

In situ layered double hydroxide for efficient remediation of acidic water

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The efficient and sustainable in situ remediation of high-strength acidic groundwater contaminated by complex micropollutants with minimal use of chemicals has been a challenge. Here we report that MgAl alloy achieves neutralization and a complete removal of 20 mg L⁻¹ Cd²⁺, Cr(VI), Cu²⁺, Ni²⁺ and Zn²⁺ in 15 min from acidic water free of chemicals. The removal rate of heavy metals and nitrate increases with decreasing pH and is not significantly reduced after 5 cycles of treating acidic water. The excellent performance of MgAl alloy in reactivity, durability and efficiency is attributed to a synergistic effect of chemical reduction and eutectic reactions, which catalyzed by intermetallic compound Mg₁₇Al₁₂ and in situ layered double hydroxide (iLDH). The pH 2.47 of an acid mine drainage sample from copper ore mines is raised to 7.4±0.4 and the concentrations of Al, Cr, Cu, Fe, Mn, Ni and Zn ions are reduced to ≤ 0.55 mg L⁻¹ from 5-559 mg L⁻¹. In contrast, quick lime treatment increases the pH to 12.45 whereas activated carbon, zerovalent iron and conventional LDH are not able to neutralize nor remove Al³⁺ and heavy metals. The findings of this study provide new insights into efficient, green and sustainable approach for acidic water remediation.

1. Introduction

Water pollution is a worldwide problem while pressing needs have been raised in Asia where 60% of South Asia's groundwater is undrinkable ^[1] and 90% of China's shallow groundwater is polluted ^[2]. Heavy metals are increasingly found in various water bodies ^[3-5] and acid mine drainage (AMD) is one of the typical pollution sources of heavy metals in surface and ground water around mining areas. Adsorption is a classical water treatment technology and has been extensively employed for removing heavy metals from contaminated water ^[6, 7]. However, the remediation of acidic wastewater by adsorption using traditional and emerging sorbent materials (e.g., activated carbon, zeolite, biochar, graphene) is insufficient in many cases and a neutralization pretreatment is required ^[8, 9]. The efficient and cost-effective in situ remediation of acidic groundwater has long been a challenge, due primarily to a lack of reactive, green and sustainable adsorbents.

Quick lime treatment has been widely employed for AMD treatment ^[8], but it produces a large quantity of hazardous solid waste and is not suitable for in situ remediation of acidic groundwater ^[8, 10]. Layered double hydroxide (LDH) is a class of anionic clays with a highly tunable brucite structure in a general molecular formula of $[M_{1-x}^{II}M_x^{III}OH_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metal cations and A^{n-} is an anion in the interlayer space. LDH is non-toxic, environmentally friendly and biocompatible and has been employed in a wide variety of fields, such as chemical synthesis, catalysis, drug delivery, imaging, targeting, biosensing, antimicrobial formulation^[11] and water remediation and treatment ^[12, 13]. The major limitation of LDH for water remediation is that the adsorption rate and capacity of toxic metal pollutants are generally not attractive ^[6]. This limitation is greatly overcome by in situ formation of LDH by dosing $MgCl_2$ and $NaOH$ in the field for remediation of AMD containing relatively high concentrations of trivalent metal ions ^[14], but it might suffer secondary contamination or insufficient remediation for acidic groundwater due to the difficulties of accurately and precisely predicting the underground contamination. In addition, adsorption is not effective and even completely ineffective for some contaminants of relatively high oxidation potentials (e.g., hexavalent chromium, $Cr(VI)$), a complete elimination of which requires prior redox transformation/degradation ^[15]. Zerovalent iron (ZVI), aluminum and magnesium were employed for acidic water remediation due to high crustal abundance of these elements and their capabilities of neutralizing H^+ , but their low selectivity towards micropollutants has limited their applications while ZVI suffers rapid surface passivation, fast agglomeration, poor mobility/flowability and secondary contamination ^[16-19]. A composite of nano zerovalent iron (nZVI) loaded on LDH was developed to integrate the redox capability of nZVI and

adsorption of LDH for the removal of Cr(VI), U(VI) and nitrate from groundwater [15, 20, 21]. However, the redox activity of nZVI in the composite is suppressed by LDH and the loading of nZVI is limited, thus reducing the durability of the composite [16].

An ideal material for in situ remediation of acidic groundwater is that the material is environmentally friendly and has sufficient mobility, redox activity, selectivity and durability (i.e., the material is sufficiently active when exposed to acidic water and becomes inert to neutral water) while the remediation is free of secondary contamination. Mg and Al metal powders are of high flowability and alloying Mg with Al significantly improves corrosion resistance of Mg metal. Therefore, MgAl alloy powder can be a good candidate to achieve a trade-off among the redox activity, selectivity and durability for acidic groundwater remediation because it has high mobility and can react with H^+ to neutralize while released Mg^{2+} and Al^{3+} could react in situ with heavy metal ions to produce LDH, thus immobilizing toxic heavy metals. Indeed, LDH coatings have been developed to improve corrosion resistance of Mg and Al alloys in salt solutions ($Zn(NO_3)_2$, NH_4NO_3 , HCO_3^- and CO_3^{2-}) [22-25].

The alloy's composition is critical to its surface reactivity [26] while the Mg/Al ratios of 2-4 are required for MgAl-LDH formation [27]. Critical resource recovery from water is becoming a promising strategy [28] and LDH has been widely applied in many fields [29, 30]. Therefore, the present study is to investigate the effects of Mg/Al ratios of MgAl alloy and water pH on the generation of in situ LDH (iLDH), the reactivity and durability and the removal rate of Cr(VI), Cu^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} and NO_3^- and a comparison of MgAl alloy with activated carbon (AC), ZVI and conventional LDH for the remediation of an AMD sample from a copper mine site, aiming at exploring potential applications of Mg and Al alloy scraps and critical resource recovery from AMD, a sustainable remediation of which has been long a challenge.

2. Experimental

2.1 Reagents and alloy samples

Chemicals and reagents were used as received: $Cu(NO_3)_2 \cdot 3H_2O$ (99.7%), $Ni(NO_3)_2 \cdot 6H_2O$ (99.7%) and ZVI powders (99.9%, 100-120 meshes) from Tianjin Fuchen Chemicals, China; $Zn(NO_3)_2 \cdot 6H_2O$ (99.7%) and $K_2Cr_2O_7$ (99.7%) from Xilong Chemicals, China; $Cd(NO_3)_2 \cdot 3H_2O$ (99.7%), HCl (99.7%) from Beijing Chemicals, China; MgAl-LDH from Heowns, China; activated carbon powders (200 meshes) from Aladdin. Stock multiple-element standard solutions (GBW(E) 081532-081535) for ICP-OES calibration were obtained from the National Institute of Metrology, China. MgAl alloys were prepared by

the melting method ^[31] in the Mg/Al mass ratios of 30/70, 40/60, 60/40 and 70/30, denoted as MgAl70, MgAl60, MgAl40 and MgAl30. The alloy ingots were crushed into different sizes (80-200 meshes). Samples of acid mine drainage (AMD) were taken from copper mining pits in South China (117.7°E, 29.0°N).

2.2 Removal experiments and sample preparation

Acidic water samples were prepared by dissolving heavy metals nitrates in ultrapure water (18.2 MΩ·cm, Millipore, USA) and adjusted to required pH using dilute HCl solutions (0.1 M and 1 M). The concentration of each heavy metal was 25 mg L⁻¹. A 500 mL glass bottle with a two-outlet tube cap was used as the reactor for the removal experiment. Alloy powders (3 g) were placed in the bottle and 300 mL acidic water samples were added. H₂ was collected by water drainage using a measuring cylinder. The solution was stirred with a magnetic bar at 350 rpm (IKA, RO10, Germany) at a temperature of 22±2 °C. A sample of 3 mL was withdrawn at a given time interval and filtered by 0.22 μm membrane filters (Jinteng, China) for the determination of Mg, Al, and pollutants concentration. At the end of removal experiments, the solution was settled for 30 min and the suspension was carefully decanted in a clean beaker and the suspended solids were collected by centrifugation and filtration. The precipitates were collected by filtration. The suspended solids and precipitates were then washed with deionized water and dried in a vacuum oven (-0.9 MPa) at 60 °C for 12 h. In the removal experiments at a constant pH 4.0, the pH of the solution was maintained at 4.0 ± 0.5 by adding 0.1-2 M HCl solutions using a pH meter (Mettler Toledo, FE 20, Switzerland) and pH controller (Hach, SC200, U. S. A.). An overall rate (mg L⁻¹ h⁻¹) of pollutant removal was calculated by equation (1)

$$\text{Removal rate} = (C_{t=0} - C_t) / t \quad (1)$$

where t is the time at which the removal of the pollutant reaches 95%.

2.3 Durability test

The durability of the MgAl alloy was tested in pure water at pH 2 (HCl) and heavy metals-containing water (pH 2). MgAl alloy powder (3 g) were mixed with 300 mL pH 2 HCl (10 g/L of the alloy's concentration) and the solution was stirred for 9 hours. Then, the suspensions and alloy residues were separated by centrifuge (8000 rpm) and filtration. The alloy residues were washed with ultrapure water and dried in a vacuum oven (-0.9 MPa) at 60 °C for 12 h. The used alloy sample was mixed with fresh pH 2 HCl solution at the same concentration of 10 g L⁻¹ and stirred for 9 h and then the alloy residues were collected and dried. This durability test was carried out in 4 cycles. During each cycle of the treatment, the concentration of Mg and Al in solution, pH and H₂ generation were measured and the precipitates were characterized by XRD. The alloy samples from above durability tests were

mixed with heavy metal contaminated water samples and stirred for a period of 9 h and the concentrations of Mg, Al and each heavy metal in the solution, pH and H₂ generation were measured and the precipitates were characterized by XRD.

