

***In situ* nanoconfinement catalysis for highly efficient redox transformation**

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ABSTRACT

The rapid reduction of Cr(VI) across a wide pH range, from acidic to alkaline pH conditions, to stable Cr(III) species for efficient remediation of Cr(VI) pollution has long been a challenge. Herein we propose a new concept of *in situ* nanoconfinement catalysis (iNCC) for highly efficient remediation of Cr(VI) by growing nanosheets of *in situ* layered double hydroxide (iLDH) on the surface of Al-Mg-Fe alloy achieving chemical reduction rates of >99% in 1 min from pH 3 to 11 for 100 mg L⁻¹ Cr(VI) with a rate constant of 201 h⁻¹. In stark contrast, the reduction rate is less than 6% in 12 h with a rate constant of 0.77 h⁻¹ by the pristine Al-Mg-Fe alloy. The ultrafast reduction of Cr(VI) is most likely attributed to the synergistic catalysis of Al₁₂Mg₁₇, Al₁₃Fe₄ and nanoconfinement of MgAlFe-iLDH and super-stable mineralization of Cr(III) by MgAlCr^{III}- and MgFeCr^{III}-iLDHs. This study demonstrates potentials of *in situ* nanoconfinement catalysis on redox transformation for environmental remediation.

Keywords: *In situ* layered double hydroxide; Hexavalent chromium reduction; Nanoconfinement catalysis; Al alloy intermetallics.

1. Introduction

Cr(VI) is a typical, highly toxic pollutant that is mobile in the environment. Chemical reduction of Cr(VI) to Cr(III) using zerovalent reactive metals Fe, Mg and Al has been extensively investigated for the remediation of Cr(VI)-contaminated groundwater and soil¹⁻⁴. It has been recognized that Fe⁰ has limitations of fast agglomeration, poor mobility, rapid passivation at pH above 4 and secondary contamination⁵⁻⁷ and the electron efficiency (selectivity) of Mg⁰ and Al⁰ is poor. Additional challenge encountered in Cr(VI) remediation is the oxidation of Cr(III) back to Cr(VI) by oxygen and/or manganese oxides and microbial action in the presence of Fe and natural organic matters (NOM)⁸⁻¹². The product of Cr(VI) reduction in real scenarios is Cr(III)-Fe(III) hydroxides/oxyhydroxide (Cr_{1-x}Fe_x(OH)₃) due to the ubiquitous presence of Fe in the environment^{9, 11, 13}. Studies have demonstrated that Cr(III) oxidation increases proportionally with the Fe/Cr ratio of Cr_{1-x}Fe_x(OH)₃¹⁰ and the generation of more stable Cr(III) minerals than Cr_{1-x}Fe_x(OH)₃ may potentially minimize Cr(III) oxidation¹².

LDH is an anionic clay with a highly adjustable brucite-like layered structure and its molecular formula is $[M_{1-x}^{II}M_x^{III}OH_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metal cations and Aⁿ⁻ is an anion in the interlayer space. LDH has been widely studied for environmental remediation and industrial catalysis owing to its high surface area, basicity, tunability and anion exchange capacity^{14, 15}. The solubility constant (K_{sp}) of LDH is typically 20-30 orders of magnitude lower than their hydroxide counterparts (e.g., the K_{sp} of MgAl-LDH, Mg(OH)₂ and Al(OH)₃ is 7.6×10⁻⁵³, 1.2×10⁻¹¹ and 6.3×10⁻¹⁹, respectively¹⁶⁻¹⁸). Therefore, Cr(III)-bearing LDH is expected to be much more stable than Cr(OH)₃ and Cr_{1-x}Fe_x(OH)₃ and retarded rates of Cr(III) oxidation can be anticipated. LDH is of high affinity and adsorption capacity for chromate relative to other anion ions such as NO₃⁻, CO₃²⁻, etc., and has been investigated for adsorption of Cr(VI) and Cr(III)^{14, 19}. However, conventional LDH is not able to provide electrons for Cr(VI) reduction and the lattice doping of Cr(III) into

conventional LDH is slow ²⁰.

The selectivity and reactivity are the major considerations in reductive transformation of contaminants in aqueous environment due to the competition of electrons between hydrogen ions and the contaminants ²¹. It has been observed that the reaction rate of a chemical reaction is significantly improved if the reaction is confined to a nanoscale space and a new concept of nanoconfinement catalysis is therefore proposed ^{22, 23}. LDH has been extensively investigated in chemical catalysis and now it is recognized that the two-dimensional interlayer nanoscale space of LDH is the major account for its catalysis effect ²⁴. Incorporating Fe(II) into the LDH's lattice and/or loading reductive materials such as nano-scale zerovalent iron (nZVI) onto LDH are effective for redox transformation of organic and inorganic contaminants including Cr(VI) ^{25, 26}. Nevertheless, the unique structure of Fe(II)-LDH collapses when the crystallized Fe(II) is oxidized ^{27, 28} and the nZVI's reactivity is significantly compromised due to the abundant OH⁻ groups of LDH in the system of nZVI/LDH ²⁹.

Alloy's intermetallic compounds are found to improve the electron transfer rate and selectivity of redox transformations ^{24, 30} and the adsorption of contaminants by *in situ* LDH (*i*LDH) is more efficient than conventional pre-made LDH while Al-Mg alloys are able to produce *i*LDH ³¹. The intermetallic Al₁₂Mg₁₇ was observed to improve the reduction efficiency of Ni²⁺ by Mg metal ³² and Al₁₃Fe₄ is a highly stable isolated iron-containing ensemble, which has a catalytic effect similar to Pd for the selective hydrogenation of C₂H₂ ^{33, 34} and catalyzes chemical reduction of nitrate, butadiene and chlorophenols ³⁵⁻³⁸. In this article, we propose a new concept of *in situ* nanoconfinement catalysis (*i*NCC) for ultrafast reduction of Cr(VI) and rapid immobilization of Cr(III) by growing nanosheets of *i*LDH laminates on the surface of Al-Mg and Al-Mg-Fe alloys. CrO₄²⁻ anions can be intercalated in between the *i*LDH laminates ³⁹ and the intermetallics serve as a dual-function material by providing electrons and catalyzing Cr(VI) reduction in tandem with *i*LDH (Fig. 1a). As such, the alloy and its intermetallics with *i*LDH could be an efficient heterojunction structural catalyst with abundant grain boundary,

interfaces and defects. The positive charged surface of nano-LDH laminates may provide an express pathway for hydrated electrons towards CrO_4^{2-} in a nanoconfinement space while super-mineralization of resultant Cr(III) could be achieved by *i*LDH's crystallization.

2. Materials and methods

The pretreatment experiments of the alloys were carried out in sealed glass vials. First, 50 mL pH 2 HCl solution was pumped into the glass containing 0.1 g of 200-mesh Al-Mg-Fe alloy using a peristaltic pump. Subsequently, the solution was reacted at 60 °C under water bath heating for 12 h and then left to room temperature to measure the ion concentration and pH of the solution. The removal experiments were performed by adding the same volume of Cr(VI) stock solution (200 mg L⁻¹) to pretreatment system. The solution pH, metal and Cl ions concentration were determined during the treatment. At the end of the reaction, the solution was centrifuged and separated, and the solid product was dried under vacuum at 60°C for 12 h to obtain the dried product. The experiments were repeated for 3 groups to minimize errors. Detailed information of chemicals and analytical methods are provided in the Supporting Information.

3. Results and discussion

3.1. Comparison of Al-Mg, Al-Fe and Al-Mg-Fe alloys

The proposed concept of *i*NCC as illustrated in Fig. 1a was investigated for Cr(VI) reduction by Al-Fe, Al-Mg and Al-Mg-Fe alloys. Al-Fe and Al-Mg alloys consist of intermetallic compound $\text{Al}_{13}\text{Fe}_4$ and $\text{Al}_{12}\text{Mg}_{17}$, respectively (Fig. 1b) and pretreating Al-Mg and Al-Mg-Fe alloys with pH 3 HCl produces one-dimensional nanosheets of LDH on the surface (Fig. 1c-h) while no LDH is observed on Al-Fe alloy. After the reaction of LDH surface modified Al-Mg-Fe alloy surface with $\text{K}_2\text{Cr}_2\text{O}_7$ solution, the FWHM of (003) reflection of LDH decreased from 1.50° to 1.04° indicating that the LDH's crystallinity is improved while the crystallite size in the c direction becomes smaller (Fig. 1d).

The removal rate of 25 mg L⁻¹ Cr(VI) at initial pH 3 in 12 h by the three alloys without pretreatment is 43%, 56% and 96% (Fig. 1i). By stark contrast, Cr(VI) reduction rate by pretreated Al-Mg-Fe alloy using pH 3 HCl solution reaches 99% in 3 min where the rate constant was increased by 200 times (155 h⁻¹ versus 0.77 h⁻¹) (Fig. 1j). The initial rate of Cr(VI) removal by pretreated Al-Mg and Al-Fe alloys in the beginning 5 min was also improved but the overall rate of Cr(VI) removal was not improved significantly. The pH, Mg²⁺ and Al³⁺ concentrations during Cr(VI) reduction by pristine and pretreated alloys are shown in Fig. 2. The pH was increased rapidly from 3 to 9 in 1 h for pristine Al-Mg and Al-Mg-Fe alloys and then slowly increased to 10 in the following 11 h (Fig. 2a). In contrast, the pH was increased from 3 to 4.3 in 1 h and then almost unchanged afterwards in the case of pristine Al-Fe alloy. The concentration of Mg²⁺ and Al³⁺ ions peaked at the beginning and then decreased rapidly (Fig. 2b, c), due to the *in situ* formation of LDH for Al-Mg and Al-Mg-Fe alloys during Cr(VI) reduction (refer to Fig. 1 g). In the case of pretreated three alloys, the pH is approximately 10, 8.3 and 5.2 for Al-Mg-Fe, Al-Mg and Al-Fe, respectively. The solution pH did not change significantly when the solution was mixed with Cr(VI) solution at pH 3 (Fig. 2d). This phenomenon can be explained by the pre-growing LDH's capacity of resisting hydrogen ions. The monotonous decrease of Mg²⁺ and Al³⁺ concentrations (Fig. 2e, f) is the result of *in situ* formation of new LDH with Cr(III). Clearly, pre-growing nanoscale *i*LDH on the alloy's surface is important to improve the Cr(VI) reduction rate (refer to Fig. 1i, j)

