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A Study on Removal of Heavy Metal Ions by MgFe-Layered Double Hydroxides

Zian Song

Abstract:

Heavy metal pollution has posed great threats to the ecological environment, food security and human health. To date, various approaches have been explored, among which mineralization of heavy metals via layered double hydroxides (LDHs) are reported as a promising way to solve the addressed issue. In line with this, the current study attempts to the fabrication of two typical MgFe-LDHs containing different intercalated anions (denoted as MgFe-CO_3 and MgFe-NO_3) for mineralization of Cd^{2+}. In the experiments, the as-prepared MgFe-NO_3 exhibited a high maximum adsorption capacity of 444.44 mg/g, which was 2.82 times higher than that of the contrast sample MgFe-CO_3 (157.48 mg/g). Such difference in adsorption capacity can be attributed to the different mineralization mechanism: For MgFe-NO_3, the mineralization process was dominated by isomorphous substitution and the CdFe-LDH was the main product, while for MgFe-CO_3, the formation of $CdCO_3$ can be observed. This work paves a way in treating Cd^{2+} by MgFe-NO_3 through super-stable mineralization and its further application in the removal of co-existent Cd^{2+} and AsO_4^{3-} ions can be expected.

Keywords: heavy metal, mineralization, hydroxides, absorption capacity, isomorphous substitution

Introduction

1.1 The situation of heavy metal pollution in the world

Since the 20th century, with the rapid development of social economy, the world's ecological environment is facing increasing challenges (Hou *et al*., 2020). The combustion of fossil fuels, the mining of minerals and the use of pesticides and fertilizers containing harmful heavy metals have caused heavy metal pollution, which severely threatens plants, animals and microorganism and results in deterioration of ecosystem. Among all types of heavy metal pollution, soil pollution has raised particular attention worldwide because it has led to serious food security problems or even ecological disasters (Borrelli *et al*., 2013). According to the 'Global Soil Pollution Assessment' raised by the Food and Agriculture Organization of the United Nations (FAO), about 33% of the soils in the world are currently degraded due to heavy metal pollution (Liu et al., 2023). In 2018, Pérez *et al*. express their concern that 2.8 million square kilometers of soil in EU are potentially contaminated (Pérez & Eugenio, 2018).

1.2 The situation of heavy metal pollution in China

In China, the heavy metal pollution is also a prominent environmental problem. According to national soil pollution investigation issued by the Ministry of Environmental Protection of China, 16.1% of the soil contains pollutants above average, and 82.8% of all pollutants come from heavy metals. This results in 12 million tons of contaminated grains and a direct loss of 20 billion yuan per year. Among all heavy metals, the Cd^{2+} contamination was the most serious, which accounts for 7% of total heavy metal pollutions (Yang *et al*., 2018). Hence, it is extremely urgent to find effective treatment of heavy metals in soil. In this regard, chemists have explored various approaches to remove heavy metals from the soil including elution, electrochemistry, phytoremediation, mineralization and etc. Existing studies show that elution, electrochemistry and phytoremediation may have such problems as high cost, long treatment cycle, harmful for soil structure and second-time contamination. Mineralization turned out to be a more reliable, safer and less expensive method (Sun et al., 2023). Based on these reported findings, the current study attempts to investigate the treatment of heavy metals with a focus on Cd^{2+} by applying mineralization methods.

1.3 The purpose of this study

Literature shows that layered double hydroxides (LDHs) have been demonstrated to be able to form very low $K_{sp,}$ showing great potential as a class of mineralizer. In line with this, the current study attempts to carry out experiments to remove Cd^{2+} in soil by adopting LDHs. The purpose of the study is threefold. Firstly, it intends to understand the mineralization mechanism of LDHs-based mineralizers by using different intercalated anions of MgFe-CO_3 and MgFe-NO_3. Secondly, it aims to optimize the mineralization conditions including the maximum adsorption capacity towards Cd^{2+}, and to investigate the thermodynamics and kinetics of mineralization process. Thirdly, it will explore the preliminary super-mineralization of LDHs in Cd^{2+}-polluted soil.

1.4 Outline of the paper

In this paper, the first chapter introduces the severe situation of heavy metal pollution in the world and in China in particular as well as the purpose of this study. In the second chapter, relevant literature is reviewed. In Chapter Three, experiments including materials, synthesis, characterization and performance investigation are presented in detail. Chapter Four gives an in-depth account of the results and discussions based on the experimental data. In the concluding chapter, findings are summarized and future study is pointed out.

LITERATURE REVIEW

2.1 Methods of heavy metal pollution treatment

Currently, a wide variety of heavy metal pollution treatment technologies have emerged, which provides solutions from multiple angles to solve the heavy metal pollution (Xu et al., 2019). However, considering the efficiency, operability, cost or energy consumption of the currently using technologies, there are still many problems to be solved.

2.1.1 Elution

The soil elution is the first used soil treatment technology, which commonly involves (1) digging out the contaminated soil; (2) screening to remove oversized components (3) using eluent to clean, remove contaminants (4) backfill the clean soil (Zhao *et al*., 2019). The elution of soil (Lestan et al., 2008) commonly requires large amounts of chelating agents and the resultant heavy metal-containing washing sewage often leads to the secondary pollution. Tsang et al. fabricate an EDDA chelating agent to deal with the heavy metals contaminated soil, which shows a high extraction efficiency of heavy metal Cu^{2+}, Pb^{2+} and Zn^{2+} (Beiyuan et al., 2017). However, such large amounts of chelating agent would not only increase the cost of treatment but also cause a serious decrease in the soil nutrient content (Jelusic et al., 2014).

2.1.2 Electrochemistry

The currently used electrochemistry remediation technology often applies a direct current (DC) in the soil, transporting and reducing heavy metals on the negative electrode (Xu et al., 2019). The electrochemistry technologies are only feasible for small volumes of heavily polluted shallow soil. Cui et al. report an electrochemistry remediation method to build an asymmetrical alternating current electrochemistry (AACE) technology, which can remove Cu^{2+}, Pb^{2+} and Cd^{2+} at initial concentrations from 100 to 10,000 ppm and enabled recycling of soil washing chemicals (Xu et al., 2019). However, considering the soil is a poor conductor of electricity and the high cost of constructing alternating current electric field, the electrochemistry technology is not suitable for of large-scale application.

2.1.3 Phytoremediation

Recently, the phytoremediation emerges as an efficient technology in soil treatment (Shen *et al*., 2022). However, the phytoremediation method normally takes long operation time. Cui et al. carry out the phytoremediation by using Solanum nigrum L (Cao et al., 2022). and Medicago sativa L., which can achieve the Cd removal (more than 80%) and PAHs dissipation (more than 90%) in the soil at the same time. Although the phytoremediation can effectively reduce costs, but the long operation time (commonly over 100 days) makes it only suitable for remote areas. Moreover, the heavy metals would accumulate in the plants, which may cause the secondary pollution.

2.1.4 In-situ Mineralization

Considering the large area of heavy metal pollution in China, it's difficult to carry out large-scale elution, electrochemistry or phytoremediation remediation, and the *in-situ* mineralization technology possesses the advantages of economic efficiency and strong operability, which shows great promise for large-scale application. In a typical *in-situ* mineralization process, the mineralizers are used to adsorb or precipitate the heavy metals ions and transform them into a mineralized state, so as to realize the remediation of contaminated soil and water (Mao et al., 2022).

To date, a number of mineralization agents have been applied for heavy metal removal. For example, attapulgite, zeolite, bentonite and biochar have been used as the stabilizers for Cd^{2+} immobilization (Tack, 2018; Rinklebe, 2019). However, these materials have to be repeatedly used (10–220 t/ha) since their affinity and adsorption capacity for Cd^{2+} are very limited. Moreover, accumulation of metals, nitrogen and phosphorus can cause further damage for the crops and soil. In contrast, the carbonate and hydroxides (soda lime) can be used for Cd^{2+} removal, resulting in the formation of $CdCO_3$ and/or $Cd(OH)_2$. However, large amounts (>15 t/ha) and frequent utilization of these mineralization materials are necessary (Bernal, 2014; Chen, 2016) due to relative larger solubility and instability of $CdCO_3$ and $Cd(OH)_2$. Moreover, the massive use of lime into soil can cause soil compaction, and have been rejected in agricultural land in UK. As a result, the development of highly efficient, cost effective, and long-term immobilization ability mineralization materials is highly desirable.