2.4 Analysis and characterization

Liquid samples were first filtered with 0.22 μm membrane filters, acidified by 2% HNO₃ and then analyzed using ICP-OES (Thermo, iCAP 6000, U.S.A.) for Al, Mg and heavy metals. The concentration of nitrate was measured by ion chromatography (Dionex, ICS-900, U.S.A.) using an IonPac AS19 (4*250 mm) analytical column and IonPac AG19 (2*50 mm) guard column with 35 mM NaOH at a flow rate of 0.5 mL min⁻¹.

Samples of the suspended solids and precipitates were ground with agate and then were characterized by scanning electron microscope (SEM, Hitachi, S4700, Japan) with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (Ultima IV, XRD-6000, Japan) at a scan rate of 5° min⁻¹ in the 2 θ range of 5–90°. X-ray photoelectron spectroscopy (XPS) was measured on KRATOS AXIS SUPRA (Shimadzu, Japan) with X-ray excitation provided by Al K α radiation. Samples of suspended solids were characterized by a transmission electron microscopy (TEM, Tecnai G² F20 S-TWIN, America) with energy dispersive X-ray spectroscopy (EDS). Fourier transform infrared spectrometer (FT-IR, Bruker, TENSOR27, German) with a resolution of 0.4 cm⁻¹, was used to test the infrared characteristic absorption peak of the materials.

3. Results and Discussion

3.1 Reactivity, durability and efficiency

In general, the higher the reactivity of an adsorbent, the greater the treatment efficiency, but the poorer its durability. It has been reported that the corrosion resistance of Mg and Al alloys was improved by coating a thin film of LDH on the surface [32]. Therefore, MgAl alloy could achieve a trade-off among the reactivity, durability and efficiency by surface self-reconstruction of iLDH formation for a wide variety of pollutants by chemical reduction with Mg and Al and eutectic reaction with iLDH (Figure 1).

The durability of the alloy was investigated by pretreatment using pH 2 HCl solution repeatedly (see Experimental section). Figure 2 shows the solution pH, Mg²⁺ and Al³⁺ concentrations, hydrogen generation and the alloy's XRD characterization for each cycle of pretreatment. The pH of the solution increases rapidly from 2 to 8.5 in the first 3 cycles of pretreatment and the slows down in the fourth and fifth pretreatment (Figure 2a). Overall, the concentrations of Mg²⁺ and Al³⁺ are similar in each cycle (Figure 2b, c). However, the hydrogen generation is significantly reduced by the pretreatment, being 150 mL in the first pretreatment and reduced to 60, 30, 28 and 26 mL in the following 4 cycles of pretreatment,

respectively (Figure 2d). The XRD characterization (Figure 2e) shows that the peak intensity of LDH and Mg metal decreases with the cycles of pretreatment. The iLDH on the surface of alloy improves the alloy's corrosion resistance and accounts for the significant decrease of hydrogen generation.

The above pretreated alloys are employed for treating heavy metal contaminated water at pH 2. The pH increase is slower and eventually it reaches neutral (Figure 2f). The removal rate of total Cr [Cr(T), Cr(VI)+Cr(III)] is slightly affected in the 5 cycles of acid water treatment (Figure 2g), but that of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} is reduced (Figure 2h-k). The dissolution of Mg decreases while the release of Al^{3+} increases with increasing the cycle of pretreatment (Figure 2l, m). Hydrogen is generated at 12-20 mL in the beginning period of 1 h and then the H_2 generation is basically terminated (Figure 2n). Clearly, hydrogen generation differs significantly in the presence of pollutants (refer to Figure 2d) implying that the electrons are preferably utilized by the pollutants. $\text{Al}_{12}\text{Mg}_{17}$ is more corrosion resistant than Mg metal [33] and the galvanic corrosion occurs between $\text{Al}_{12}\text{Mg}_{17}$ (the cathodic phase) and Mg (the anodic phase) [34]. The concentration of Mg metal in the alloy decreases with increasing the cycles of pretreatment and MgAl alloy can maintain its capability of chemical reduction until it is completely consumed. By contrast, ZVI is passivated when the treated water's pH is greater than 4 [31]. In this context, a further neutralization by injecting additional alkaline chemicals is required in the ZVI-based technology for in situ remediation of acidic groundwater.

The capability of neutralization, pollutant removal and secondary contamination by leached components are important to evaluate the performance of an adsorbent for acidic water remediation. MgAl alloy and ZVI are compared for treating $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Cr}(\text{NO}_3)_3$ solutions at different concentrations (Figure S1 and Figure S2). The removal rate of Cr(T) decreases with increasing Cr(VI) concentration in both cases of MgAl alloy and ZVI, the removal of 25 mg L^{-1} Cr(VI) by MgAl alloy is complete in 2 h while ZVI requires 4 h (Figure S1a, b). Al^{3+} concentration reaches a peak of 2.5 mg L^{-1} at 1 h and then rapidly decreases to < 0.12 mg L^{-1} at 12 h by MgAl alloy (Figure S1c) while Fe concentration reaches 60 mg L^{-1} by ZVI (Figure S1d). Water pH in the MgAl alloy system is lifted to 8 in 1 h and then remains almost unchanged for next 8 h (Figure S1e) whereas the pH in the ZVI system is below 4.93 after 12 h reaction (Figure S1f). LDH is identified and $\text{Cr}(\text{OH})_3$ is not found in the reaction product in the MgAl alloy system (Figure S1g), indicating that the resultant Cr^{3+} is crystalized by LDH. The reaction product is mainly $\gamma\text{-Fe}_3\text{O}_4$ magnetite in the ZVI system (Figure S1h) and Fe concentration is greater than 14.0 mg L^{-1} .

The treatment of $\text{Cr}(\text{NO}_3)_3$ solution at 25-3000 mg L^{-1} Cr^{3+} by MgAl alloy and ZVI is shown

in Figure S2. The removal of 25-3000 mg L⁻¹ Cr³⁺ by MgAl alloy is all greater than 99.5% (Figure S2a) whereas the removal rate by ZVI is 91.0% at 25-300 mg L⁻¹ Cr³⁺ and it decreases significantly at higher Cr³⁺ concentration (from 40% at 500 mg L⁻¹ to 10% at 3000 mg L⁻¹) (Figure S2b). Nitrate reduction by MgAl alloy is much faster than that by ZVI (Figure S2c, d). Leached Al³⁺ concentration increases with increase of Cr³⁺ concentration and a peak of 226 mg L⁻¹ Al³⁺ is observed at 2 h for 3000 mg L⁻¹ after which the concentration decreases to < 0.1 mg L⁻¹ (Figure S2e). Fe leaching from ZVI increases with the increase of Cr³⁺ concentration, from 179 mg L⁻¹ at 25 mg L⁻¹ Cr³⁺ to 2717 mg L⁻¹ at 3000 mg L⁻¹ Cr³⁺ (Figure S2f). The pH profile of the solution at the beginning period of 6 h is diversified with different Cr³⁺ concentrations but the final pH stabilizes at 8.5-9.1 for all of Cr³⁺ concentrations in the MgAl alloy system (Figure S2g). The final pH values in the ZVI system are between 3.2-4.7 (Figure S2h). LDH is produced and Cr(OH)₃ is not observed in all cases of 25-3000 mg L⁻¹ Cr³⁺ while Al(OH)₃ is found with 1000-2000 mg L⁻¹ Cr³⁺ (Figure S2i), indicating that part of Al³⁺ are not able to crystalized into LDH at higher Cr³⁺ concentrations. Extremely high concentrations of Fe in the ZVI system (Figure S2f) are attributed to nanoparticles of FeO(OH) goethite and ZVI (Figure S2j).

3.2 Effect of MgAl alloy's composition on metal ions removal and AMD remediation

The above results demonstrate the importance of iLDH to efficient remediation of acidic water in terms of efficiency, durability and secondary contamination. The Mg/Al atomic ratios of 2-4 are required to form a well-structured MgAl-LDH [27, 35]. Therefore, the MgAl alloys with 4 different Mg/Al ratios of 30/70, 40/60, 60/40 and 70/30 were investigated (Figure 3), which shows the concentration of Cd, Cr(VI), Cu, Ni, Zn, Mg and Al ions, the pH of the solution, and the XRD characterization of the pristine alloys and the 48-h reaction products. Clearly, the removal rates of heavy metals and pH increase with increasing the Mg/Al ratio from 30/70 to 70/30 (Figure 3a-d). For Mg30Al70 (Figure 3a), the pattern of Cr(VI) concentration decline is significantly different from that of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ where Cr(VI) concentration decreases instantly in a pseudo-first order of reaction (k=0.60) while Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ concentrations experience different induced periods with the shortest for Cu²⁺ (~ 0.5 h), the second shortest for Zn²⁺ (~2 h) and the longest for Cd²⁺ and Ni²⁺ (~3 h) and then decrease rapidly after the induced period. The pH rise is in three stages, the fastest in the beginning of 0.5 h, then a slower period from 0.5 to 6 h and finally stabilized at pH 9.35 from 6 h to 48 h. The concentration of the five heavy metals decreases to < 0.53 mg L⁻¹ at 6 h when the pH stabilizes.