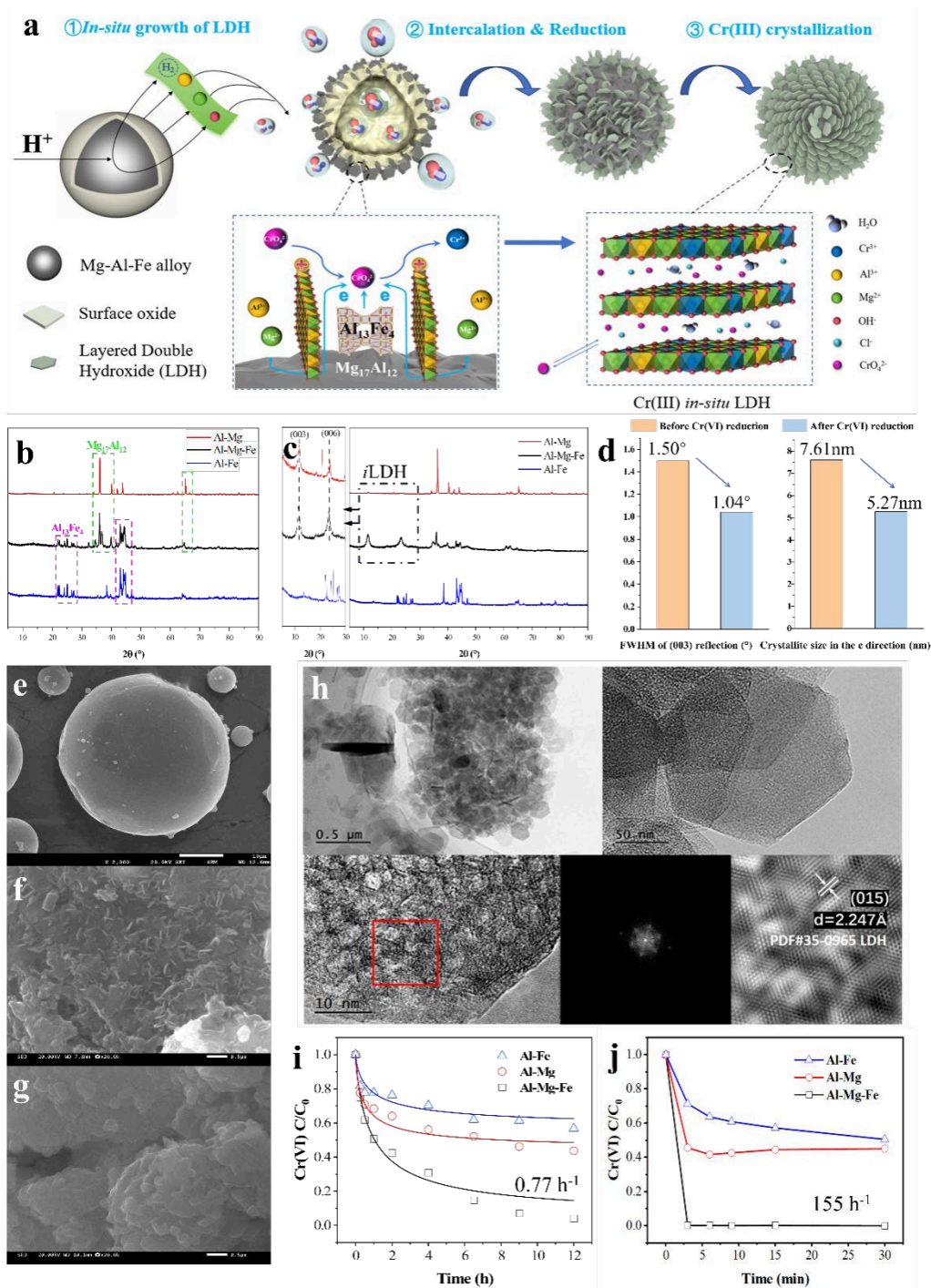


Fig. 1. Chemical reduction of Cr(VI) by Al alloys. (a) Schematic illustration of Cr(VI) reduction by *in-situ* nanoconfinement catalysis (*iNCC*) of MgAlFe-*i*LDH; (b) XRD characterization of pristine Al-Fe, Al-Mg and Al-Mg-Fe alloys; (c) XRD characterization of the three alloys after pretreatment; (d) Lattice parameters of *i*LDH before and after Cr(VI) reduction; (e) SEM of Al-Mg-Fe alloy; (f) SEM of MgAlFe-*i*LDH; (g) SEM of MgAlFe-*i*LDH after Cr(VI) reduction. (h) TEM of MgAlFe-*i*LDH; (i) Cr(VI) concentration ratio C/C_0 by different alloys; (j) Cr(VI) concentration ratio C/C_0 by different alloys after pretreatment. $Cr(VI) C_0 = 25\text{ mg L}^{-1}$.

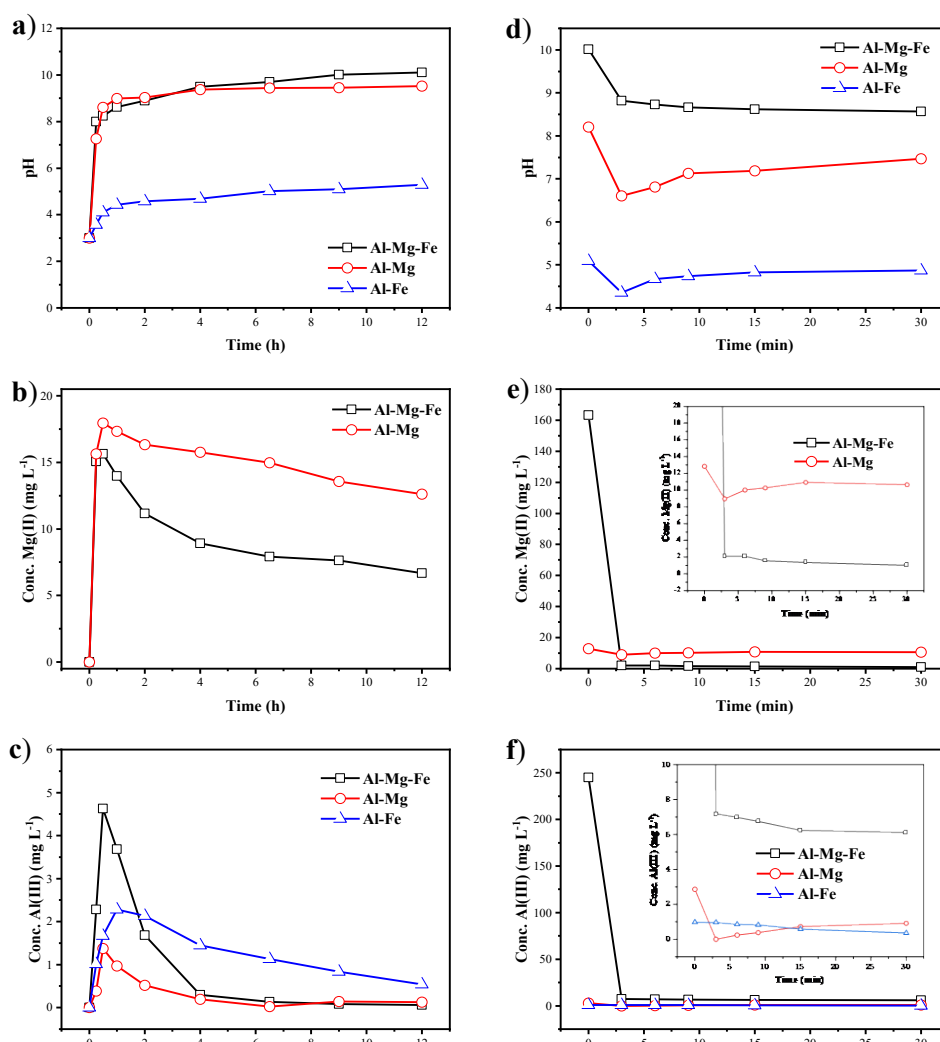


Fig. 2. pH, Mg^{2+} and Al^{3+} concentrations as a function of time during $Cr(VI)$ reduction by (a-c) pristine and (d-f) pretreated Al-Mg, Al-Fe and Al-Mg-Fe alloys. Pretreatment: pH 3 HCl, 60 ± 0.5 °C, magnetic stirring 300 rpm, 12 h; $Cr(VI)$ reduction: initial $Cr(VI)$ concentration 25 mg L⁻¹, initial pH 3, alloy dosage 10 g L⁻¹, room temperature.

3.2 Effect of initial pH of pretreatment solution

Results outlined in Table S1 display the final pH of the treating solution and the concentrations of leached metal ions. Upon pretreatment with HCl at pH 0.5 and 1.0, the solutions were clear, with minimal tiny particle residues, and the pH values increased to 1.3 and 4.1, respectively. Elevated concentrations ranging between 156-380 mg L⁻¹ for Al, Mg, and Fe ions suggest substantial dissolution of the alloy in these cases. Contrastingly, when employing pH 2 and 3 pretreating solutions, the treating solutions become visibly turbid, and the pH values shift towards alkalinity (pH > 8). The concentrations of dissolved Al, Mg, and

Fe ions remained below 10 mg L⁻¹, indicating limited dissolution of the alloy under these conditions.

Upon introducing Cr(VI) into the pH 0.5 pretreated alloy system, the solution turned immediately to light green. In contrast, the pH 1 pretreated alloy system produced yellow-brown suspension. After 2-h reaction, the pH values reach 1.8, 3.7, 7.7 and 10.3 (Fig. S1a) and the concentrations of Cr(VI), total Cr and Cr(III) were 0, 94.7 and 94.7 mg L⁻¹ in Fig. S1b-d. Cr(VI) reduction reaches >99% within 1 min at pH 0.5 and pH 1.0 pretreatment, with no further reduction observed subsequently (Fig. S1b). The removal efficiency of total Cr [Cr(T)] in the pH 2 and 3 pretreatments corresponded closely to the reduction of Cr(VI), while the removal of Cr(T) is not observed in the cases of pH 0.5 and 1.0 pretreatment (Fig. S1b, c). This is mainly due to the complete reduction of Cr(VI) to Cr(III) at pH 2 and 3 pretreatment systems, leading to its precipitation from the solution. In contrast, Cr(III) remained dissolved in the pH 0.5 and 1.0 pretreatment systems, where the final pH is acidic pH 1.3 and 4.1 (Fig. S1a and Table S1).

3.3 Effect of pretreatment time

The above section has demonstrated that lower pH of the pretreating solution consumes more alloy and thus produces more *i*LDH. For the sake of Cr(VI), an ultrathin layer of *i*LDH on the alloy's surface is expected to be sufficient. Therefore, the effect of the pretreatment time using pH 3 HCl was investigated (Table S2 and Fig. S2). After 1-12 h pretreatment, the final pH was between 8.6 and 9.5 and Al and Mg ion concentrations decrease with increasing pretreatment time, indicating the progressing formation of *i*LDH. The area of the pristine Al-Mg-Fe alloy's smooth surface decreases with increasing the pretreatment time and the smooth surface disappears after 3 h pretreatment. *i*LDH grows perpendicularly on the surface and the surface morphology changes significantly after Cr(VI) reduction (Fig. 1e-g and Fig. S3), indicating that Cr(VI) reduction may cause the transformation of *i*LDH by the Cr(III) substitution. Interestingly, the smooth surface of unpretreated Al-Mg-Fe alloy still exists after

its reaction with Cr(VI) despite that the formation of petaloid *i*LDH is observed on the surface (Fig. 3b and Fig. 3e, f). The XPS characterization (Table S3) shows that the ratio of Cr(III)/Cr(VI) increases with prolonged pretreatment time, reflecting that the absorbed amount of Cr(VI) decreases. The XRD characterization reveals that the diffraction peak intensities of Mg, Al₁₂Mg₁₇ and Al₁₃Fe₄ decline with increasing pretreatment time and the amount of *i*LDH increases (Fig. 3a). The increase of *i*LDH is also supported by the significant increase of O concentration (Table S4). Due to the order of galvanic corrosion in Al-Mg-Fe alloy's micro-cell system, Al₁₃Fe₄ is still well preserved after pretreatment.

The structural parameters of *i*LDH after pretreatment and Cr(VI) reduction are given in Table 1. The average crystallite size in the *c* direction of *i*LDH after reduction increases from 3.78 nm at 1 h pretreatment to 5.27 nm at 12 h pretreatment, indicating that the pretreatment time affects the growth and structure of *i*LDH during Cr(VI) reduction. Based on the characteristic peaks observed for crystal faces (003) and (006), the average crystallite size of *i*LDH after 12 hours of pretreatment is estimated to be 7.61 nm and reduced to 5.27 nm after Cr(VI) reduction. The FT-IR characterization (Fig. 3c, d) shows that the vibration of each absorption peak by 12 h pretreatment is strongest, further confirming that the amount of *i*LDH increases with increasing pretreatment time as observed by XRD. The vibration absorption peaks at 3698 cm⁻¹ and 448 cm⁻¹ are the Mg-OH bond and the peak near 557 cm⁻¹ is the Al-OH bond ⁴². These peaks are reduced after the Cr(VI) reduction. The vibration absorption peaks of Fe-O-Mg ⁴³ and Mg-Cr-O ⁴⁴ at 784 cm⁻¹ and 673 cm⁻¹ indicate the presence of MgFe- and MgCr- hydroxides or LDHs while the Cr-O peak at 882 cm⁻¹ is the reflection of CrO₄²⁻ intercalation into the LDH layers ⁴⁵. Therefore, the changes in the crystallite parameters after Cr(VI) reduction are most likely due to the substitution of Cr(III) in the *i*LDH, i.e., the generation of Cr(III)-containing LDH, e.g, MgAlCr^{III}-, MgFeCr^{III}- and/or MgCr^{III}- LDHs.

