn/2023/0105/c2514a175422/page.htm>.
- [42] N. He, L. Hu, C. Jiang, M. Li, *Sci. Total Environ.* **2022**, 850, 157995, <https://doi.org/10.1016/j.scitotenv.2022.157995>.

License and Terms



This is an Open Access article under the terms of the Creative Commons Attribution License CC BY 4.0. The material may not be used for commercial purposes.

The license is subject to the CHIMIA terms and conditions: (<https://chimia.ch/chimia/about>).

The definitive version of this article is the electronic one that can be found at <https://doi.org/10.2533/chimia.2023.733>