For Mg40Al60, the induced period is significantly reduced and the reaction time reaching a stabilized pH of 9.4 is shorten to 1.5 h at which the five heavy metals concentration are all

decreased to $< 0.3 \text{ mg L}^{-1}$ (Figure 3b). For Mg60Al40 and Mg70Al30 (Figure 3c, d), the concentration of the five heavy metals decreases sharply to $< 0.3 \text{ mg L}^{-1}$ in 0.5 h at which the pH is lifted to 9.4 and stabilizes. The variation of Mg^{2+} and Al^{3+} concentration is similar for the four alloys (Figure 3e-h) where the concentration of Mg^{2+} is lifted to 129.0-144.5 mg L^{-1} and then gradually declines with reaction time; the peaking time and width decrease with the increase of Mg/Al ratio and the peaking time is the turning point of pH to a constant value. The concentration of Al^{3+} is in a similar pattern but it is significantly lower. The above results indicate that the reactivity of MgAl alloys increases with the increase of Mg/Al ratio in the alloy. The decrease of Mg^{2+} and Al^{3+} is attributed to the formation of LDH, $\text{Al}(\text{OH})_3$ and/or $\text{Mg}(\text{OH})_2$ phases, as shown by the XRD characterization (Figure 3i-l), which indicates that a relatively pure LDH phase is produced by Mg60Al40.

The comparison of MgAl alloys with AC, lime, ZVI and conventional LDH for AMD sample from a copper ore mine was studied (Table 1). The AMD's pH is 2.47 and Cu, Ni, Zn, Cr, Fe, Mn and Al are the major contaminants. MgAl alloys remove $>90\%$ for each contaminant of Cu, Ni, Zn, Fe, Mn, Cr and Al, raise the acidic pH to neutral pH and produce LDH. In this context, the proposed method for AMD remediation is of potential because LDH doped with transition metals (e.g., Fe, Co, Ni, Mn, Cr, Ce, Ti, and Cu) has been widely used in heterogeneous catalysis, photocatalysis, and photoelectrocatalysis^[12]. ZVI removes 99% of Cu and 47% of Al, but it is not effective for Ni, Zn, Mn and Cr. ZVI treatment fails neutralizing the acidic pH and causes a secondary contamination by high concentrations of Fe. Clearly, ZVI is not suitable for acidic water remediation as Fe is one of the major pollutants in AMD^[36]. Conventional LDH removes 28% of Cu, 99% of Fe and 84% of Cr but the water sample is still at acidic pH 4 after treatment whereas AC does not work at all. Lime neutralization is the traditional process for AMD treatment, but the further treatment of a tremendous amount of the hazardous solid waste has been problematic^[8]. Table 2 shows a comparison with other studies on AMD remediation regarding pH and metal ions concentrations, material dosage and removal rate of metal contaminants. Clearly, Tables 1 and 2 demonstrate the strength of the MgAl alloy for AMD remediation in terms of the neutralization capability and removal efficiency of different metal contaminants. It is noted that MgO has a high neutralization capability for AMD remediation, but it lacks redox capability and its product is not amenable to resource recovery.

3.3 Removal mechanism

The pH value is critical to the dissolution of Mg and Al from MgAl alloy, the precipitation of heavy metal hydroxides and the formation of LDH and therefore, it is of interest to investigate the mechanism of heavy metals removal by Mg60Al40 alloy via hydroxide

precipitation and/or LDH crystallization/eutectic reactions. Figure 4 shows the effect of initial pH 1.5-4.7 on the concentrations of heavy metals, Mg^{2+} and Al^{3+} and active pH of the solution during the alloy's reaction with the contaminated water in a period of 24 h and XRD characterization of the solid phase after the reaction. Interestingly, the removal rate of heavy metals increases with decreasing initial pH and the average removal rate of the five heavy metals at initial pH 1.5 is significantly higher than that at initial pH 2.5 (49.1 versus 12.1 $\text{mg L}^{-1} \text{ h}^{-1}$) (Figure 4a, b). This trend is opposite to many of traditional and contemporary absorbents, which exhibit lower adsorption rates at lower pH [11, 41, 42].

At initial pH 1.5, the solution pH is lifted straight to pH 9.1 in 0.5 h in which the five heavy metals are all removed by 99.7%. By contrast, the increase of solution pH is much slower for initial pH 2.5-4.7 (Figure 4c-e); the solution pH is increased to around 7 in 0.5 h and remains almost unchanged in 9 h and then slowly decreased to 7.7-8.8 in the following period of 15 h. Overall, the removal rate for each metal decreases with increasing initial pH and is in an order of $\text{Cd} < \text{Ni} < \text{Cr} < \text{Zn} < \text{Cu}$. The removal rate is positively correlated to the corrosion rate of the alloy, which is reflected by Mg^{2+} concentration (Figure 4f-j), with an exception of Cu^{2+} , which is almost completely removed in all cases of initial pH 1.5-4.7 in 0.5 h. Greater than 50% of Cr(VI) are removed in 0.5 h in which pH is < 7 and the remaining amounts of Cr(VI) are removed in the following period of 15 h in which pH is > 7 . Therefore, it is likely that Cu(II) and Cr(VI) are removed primarily by chemical reduction to Cu(0) and Cr(III), respectively while Cd(II), Ni(II) and Zn(II) are removed by hydroxide coprecipitation, iLDH eutectic reaction or their combination. iLDH eutectic reaction is most likely to account for the removal of Cd(II), Ni(II) and Zn(II), which is supported by XRD characterization (Figure 4k-o). Chemical reduction accounted for the removal of Cu(II) and Cr(VI) while hydroxide precipitation explained the removal of Ni(II), Cd(II), Zn(II) and Cr(III) by Al/Fe bimetal [43]. In general, the hydroxide precipitation of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) requires greater than pH 4 [44] and therefore, the removal of these metals should not occur if the solution pH were maintained to below 4. In this context, the removal mechanism of these five heavy metals is investigated by examining the effect of solution pH in the following 4 scenarios. When the initial pH increases from 1.5 to 4.7, the maximum pollutant removal capacity remains stable at $2.70 \pm 0.10 \text{ mg g}^{-1}$, while the minimum value gradually decreases: from 2.35, 2.26, 2.27, 2.07 to 1.66 mg g^{-1} .

In the first scenario ("6+0"), a constant pH 4.0 (± 0.5) was maintained for a period of 6 h to determine the contributions of chemical reduction, hydroxide coprecipitation and *in-situ* LDH formation to heavy metals removal by monitoring pH and the concentrations of Mg^{2+} , Al^{3+} and heavy metals (Figure 5a, b) and XRD and SEM characterization of the solid phase

after the reaction (Figure 5c, d). Mg^{2+} concentration increases rapidly to 500 mg L^{-1} in 1 h and then slowly to 1000 mg L^{-1} in the following 5 h while Al dissolution is relatively slow at the beginning (1 h) and then its concentration gradually increases to 200 mg L^{-1} (Figure 5a). Correspondingly, the concentration of Cd, Cr and Cu is rapidly reduced from initial concentration of 25 mg L^{-1} to $< 1.3 \text{ mg L}^{-1}$ within 1 h. Ni and Zn are also rapidly reduced to $< 9.9 \text{ mg L}^{-1}$ in 0.75 h but part of them are quickly released back to the solution and their concentrations remain almost unchanged at 13.7 and 16.5 mg L^{-1} , respectively (Figure 5b). The desorption and re-sorption might explain the removal behaviour of Ni(II) and Zn(II) during the 6 h period of a constant pH 4.0 at which no LDH phases are observed (Figure 5c, d). Cr(VI) and Cu(II) are removed by chemical reduction while Cr(III), Cd(II), Ni(II) and Zn(II) are partially removed by hydroxide precipitation. It was found that Cu(0) was a catalyst for Cr(VI) reduction by sulfidated zerovalent iron [45]. Similarly, the transformation of Cu(II) to Cu(0) may also promote Cr(VI) reduction in this study.

In the second scenario (“6+6”), pH of the solution was maintained at pH 4.0 for 6 h and then the pH was not controlled for the next period of 6 h, during which the solution pH increases and peaks to 7.74 and Mg^{2+} reaches a peak of 1044 mg L^{-1} while Al^{3+} concentration declines to $< 0.05 \text{ mg L}^{-1}$ in 10 h (Figure 5e). Ni and Zn are quickly re-removed and their removal rates are greater than 99.8% (Figure 5f). The formation of LDH is clearly observed (Figure 5g, h) and the decrease of Mg^{2+} and Al^{3+} ion concentration (Figure 5e) is the result of MgAl-LDH formation. In this context, it can be concluded that Cu(II) and Cr(VI) are removed by chemical reduction while in situ formation of LDH phases accounts primarily for removing Zn(II), Ni(II), Cd(II) and Cr(III).

In the third scenario (“1+11”), the pH of the solution was maintained at 4.0 for 1 h and then the reaction continued for 11 h without pH control (Figure 5i-l). The pH increases rapidly from 4.0 to 8.8 in 2 h at which Mg^{2+} ion concentration reaches 580 mg L^{-1} and then declines very slowly while Al^{3+} concentration increases to 17.3 mg L^{-1} and then becomes undetectable after 2 h (Figure 5i). Concentrations of Cu, Cr, Cd, Ni and Zn decreased from 25 mg L^{-1} to 4 mg L^{-1} in 0.75 h, but Ni and Zn are released back to the solution at 7.1 - 8.6 mg L^{-1} at 1 h and then are rapidly removed to less than 0.05 mg L^{-1} when the pH 4.0 control is stopped for 1 h (Figure 5j). This is the result of MgAl-LDH formation as the LDH phases are clearly observed (Figure 5k-l).