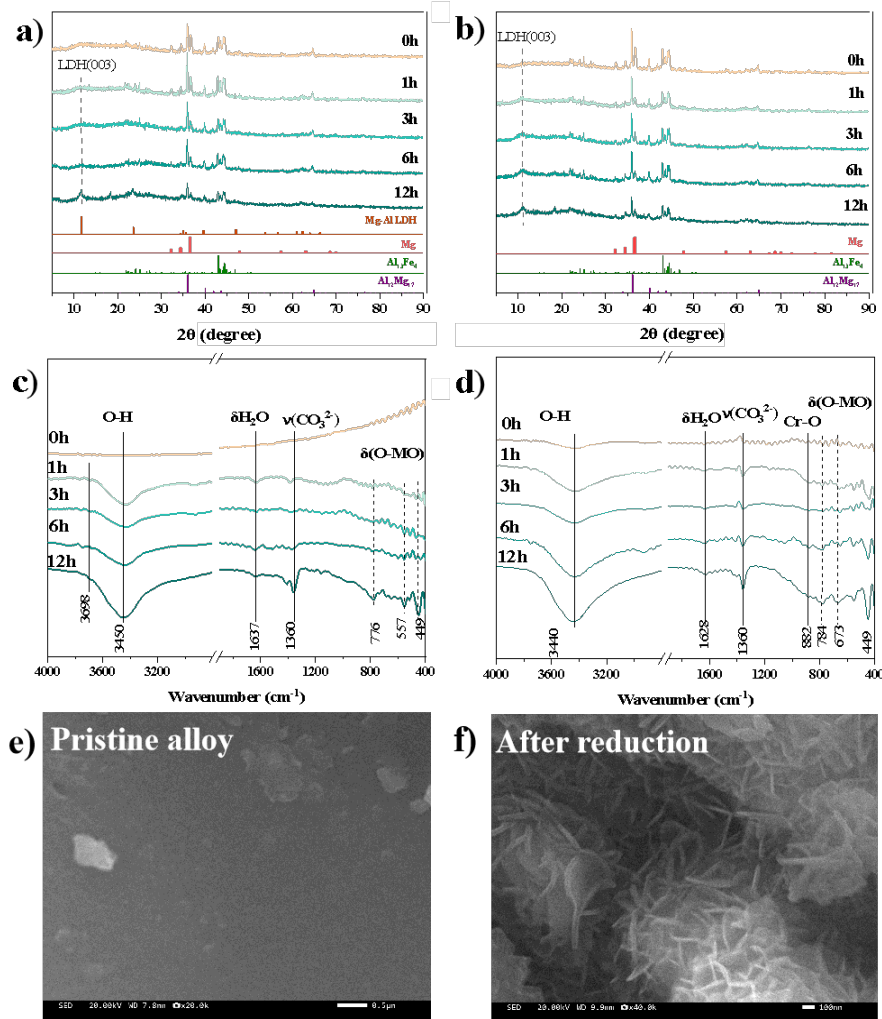


Fig. 3. Effect of pretreatment time (0-12 h) and Cr(VI) reduction on Al-Mg-Fe alloy's surface *i*LDH. **(a)** XRD characterization of *i*LDH before and **(b)** after Cr(VI) reduction; **(c)** FT-IR characterization before and **(d)** after Cr(VI) reduction; **(e)** SEM characterization of pristine alloy before and **(f)** after Cr(VI) reduction. Pretreatment: pH 3 HCl, 60 ± 0.5 °C, magnetic stirring 300 rpm. 2 g L^{-1} Al-Mg-Fe alloy, 100 mg L^{-1} Cr(VI), initial pH 4.5.

Table 1 XRD structure parameters of Al-Mg-Fe alloy's *i*LDH with different pretreatment time (1, 3, 6 and 12 h) before and after Cr(VI) reduction

LDH structure parameters	After Cr(VI) reduction				Before reduction
	1 h	3 h	6 h	12 h	12 h
d_{003} (Å)	7.93	8.02	8.03	7.95	7.84
2θ (003)	11.15	11.03	11.00	11.12	11.58
FWHM of (003) reflection (°)	2.09	1.97	1.78	1.50	1.04
Lattice parameter c (nm)	2.38	2.41	2.41	2.39	2.35
Crystallite size in the c direction (nm)	3.78	4.01	4.44	5.27	7.61

As discussed above, *i*LDH formation is important to Cr(VI) reduction. MgAlCr-CrO₄²⁻-LDH has also been investigated as an efficient catalyst for photocatalytic degradation of organic pollutants⁴⁶. Therefore, the ageing of *i*LDH (23 h and 36 h) was also investigated.

Clearly, increasing ageing time from 0 to 36 h increases the removal rate of Cr(VI) from 95% to >99% (Fig. S4) and improves the transformation of Al(OH)₃ into stable octahedral MgAl-*i*LDH (Fig. S5). The pH, Mg and Al ion concentration and their ratio, reaction temperature and ageing time are the key parameters to the formation of LDH in the coprecipitation process, where the initial concentration of Mg²⁺ and Al³⁺ and their ratio are critical to LDH nucleation. Generally, the optimal parameters are pH 9-10, Mg²⁺/Al³⁺ ratio 2-4, temperature 60-80 °C and ageing time 12-24 h⁴⁷⁻⁴⁹. In the present system, Mg and Al ions concentration in the pretreating solution increases from zero to a peak and then declines when *i*LDH is generated.

3.4 Effect of pretreatment acids (HCl, H₂SO₄, H₃PO₄)

The interlayer spacing of LDH is important in the adsorption capacity of CrO₄²⁻⁵⁰ while the counterparts of anions (e.g., PO₄³⁻, SO₄²⁻, CO₃²⁻ and Cl⁻) affect the adsorption of CrO₄²⁻⁵¹. Moreover, the etching effect of acid on the alloy significantly influences the nucleation of *i*LDH on its surface during the reaction with Cr(VI). The removal rates of Cr(VI) by pretreated alloy using dilute HCl, H₂SO₄ and H₃PO₄ (pH 2) were 95%, 38% and 1%, respectively (Fig. S6b). No LDH is generated in the case of H₃PO₄ pretreatment (Fig. S6c) and the amount of *i*LDH produced by H₂SO₄ pretreatment (Fig. S6d) is much less than that by HCl pretreatment (Fig. 1c). The low Cr(VI) removal rates by H₃PO₄ and H₂SO₄ pretreatment is most likely owing to the deactivation by the formation of MgHPO₄(H₂O)₃ and CrO(OH). The H₃PO₄ pretreatment has been extensively employed to improve corrosion resistance of AZ31 Mg alloy⁵² and deactivates Cr(VI) reduction by Al metal due to the formation of AlPO₄⁵³. Cl⁻ is notorious in surface pitting corrosion of metals and alloys, particularly when the solution is acidic as H⁺ ions etch the surface of the metal to create defects⁵⁴. The specific surface area of Al-Mg-Fe alloy is increased from 2.06 m² g⁻¹ of alloy to 17.99 m² g⁻¹ after pH 2 HCl pretreatment for 12 h. The “armour” structure of *i*LDH on the surface of Al-Mg-Fe alloy produces many edge interfaces and grain boundary to improve electron transfer from the alloy to Cr(VI).

3.5 Effect of initial pH of Cr(VI) solution

Cr(VI) species are mainly in the form of HCrO_4^- in pH 1-6 and the free energy of HCrO_4^- is higher than that of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Consequently, electrostatic attraction of Cr(VI) species is stronger in an acidic environment⁵⁵ and Cr(VI) reduction is much more favorable in acidic pH than in alkaline pH. After pretreatment using pH 2 HCl, the solution pH of the Al-Mg-Fe alloy system is 7.3 and then the Cr(VI) solutions at three initial pH values (4.5, 7 and 11) were added. Fig. 4 shows the solution pH and Cr(VI) concentration profiles. For comparison, the pristine alloy reacting with these three pH Cr(VI) solutions was conducted. The finished pH values of pretreated alloy system are 7.1, 7.7 and 8.8 after 2 hours of reaction (Fig. 4a) and greater than 91% of Cr(VI) are removed by pretreated alloy within 1min in different pH environments (Fig. 4b). In stark contrast, Cr(VI) reduction is almost zero, even at pH 4.5 by the pristine alloy.

The XRD and FT-IR characterizations of pretreated Al-Mg-Fe alloy reacting with Cr(VI) solutions with three initial pH values (4.5, 7 and 11) are shown in Fig. 4c, d and the structural parameters of the resultant *i*LDHs are given in Table S5. The crystallite size in the *c* direction of *i*LDH in the initial pH 4.5 is 5.23 nm and the size increases with increasing the initial pH value while other parameters do not change significantly. The intercalation of CrO_4^{2-} between layers of *i*LDH is confirmed (Fig. 4d, 887 cm^{-1}) and the distribution of Cr on the surface (Table 2 and Fig. 4e) reveals higher amounts of Cr(III) produced at lower pH. Upon addition of acidic Cr(VI) solution, local accumulation of H^+ may trigger the decomposition of *i*LDH in part and therefore, increases the exposure of the alloy to Cr(VI), thereby enhancing electron transfer, releasing OH^- and promoting reassembly of *i*LDH. XRD characterization (Fig. 4c and Table S5) demonstrates higher interlayer charge density and narrower half-peak width of *i*LDH at initial pH 7 and 11 than at initial pH 4.5. At initial pH 4.5, 7 and 11, the half-peak width of *i*LDH is 1.51° , 1.22° and 1.17° respectively. The corresponding crystallite size in the *c* direction is 5.23, 6.46 and 6.76 nm. The higher interlayer charge density and narrower half-

peak width reflect better crystallinity of *i*LDH generated at neutral and alkaline pH than at acidic pH. The XRD characterization also indicates the presence of intermetallic $\text{Al}_{12}\text{Mg}_{17}$ and $\text{Al}_{13}\text{Fe}_4$ after Cr(VI) reduction. It is believed that the reduction rate of $>99\%$ for $25\text{--}100\text{ mg L}^{-1}$ Cr(VI) in 1 min from acidic to alkaline pH is most likely due to the effect of *i*NCC. In general, the reduction rate of Cr(VI) decreases with the increase of solution pH. The reduction rate of 2.1 mg L^{-1} Cr(VI) at pH 2 by ZVMg is 99% in 30 min, which is less than 50% at pH 7 even in an extended period up to 5 h⁵⁶. Nano-scale Fe^0 was observed on the surface of the material after reaction when the initial pH of the Cr(VI) solution was alkaline (Fig. 4f).