2.2 Studies of Layered Double Hydroxides for treatment of heavy metal ions

2.2.1 Overview of Layered Double Hydroxides

Layered double hydroxides (LDHs), a class of two-dimensional (2D) layered metal-containing clays, are composed of positively charged brucite-like host layers, the intercalated guest anions for charge balance, and solvent molecules (Feng et al., 2015). The general chemical formula of LDHs is $[M(II)_{1-x}M(III)_x(OH)_2]_x^+[A_{x/n}\ H_2O]^{x-}$, where M^{2+} and M^{3+} represent the divalent and trivalent metal cations (such as Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, etc.), while A^{x-} denotes the interlayer anion.(Tan *et al*., 2019) More importantly, Duan *et al* proposed the concept of super-stable mineralization of LDHs towards heavy metals for the first time in 2021 (Kong *et al*., 2021). LDHs can be finely tuned from different perspective: (1) the metal cations on the laminate of LDHs can be adjusted;(Ning *et al*., 2021) (2) the interlayer anions are able to be regulated such as CO_3^{2-}, NO_3^-, SO_4^{2-}; organic anions and polyoxometalates *etc.* (Chang et al., 2020); (3) the abundant -OH groups on LDH layers provide ample binding sites(Wright et al., 2017). Various functional groups (-SH, -COOH, $-NH_2$, etc.) can be introduced either on the LDH laminates surface or interlayer spacing (Li *et al*., 2020). These structural features endow LDHs to be able to adsorb heavy metals by surface adsorption, coordination by interlayer anions, and anion exchange *etc*.

2.2.2 Removal and mineralization of heavy metal ion by LDHs

In recent years, LDHs are demonstrated to be effective in adsorbing heavy metal ions, which have attracted widespread interest of the academic community (Xu et al., 2022). For example, Ma and coworkers documented that the substitution of CO_3^{2-} with MoS_4^{2-} in MgAl-LDH resulted in exceptional removal efficiency for metal ions, particularly demonstrating remarkable selectivity for Ag^+ and Hg^{2+} (Ma *et al*., 2016). In another recent study, Kong and his team utilized a CaAl-LDH to facilitate the mineralization of Cd^{2+} ions, resulting in the formation of CdAl-LDH. Impressively, this CdAl-LDH displayed outstanding stability during the practical remediation of Cd^{2+} ions, maintaining its effectiveness for a period spanning 3 to 4 years (Kong *et al*., 2021).

Moreover, Song *et al*. reported the use of a CaFe-LDH stabilizer capable of super-stable mineralization of Ni^{2+} ions, with a maximum saturation removal capacity of 321 mg^{-1} (Chi *et al*., 2021). Notably, Song *et al*. firstly demonstrated the isomorphous substitution of CaFe-LDH during the mineralization of Ni^{2+} by using ex situ X-ray diffraction and X-ray absorption fine structure (XAFS) characterization.

Given the presence of an abundant -OH groups on the primary layers of LDHs, the -OH groups on the LDH surface readily form coordination bonds with heavy metals. For instance, in a study conducted by Wu *et al.*, a calcined $MgZnFe-CO_3$ (CMZF) adsorbent was employed to effectively remove AsO_3^{3-} and Cd^{2+}, achieving a remarkable removal rate of 99.7% (Liu et al., 2019). The X-ray Photoelectron Spectroscopy (XPS) analysis was employed to reveal that Cd^{2+} and AsO_4^{3-} coordinated with -OH sites on the LDH laminates after adsorption.

In this study, we choose MgFe-LDH for Cd^{2+} removal is due to the following reasons: (1) For soil in south part of China, it is generally lack of Mg^{2+}. As such, the Mg^{2+} ions can be released into soil during the isomorphous substitution of Mg^{2+} by Cd^{2+}, which is the key for soil nourishment in South part of China; (2) Future study for treatment of AsO_4^{3-} and Cd^{2+} contaminated soil and water, due to the formation of FeAs associated core that is frequently observed in nature, it is necessary to design Fe-containing LDHs.

2.3 Hypotheses

Based on the discussion above, this study hypotheses:

H1. MgFe-LDH will be successfully prepared by co-precipitation method and ion exchange method.

H2. The prepared MgFe-LDH will have good adsorption properties for Cd^{2+}.

H3. MgFe-NO3 will be isomorphic substitution to form CdFe-LDH. MgFe-CO3 will be direct precipitation to form CdCO3.

EXPERIMENTAL SECTION

3.1 Material and synthesis

3.1.1 Experimental material

Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99%, Sigma-Aldrich), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99%, Sigma-Aldrich), nitric acid (HNO_3, Sinopharm), sodium carbonate (Na_2CO_3, 99.8%, Fuchen Chemical), sodium hydroxide (NaOH, 96%, Fuchen Chemical) and hexamethylenetetramine (HMT, 98%, Energy Chemical) were used without any further purification.

3.1.2 Material synthesis

Preparation of MgFe-CO_3: The MgFe-CO_3 was synthesized by co-precipitation method. Firstly, 1.76 g $Fe(NO_3)_3 \cdot 9H_2O$ and 2.18 g $Mg(NO_3)_2 \cdot 6H_2O$ were added into 25 mL of deionized water to form the solution A. Whereas 100 mL aqueous solution of NaOH (4 g) and Na_2CO_3 (10.75 g) was recorded as solution B. At 65°C, solution A and solution B were injected dropwise into 50 mL deionized water under magnetic stirring, and the resulting reaction mixture maintained at pH = 10. Then, MgFe-CO_3 powder was obtained after centrifugation, washing and drying (60 °C) overnight.

Preparation of MgFe-NO_3: The MgFe-NO_3 was synthesized by the method of anion-exchange. Firstly, 100 mL methanol and 500 mg MgFe-CO_3 were mixed and stirred under N_2 flow (600 mL/min) at room temperature for 3 h. Subsequently, a solution of HNO_3 and 45 mL methanol was added in the above solution drop by drop, and stirred for 1 h. The resulting suspension was filtered, washed with methanol and vacuum-dried to yield white powder of MgFe-NO_3.

3.2 Characterization

3.2.1 Characterization technique

Fourier transform infrared (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), High-resolution transmission electron microscopy (HRTEM) and Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were carried out to characterize the structure of the MgFe-CO_3, MgFe-NO_3, MgFe-CO_3-bulk and their mineralization products.

3.2.2 Sample making

The XRD sample was prepared by filling the mold directly with the powder.

The FT-IR was obtained by using KBr pellet method. Firstly, the 2 mg as-synthesized sample was mixed in 200 mg KBr, the resulting mixture was evenly ground and filled into a tableting mold under certain pressure to form a transparent slice.

The SEM and HRTEM samples were obtained by ultrasonic mixing of ethanol and LDH powder, and then, the mixture was dropped on a silicon wafer or microgrid for observation after drying.

The ICP-AES samples were prepared by 20 times dilution after fixed time (0-60 min) mineralization.

3.2.3 Material characterization

X-ray diffraction (XRD) patterns were carried out by a Rigaku XRD-6000 diffractometer (λ of Cu Kα radiation = 1.5405 Å). Fourier transform infrared (FT-IR) spectra were characterized on a Bruker Vector 22 infrared spectrometer. Scanning electron microscopy (SEM) images were obtained with a Zeiss Supra 55 SEM, which was equipped with an Energy dispersive spectroscopy (EDS) detector. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2010 transmission electron microscope operating at an acceleration voltage of 200 kV.

3.3 Performance investigation

3.3.1 Kinetic experiment

The adsorption kinetic for Cd^{2+} was explored using various mineralization times (0-60 min) were conducted. For each experiment, 50 mg LDH was placed in a 100 mL beaker and then 50 mL of an aqueous solution containing 300 mg/L Cd^{2+} ions were added, respectively. At specific time intervals as displayed in Figure 5A, 1 mL of suspension was collected and analysed by ICP-AES to determine the heavy metal contents. Other processes were the same as above. The mineralization capacities at contact time (t) and at equilibrium, q_t (mg/g) and q_e (mg/g), respectively, were calculated as displayed below (equations 1-2). The percentage removal was calculated following equation 3. The adsorption kinetics of Cd^{2+}ions on LDHs were investigated according to the pseudo-first-order and pseudo-second-order kinetics equations (equations 4 and 5).

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

$$\%\ \text{removal} = 100^* \ \frac{(C_o - C_t)}{C_0} \tag{3}$$

$$\log(\, q_e - q_t\,) = logq_e - \frac{k_1}{2.33} t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2} q_e{}^2 + \frac{t}{q} \tag{5}$$

C_0 and C_t are the initial and equilibrium concentrations of Cd^{2+} ions (mg/L), respectively, and V and m are the amounts of solvent (mL) and mass (g) of adsorbent. k_1 and k_2 were rate constants for pseudo-first-order and pseudo-second-order equations, respectively.