Finally (“0+12”), the experiment was conducted at initial pH 4.0 without pH control for 12 h (Figure 5m-p). The pH of the solution rapidly increases from 4.0 to 7.0 in 20 min and then remains unchanged where Mg^{2+} and Al^{3+} concentration is 13.7 and 0.5 mg L^{-1} , respectively (Figure 5m). The removal rate of heavy metals is very slow with an exception of Cu (Figure

5n) and LDH is not observed (Figure 5o-p). In this scenario, the rapid removal of Cu^{2+} is attributed to chemical reduction.

The XPS results of the solid products in the above 4 scenarios (6+0, 6+6, 1+11 and 0+12) are shown in Figure 6. Cr(III), Cu(0), Cu(II) and Cd(II) are detected and Cr(VI), Ni(II) and Zn(II) are not identified in the 6+0 scenario (Figure 6a). Cr(VI) is completely reduced to Cr(III) and the presence of Cu(II) is likely re-oxidation of Cu(0). The oxidation of freshly formed Cu(0) by O_2 was observed during the process of Cu(II) removal by ZVI [46] and the adsorption of metal ions (e.g., Cr, Ni, As) by CuO nanoparticles was found in water matrices from acidic to alkaline pH [47, 48].

Interestingly, no heavy metals are detected in the XPS characterization in both cases of 6+6 and 1+11 h (Figure 6b, c) although heavy metals are all removed out of the solution in 2 h (see Figure 5f, j). This is likely that the heavy metals are concealed by relatively thick MgAl-LDH phases because the thickness of XPS detection is generally no more than 8 nm [49]. In the case of 0+12 h scenario, Cr(VI), Cr(III), Cd(II), Cu(II), Ni(II) and Zn(II) are observed and Cu(0) is not found (Figure 6d). This can be explained that part of Cr(VI) is reduced to Cr(III) in the beginning and then Cr(III), Cd(II), Cu(II) Ni(II) and Zn(II) form hydroxide precipitates when the pH of the solution increases to alkaline (see Figure 5m, n).

The SEM-EDS mapping of the reaction solid product in the 6+6 experiment is shown in Figure S3. Clearly, the element distribution is dominated by Mg, Al, O and Cl and the five heavy metals Cd, Cu, Cr, Ni and Zn, and N are also observed. The FTIR spectra of MgAl40 alloy and its reaction product from “0+12” experiment are displayed in Figure 7. A broad peak at 3439 cm^{-1} is related to the vibration of -OH in LDH structure, and the peak at 1623 cm^{-1} is related to water molecules on the surface of LDH [50, 51]. The band at 1350 cm^{-1} is ascribed to NO_3^- stretching group [52]. The bands recorded at 443, 503, 537, 563, 570 and 626 cm^{-1} are ascribed to stretching vibration of Al-O [53, 54], Mg-O [53, 54], Zn-O [55], Ni-O [56], Cd-O [57] and Cr(III)-O [58].

TEM characterization is given in Figure 8 and the corresponding EDS elemental mapping is presented in Figure S4. The hexagonal sheet structure is consistent with the typical MgAl-LDH morphology [59] and the particle size is relatively uniform in a diameter of 500 nm. The lattice spacings between adjacent planes in the microsheets are $2.57\text{ \AA}$ and $1.49\text{ \AA}$ (Figure 8), corresponding to those between the (012) and (113) crystal planes of LDH, respectively. The EDS spectrum of the microsheets shows strong signals of Mg, Al, O and C (carbon signal coming from the substrate) and weak signals of five heavy metal elements (Figure S4). The determined atomic ratio of M^{2+} , M^{3+} , A^- and OH^- is 2.6:1.0:1.0:7.6. Previously, we showed that the chemical formula of the MgAl-LDH from the hydrolysis of $\text{Mg}_{70}\text{Al}_{30}$

alloy at initial pH 1 HCl is $[\text{Mg}_{18}\text{Al}_7(\text{OH})_{50}][\text{Cl}_3(\text{CO}_3)_{25}\text{H}_2\text{O}]$ [26]. Here, the chemical formula of LDH after heavy metals removal by MgAl alloy is determined to be $\text{M}_3^{2+}\text{M}^{3+}\text{A}^-(\text{OH})_8^-$.

In summary, mixtures of Cr(VI), Cd(II), Cu(II), Ni(II), Zn(II) and nitrate are efficiently removed by MgAl alloys in a synergistic effect of chemical reduction and iLDH's eutectic reactions. Cr(VI), Cu(II) and nitrate are removed by chemical reduction to Cr(III), Cu(0) and NH_4^+ , respectively while Mg(II), Al(III), Cd(II), Cr(III), Ni(II), Zn(II) and OH^- react to generate hybrid LDH precipitates. Hydroxide precipitation may also account for partial removal, but it is not the dominant mechanism in the present system, especially for amphoteric metals such as Al, Cd, Ni and Zn. This conclusion is supported by significantly lower solubility constant K_{sp} of M/Al-LDH (M = Zn, Cd, Ni) than their hydroxide counterparts (e.g., ZnAl-LDH $K_{\text{sp}} = 1 \times 10^{-58}$, $\text{Zn}(\text{OH})_2$ $K_{\text{sp}} = 3 \times 10^{-17}$ and $\text{Al}(\text{OH})_3$ $K_{\text{sp}} = 6.3 \times 10^{-19}$) [60-63].

3.4 Effect of temperature, pollutant concentration, alloy dosage and particle size

The removal rates of pollutants by ZVI and ZVAl increase with increasing temperature [16, 17, 19], and a similar effect is observed in the present study (Figure S5). It was found that the removal rate is almost same between 45 °C and 35 °C while hydrogen generation is increased significantly at 45 °C. The removal rate increases with decreasing pollutant concentration (Figure S6), increasing alloy's dosage (Figure S7) and decreasing alloy particle size (Figure S8).

4. Conclusion

This study provides a highly efficient process for acidic water remediation by MgAl alloy without dosing any other chemicals. The reactivity of the MgAl alloy increases with increasing Mg/Al ratio and decreasing the pH of acidic water. The 70% Mg and 30% Al alloy achieves a full neutralization and complete removal of 20 mg L⁻¹ Cd²⁺, Cr(VI), Cu²⁺, Ni²⁺ and Zn²⁺ in 15 min from acidic water at pH 2. Cr(VI) and Cu²⁺ are removed by chemical reduction to Cr³⁺ and Cu0 while Cd²⁺, Cr(III), Ni²⁺ and Zn²⁺ are incorporated into the lattice of LDH via eutectic reactions. The reactivity and durability of the alloy and the remediation efficiency are well integrated by in situ surface re-construction of the alloy to produce environmentally benign LDH. The MgAl alloy outperforms benchmark materials activated carbon, lime, zerovalent iron and conventional layered double hydroxide for acidic water remediation in terms of pollutants removal efficiency, secondary contamination, biocompatibility and resource recovery. This study provides an opportunity of exploring new applications of Mg and Al alloy scraps to environmental remediation, which has been facing great challenges.

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Table 1. Treatment of acid mine drainage (AMD) from a copper ore site (117.7°E, 29.0°N).

	Before treatment	After treatment							
		MgA30	MgA40	MgA60	MgAl70	LDH	ZVI	AC	CaO
pH	2.47	7.02	7.37	7.50	7.81	3.96	4.18	2.33	12.45
Cu	88.5	<0.05	<0.05	<0.05	<0.05	59	0.73	83	<0.05
Ni	5.34	2.23	<0.05	<0.05	<0.05	4.84	3.17	5.11	<0.05
Zn	6.14	0.92	0.14	0.12	0.13	19.7	5.53	5.97	0.17
Fe	559	0.45	0.45	0.55	0.45	2.73	2039	474	0.55
Mn	117	23	19	10	1.37	111	128	115	0.05
Cr	1.63	0.23	0.06	<0.05	0.06	0.10	1.64	0.65	0.10
Ca	441	429	314	373	391	473	448	447	929
Al	731	<0.1	<0.1	<0.1	<0.1	622	383	711	1.29
Mg	1527	2587	2597	2576	2338	1626	1523	1530	0.74
K	2.69	3.41	4.21	3.74	3.21	4.92	3.03	10.55	3.487

Note: The concentration of metals is in mg L⁻¹.

Table 2. Different materials for acid mine drainage remediation reported in literature

Metals	Phosphate limestone waste ^[37]			α -Fe ₂ O ₃ nanoparticle ^[38]			Magnesium oxide ^[39]			Bentonite clay ^[40]		
	Dosage: 1000 g L ⁻¹			Dosage: 1 g L ⁻¹			Dosage: 0.33 g L ⁻¹			Dosage: 20 g L ⁻¹		
	Initial AMD pH: 2.5			Initial AMD pH: 2.4			Initial AMD pH: 2.9			Initial AMD pH: 2.3		
	Treated AMD pH: 5.0			Treated AMD pH: 4.1			Treated AMD pH: 9.5			Treated AMD pH: 6.0		
	Initial (mg L ⁻¹)	Treated (mg L ⁻¹)	Removal (%)	Initial (mg L ⁻¹)	Treated (mg L ⁻¹)	Removal (%)	Initial (mg L ⁻¹)	Treated (mg L ⁻¹)	Removal (%)	Initial (mg L ⁻¹)	Treated (mg L ⁻¹)	Removal (%)
Al	1201	90	92.52	0.90	0.00	100.00	156	1.56	99.00	190	1.10	99.42
Mg	868	871	-0.40	385	0.00	100.00	-	-	-	183	192	-4.92
Ca	201	599	-198.24	561	256	54.37	-	-	-	762	566	25.72
Cu	94	33	65.11	-	-	-	4.20	0.00	100.00	7.80	0.10	98.72
Fe	232	0.39	99.83	835	79	90.54	341	0.34	99.90	259	15	94.21
Cr	-	-	-	-	-	-	-	-	-	20	0.10	99.50
Zn	24	17	29.86	0.90	0.10	88.89	7.16	0.20	97.20	7.90	6.30	20.25
Mn	38	34	10.91	30	0.00	100.00	38	0.50	98.68	40	35	12.50
Ni	-	-	-	1.80	0.50	72.22	3.90	0.00	100.00	17	24	-46.99
Co	5.62	5.27	6.23	0.80	0.30	62.50	-	-	-	41	45	-8.23
Pb	<0.10	<0.10	-	-	-	-	-	-	-	6.30	0.10	98.41
Cd	-	-	-	-	-	-	-	-	-	-	-	-
As	-	-	-	-	-	-	-	-	-	20	0.05	99.75