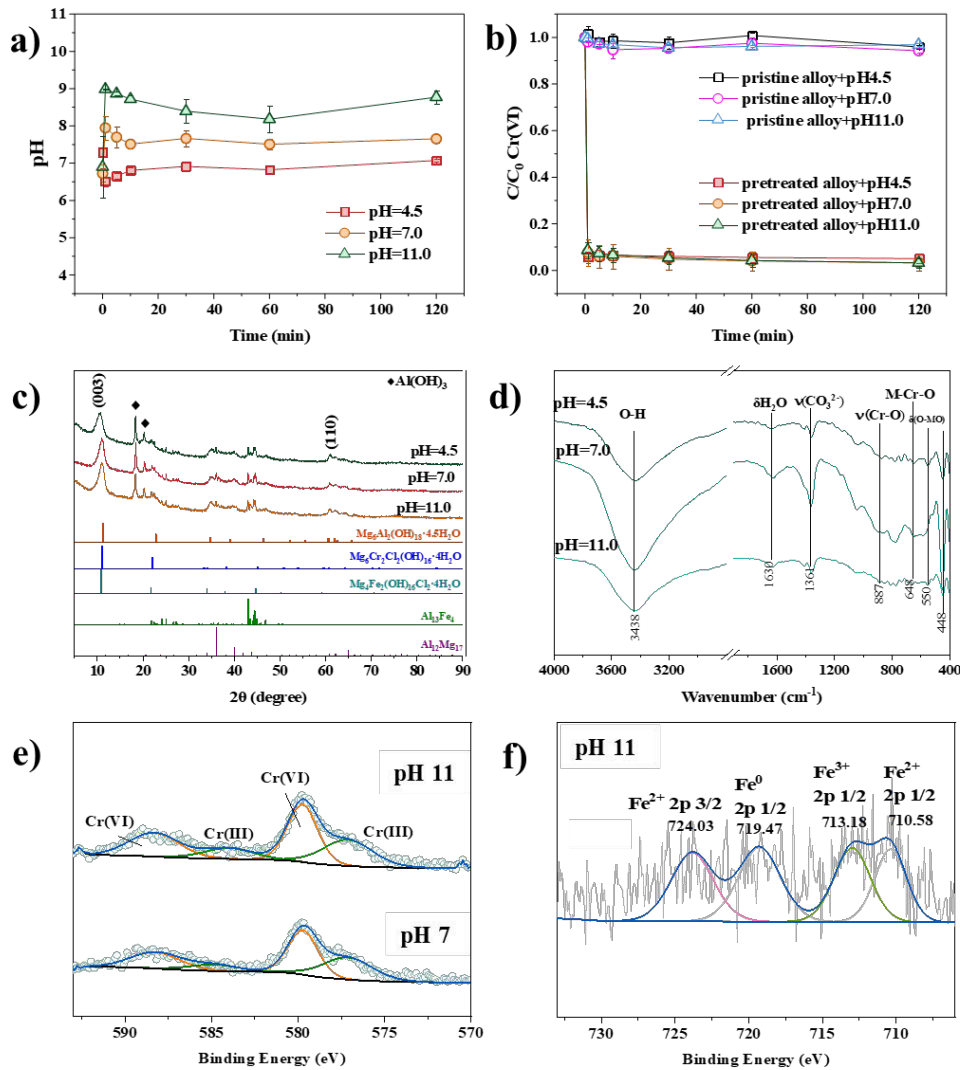


Fig. 4. Effect of initial pH (4.5, 7.0, 11.0) of Cr(VI) solution. (a) pH as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 , (c) XRD and (d) FT-IR characterization of Al-Mg-Fe alloy's *i*LDH after Cr(VI) reduction, XPS characterization of (e) Cr 2p high resolution spectra at pH 7 and pH 11 and (f) Fe 2p high resolution spectra at pH 11. Initial Cr(VI) concentration 100 mg L^{-1} , 1 g L^{-1} Al-Mg-Fe alloy.

Table 2 Area of Cr 2p XPS after Cr(VI) reduction at different initial pH

Cr(VI) pH	Area (CPS. eV)		
	Cr(III)	Cr(VI)	Cr(III)/Cr(VI)
4.51	10850	13525	0.80
7.05	8827	13267	0.67
11.01	11473	18208	0.63

3.6 Effect of Cr(VI) concentration

The pH and Cr(VI) and other metal concentrations with different initial Cr(VI) concentrations (pH 4.5) are shown in Fig. S7. After the pretreatment, the pH of MgAlFe-*l*LDH system is 8.5 and it turns to 7.8, 7.9 and 8.0 when reacting with 100, 200, 300 mg L⁻¹ Cr(VI) for 18 h, respectively. The removal rate within 1 min is 99%, 56% and 45% respectively and the maximum removal capacity of Cr(VI) is estimated to be 118.7 mg g⁻¹. In stark contrast, 0.1g L⁻¹ nZVI@Mbenes required 8 h to achieve 84% removal of 10 mg L⁻¹ Cr(VI) and the removal rate capacity was 68.6 mg g⁻¹ ⁵⁷. The concentration of dissolved Al, Cr(T) and Fe ions is below 0.4 mg L⁻¹. Mg²⁺ concentration increases with increasing initial Cr(VI) concentration to 25, 50 and 65 mg L⁻¹ within the beginning 1 h and then does not change significantly during the following reaction time of 17 h (Fig. S7d). This demonstrates that the alloy's corrosion rate increases with the increase of Cr(VI) concentration and as a result, more *l*LDH and hydroxides are produced, leading to low concentrations of soluble trivalent metal ions (Al and Cr), and the alloy's surface is then passivated to a larger extent at higher Cr(VI) concentration. Mapping and EDS characterization (Fig. S8) shows that the atomic proportion of O, Fe and Cr in the surface of the alloy increases with the initial concentration of Cr(VI) supporting this passivation inference. Indeed, high concentrations of Cr(VI) aggravated the precipitates of Cr(III) hydroxides, which passivated the surface of nZVI ⁵⁸. The passivation was also observed in Cr(VI) reduction by Al-Fe alloys ⁵⁹.

3.7 Effect of Cr(VI) reaction time

Fig. 5a shows that 95% of Cr(VI) reduction (100 mg L^{-1}) is achieved within 1 min and then the reduction slowly increases to >99.9% by 72 h. The pH of the solution stabilizes at around 7.7 after 1 min reaction (Fig. 5a) while Mg ion concentration increases linearly with reaction time to 37 mg L^{-1} in 28 h and then remains unchanged by the end of 72 h reaction (Fig. 5b). In contrast, Al and Fe ions reach 6.8 and 1.6 mg L^{-1} , respectively at 0 min and then decline to $< 0.2 \text{ mg L}^{-1}$ by 28 h. The Cr(VI) reduction process is in a pseudo first-order (PFO) reaction with a rate constant $k = 201.6 \text{ h}^{-1}$ (Table S6). To the best of our knowledge, such a rapid rate of >99% Cr(VI) reduction in 1 min for 100 mg L^{-1} from acidic to alkaline pH has not been found. For example, the removal efficiency of 10 mg L^{-1} Cr(VI) in 2 h at initial pH 5 by rGO/nZVI was 99.5% and its PFO constant was 13.68 h^{-1} ⁶⁰. A comparison for different materials (zerovalent Al, nZVI, Green Rust) reported in the literature and our results is given in Table S7. Clearly, our material MgAlFe-*i*LDH outperforms other materials significantly. The kinetic data fitted well with both PFO and PSO dynamic model (>0.99), suggesting that the removal of Cr(VI) exists both physical diffusion and a chemical process determined by valence bonding forces or electro-transfer⁶¹.

XPS characterization (Fig. 5e, f) indicates the Cr(III)/Cr(VI) ratio of 0.55 for 1 min and 0.75 for 72 h reaction and the binding energy position of Cr(III) 2p 1/2 orbital peak shifted from 584.9eV at 1min to 586.7eV at 72h. The spin splitting peak shifts to a position with higher binding energy, which indicates that Cr(III) binds to oxygen atoms with higher electronegativity, and the shielding effect of outer electrons decreases, resulting in an increase in the binding energy of inner electrons^{62, 63}. The connection of Cr (III) to the M-O bond also confirms the formation of Cr(III)-LDH. FT-IR characterization (Fig. 5c) reveals that no CrO_4^{2-} intercalation is identified in the case of 1 min reaction. During the reaction period, $\text{Al}_{12}\text{Mg}_{17}$ undergoes galvanic corrosion while *i*LDH continuously generated. SEM and EDS characterization (Fig. S9) shows that the surface morphology of the *i*LDH at the initial stage

of reaction is in a square shape, which is probably newly nucleation structure of *i*LDH. The square block gradually undergoes morphological transformation into rounded sheets and irregular shapes with reaction time. As the metal ions in the solution form the cation layer of *i*LDH, crystal growth occurs in all directions, resulting in the rounding of edges ⁶⁴. The diffraction peak intensity of the LDH (003) crystal plane increases with reaction time while its half-peak width shrinks (Fig. 5d), indicating that the crystallinity of *i*LDH increases. The lattice parameter of $a = 2d(110)$ reflects the distance between the two metal cations and the value of c represents the interlayer distance in the LDH. Both the two metal ion and the interlayer distances in LDH become larger when larger trivalent cations of Cr(III) and Fe(III) replace smaller Al(III) ion (their radius is 0.69, 0.64 and 0.50 Å), thus leading to higher anion exchange capacity ^{13, 46, 65}. The *i*LDH laminate grows in both a and c directions with the reaction time (Table S8), indicating that both the substitution of Cr(III) in cationic laminates and intercalation of CrO_4^{2-} increase with reaction time.

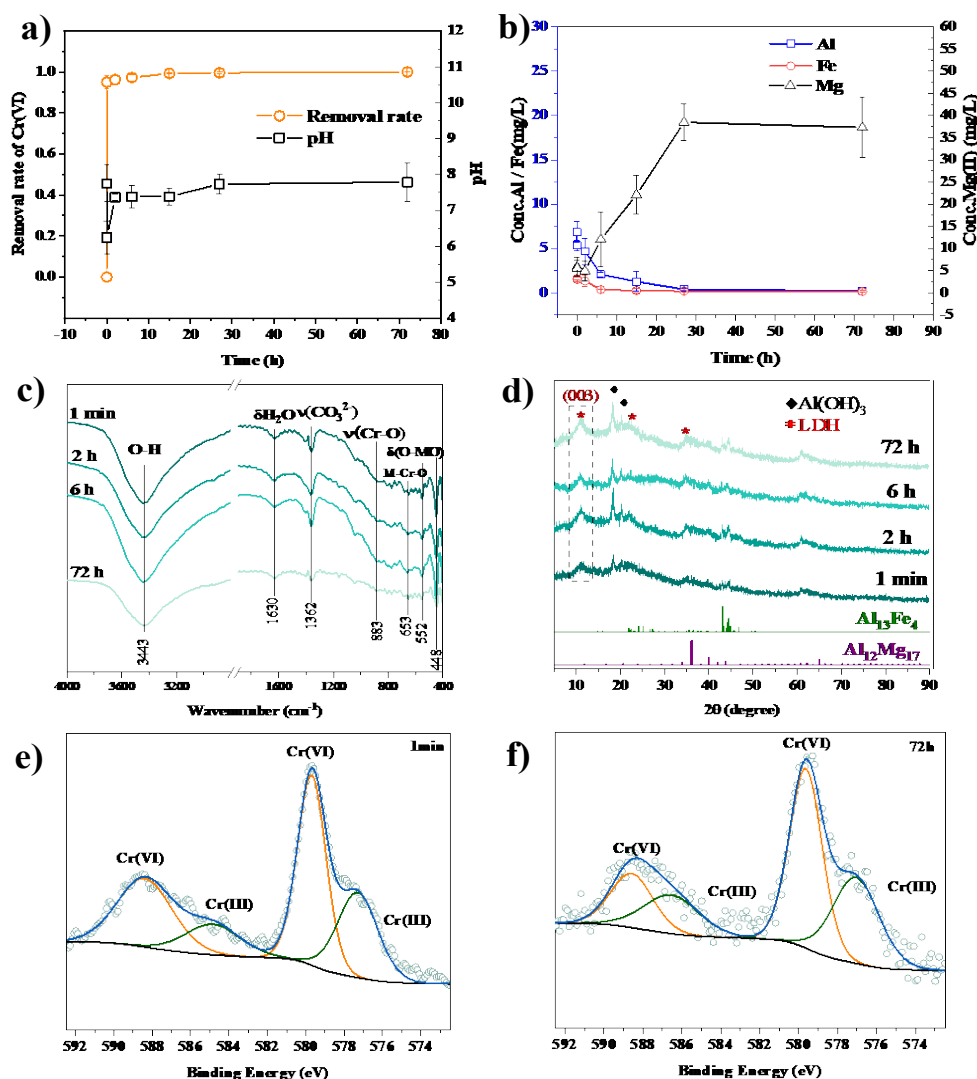


Fig. 5. Cr(VI) reduction by MgAlFe-iLDH in a prolonging reaction time. (a) Cr(VI) removal rate and solution pH variation as a function of reaction time, (b) concentration of Al(III), Mg(II) and Fe(T); (c) FT-IR characterization, (d) XRD characterization of MgAlFe-iLDH at different reduction times; (e) and (f) Cr 2p XPS high resolution spectra of MgAlFe-iLDH in 1 min and 72 h of reaction time. Initial concentration of Cr(VI) 100 mg L⁻¹, initial pH 4.5, Al-Mg-Fe alloy 1 g L⁻¹.