3.3.2 Thermodynamic experiment

Mineralization isotherms for Cd^{2+} was performed to investigate the mineralization capacity. The removal performances of LDHs were investigated in 100-600 mg/L Cd^{2+}, ions solution, respectively. The experiment data were fitted by the Langmuir isotherm model (Equation (6)) and Freundlich isotherm model (Equation (7)):

$$q_e = \frac{C_e k_L q_m}{1 + k_L C_e} \tag{6}$$

$$q_e = k_F C_e^{\frac{1}{n}} \qquad (7)$$

where q_m and C_e are maximum removal capacity and equilibrium concentration, k_L and k_F are Langmuir mineralization and Freundlich mineralization constant, respectively. And n is the heterogeneity factor.

RESULTS AND DISCUSSION

4.1 Structural and Morphological characterization of MgFe-LDH

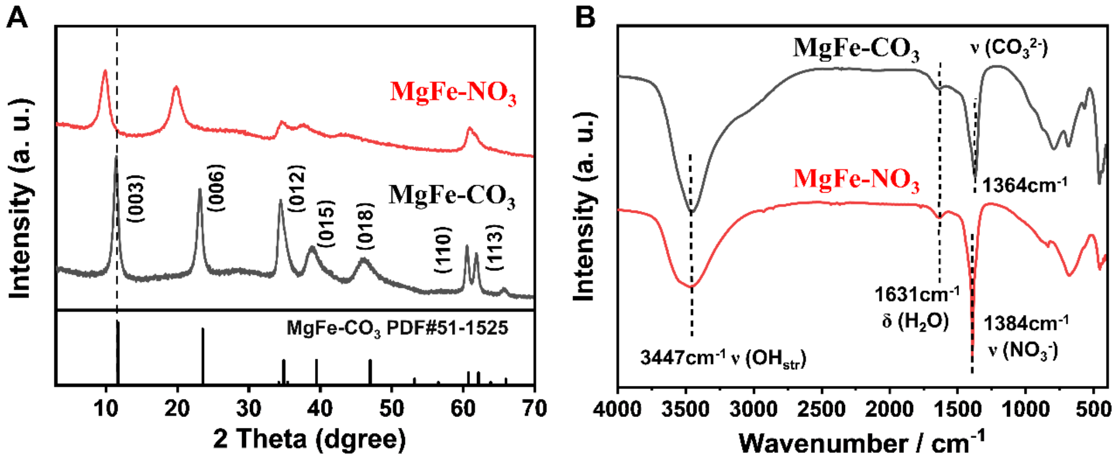

Figure 1 (A) XRD patterns for MgFe-CO_3 and MgFe-NO_3; (B) FT-IR spectra for MgFe-CO_3 and MgFe-NO_3.

Firstly, we fabricated the catalyst of CO_3^{2-} intercalated MgFe-LDH (denoted as MgFe- CO_3) and NO_3^- intercalated MgFe-LDH (denoted as MgFe -NO_3) by using co-precipitation method and ion exchange method, respectively. The XRD patterns (Figure 1A) of the as-prepared MgFe-LDHs (MgFe-CO_3 and MgFe-NO_3) both exhibited the typical LDHs diffraction peaks of (00*l*) and (110). Compared with MgFe-CO_3, the (003) and (006) peaks of MgFe-NO_3 presented a significant shift to lower degree, indicating a larger basal spacing originated from the vertical intercalation of NO_3^- (Ning *et al.*, 2021). Moreover, the Fourier transform-infrared spectrometer (FT-IR) was used to further prove the MgFe-CO_3 and MgFe-NO_3 were successfully fabricated. Both of them exhibited characteristic absorption peaks at 3447 cm^{-1} and 1631 cm^{-1}, which can be attributed to -OH group stretching vibration of metal hydroxide layers and the deformation vibration of the interlaminar water, respectively. Notably, the MgFe-CO_3 exhibited an absorption peak at 1364 cm^{-1}, which belonged to asymmetric stretching vibration of at CO_3^{2-}. By comparison, for MgFe-NO_3, the sharper absorption peak at 1384 cm^{-1} can be ascribed to symmetric stretching vibrations of NO_3^- (Tan *et al.*, 2019).

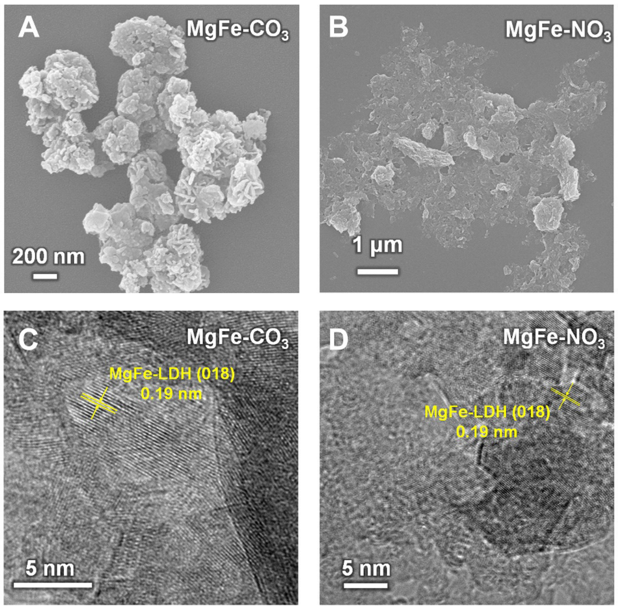

Figure 2 (A-B) SEM images of MgFe-CO_3 and MgFe-NO_3; (C-D) HRTEM images of MgFe-CO_3 and MgFe-NO_3.

The scanning electron microscope (SEM) was employed to obtain the morphology of as-prepared catalysts. It can be seen from Figure 1A-B that the MgFe-CO_3 and MgFe-NO_3 both exhibited classic layered structure of LDHs (Tan et al., 2023). However, the stacking degree of laminates in MgFe-NO_3 were apparently lower than MgFe-CO_3, which led to more metal sites in the laminates to be exposed. The corresponding HRTEM images were displayed in Figure 1C-D, in which both of the MgFe-CO_3 and MgFe-NO_3 showed the lattice spacing of 0.19 nm, indicating the (018) facet exposure on the surface of Mg-Fe-LDH. The above characterizations all demonstrated the successful synthesis of MgFe-CO_3 and MgFe-NO_3.

4.2 Heavy metal mineralization performance of MgFe-LDH

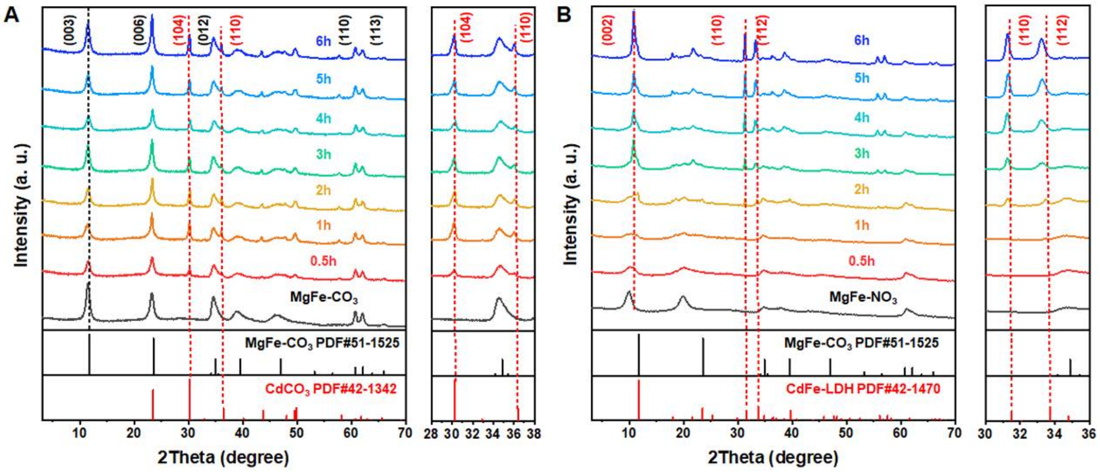

Figure 3. XRD patterns of the mineralization product recovered after the removal of Cd^{2+} using (A) MgFe-CO_3 and (B) MgFe-NO_3 for 0.5, 1, 2, 3, 4. 5 and 6 h, respectively. (Conditions: LDHs = 1 g/L, C_0 = 300 mg/L, V = 50 mL, 25 °C)

The XRD characterization was performed to explore the structural and compositional change of MgFe-CO_3 and MgFe-NO_3 in Cd^{2+} solution, respectively. As displayed in Figure 3A, the characteristic peaks of MgFe-CO_3 maintained the same as the increase of mineralization time (0-6 h), indicating the existing of MgFe-CO_3 in the mineralization products. Interestingly, after 0.5 h of mineralization, two new peaks situated at 30.2^o and 36.5^o appeared and increased along with the adsorption time, which can be well matched with the (104) and (110) crystal planes of $CdCO_3$ (JPCDS cards No. 42-1342).