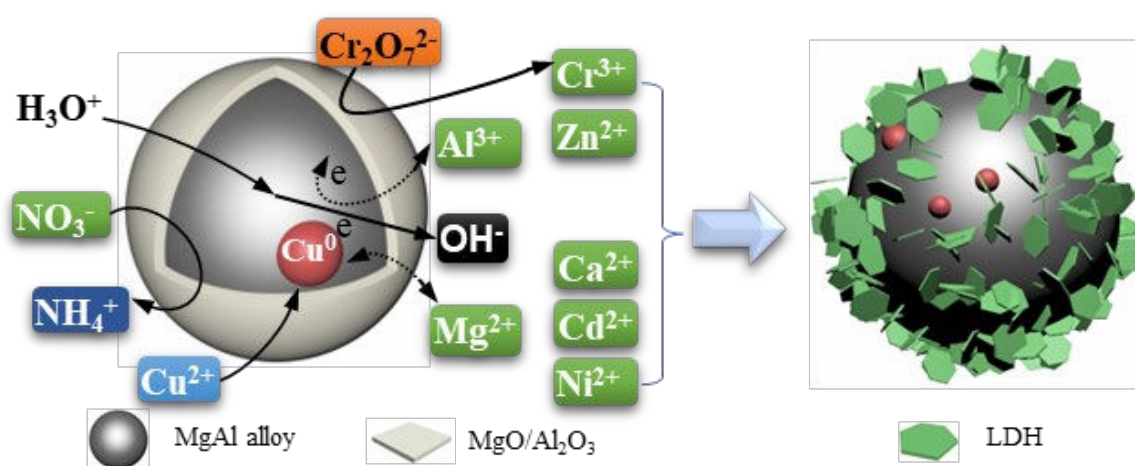


Figure 1. Schematic illustration of in situ layered double hydroxide (iLDH) for acidic water remediation using MgAl alloy. A general molecular formula of LDH is $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}\text{OH}_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} are divalent and trivalent metal cations and A^{n-} is an anion in the interlayer space. Zerovalent Mg and Al provide electrons for H^+ and oxidative pollutants (e.g., Cr(VI) , Cu^{2+} and NO_3^-) and the eutectic reaction takes place between LDH and other divalent and trivalent metal ions (Cd^{2+} , Ni^{2+} , Cr^{3+} , etc.).

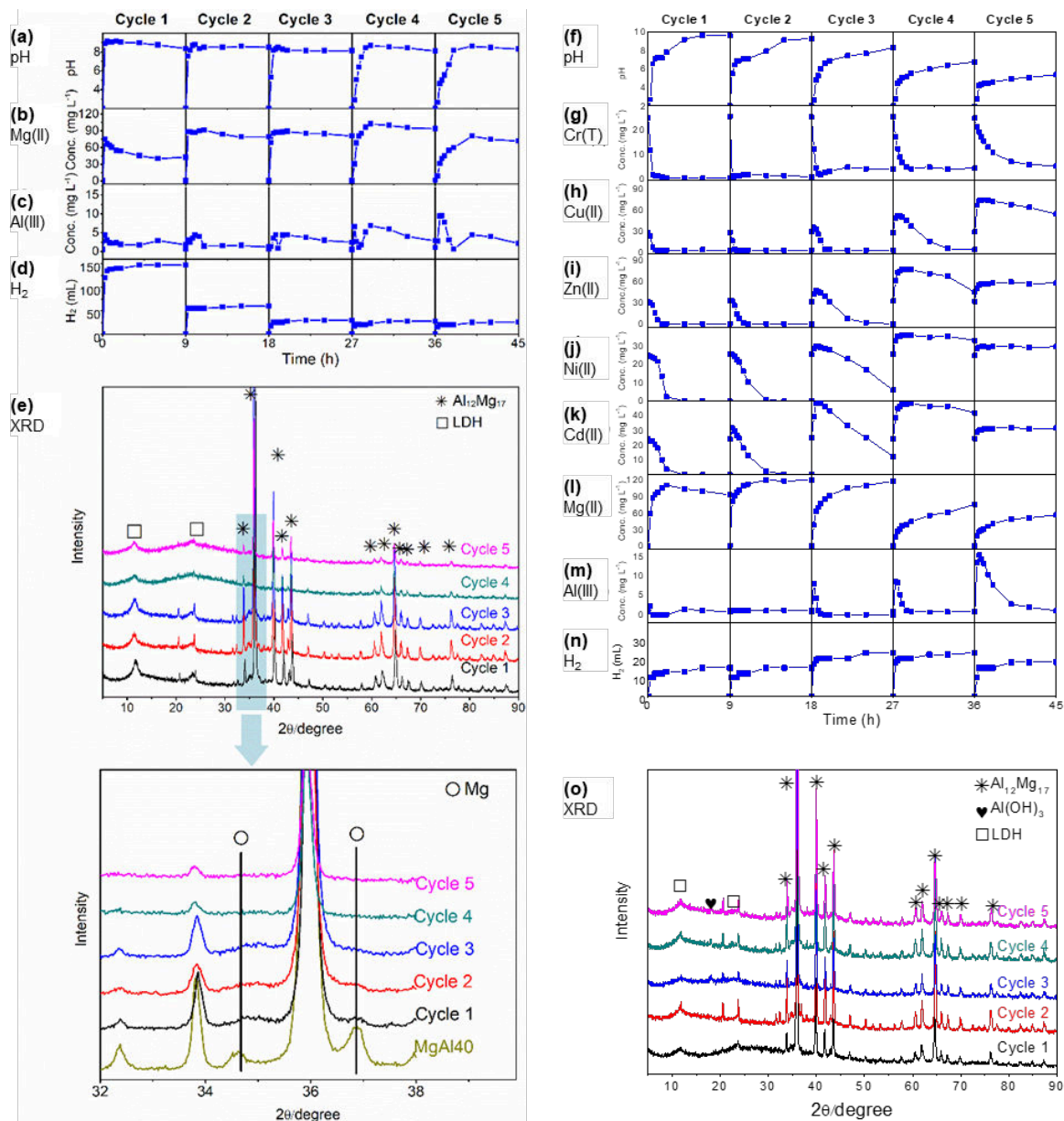


Figure 2. Metal ion concentration, pH variation, H_2 generation and XRD characterization of Mg60Al40 alloy after pretreatment with pH 2 HCl in 5 cycles (Left panel) and the pretreated alloy's reaction with pH 2, heavy metal-containing water in 5 cycles (Right panel). Initial concentration of each heavy metal is 25 mg L⁻¹ and initial pH is 2; alloy particle size -200 mesh; solution volume 300 mL; alloy loading 3 g; stirring speed 300 rpm, temperature 22±2 °C.