3.8 Effect of alloy loading

The solution pH and Cr(VI) removal rate by different dosages (0.1-2.0 g L⁻¹) of alloy pretreated with pH 2 HCl are shown in Fig. S10. For 0.1 and 0.2 g L⁻¹ dosages, the alloys are completely dissolved by the pretreating solution of pH 2 HCl and the pH is increased to 4.2 and 5.0, respectively (Fig. S10a, t=0 h). By contrast, solid residues remain and the pH reaches 7.1, 7.3 and 8.4 after pretreatment in the cases of 0.5, 1.0 and 2.0 g L⁻¹ alloy dosages. Consequently, Cr(VI) reduction is extremely low (< 10%) in the cases of 0.1 and 0.2 g L⁻¹

dosages and it reaches 35.5%, 94.4% and >99.9% at a dosage of 0.5, 1.0 and 2.0 g L⁻¹, respectively (Fig. S10b). After 2-h reduction (Fig. S10c) shows that both Al₁₂Mg₁₇ and Al₁₃Fe₄ are consumed to a large extent for 0.5 g L⁻¹ alloy, Al₁₂Mg₁₇ is preferably dissolved for 1.0 g L⁻¹ alloy and both remain in considerable amounts for 2.0 g L⁻¹ alloy. The XRD peak pattern of 0.5 g L⁻¹ is more disordered than the others, which is likely that a large number of by-products of Fe(III), Al(III) and Cr(III) hydroxides are produced. However, Al₁₃Fe₄ is consumed, indicating that Al₁₃Fe₄ plays the role of electron donor rather than catalyst in this process, resulting in poor removal rate. LDH is clearly identified for 1.0 and 2.0 g L⁻¹ alloy dosages (Fig. S10c) while the Cr-O absorption peaks demonstrate the intercalation of CrO₄²⁻ into the LDH layers (Fig. S10d). After the reaction, both Cr(VI) and Cr(III) are detected in the three cases of 0.5, 1.0 and 2.0 g L⁻¹ alloy dosages (Fig. S11a) and Cr(III)/Cr(VI) ratio is the highest (0.8) for 1g L⁻¹ (Table S9). Compared with the case of 0.5 g L⁻¹, the 2p orbital binding energy of Fe at 1.0 and 2.0 g L⁻¹ alloy dosages slightly shifts to the direction of low binding energy (Fig. S11b), indicating that the central electronic structure of Fe is affected⁶⁶, which further confirms the site isolation strategy and the importance of Al₁₃Fe₄ in the catalytic system. The results demonstrate the synergy between *i*LDH and intermetallic compounds, which significantly improves the electron supplement to Cr(VI) reduction.

3.9 Catalytic reduction of Cr(VI) by *i*NCC

Al and Mg metals are not suitable for highly selective reduction of targeted pollutants in aqueous solutions due to the electron competition with O₂, H₂O (H⁺)^{3,4}. Al-Mg intermetallic Al₁₂Mg₁₇ belongs to bcc structure and improves corrosion resistance of Mg and Al and can serve as a catalyst for rapid electron transfer between Mg⁰ and Ni²⁺ cation due to its fine interdendritic networks³². For CrO₄²⁻ anion, the reduction rate of Cr(VI) is improved in the beginning period of 5 min by pre-growing *i*LDH on the Al-Mg alloy's surface (refer to Fig. 1i, j). Al-Fe intermetallic Al₁₃Fe₄ holds the potential to improve the electron selectivity of reduction assigned to the combination of site-isolation and the alteration of the electronic

structure by the chemical bonding and has been employed as the catalyst for hydrogenation of C_2H_2 and chemical reduction of nitrate, butadiene and chlorophenols^{33, 34, 40}. The poor performance of Al-Fe alloy even pretreated for Cr(VI) reduction is most likely attributed to improved corrosion resistance by $Al_{13}Fe_4$ and a lack of *i*LDH.

The distinct performance of Al-Mg-Fe alloy developed in this study for Cr(VI) reduction is attributed to a synergistic effect of $Al_{12}Mg_{17}$, $Al_{13}Fe_4$ and *i*LDH. The lattice doping of multi-metal components in the Al-Mg-Fe alloy is capable of isolating continuous metal sites, modulating the electronic properties of the main metal active substances, and establishing specific geometric configurations and electronic structures. Importantly, the *in situ* growth of one-dimensional LDH generates abundant surface defects, creates numerous heterogeneous interfaces and offers plentiful adsorption, nucleation and active sites. The intercalation of CrO_4^{2-} into the nano-scale interlayer space of *i*LDH enhances the electron efficiency between CrO_4^{2-} and Mg and Al metals while the *in situ* generation of Cr^{3+} -bearing LDH continues to renew the surface and interphase. Consequently, the electronic metal–support interaction (EMSI)^{41, 67} is significantly enhanced. Although we focus on CrO_4^{2-} anion in this study, we have obtained encouraging results for other contaminants including nitrate, chlorophenols and other heavy metal cations and considered that the *in situ* generation and re-construction of nanoscale LDH are critical.

4. Conclusions

This study demonstrates a novel approach to Cr(VI) remediation through the selective pretreatment of Al–Mg–Fe alloy with dilute HCl, which creates a unique surface structure featuring $Al_{13}Fe_4$ phases and *in situ* growth of MgAlFe-*i*LDH nanosheets. The resulting architecture, rich in grain boundaries and scaffold-like structures, facilitates high Cr(VI) removal efficiency, rapid reduction across a wide pH range, and eliminates secondary contamination. A central contribution of this work is the introduction of *in situ* nanoconfinement catalysis (*i*NCC), where synergistic interactions between *i*LDH nano-sheets

and Al–Mg/Al–Fe intermetallics significantly enhance catalytic activity. This iNCC framework, coupled with the stability of LDH phases and MgAlCr–CrO₄^{2–}-LDH's photocatalytic potential for organic pollutant degradation, suggests a powerful dual-function mechanism. It effectively limits Cr(III) reoxidation while promoting degradation and mineralization of organic contaminants, underscoring the approach's applicability in sustainable environmental remediation. Thus, the findings offer valuable insights into advanced catalytic materials for diverse contaminant removal strategies.

ASSOCIATED CONTENT

Supporting information

All data are presented in the Article and its Supplementary Information.

Detailed information of chemicals and analytical methods; Effect of pretreating HCl solution pH (0.5, 1, 2 and 3); Effect of pretreatment time 0-12 h; SEM images of MgAlFe-*i*LDH with pretreatment times of 1, 3, 6, and 12 h; Effect of prolonging LDH ageing time (23h, 36h) after the pretreatment; XRD characterization of MgAlFe-*i*LDH after pretreatment with prolonging 23 and 36 h LDH ageing time (AT) before and after Cr(VI) reduction; Effect of different acids solution pretreatment; Effect of Cr(VI) concentration (100, 200, 300 mg L⁻¹); SEM and Mapping image of MgAlFe-*i*LDH after reaction with different Cr(VI) concentration solution; SEM and EDS images of MgAlFe-*i*LDH at different reaction times with 100mg L⁻¹ Cr(VI); Effect of alloy dosages (0.1-2.0 g L⁻¹); XPS high resolution spectra of MgAlFe-*i*LDH after reaction with Cr(VI) at different alloy dosages.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

NA.

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Supporting Information

***In situ* nanoconfinement catalysis for highly efficient redox transformation**

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Number of pages:16

Number of figures:11

Number of tables:9

Table of Contents

Experimental Section	S3
Table S1 Effect of initial pH on finished pH, Al(III), Mg(II) and Fe(T) ion concentrations in the HCl pretreatment solutions of Al-Mg-Fe alloy.	S5
Table S2 Effect of pretreatment time on finished pH, Al(III), Mg(II) and Fe(T) ion concentrations in the HCl pretreatment solutions of Al-Mg-Fe alloy.....	S5
Table S3 Binding energy and area of Cr 2p XPS with different pretreatment time after Cr(VI) reduction	S5
Table S4 Atomic proportions of surface elements of Al-Mg-Fe alloy with different pretreatment time after pretreatment.....	S5
Table S5 XRD structure parameters of Al-Mg-Fe alloy's iLDH after reduction with different initial pH of Cr(VI) solution	S6
Table S6 Reaction kinetics fitting in Al-Mg-Fe alloy reaction with Cr(VI) with different condition.....	S6
Table S7 Rate constants of Cr(VI) reduction by different materials reported in the literature and by MgAlFe-iLDH	S6
Table S8 XRD structure parameters of Al-Mg-Fe alloy's iLDH at different reaction time with Cr(VI)....	S7
Table S9 Binding energy and area of Cr 2p XPS after reduction with different alloy dosages	S7
Fig. S1 Effect of pretreating HCl solution pH (0.5, 1, 2 and 3).	S8
Fig. S2 Effect of pretreatment time 0-12 h.....	S9
Fig. S3 SEM images of MgAlFe-iLDH with pretreatment times of 1, 3, 6, and 12 h.	S9
Fig. S4 Effect of prolonging LDH ageing time (23h, 36h) after the pretreatment.	S10
Fig. S5 XRD characterization of MgAlFe-iLDH after pretreatment with prolonging 23 and 36 h LDH ageing time (AT) before and after Cr(VI) reduction.	S10
Fig. S6 Effect of different acids solution pretreatment.	S11
Fig. S7 Effect of Cr(VI) concentration (100, 200, 300 mg L ⁻¹).	S12
Fig. S8 SEM and Mapping image of MgAlFe-iLDH after reaction with different Cr(VI) concentration solution.....	S13
Fig. S9 SEM and EDS images of MgAlFe-iLDH at different reaction times with 100mg L ⁻¹ Cr(VI).	S14
Fig. S10 Effect of alloy dosages (0.1-2.0 g L ⁻¹).	S15
Fig. S11 XPS high resolution spectra of MgAlFe-iLDH after reaction with Cr(VI) at different alloy dosages.	S15
References	S16

Experimental Section

Chemicals.

Al-Mg (Mg 50 w.t%), Al-Fe (Fe 20 w.t%) and Al-Mg-Fe (Mg 40 w.t% Fe 20 w.t%) alloys were prepared by high temperature melting process and crushed into 200 mesh powder after cooling. Anhydrous MgCl_2 (99.7%) were purchased from Tianjin Fuchen Chemical Reagent Factory (China). $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$ (99.7%), NaOH (99.7%), NaCl (99.7%), HCl (99.7%), H_2SO_4 (99.7%), HNO_3 (99.7%), H_3PO_4 (99.7%), $\text{K}_2\text{Cr}_2\text{O}_7$ (99.7%), CH_3COCH_3 (99.7%) were purchased from Beijing Chemical Works (China). KBr (99.9%) were purchased from Aladdin. $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ were purchased from Shanghai Bide Medical Technology.