In contrast, MgFe-NO_3 displayed different variation of diffraction peaks compared with that of MgFe-CO_3 (Figure 3B). Firstly, the characteristic diffraction peak intensity of MgFe-NO_3 weakened during the first 1 h of mineralization. With the extension of mineralization time, new diffraction peaks appeared and became dominant at 2θ=11.7^o, 31.6^o and 33.8^o, respectively, which can be corresponding to the (002), (110) and (112) basal XRD patterns of Cd-Fe-LDH (JPCDS cards No. 42-1470). Ultimately, after 6 h of mineralization, the characteristic peaks of MgFe-NO_3 completely disappeared. Hence, we concluded that Mg-Fe-NO_3 has been completely converted to CdFe-LDH after 6 h of mineralization.

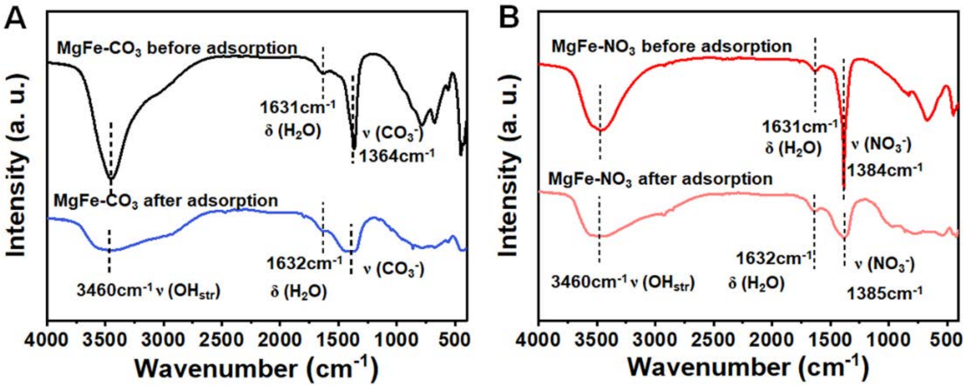

Figure 4. FT-IR spectra of the mineralization product recovered after the removal of Cd^{2+} using (A) MgFe-CO_3 and (B) MgFe-NO_3 for 6 h (conditions: LDHs = 1 g/L, C_0 = 300 mg/L, V = 50 mL, 6 h, 25 °C)

Furthermore, the precipitates after the mineralization of Cd^{2+} by MgFe-CO_3 and MgFe-NO_3 for 6 h were subjected to FT-IR analysis, respectively (Figure 4A and 4B). As was observed, the infrared characteristic peaks of precipitates after the mineralization had no obvious shift compared with that of MgFe-CO_3 and MgFe-NO_3. In addition, the stretching vibration at 1364 cm^{-1} (CO_3^{2-}) and 1384 cm^{-1} (NO_3^-) remained in position after mineralization, indicating that there was no obvious change in the types of interlayer anions.

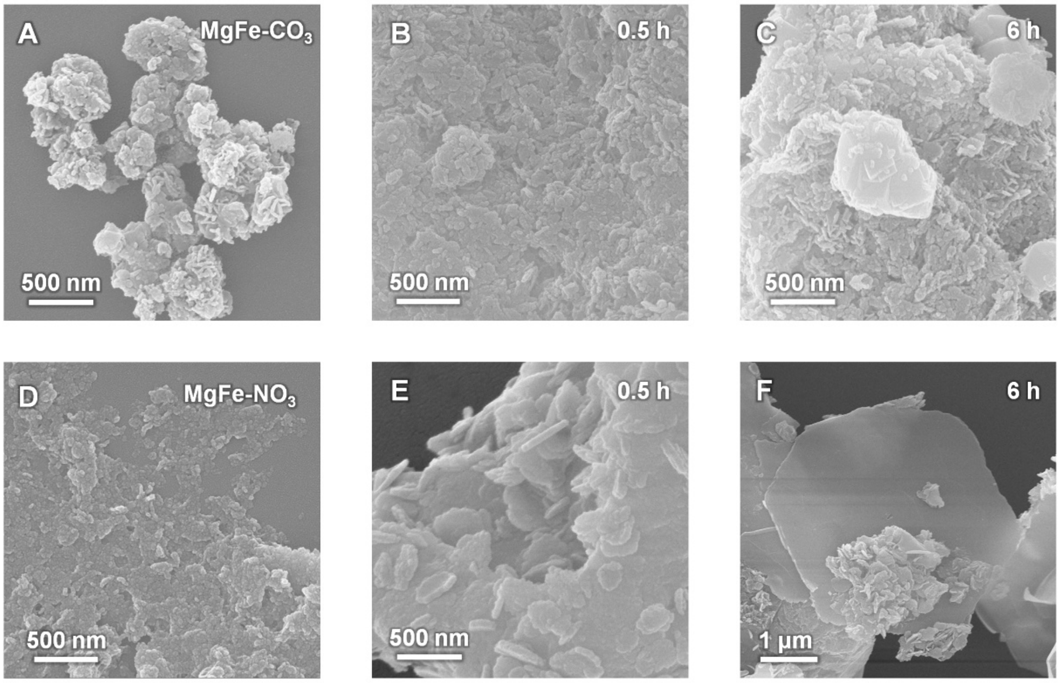

Figure 5. SEM images of (A-C) MgFe-CO_3, and (D-F) MgFe-NO_3 before and after adsorption in Cd^{2+} solution for 0.5h and 6h, respectively.

The morphology change of both MgFe-CO_3 and MgFe-NO_3 in the process of mineralization were examined by SEM (Figure 5). As shown in Figure 5A, the pristine morphology of MgFe-CO_3 showed a flower-like shape with a diameter of about 200 nm (Figure 5A). After 0.5 h of mineralization, the size of the LDHs sheets did not change significantly. Subsequently, it can be clearly observed that after 6 h of mineralization, many cubes with diameters of about 500 nm appeared on the surface of MgFe-CO_3, indicating that a new substance was generated (Figure 5C). Combing with the results of XRD, such cubes can be designated as $CdCO_3$. Interestingly, the sheets of as-prepared MgFe-NO_3 exhibited an average size of ~ 10 nm (Figure 5D). With the extension of mineralization time, the diameter of the sheets increased significantly to 200 nm in 0.5 h. After 6 h, hexagonal nanosheets with diameters of 5 μm generated eventually (Figure 5F), which can be attributed to the formation of CdFe-LDH.

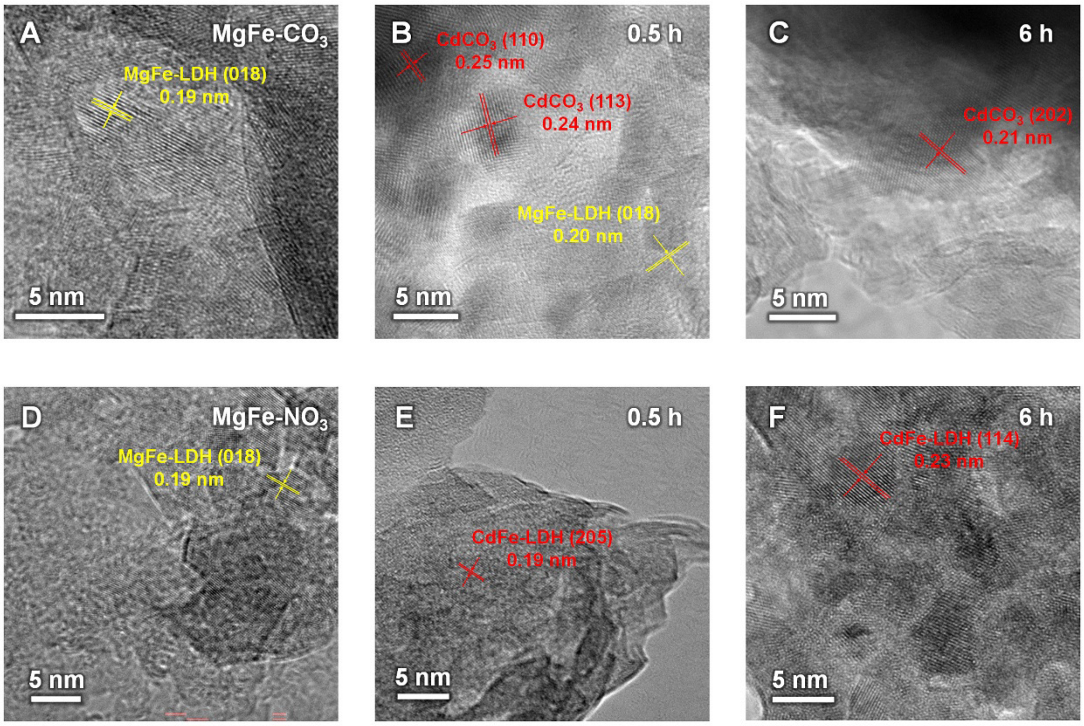

Figure 6 HRTEM images of (A-C) MgFe-CO_3, and (D-F) MgFe-NO_3 before and after adsorption in Cd^{2+} solution for 0.5h and 6h, respectively.