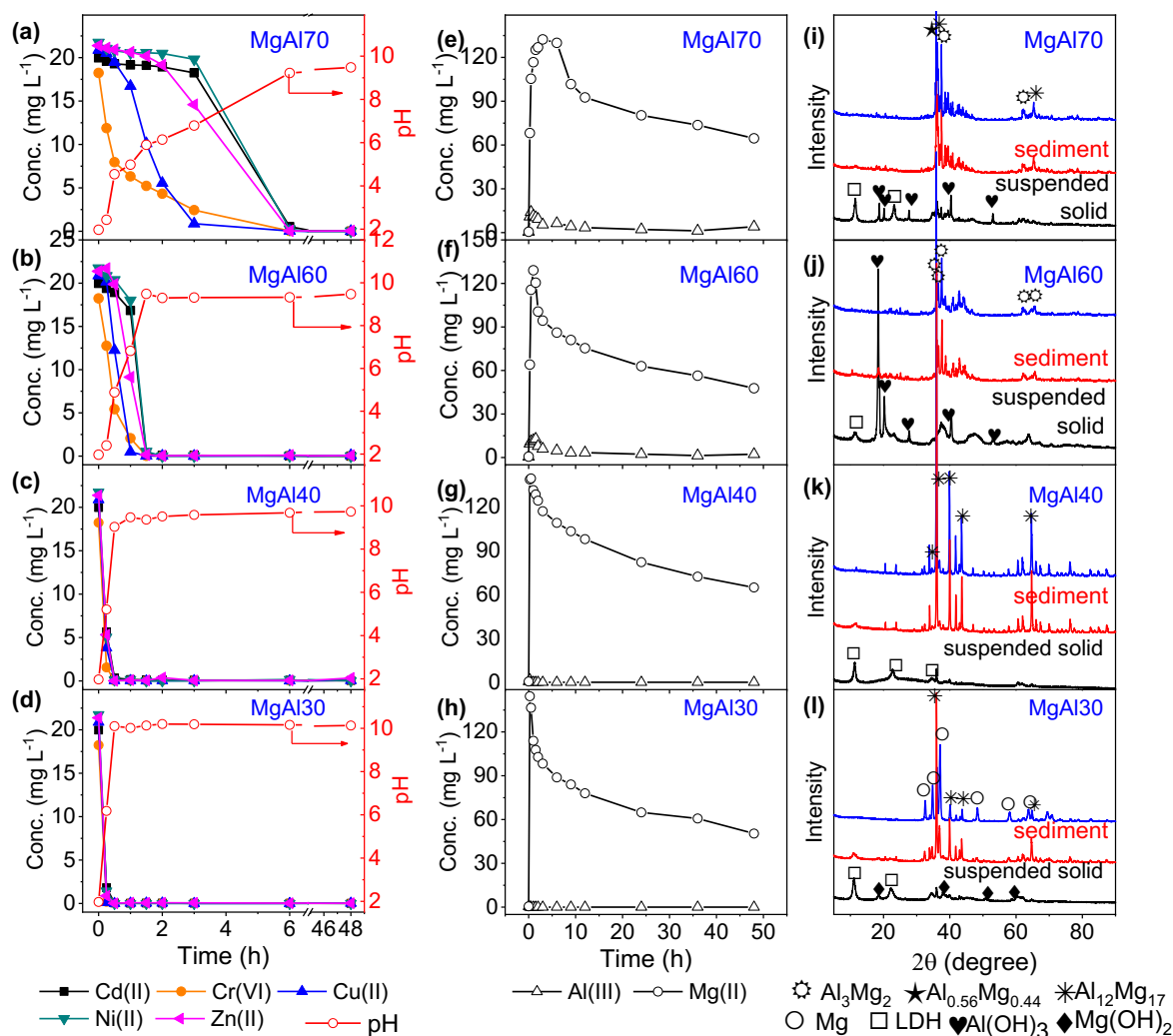


Figure 3. Effect of alloy's Mg/Al ratio on (a-d) the concentrations of heavy metals and pH as a function of reaction time, (e-h) the concentrations of Mg²⁺ and Al³⁺ ions, (i-l) the formation of LDH, Al(OH)₃ and Mg(OH)₂. The XRD characterization (i-l) is the pristine alloy and the lower and upper phases of the solution after reaction. Alloy loading 3 g, alloy particle size -200 mesh, solution volume 300 mL, pH 2 (HCl), reaction time 48 h, stirring speed 300 rpm, temperature 22±2 °C. The powder diffraction files (PDF) matched are Mg (PDF #35-0821), Mg₂Al₃ (PDF #29-0048), Al₁₂Mg₁₇ (PDF #01-1128), Mg_{0.44}Al_{0.56} (PDF #51-0799), LDH (PDF #89-0460), Al(OH)₃ (PDF #74-1775), Mg(OH)₂ (PDF #82-2453).

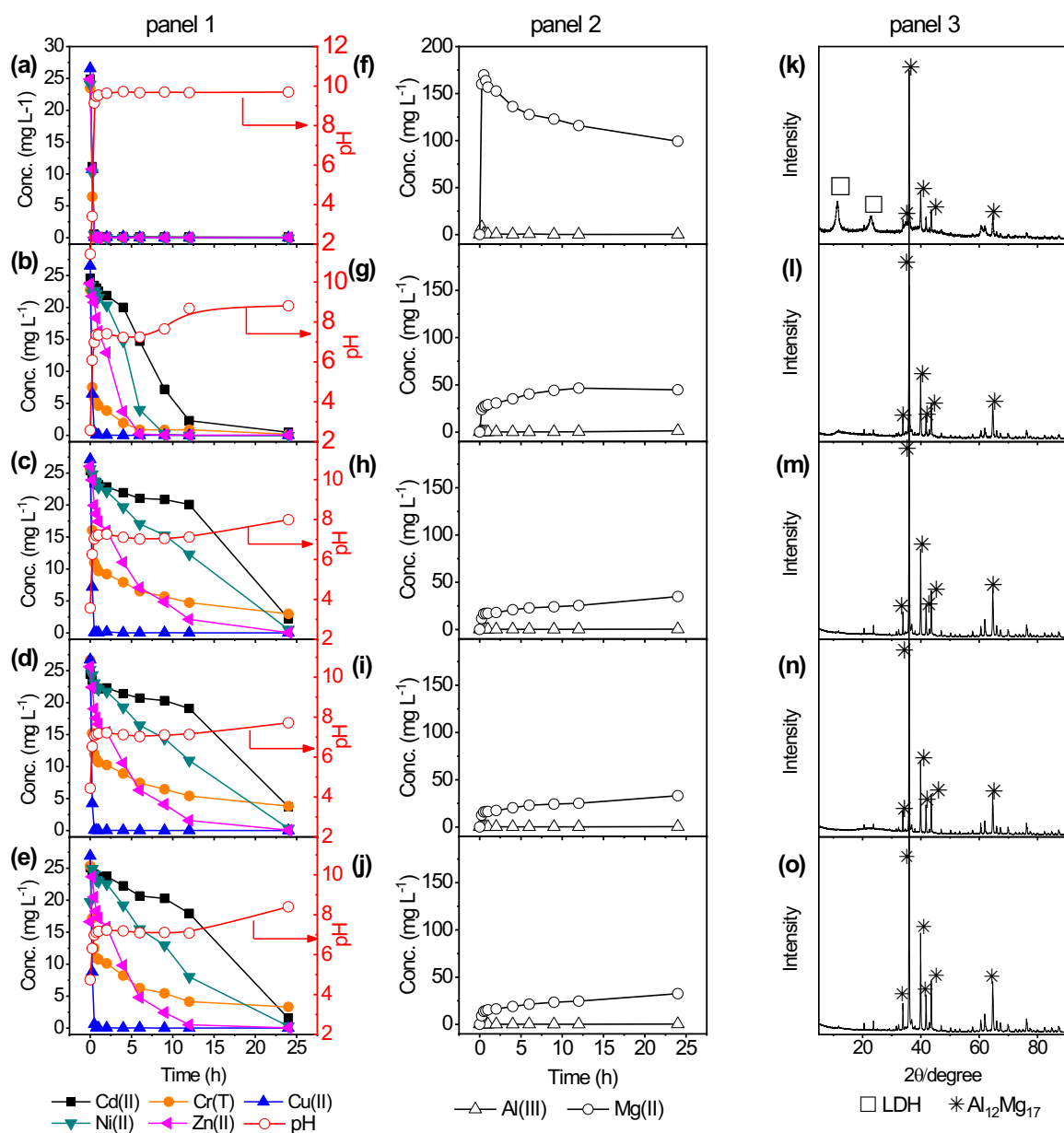


Figure 4. Effect of initial pH of heavy metals contaminated water on (a-e) the concentrations of heavy metals and active pH with reaction time (0-24 h), (f-j) the concentrations of Mg^{2+} and Al^{3+} ions, (k-o) XRD characterization of the solids from solution at the end of reaction. Heavy metals contaminated water was prepared by dissolving K_2CrO_7 and metal nitrates in deionized water and adjusted to pH 1.5-4.5 using dilute HCl solutions. pH 4.7 is the native pH of the solution. Solution volume 300 mL, 3 g Mg60Al40 alloy (-200 mesh), reaction time 24 h, stirring speed 300 rpm, temperature 22 ± 2 °C.