Analytical Methods.

The crystal structure of the materials were characterized by X-ray diffraction (XRD, Ultima IV, XRD- 6000, Japan) at 40 kV/ 40 mA with Cu Ka radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan rate of $10^\circ \text{ min}^{-1}$ in the 2θ range of $5\text{--}90^\circ$. The test results were analyzed by Jade software. The grain size is estimated by Scherrer formula:

$$D = R\lambda/(\beta\cos\theta)$$

where D is the grain size, R is the Scherrer constant ($R=0.89$), λ is the radiation wavelength ($\lambda = 0.1542$), and β is the half-maximum width at the Bragg diffraction angle θ .

The nanostructure of pretreated materials was studied by Transmission Electron Microscopy (TEM) (FEI Tecnai G2 F20 S-Twin, U.S.A) at 160 KV. The sample was dispersed in ethanol solution by ultrasound and then deposited on a hollow Cu net for detection.

The changes of functional groups and chemical bonds on the surface of materials were determined by Fourier Transform Infrared absorption spectrum (FT-IR, BRUKER, TENSOR27, Germany). The scanning range was $400\text{--}4000 \text{ cm}^{-1}$, scanning speed 4 cm s^{-1} , and the carrier material was KBr . The BET specific surface area was determined using N_2 adsorption and desorption isotherms at 77 K collected from the Autosorb-IQ gas adsorption analyzer (Quantachrome, U.S.A.).

The changes of elemental valence (Fe and Cr) during adsorption were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+, U.S.A.) The surface morphology was observed Scanning Electron Microscope (SEM, JSM-F100/ JSM-7610FPlus, Japan), and the surface of the material was treated with carbon spraying before testing. The distribution of elements on the surface of materials was analyzed by Energy Dispersive Spectrometer (EDS) and Mapping.

The concentration of heavy metals (Cr total, Al, Mg, and Fe total) was determined by ICP-OES (Thermo, iCAP 6000, U.S.A.). The Chloride ion concentration was quantified using ion chromatography (Dionex, ICS-900, U.S.A.) with an IonPac AS11-HC analytical column and an IonPac AG11-HC guard column. The analysis was performed at a flow rate of 1 mL min⁻¹ with a 6 min retention time and the eluant was the mixture of 0.0045 M Na₂CO₃ and 0.0008 M NaHCO₃. The concentration of Cr (VI) was determined by UV-vis photometer (TU- 1900, Persee, China) at a wavelength of 540 nm, and diphenyl carbazide was used as color developing agent.

Table S1 Effect of initial pH on finished pH, Al(III), Mg(II) and Fe(T) ion concentrations in the HCl pretreatment solutions of Al-Mg-Fe alloy.

Initial pH	Finished pH	Al(III) (mg L ⁻¹)	Mg(II) (mg L ⁻¹)	Fe(T) (mg L ⁻¹)
3.0	8.65	3.80	0.70	0.22
2.0	8.35	3.88	9.87	0.52
1.0	4.07	319.98	296.29	156.51
0.5	1.25	380.24	283.21	175.04

Table S2 Effect of pretreatment time on finished pH, Al(III), Mg(II) and Fe(T) ion concentrations in the HCl pretreatment solutions of Al-Mg-Fe alloy.

Pretreatment time (h)	Finished pH	Al(III) (mg L ⁻¹)	Mg(II) (mg L ⁻¹)	Fe(T) (mg L ⁻¹)
1	9.45	11.03	9.45	0.38
3	9.43	10.39	5.48	0.46
6	9.38	8.96	5.80	0.66
12	8.65	3.80	0.70	0.22

Table S3 Binding energy and area of Cr 2p XPS with different pretreatment time after Cr(VI) reduction

Pretreatment time (h)	Binding Energy (eV)				Area (CPS.eV)		
	2p 3/2		2p 1/2				
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)/Cr(VI)
1	576.66	579.46	583.40	587.95	5828	9768	0.60
3	576.59	579.38	586.13	588.72	5722	8118	0.70
6	576.93	579.55	585.92	588.60	8547	10487	0.81
12	576.99	579.55	586.17	588.75	8128	9187	0.88

Table S4 Atomic proportions of surface elements of Al-Mg-Fe alloy with different pretreatment time after pretreatment.

Element	Pretreatment time (h)				
	0	1	3	6	12
C	—	31.42	32.42	36.44	33.5
O	10.08	20.92	36.72	40.54	48.08
Mg	43.76	19.8	17.62	12.98	10.41
Al	35.39	22.12	10.18	8.09	6.36
Cl	—	0.19	0.3	0.15	0.14
Fe	10.76	5.54	2.76	1.8	1.51

Table S5 XRD structure parameters of Al-Mg-Fe alloy's iLDH after reduction with different initial pH of Cr(VI) solution

LDH structure parameters	Initial and finished pH of Cr(VI) solution		
	4.51 / 7.07	7.05 / 7.65	11.0 / 8.77
d ₀₀₃ (Å)	8.39	8.03	8.04
d ₁₁₀ (Å)	1.51931	1.5204	1.5214
2θ (003)	10.54	11.02	11.01
FWHM of (003) reflection (°)	1.51	1.22	1.17
Lattice parameter c (nm)	2.517	2.409	2.412
Lattice parameter a (nm)	0.3039	0.3041	0.3043
Crystallite size in the c direction (nm)	5.23	6.46	6.76

Table S6 Reaction kinetics fitting in Al-Mg-Fe alloy reaction with Cr(VI) with different condition

Conditions	Pseudo first order dynamic model			Pseudo second order dynamic model		
	q _e (mg/g)	k ₁ (h ⁻¹)	R ₁ ²	q _e (mg/g)	k ₂ (g mg ⁻¹ h ⁻¹)	R ₂ ²
Pristine alloy	2.167	0.765	0.924	2.460	0.397	0.970
-pH 3 Cr(VI)						
pH 2 HCl pre	103.884	201.567	0.999	103.898	15.878	0.999
-pH 4.5 Cr(VI)						
pH 2 HCl pre	99.326	201.703	0.998	99.741	13.276	0.999
-pH 11 Cr(VI)						

Table S7 Rate constants of Cr(VI) reduction by different materials reported in the literature and by MgAlFe-iLDH

Materials	Pseudo first order dynamic model		Pseudo second order dynamic model	
	k ₁ (h ⁻¹)	R ₁ ²	k ₂ (g mg ⁻¹ h ⁻¹)	R ₂ ²
ZVAl ¹	0.67	0.980	0.22	1.000
nZVI ²	21.6	0.964	8.4×10 ⁻³	0.972
Green Rust ³	11.58	0.993	1.92	0.999
MgAlFe-iLDH (This work)	201.6	0.999	15.878	0.999

Table S8 XRD structure parameters of Al-Mg-Fe alloy's iLDH at different reaction time with Cr(VI)

LDH structure parameters	Reaction time			
	1 min	2 h	6 h	72 h
d ₀₀₃ (Å)	7.879	7.961	7.999	8.008
d ₁₁₀ (Å)	1.518	1.520	1.523	1.524
2θ (003)	11.230	11.105	11.061	11.049
2θ (110)	60.979	60.882	60.783	60.777
FWHM of (003) reflection (°)	2.118	1.974	1.521	1.511
FWHM of (110) reflection (°)	0.510	0.507	0.500	0.498
Lattice parameter c (Å)	23.637	23.883	23.997	24.024
Lattice parameter a (Å)	3.036	3.040	3.046	3.048
Crystallite size in the c direction (nm)	3.732	4.004	5.197	5.231
Crystallite size in the a direction (nm)	17.898	17.995	18.238	18.311

Table S9 Binding energy and area of Cr 2p XPS after reduction with different alloy dosages

Alloy dosage (g L ⁻¹)	Binding Energy (eV)				Area (CPS.eV)		
	2p 3/2		2p 1/2				
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)/Cr(VI)
2	576.34	579.61	585.85	588.90	7255	10008	0.72
1	577.47	579.75	585.32	588.37	10850	13525	0.80
0.5	576.56	579.60	584.45	588.20	10431	14144	0.74

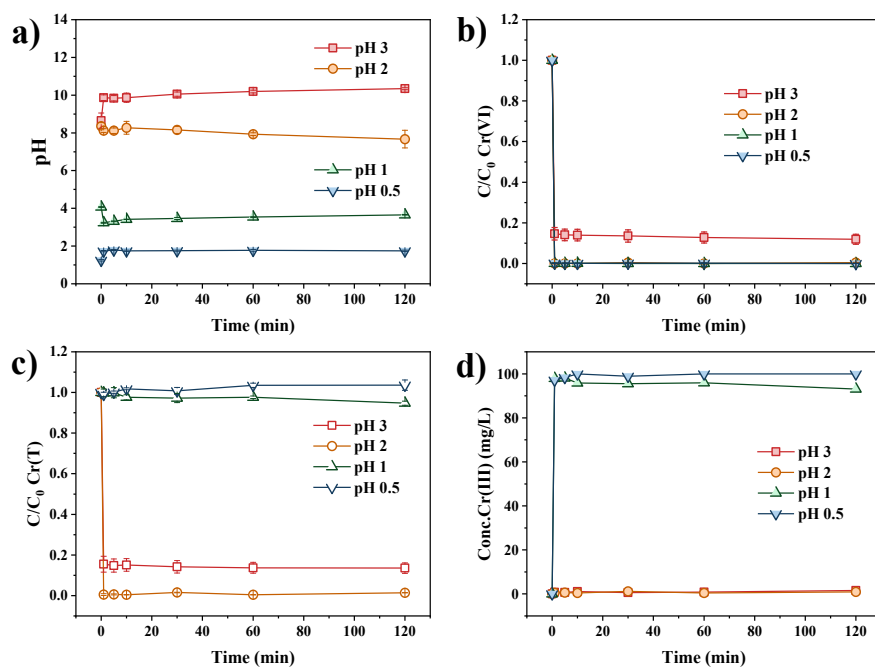


Fig. S1 Effect of pretreating HCl solution pH (0.5, 1, 2 and 3). (a) pH variation upon the addition of pH 4.5 Cr(VI) solution, (b) Cr(VI) concentration ratio C/C_0 , (c) Total Cr [Cr(T)] concentration ratio C/C_0 , and (d) Cr(III) concentration. Initial Cr(VI) concentration 100 mg L⁻¹, 2 g L⁻¹ Al-Mg-Fe alloy.