The HRTEM images further proved the mineralization of Cd^{2+} by MgFe-CO_3 and MgFe-NO_3 went through different process from a more microscopic perspective. For the MgFe-CO_3, only MgFe-LDH lattice fringe can be detected at the beginning (Figure 6A). When the removal process extended to 0.5h, the 0.24 and 0.25 nm lattice spacing were observed, which can be assigned to the exposure of (110) and (113) facets of $CdCO_3$ (Figure 6B). Besides, the lattice fringe of MgFe-LDH was also existed, indicating the incomplete transformation of MgFe-LDH towards $CdCO_3$. After 6h mineralization of Cd^{2+} (Figure 6C), the lattice fringe of MgFe-LDH was not visible, illustrating the structure of MgFe-LDH was fully destroyed by the formation of $CdCO_3$. For the MgFe-NO_3 in Figure 6D-F, compared with the initial MgFe-NO_3, the lattice fringe of CdFe-LDH started to appear after 0.5h mineralization of Cd^{2+}. After 6h, the lattice fringe of the large planner sheets was totally belonged to CdFe-LDH. The above results were in good line with the SEM and XRD tests.

4.3 Heavy metal adsorption performance of MgFe-LDH

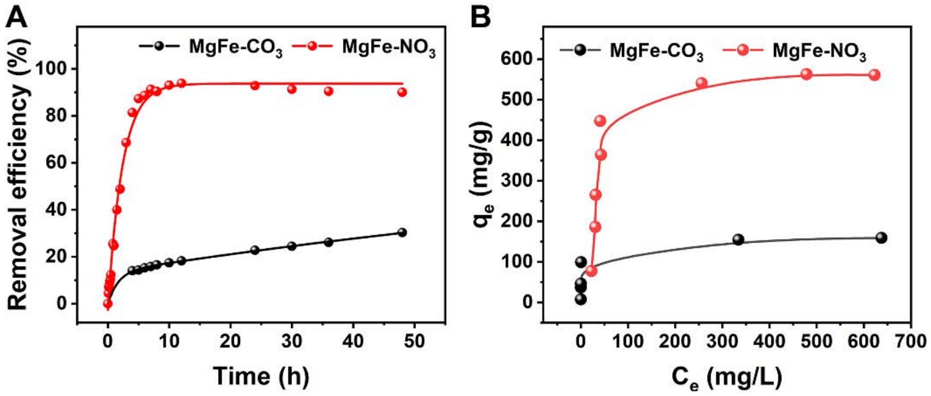

Figure 7. Mineralization capacity of Cd^{2+} using (A) MgFe-CO_3, and MgFe-NO_3 for 6 h, removal performance of (B) MgFe-CO_3 and MgFe-NO_3 in Cd^{2+} solution with a concentration range of 10–1200 ppm (dose=1 g/L, 25 ^{o}C, pH=6).

The removal performance of MgFe-CO_3 and MgFe-NO_3 were studied in the same concentration of Cd^{2+} (dose=1 g/L, C_0=300 mg/L, Figure 7A). As shown in Figure 7A, the MgFe-CO_3 did not reach the mineralization equilibrium after about 50 h, by contrast, MgFe-NO_3 showed a shorter mineralization equilibrium time of 10 h. Moreover, compared with MgFe-CO_3, MgFe-NO_3 exhibited a higher removal efficiency toward Cd^{2+}, which can reach to more than 97% within 10 h, while MgFe-CO_3 only showed low removal efficiency of 30% after 50 h of mineralization. Additionally, the adsorption kinetics of Cd^{2+} ions using MgFe-CO_3 and MgFe-NO_3 as adsorbents were further investigated (Table 1). For MgFe-NO_3, t/q_t as a function of time for Cd^{2+} was well consistent with the pseudo-second-order kinetic model with R^2 = 0.9952. In contrast, $\log(q_e - q_t)$ as a function of time was not well in line with the pseudo-first-order kinetic model (R^2 = 0.9651), indicating that the mineralization process tended to be chemisorption rather than physisorption (Kong *et al*., 2021). However, compared with pseudo-second-order kinetic model, MgFe-CO_3 can be fitted well with pseudo-first-order kinetic model(R^2 = 0.9970).

To investigate the mineralization capacity of the MgFe-CO_3 and MgFe-NO_3, the equilibrium adsorption isotherm was carried out in different concertation of Cd^{2+} solution (10 - 1200 mg/L, Figure 7B). The mineralization results were fitted by Langmuir and Freundlich models, respectively. For both of MgFe-CO_3 and MgFe-NO_3, the R^2 value fitted from the Langmuir isotherm model (Table 2, R^2 = 0.9998 and 0.9937) were much higher than that of Freundlich isotherm model (R^2 = 0.5610 and 0.9297), respectively, demonstrating that the Cd^{2+} adsorbed monolayer on both MgFe-CO_3 and MgFe-NO_3 (Chen *et al*., 2021). Meanwhile, the MgFe-NO_3 showed an ultra-high theoretical maximum saturated adsorption capacity (q_m) value of 444.44 mg/g fitting based on Langmuir model, while that of the MgFe-CO_3 was much lower (157.48 mg/g), illustrating that the Cd^{2+} adsorption driven by isomorphic substitution of MgFe-NO_3 was beneficial to the mineralization capacity (Kong *et al*., 2021).

Table 1. Kinetic parameters obtained after applying pseudo-first and second-order kinetics equations

Materials	Pseudo-first Order			Pseudo-second Order		
	q_e (mg/g)	k_1 (L/min)	R^2	q_e (mg/g)	k_2 (g/(mg/min))	R^2
MgFe-CO_3	63.38	0.04	0.9970	10.60	1.003	0.9675
MgFe-NO_3	317.96	0.43	0.9651	194.17	0.008	0.9952

Table 2. The fitting results of Langmuir model and Freundlich model for MgFe-CO_3 and MgFe-NO_3, respectively.

Materials	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	k_l (L/g)	R^2	n	k_f (mg/g)*(L/mg)$^{1/n}$	R^2
MgFe-CO_3	157.48	-9.39	0.9998	1.96	0.034	0.5610
MgFe-NO_3	444.44	0.13	0.9937	2.04	2.24	0.9297

Conclusion

5.1 Summary of findings

To summarize, this study demonstrates the successful fabrication of MgFe-NO_3 and MgFe-CO_3 by using co-precipitation method and ion exchange method, respectively. The as-prepared mineralizer was fully characterized by XRD, FT-IR, SEM, and HRTEM. When applied for the adsorption of Cd^{2+} ions in water, it was demonstrated that the adsorption process of MgFe-NO_3 was in good line with the pseudo-second-order adsorption and Langmuir adsorption model, whereas the MgFe-CO_3 followed pseudo-first-order adsorption and Langmuir adsorption model. The maximum adsorption capacity can reach 444.44 and 157.48 mg/g for MgFe-NO_3 and MgFe-CO_3, respectively. Detailed characterization showed that for MgFe-NO_3, the isomorphous substitution dominated the adsorption process, while for MgFe-CO_3, the formation of $CdCO_3$ was observed.

5.2 Limitations of the study

Although, some preliminary results on remediation of Cd^{2+} contaminated soil was carried out, systematic investigation of LDHs application for heavy metals contamination need to be performed in the future.

5.3 Future study

In the future study, these following areas can be explored. (1) In Hunan and Hainan provinces of China, the soil is mainly polluted by Cd and As simultaneously. Due to the formation of FeAs associated core that is frequently found in nature, future work can focus on the use of MgFe-LDH for the remediation of co-existence of Cd^{2+} and AsO_4^{3-} in soil, which is significant for ensuring food security; (2) Rational design of highly selective LDHs for different heavy metal contamination needs to be studied in the next step; (3) Regarding the large-scale preparation of LDHs, it is necessary to take into consideration the green synthesis of LDHs in order to meet with the requirement of practical application.

EVALUATION

EPQ performance

I have long been interested in chemistry and environment related things. I was really shocked one day when I watched TV news about the seriousness of the soil pollution especially heavy metal pollution in China. When I searched the internet, I realized that it is not a problem only in China but a worldwide one. I continued to search for solutions and found out there are different ways to tackle the problem including those in chemistry, which seem promising. Therefore, I decided to choose the removal of heavy metal as my EPQ research direction. Under the guidance of my supervisor, I started to read research papers and I found the most suitable way to deal with Cd^{2+}pollution is mineralization by adopting LDHs. Hence, I think it is feasible to design a study to remove Cd^{2+} in soil by adopting LDHs.