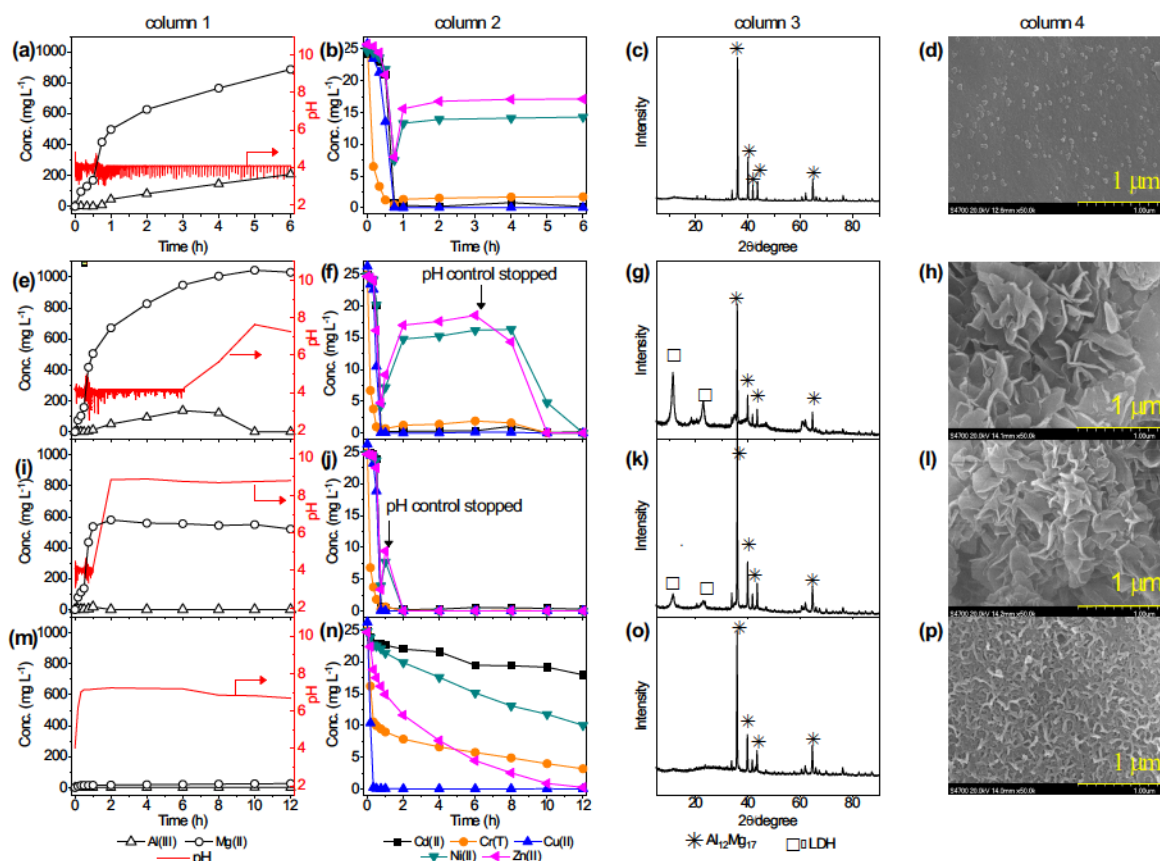


Figure 5. Effect of heavy metals solution pH control scenarios. (a-d) “6+0”, pH is controlled at 4.0 for 6 h, (e-h) “6+6”, pH is controlled at 4.0 for 6 h and then uncontrolled for 6 h, (i-l) “1+11”, pH is controlled at 4.0 for 1 h and then uncontrolled for 11 h, (m-o) “0+12”, initial pH is made to 4.0 and the pH is not controlled for 12 h. Column 1, concentrations of Mg and Al ions and pH of the solution; Column 2, concentrations of heavy metals; Column 3, XRD of reaction products; Column 4, SEM characterization of reaction products. Heavy metals solution 300 mL, MgAl40 alloy (-200 mesh) 3 g, stirring speed 300 rpm, temperature 22 ± 2 °C.

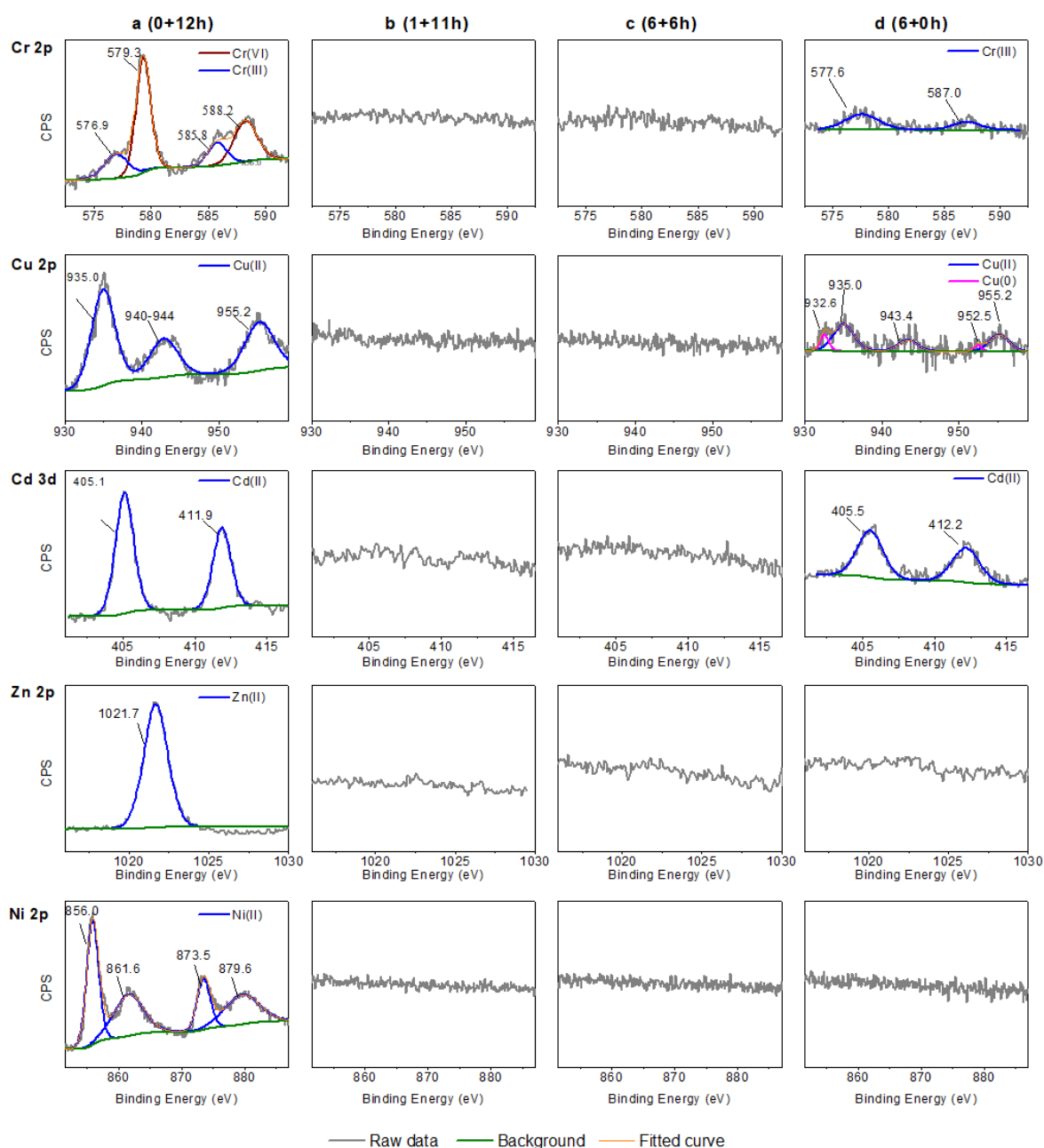


Figure 6. XPS characterization of reaction products of MgAl40 alloy with heavy metals solution in 4 scenarios of pH control. Column represents the result of XPS characterization for pH control scenarios (a) 0+12, (b) 1+11, (c) 6+6, (d) 6+0, these terms are explained in the caption of Figure 5.

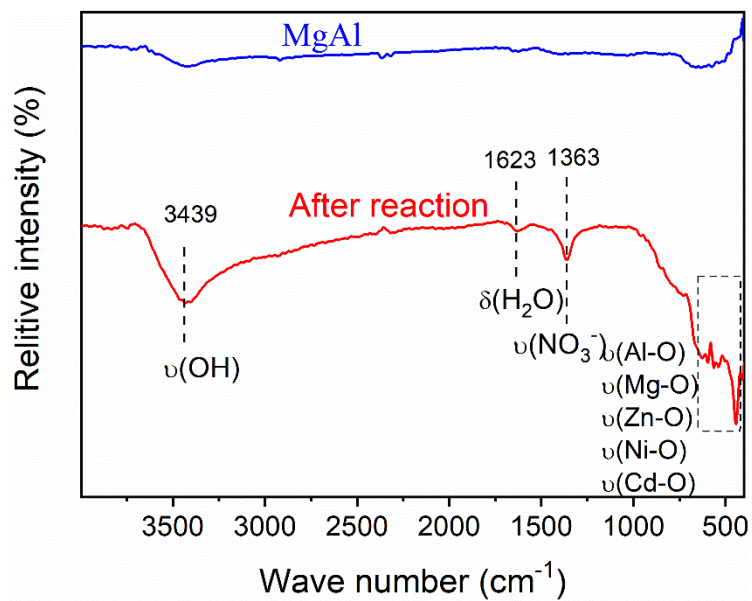


Figure 7. FTIR of MgAl40 alloy and its reaction product with heavy metals solution in the 0+12 experiment.

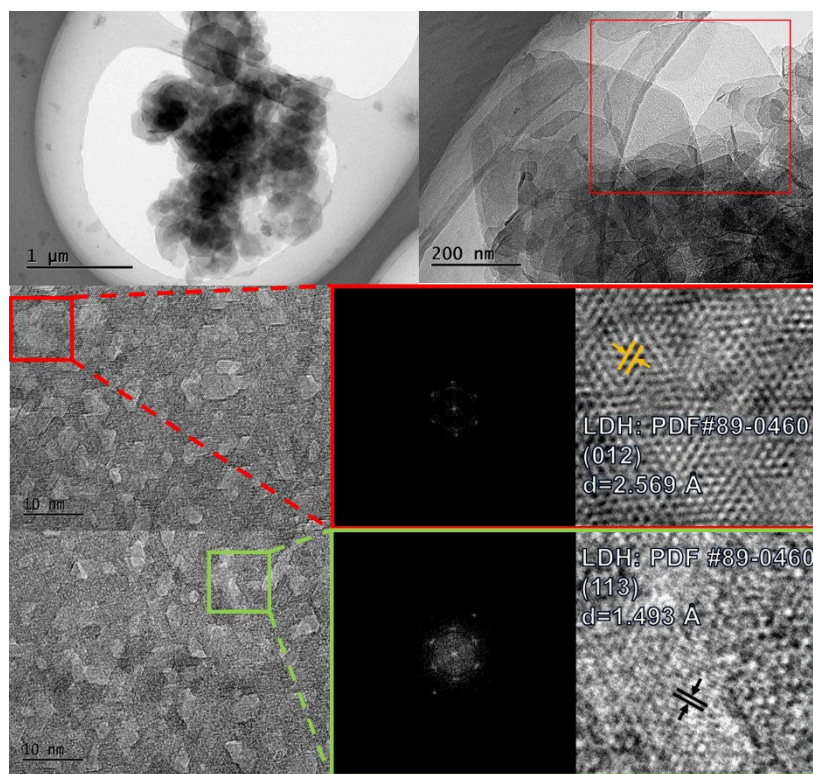


Figure 8. TEM characterization of reaction products of MgAl40 alloy with heavy metals