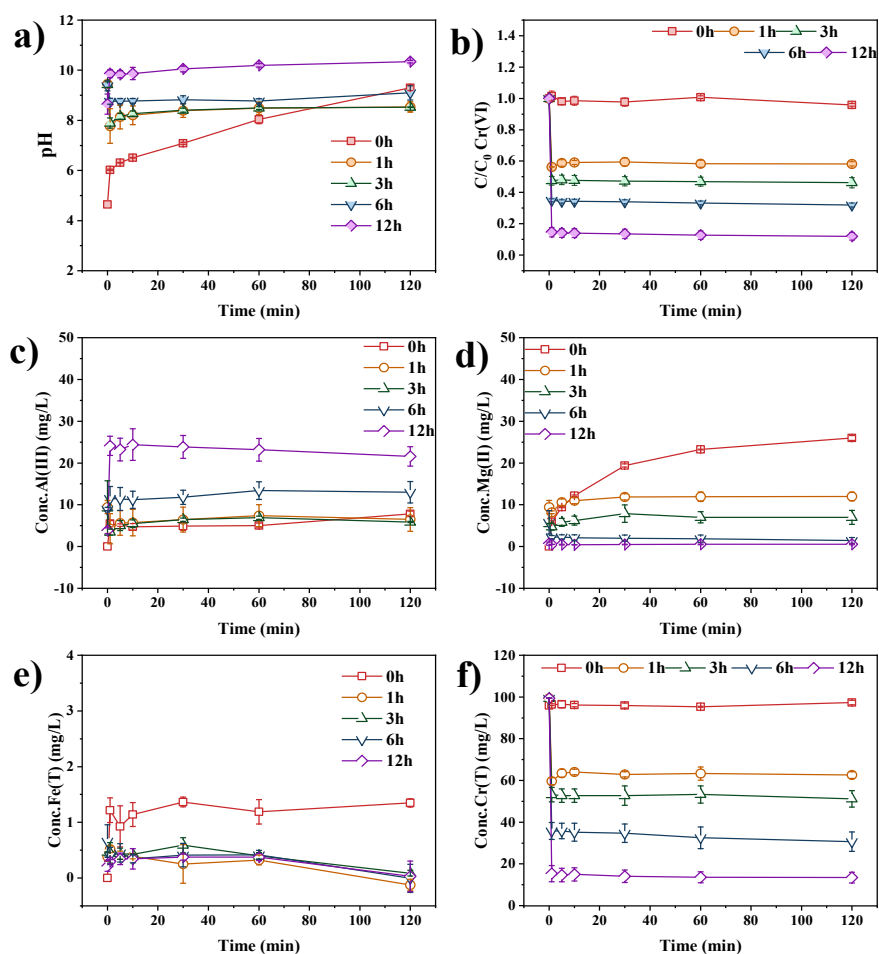


Fig. S2 Effect of pretreatment time 0-12 h. (a) solution pH variation as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 , (c) Al(III) concentration, (d) Mg(II) concentration, (e) total Fe [Fe(T)] concentration, (f) total Cr [Cr(T)] concentration. Initial Cr(VI) 100 mg L^{-1} , pH 4.5, 2 g L^{-1} Al-Mg-Fe alloy.

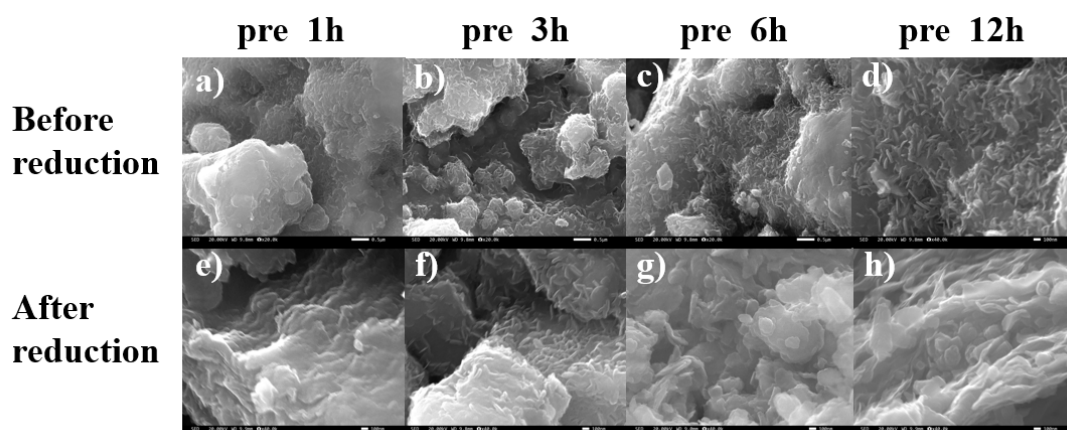


Fig. S3 SEM images of MgAlFe-iLDH with pretreatment times of 1, 3, 6, and 12 h. (a)-(d) before Cr(VI) reduction ($\times 20k$), (e)-(h) after Cr(VI) reduction ($\times 40k$).

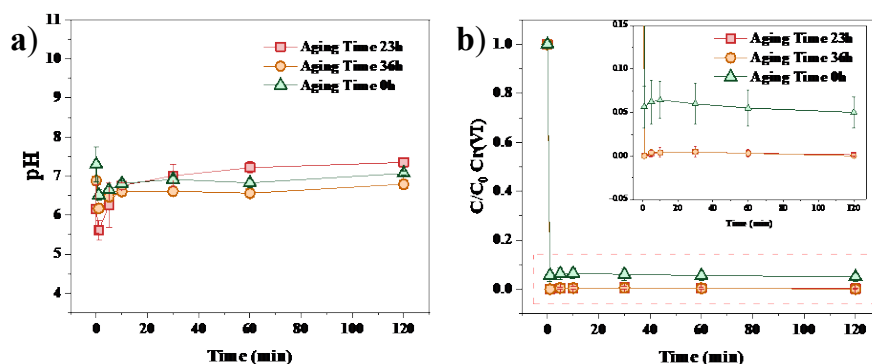


Fig. S4 Effect of prolonging LDH ageing time (23h, 36h) after the pretreatment. (a) solution pH variation as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 . Initial Cr(VI) concentration 100 mg L^{-1} , pH 4.5, 1 g L^{-1} Al-Mg-Fe alloy.

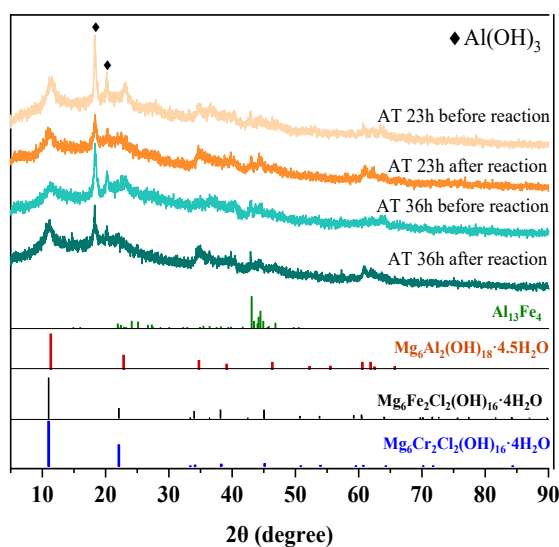


Fig. S5 XRD characterization of MgAlFe-iLDH after pretreatment with prolonging 23 and 36 h LDH ageing time (AT) before and after Cr(VI) reduction.

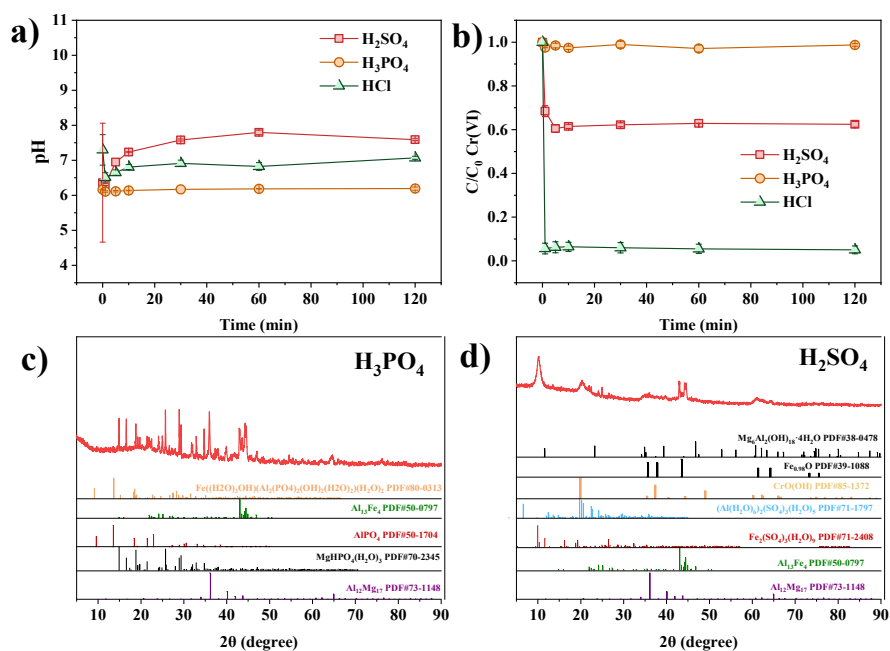


Fig. S6 Effect of different acids solution pretreatment. (a) solution pH variation as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 . XRD characterization of Al-Mg-Fe alloy pretreated with (c) pH 2 H₃PO₄, (d) pH 2 H₂SO₄ after Cr(VI) reduction. Alloy 0.1 g, 50 mL solution, pretreatment temperature 60 ± 0.5 °C, magnetic stirring 300 rpm, 12 h. Initial Cr(VI) concentration 100 mg L^{-1} , initial pH 4.5, 1 g L^{-1} Al-Mg-Fe alloy.

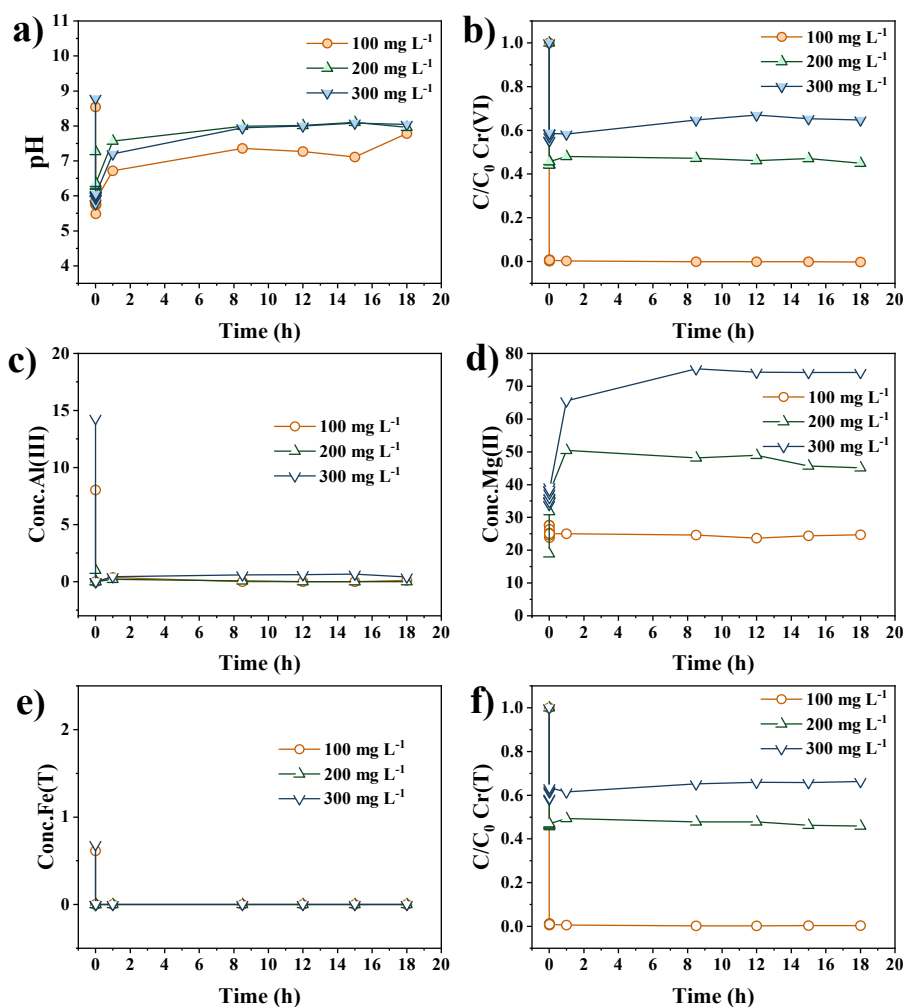


Fig. S7 Effect of Cr(VI) concentration (100, 200, 300 mg L⁻¹). (a) solution pH variation as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 , (c) Al(III) concentration, (d) Mg(II) concentration, (e) total Fe [Fe(T)] concentration and (f) total Cr [Cr(T)] concentration ratio. Initial Cr(VI) solution pH 4.5, 1 g L⁻¹ Al-Mg-Fe alloy.