It is a huge challenge to complete a scientific research project by my own and write up a long paper, which I have never done before. For the first time, I read many research papers, made a detailed plan, design experiments, do the experiments, observe and record the progress of each experiment, collect data and do the statistics, analyzed the results and wrote the paper. This is indeed a long and hard process and very challenging in many ways. In the face of a large number of professional literatures, I was very confused at first. There are a lot of professional words and it took a lot of time to look them up at beginning. However, with continuous effort in remembering them, I became more skilled in reading journal papers and can find the part I need. Then, the experimental part is no easy job at all. Doing experiments are fun. However, I do not have much experience. Even with the help of my supervisor, I made a lot of mistakes. The process is painful but happy. I often had to work for up to 10 hours a day and ended up with sore legs. But after seeing the results, I felt great and my efforts were paid off. The results kept motivating me to enjoy the experiments more. Finally, the long thesis required for the EPQ project is an enormous task. I have never written a paper of this length, and I lack research paper writing training. Fortunately, with the help of my thesis supervisor, I revised my paper over and over again, and also learned from other people's articles. Finally, I have a decent academic paper of my own.

This EPQ project not only improved my skills in literature collection and a critical review of previous research, but also improved my time management skills and perseverance in doing research. What's more, I have learnt from the failures and improved my chemistry knowledge and experiment skills. Finally, my writing skills and logical thinking have been trained.

I have to admit that my paper only studied the removal of the heavy metal ions Cd^{2+} by specific LDH. The limitations are obvious. Systematic investigation of LDHs application for heavy metal contamination needs to be performed in the future.

The EPQ project allowed me to experience the complete process of scientific research for the first time, from topic selection to planning, to searching for literature, to doing experiments and to paper writing. Not only has it enriched my scientific research experience, but also I have developed a passion for the topic and chemistry study in general. In my future university life, when I encounter a scientific research project, I would not be afraid and can follow the steps and principles that I learned from this EPQ project. I can take advantage of the skills I gained from this project and further develop my knowledge and skills in research and in study in general.

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Appendix A Gantt Diagram of Time- line

Name: Zian Song		Date		5.31-6.6	6.7-6.13	6.14-6.20	6.21-6.27	6.28-7.4	7.5-7.11	7.12-7.18	7.19-7.25	7.26-8.1	8.2-8.8	8.9-8.15	8.16-8.22	8.23-8.29	8.30-9.5	9.6-9.12
Time line (week)		Begin Week	Finish Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Search for information online	plan	1	2															
	actual	1	2															
Decide the general topic	plan	2	3															
	actual	2	3															
Create a mind map with contents	plan	3	5															
	actual	3	8															
Detail the subject	plan	3	4															
	actual	3	6															
Find and evaluate the data	plan	4	11															
	actual	4	14															
Build the framework of the paper	plan	4	5															
	actual	4	5															
Time planning	plan	5	6															
	actual	5	6															
Write a research proposal	plan	6	8															
	actual	6	8															
Abstract	plan	7	8															
	actual	7	8															
Introduction	plan	9	10															
	actual	9	10															
Literature review	plan	11	16															
	actual	11	16															
Data collection and analysis	plan	13	18															
	actual	13	18															
Discussion	plan	19	22															
	actual	19	22															
Conclusion	plan	22	23															
	actual	22	23															
Review	plan	24	25															
	actual	24	25															
Proofreading the dissertation	plan	25	27															
	actual	25	27															
Prepare and practice presentation	plan	27	29															
	actual	27	29															

Name: Zian Song		Date		9.13-9.19	9.20-9.26	9.27-10.3	10.4-10.10	10.11-10.17	10.18-10.24	10.25-10.31	11.1-11.7	11.8-11.14	11.15-11.21	11.22-11.28	11.29-12.5	12.6-12.12	12.13-12.19
Time line (week)		Begin Week	Finish Week	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Search for information online	plan	1	2														
	actual	1	2														

Decide the general topic	plan	2	3														
	actual	2	3														
Create a mind map with contents	plan	3	5														
	actual	3	8														
Detail the subject	plan	3	4														
	actual	3	6														
Find and evaluate the data	plan	4	11														
	actual	4	14														
Build the framework of the paper	plan	4	5														
	actual	4	5														
Time planning	plan	5	6														
	actual	5	6														
Write a research proposal	plan	6	8														
	actual	6	8														
Abstract	plan	7	8														
	actual	7	8														
Introduction	plan	9	10														
	actual	9	10														
Literature review	plan	11	16														
	actual	11	16														
Data collection and analysis	plan	13	18														
	actual	13	18														
Discussion	plan	19	22														
	actual	19	22														
Conclusion	plan	22	23														
	actual	22	23														
Review	plan	24	25														
	actual	24	25														
Proofreading the dissertation	plan	25	27														
	actual	25	27														
Prepare and practice presentation	plan	27	29														
	actual	27	29														

Appendix B Resources assessment

Title	Resource type	Author(s)	Publisher	Publication date	Summary	Evaluation	Link	Usefulness (out of 5)	Reliability (out of 5)	Final decision
Guangdong found nine batches of cadmium excessive rice Hunan three manufacturers stopped production	news	——	CCTV NEWS	2013 5 21	The situation of heavy metal pollution in cultivated land in China is severe, and mass incidents often occur because of heavy metal pollution in soil	In the news broadcast a few years ago, the food security problem caused by soil pollution was reported, which made people realize that soil safety is very important, after all, "food is the heaven, food safety is the first." This kind of soil pollution caused by heavy metal ions has become my research background, and the facts in front of people also make this research more meaningful and convincing	http://www.ce.cn/cysc/sp/info/201305/21/t20130521_21493483.shtml	4	5	√
Metal contamination and bioremediation of agricultural soils for Food Safety and Sustainability	journal	Deyi Hou David O'Connor Avanthi D. Igalavithana Daniel S. Alessi Jie Luo Daniel C. Tsang Donald L. Sparks Yusuke Yamauchi Jörg Rinklebe Yong Sik Ok	Nature Reviews Earth & Environment, 1(7), pp. 366–381.	2020	Natural causes and human activities led to a large number of heavy metals entering cultivated land and causing pollution.	The article has high timeliness and credibility, and the main points it puts forward trigger me to conduct experiments and investigations. Help me clear the direction of the experiment, and serve as a powerful basis and point of view behind my experiment	https://www.nature.com/articles/s43017-020-0061-y	4	5	√

Heavy metals in soils: Trace metals and metalloids in soils and their bioavailability.	journal	Brian J. Alloway	Dordrecht, Netherlands: Springer.	2013	localised contamination from a predominant single source, such as a metal smelter can have a marked effect on soils, vegetation and possibly also on the health of the local population, especially in countries where there are inadequate emission controls and soil quality standards. Soils in all urban areas are generally contaminated with lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu) from traffic, paint and many other non-specific urban sources.	The article clearly describes the source of soil pollution and its impact on human beings. Narrowed my research once again in a short period of time. The pollution of lead, zinc, cadmium and copper mentioned in the article made me focus on the investigation and research of these heavy metal ions. His mention of different pollution treatment methods in different countries also gave me a new inspiration.	https://link.springer.com/book/10.1007/978-94-007-4470-7	5	5	√
Current status of agricultural soil pollution by heavy metals in China: A meta-analysis	journal	Ying Huang Lingyu Wang Wenjia Wang Tingqiang Li Zhenli He Xiaoe Yang	Science of The Total Environment, 651, pp. 3034–3042.	2019	Through the understanding of food safety and cultivated land pollution in China found: The total rate of soil exceeding the standard was 16.1%. The total amount of soil pollution is enormous Types of pollutants: Mainly inorganic heavy metals (82.8%), cadmium pollution is the most serious (7%)	The authoritative national soil survey data clearly shows that food safety and cultivated land pollution in our country are urgent problems. The analysis of the types of pollutants shows that inorganic heavy metals are the main pollutants, and cadmium is the most serious pollution. With such a large number of data, let me narrow my focus to cadmium, a heavy metal contaminant. The enormous impact of soil pollution and the urgent need to deal with it also reflect the need for this research.	https://www.sciencedirect.com/science/article/pii/S0048969718340762	5	5	√