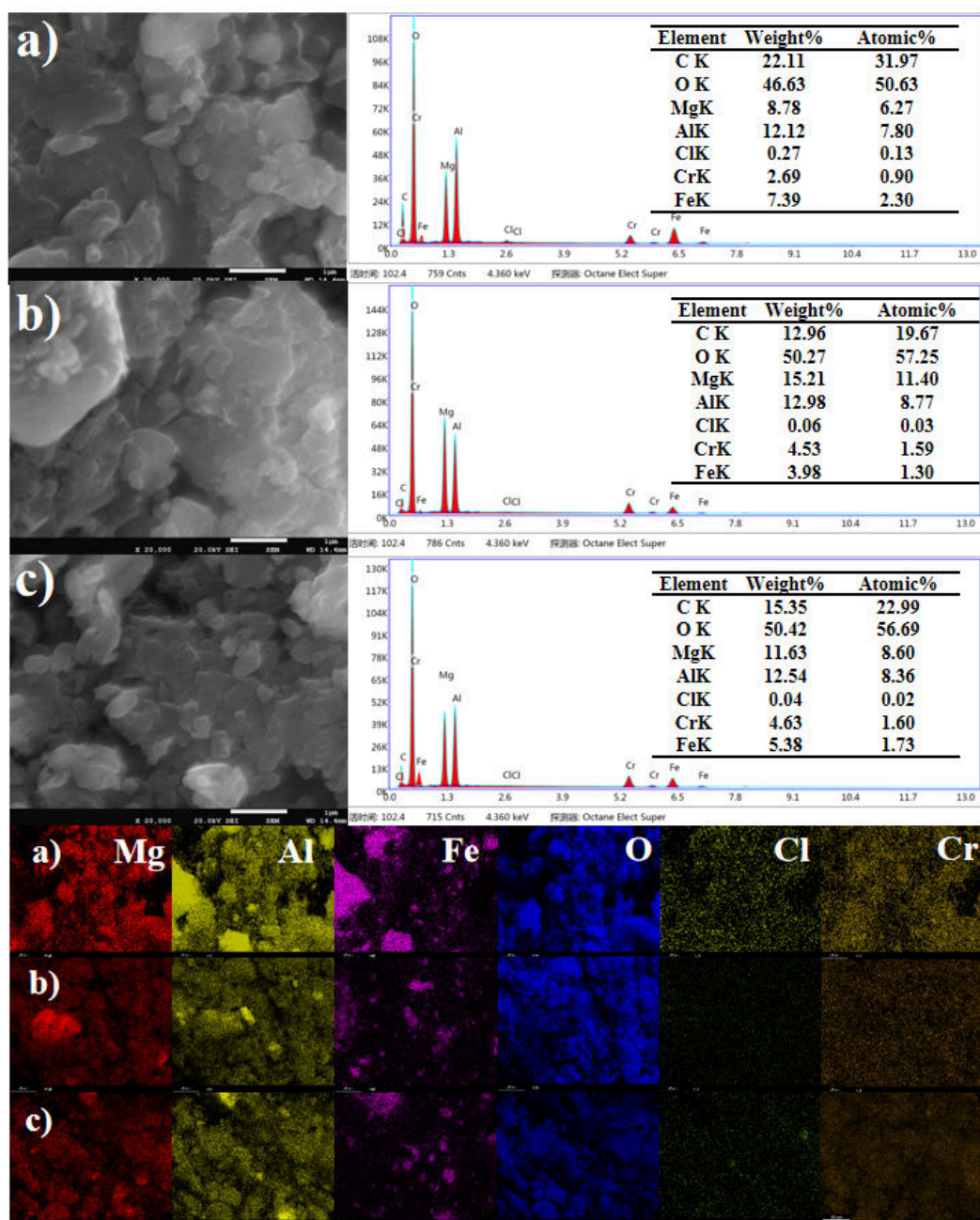


Fig. S8 SEM and Mapping image of MgAlFe-iLDH after reaction with different Cr(VI) concentration solution. (a) 100 mg L⁻¹, (b) 200 mg L⁻¹, (c) 300 mg L⁻¹.

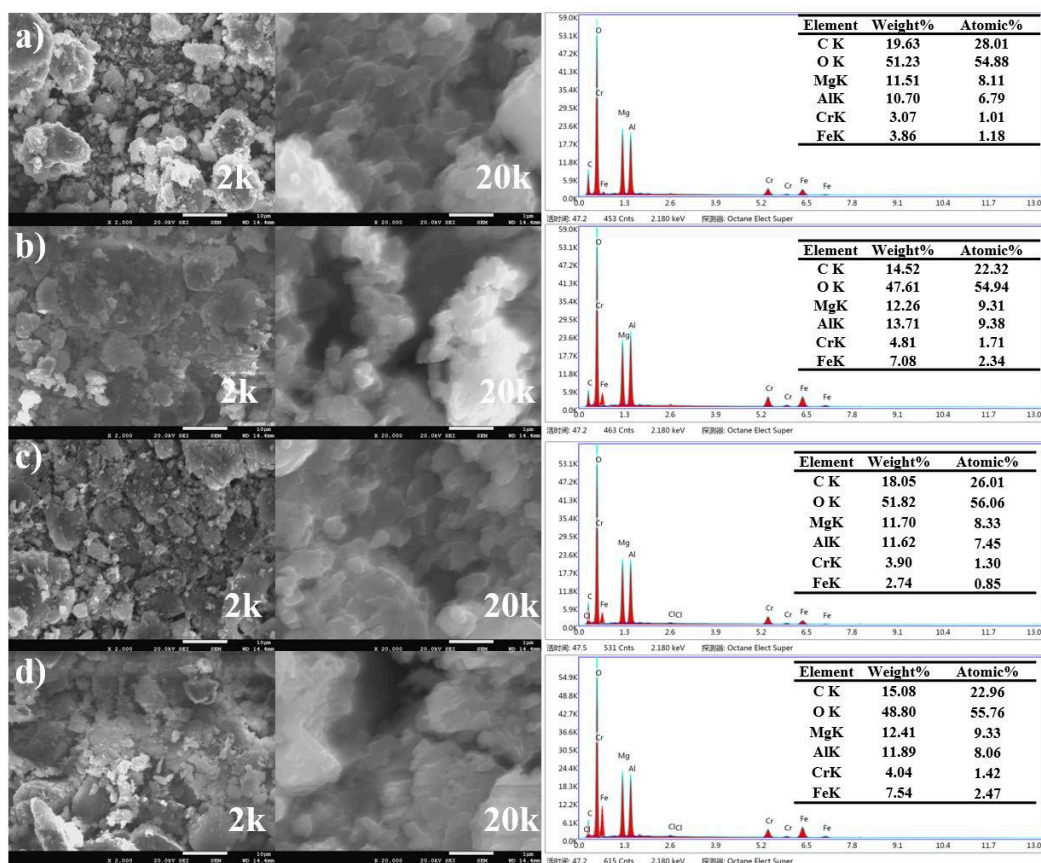


Fig. S9 SEM and EDS images of MgAlFe-iLDH at different reaction times with 100mg L^{-1} Cr(VI). (a) 1 min, (b) 2 h, (c) 6 h, (d) 12 h.

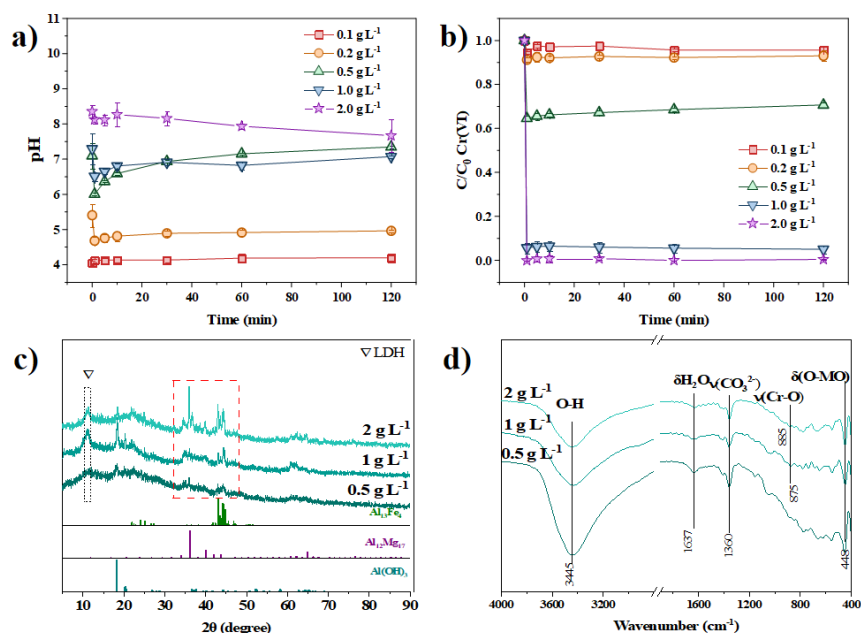


Fig. S10 Effect of alloy dosages (0.1-2.0 g L⁻¹). (a) solution pH variation as a function of reaction time, (b) Cr(VI) concentration ratio C/C_0 . (c) XRD and (d) FT-IR characterization of MgAlFe-iLDH after Cr(VI) reduction with different alloy dosages (0.5, 1.0, 2.0 g L⁻¹). Initial Cr(VI) 100 mg L⁻¹, pH 4.5.

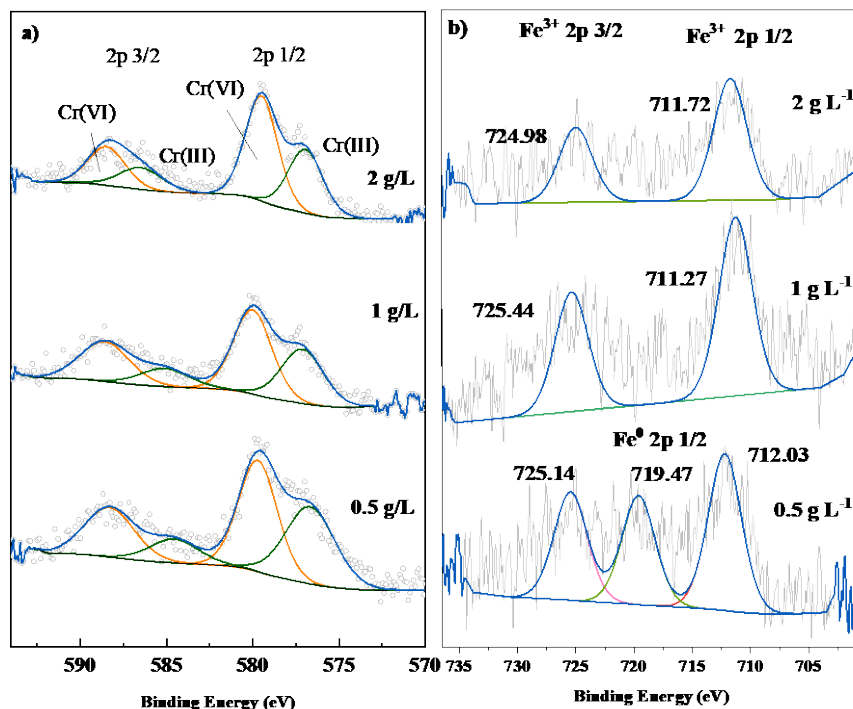


Fig. S11 XPS high resolution spectra of MgAlFe-iLDH after reaction with Cr(VI) at different alloy dosages. (a) Cr 2p, (b) Fe 2p.

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Chen, Yuhan; Tan, Jisheng; Chao, Jingbo; Zhang, Jingqi; Tang, Yang ...

2024-11-13

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<https://doi.org/10.1021/acsami.4c12409>

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