Selective dissolution followed by EDDS washing of an e-waste contaminated soil: Extraction efficiency, fate of residual metals, and impact on soil environment	journal	Jingzi Beiyuan Daniel C.W. Tsang Marjorie Valix Weihua Zhang Xin Yang Yong Sik Ok Xiang-Dong Li	Chemosphere, 2017, 166, pp. 489-496	2017	In this study, the authors sequentially use reducing agents, oxidants, alkaline solvents, and organic acids in a two-stage soil washing, followed by a biodegradable chelating agent (EDDS, [S,S] -ethylenediamine-disucinic acid). The result comes that the heavy metals (Cu, Zn, Pb) can be successfully removed.	This study provides a way to simultaneously remove the heavy metal Cu, Zn and Pb in soil by a two-stage soil washing method using EDDA as washing agent. However, to avoid the soil damage, plenty of oxidants, alkaline solvent and organic acid are added during the washing process. Such two-stage washing method is low efficient and time consuming. Hence, this work inspired me to seek another technology to deal with the heavy metal pollution in soil.	https://www.sciencedirect.com/science/article/pii/S004565351631311X?via%3Dihub	3	5	√
An assessment of the global impact of 21st century land use change on soil erosion	journal	Pasquale Borrelli David A. Robinson Larissa R. Fleischer Emanuele Lugato Cristiano Ballabio Christine Alewell Katrin Meusburger Sirio Modugno Brigitta Schütt Vito Ferro Vincenzo Bagarello Kristof Van Oost Luca Montanarella Panos Panagos	Nature Communications, 2017, 8, pp. 2013	2017	In this work, the authors present an unprecedentedly high resolution (250×250 m) global potential soil erosion model, using a combination of remote sensing, GIS modelling and census data. Moreover, the authors estimate the spatial and temporal effects of land use change between 2001 and 2012 and the potential offset of the global application of conservation practices. Their findings indicate a potential overall increase in global soil erosion driven by cropland expansion, especially in the economically underdeveloped areas	This study clearly expound the sever situation of soil erosion in the 21th century and predict the soil pollution in 2030, making me realize that the treatment of heavy metal pollution is urgent. Meanwhile, the authors' mention of the pollution will be more serious in the undeveloped area also remind me that the seek of an efficient and cost-effective technology to solve the addressed problem is important.	https://www.nature.com/articles/s41467-017-02142-7#citeas	4	5	√

Super-Stable Mineralization of Ni2+ Ions from Wastewater using CaFe Layered Double Hydroxide	journal	Haoyuan Chi Jikang Wang Huijuan Wang Shaoquan Li Mufei Yang Sha Bai Changjuan Li Xiaoliang Sun Yufei Zhao Yu-Fei Song	Advanced Functional Materials, 2021, 32, pp. 2106645	2021	In this work, the authors report the application of a CaFe-LDH stabilizer which is capable of mineralizing of Ni with a maximum saturation removal capacity of 321 mg/g. Meanwhile, Song et al. firstly demonstrate the isomorphous substitution of CaFe-LDH during the mineralization process of Ni2+ by using ex-situ X-ray diffraction and X-ray absorption fine structure (XAFS) characterization.	This study demonstrates that the heavy metals can be efficiently mineralized through the isomorphous substitution process by using LDHs as mineralizer, which inspired me to use LDHs-based mineralizer to deal with other heavy metal pollutions in soil.	https://onlinelibrary.wiley.com/doi/10.1002/adfm.202106645	5	5	√
Supported catalysts based on layered double hydroxides for catalytic oxidation and hydrogenation: general functionality and promising application prospects	review	Junting Feng Yufei He Yanan Liu Yiyun Dua Dianqing Li	Chemical Society Reviews, 2015, 44, pp. 5291-5319	2015	Layered double hydroxides (LDHs) with the advantages of unique structure, composition diversity, high stability, ease of preparation and low cost have shown great potential in the design and synthesis of novel supported catalysts. This review summarizes the recent progress in supported catalysts by using LDHs as supports/precursors for catalytic oxidation and hydrogenation.	In this review, the authors introduce the fine structure of layered double hydroxides and its application in catalysis, which help me better understand the basic host-gust intercalation structure and the potential applications of layered double hydroxides.	https://pubs.rsc.org/en/content/articlelanding/2015/CS/C5CS00268K	4	5	√

Synergistic deep removal of As(III) and Cd(II) by a calcined multifunctional MgZnFe-CO3 layered double hydroxide: Photooxidation, precipitation and adsorption	journal	Junqin Liu Pingxiao Wu Shuaishuai Li Meiqing Chen Wentin Cai Dinghui Zou Nengwu Zhu Zhi Dang	Chemosphere, 225, pp. 115-125	2019	In this study, a high removal rate (>99.7%) of combined arsenite (As(III)) and Cd (Cd(II)) in low concentration (1000 μg/L) from contaminated water was achieved by a calcined MgZnFe-CO3 layered double hydroxide (CMZF) adsorbent. Meanwhile, the synergistic interaction among As(III) molecule, As (V) anion and Cd(II) cation in removal process is proposed. Moreover, the As(III) and Cd(II) in actual water were removed simultaneously and efficiently to satisfy drinking water provision.	In this work, the authors achieve the simultaneous removal of Cd and As in actual water by using MgZnFe-LDHs as absorbent. Particularly, the Fe ions in LDHs is capable of oxidating As(III) to As (V) under light irradiation. These results help me to better understand the minerlization mechanism of LDHs in the multiple heavy metal polluted water and inspired me that the Fe-based LDHs are expected to be an efficient mineralizer.	https://www.sciencedirect.com/science/article/pii/S0045653519304412?via%3Dihub	4	5	√
Highly Selective Photoreduction of CO2 with Suppressing H2 Evolution over Monolayer Layered Double Hydroxide under Irradiation above 600 nm.	journal	Ling Tan Si-Min Xu Zelin Wang Yanqi Xu Xian Wang Xiaojie Hao Sha Bai Chenjun Ning Yu Wang Wenkai Zhang Yun Kyung Jo Seong-Ju Hwang Xingzhong Cao Xusheng Zheng Hong Yan Yufei Zhao Haohong Duan Yu-Fei Song	Angewandte Chemie International Edition, 2019, 58, pp. 11543-11922	2019	In this work, the authors report a heterogeneous photocatalyst system consisting of a ruthenium complex and a monolayer nickel-alumina layered double hydroxide (NiAl-LDH), which act as light-harvesting and catalytic units for selective photoreduction of CO2 and H2O into CH4 and CO under irradiation with λ>400 nm. By precisely tuning the irradiation wavelength, the selectivity of CH4 can be improved to 70.3%, and the H2 evolution reaction can be completely suppressed under irradiation with λ>600 nm.	This work clearly shows the XRD patterns and FT-IR spectra of layered double hydroxides with different thickness, which help me verify whether the as-prepared MgFe-LDHs is synthesized successfully.	https://onlinelibrary.wiley.com/doi/10.1002/anie.201904246	5	5	√

Dual Engineering of Lattice Strain and Valence State of NiAl-LDHs for Photoreduction of CO_2 to Highly Selective CH_4	journal	Ling Tan Xiaoliang Sun Sha Bai Ziheng Song Yu-Fei Song	Small, 2023, 19, pp. 2205770	2023	In this work, the authors fabricated different surfactants ($C_{11}H_{23}COONa$, $C_{12}H_{25}SO_4Na$, $C_{16}H_{33}SO_4Na$) intercalated NiAl-layered double hydroxides (NiAl-LDH), resulting in the formation of LDH-S1 (S1 = $C_{11}H_{23}COO^-$), LDH-S2 (S2 = $C_{12}H_{25}SO_4^-$) and LDH-S3 (S3 = $C_{16}H_{33}SO_4^-$) with curved morphology. Compared with NiAl-LDH with a 1.53% selectivity of CH_4, LDH-S2 shows higher selectivity of CH_4 (83.07%) and lower activity of HER (3.84%) in CO_2 photoreduction reaction (CO_2PR).	This work introduce the synthesize method of layered double hydroxides and shows the SEM and TEM ofLDHs with intercalated ions, which help me verify whether the morphology of the as-prepared MgFe-LDHs is analogous with the reported literature.	https://onlinelibrary.wiley.com/doi/10.1002/smll.202205770	5	5	√
Controlling the Surface Hydroxyl Concentration by Thermal Treatment of Layered Double Hydroxides	journal	Christopher M. R.Wright Kanittika Ruengkajorn Alexander F. R. Kilpatrick Jean-Charles BuffetOrcid Dermot O'Hare*Orcid	Inorganic Chemistry, 2017, 56, pp. 7842-7850	2017	In this work, the authors report that the surface hydroxyl concentration of layered double hydroxides can be controlled by thermal treatment of these materials under vacuum, leading to hydroxyl numbers (αOH) similar to those of dehydroxylated silica, alumina, and magnesium hydroxide.	This work finely introduce hydroxyl groups on the surface of the layered double hydroxides and their application in catalysis, which inspire me that the abundant -OH groups on LDH can also provide ample binding sites for heavy metal minerlization.	https://pubs.acs.org/doi/10.1021/acs.inorgchem.7b00582	4	5	√

The use of chelating agents in the remediation of metal-contaminated soils: A review	journal	Domen Lestan Chun-ling Luo Xiang-dong Li	Environ. Pollut. 2008, 153, pp. 3.	2008	This paper reviews current remediation technologies that use chelating agents for the mobilization and removal of potentially toxic metals from contaminated soils. These processes can be carried out in situ as enhanced phytoextraction, chelant enhanced electrokinetic extraction and soil flushing, or ex situ as the extraction of soil slurry and soil column leaching. Finally, the treatment and secondary pollution of the chelating agent has been discussed.	This review discusses the advantages and disadvantages of the soil elution technology of soil remediation. The review shows that the resultant heavy metal-containing washing sewage often leads to the secondary pollution.	https://www.sciencedirect.com/science/article/pii/S0269749107005623?via%3Dihub	4	5	√
Super-stable mineralization of cadmium by calcium-aluminum layered double hydroxide and its large-scale application in agriculture soil remediation	journal	Xianggui Kong Ruixiang Ge Tian Liu Simin Xu Peipei Hao Xiaojie Zhao Zhenhua Li Xiaodong Lei Haohong Duan	Chemical Engineering Journal, 2021, 407, pp. 127178.	2021	This article report a CaAl-layered double hydroxide as an efficient stabilizer for Cd2+ in-situ immobilization both in lab scale and practice remediation. This material presents fast sorption rate (ca. 5 min) and high capture capacity (592 mg/g) towards Cd2+ in solution, and high immobilization efficiency (up to 96.9%) in soil remediation. The concept of Super-stable mineralization has been first proposed in the article.	This article confirms that LDH has a good mineralization performance towards Cd, which can provide a guidance for the design of my experiments.	https://www.sciencedirect.com/science/article/pii/S1385894720333052	5	5	√

Soil contamination in nearby natural areas mirrors that inurban greenspacesworldwide	journal	Yu-Rong Liu Marcel G A van der Heijden Judith Riedo Carlos Sanz-Lazaro David J Eldridge Felipe Bastida et al.	Nature Communications, 2023, 14, pp. 1706.	2023	There are many kinds of contamination similar levels of multiple soil contaminants (metal(loid)s, pesticides,microplastics, and antibiotic resistance genes) across the globe, however, the importance of human and natural factors in explaining soil contamination across contrasting ecosystems remains virtually unknown. So that the aritcle demonstrates the soil contamination in nearby natural areas mirrors that inurban green spaces worldwide.	In the article, the author points out human-driven soil contamination in nearby natural areas mirrors that in urban greenspaces globally, and highlights that soil contaminants have the potential to cause dire consequences for ecosystem sustainability and human wellbeing.	https://doi.org/10.1038/s41467-023-37428-6	5	5	√
Super-stable mineralization of Cu, Cd, Zn and Pb by CaAl-layered double hydroxide: Performance, mechanism, and large-scale application in agriculture soil remediation	journal	Zewen Sun Yiping Wang Tian Liu Xianggui Kong Tianzun Pan Fazhi Zhang Xiaodong Lei Xue Duan	Journal of Hazardous Materials, 2023, 447, pp. 130723.	2023	The synthesized CaAl-layered double hydroxide (CaAl-LDH) shows excellent performance in potentially toxic metals (PTMs) removal, with the high removal capacity of 502.4, 315.2 and 600.0 mg/g respectively towards Cu2+, Zn2+ and Pb2+ in aqueous solution. Also, the as-prepared CaAl-LDHs can mineralize the Cu2+, Zn2+ and Pb2+ in soil with the removal efficiency of 30.15 %, 67.30 % and 38.71 %, respectively.	This article illustrates that the mineralization technology turns out to be a reliable, safe and economical method in the remediation of Cu2+, Pb2+ and Zn2+ contaminated soil.	https://www.sciencedirect.com/science/article/pii/S0304389423000055	4	5	√

Highly Selective and Efficient Removal of Heavy Metals by Layered Double Hydroxide Intercalated with MoS_4-ion	journal	Lijiao Ma Qing Wang Saiful M. Islam Yingchun Liu Shulan Ma Mercouri G. Kanatzidis	Journal of the American Chemical Society, 2016, 138(8), pp. 2858-2866.	2016	The author synthesized the MgAl-MoS_4, which can rapidly lower the concentrations of Cu^{2+},Pb^{2+},Hg^{2+}, and Ag^{+} from ppm levels to trace levels of≤1 ppb. For the highly toxic Hg^{2+} (at 30 ppm concentration), the adsorption is exceptionally rapid and highly selective, showing a 97.3% removal within 5 min, 99.7% removal within 30 min, and 100% removal within 1 h.)	The article demonstrates the coordination and intercalation structures of MgAl-MoS_4 can promote the adsorption of heavy metal ions. The results can help us to understand the multiple interactions of the mineralization products in the host-guest structure of LDHs.	https://pubs.acs.org/doi/10.1021/jacs.6b00110	5	5	√
Remediation of heavy metal contaminated soil by asymmetrical alternating current electrochemistry	journal	Jinwei Xu Chong Liu Po-Chun Hsu Jie Zhao Tong Wu Jing Tang Kai Liu Yi Cui	Nature Communications, 2019, 10(1), pp. 2440.	2019	The article reports the design of a remediation method based on electrochemistry that achieves high degrees of contaminant removal for different heavy metals (copper, lead, cadmium), all reaching corresponding regulation levels for residential scenario after rational treatment time (from 30 min to 6 h). No excessive nutrient loss in treated soil is observed and no secondary toxic product is produced. Long-term experiment and plant assay show the high sustainability of the method and its feasibility for agricultural use.	The study proposes a new electrochemistry remediation method of heavy metal contaminated soil. Such method provides a fast and efficiency pathway to deal with the seriously polluted soil. However, However, considering the soil is a poor conductor of electricity and the high cost of constructing alternating current electric field, the electrochemistry technology is not suitable for of large-scale application.	https://www.nature.com/articles/s41467-019-10472-x?utm_source=xmol&utm_medium=affiliate&utm_content=meta&utm_campaign=DDCN_1_GL01_metadata	5	5	√

Layered double hydroxides: Scale production and application in soil remediation as super-stable mineralizer	journal	Fangqi Mao Peipei Hao Yuquan Zhu Xianggui Kong Xue Duan	Chinese Journal of Chemical Engineering, 2022, 41, pp. 42-48.	2021	This work mainly focused on the scale production strategy of LDHs with low-cost, and its application in soil remediation. Besides, several key challenges in using LDHs as amendments for immobilization of heavy metal ions are presented.	This mini-review shed light on the applications of LDHs in the remediation of heavy metal contamination. Also, the review proves the feasibility of the design of my experiments.	https://www.sciencedirect.com/science/article/pii/S1004954121005036	3	5	√
A critical review on the phytoremediation of heavy metals from environment: Performance and challenges	journal	Xing Shen Min Dai Jiawei Yang Lin Sun Xiao Tan Changsheng Peng Imran Ali d Iffat Naz	Chemosphere,2022, 291, pp. 132979.	2022	The review mainly focuses on the exploration of different forms of heavy metals in plants, which can help to explore appropriate disposal methods. Meanwhile, according to the challenges of phytoremediation, the author put forward some views and recommendations for the sustainable and rapid development of phytoremediation technology.	The study proves that the phytoremediation technology has been considered as an efficient technology in soil treatment. However, the phytoremediation method normally takes long operation time. Hence, this work reminds me to focus on the advantages and disadvantages of the various remediation technologies, in order to find a most suitable remediation methods towards different working conditions.	https://www.sciencedirect.com/science/article/pii/S0045653521034512	3	5	√

How to prevent soil pollution in the future	video	——	CCTV 2	2020 8 30	In the video, Mr. Zhu Zhu, academician of the Chinese Academy of Engineering and expert in environmental engineering, as the keynote speaker, discussed how to prevent soil pollution in China in the future from four aspects: pollution prevention, establishing a risk management platform, and the help of science and technology to ensure soil safety and constantly check shortcomings and fill gaps. He proposed that China should use natural ecological methods to control heavy metal pollution, and conduct large-scale data management to count and predict soil pollution. At the same time, it is also necessary to carry out coordinated remediation, and do a good job of multi-media remediation of water, soil and air. It is necessary to adjust the layout of soil, plan the use of soil, adhere to the concept of green development, and protect the environment.	As an academician of the Chinese Academy of Engineering and an expert in environmental engineering, the speaker of this video has made considerable achievements in the field of environment and enjoys a high reputation, which makes his speech highly credible. The specific description of the four aspects makes people have a clear understanding of the current status and limitations of soil pollution control in China. The speech mentioned two treatment methods for moderate and mild heavy metal contaminated soil, using phytoremediation and mineralization technology respectively, which provided help for my research. It supplemented my knowledge of phytoremediation and made me realize that a combination of pollution treatment techniques can sometimes achieve better results.	https://tv.cctv.com/2020/08/30/VIDEQ4tsnNNJV2pVZxoyO4Un200830.shtml	4	5	√

Appendix C Mindmap