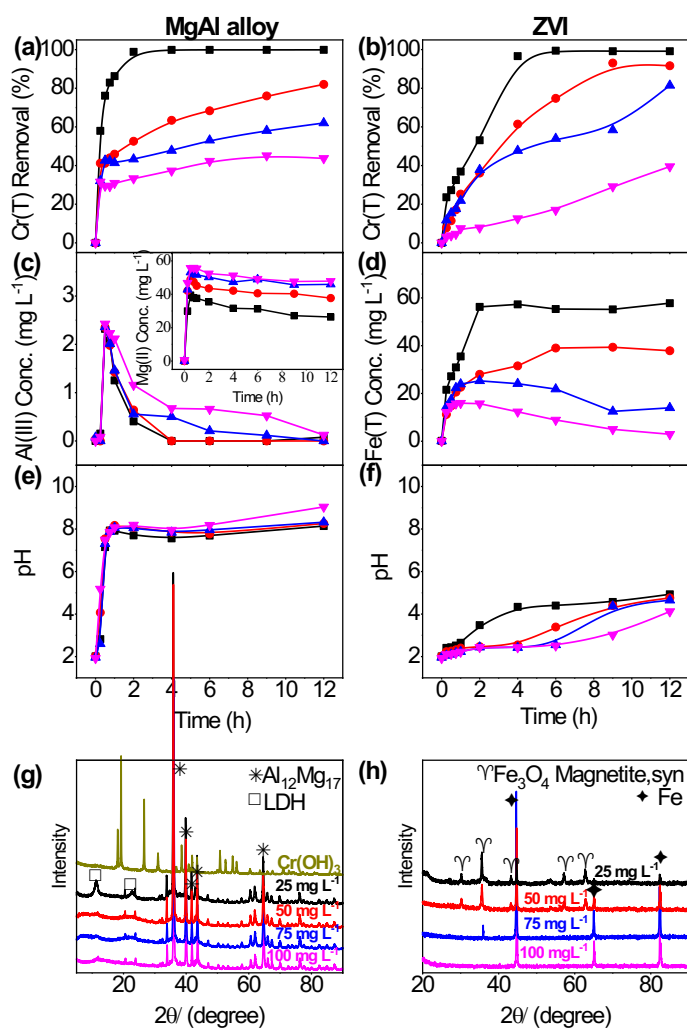


Figure S1. Reaction of different $K_2Cr_2O_7$ concentrations with MgAl alloy (left panel) and ZVI (right panel). (a) removal rate of Cr(VI) and Cr(III) [Cr(T)], (b) concentration of Mg, Al or Fe ions, (c) pH of solution, (d) XRD characterization of reaction product. $K_2Cr_2O_7$ solution 300 mL pH 2 (HCl); 3 g alloy (-200 mesh), stirring speed 300 rpm, temperature 22 ± 2 °C. The initial concentration of Cr(VI): ■=25, ●=50, ▲=75, ▼=100 mg L⁻¹.

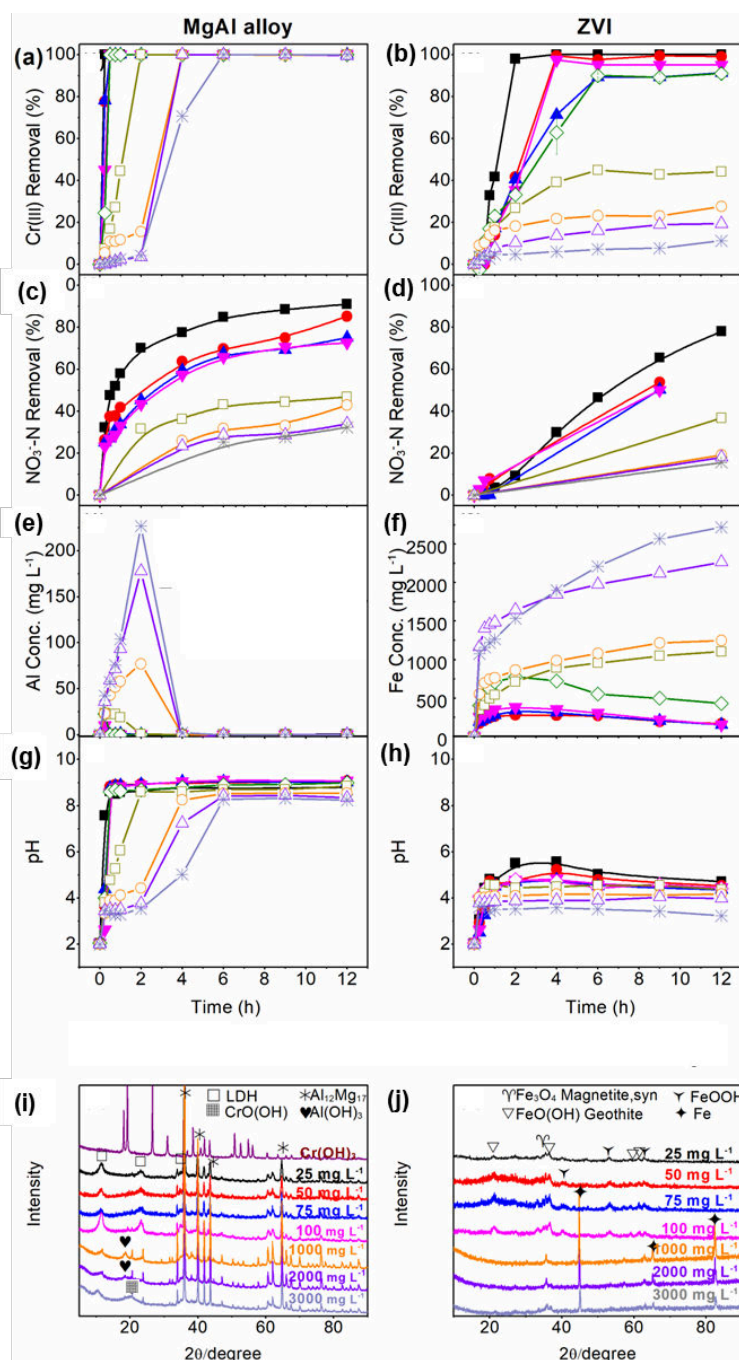


Figure S2. Reaction of different $\text{Cr}(\text{NO}_3)_3$ concentrations with MgAl alloy (left panel and ZVI (right panel). (a) Cr(III) removal, (b) NO_3^- removal, (c) Concentration of Al, Mg or Fe ions, (d) pH of solution, (e) XRD characterization of reaction product. $\text{Cr}(\text{NO}_3)_3$ solution 300 mL, pH 2 (HCl); 3 g alloy (-200 mesh), stirring speed 300 rpm, temperature 22 ± 2 °C. The initial concentration of Cr(III): ■=25, ●=50, ▲=75, ▼=100, ◇=300, □=500, ○=1000, △=2000, ※=3000 mg L^{-1} .

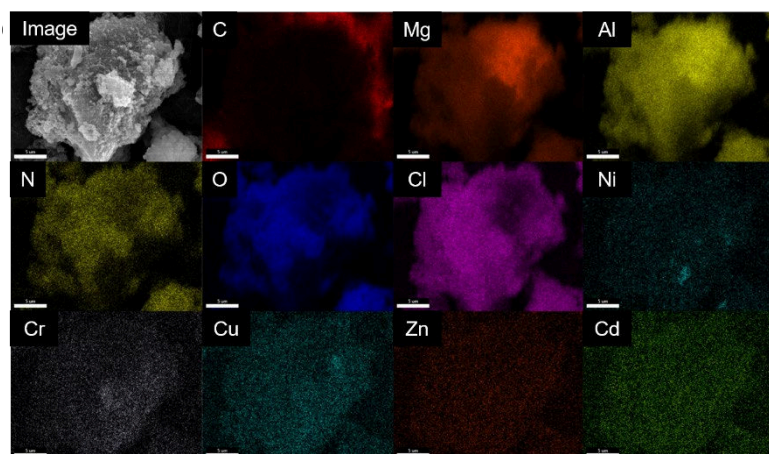


Figure S3 EDS elemental maps of the corresponding SEM image of reaction products of MgAl40 alloys with heavy metals solution. Reaction condition: pH controlled at 4.0 for 6 h and then uncontrolled for 6 h (6+6 h). Solution volume 300 mL, alloy (-200 mesh) 3g, stirring speed, temperature 22 ± 2 °C.

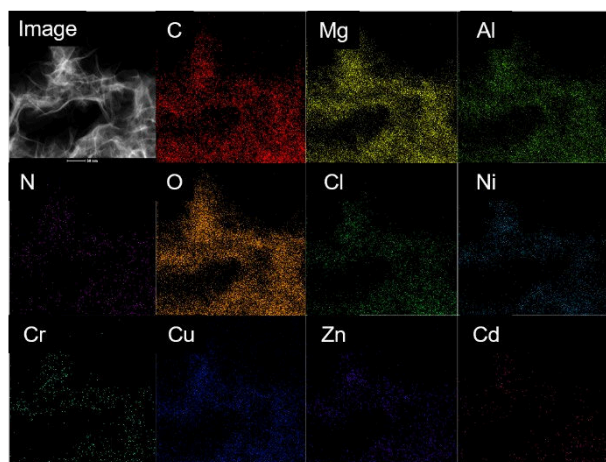


Figure S4. EDS elemental maps of the corresponding TEM image of reaction products of MgAl40 alloy with heavy metals solution. Reaction condition: pH controlled at 4.0 for 6 h and then uncontrolled for 6 h (6+6 h). Solution volume 300 mL, alloy (-200 mesh) 3g, stirring speed, temperature 22 ± 2 °C.

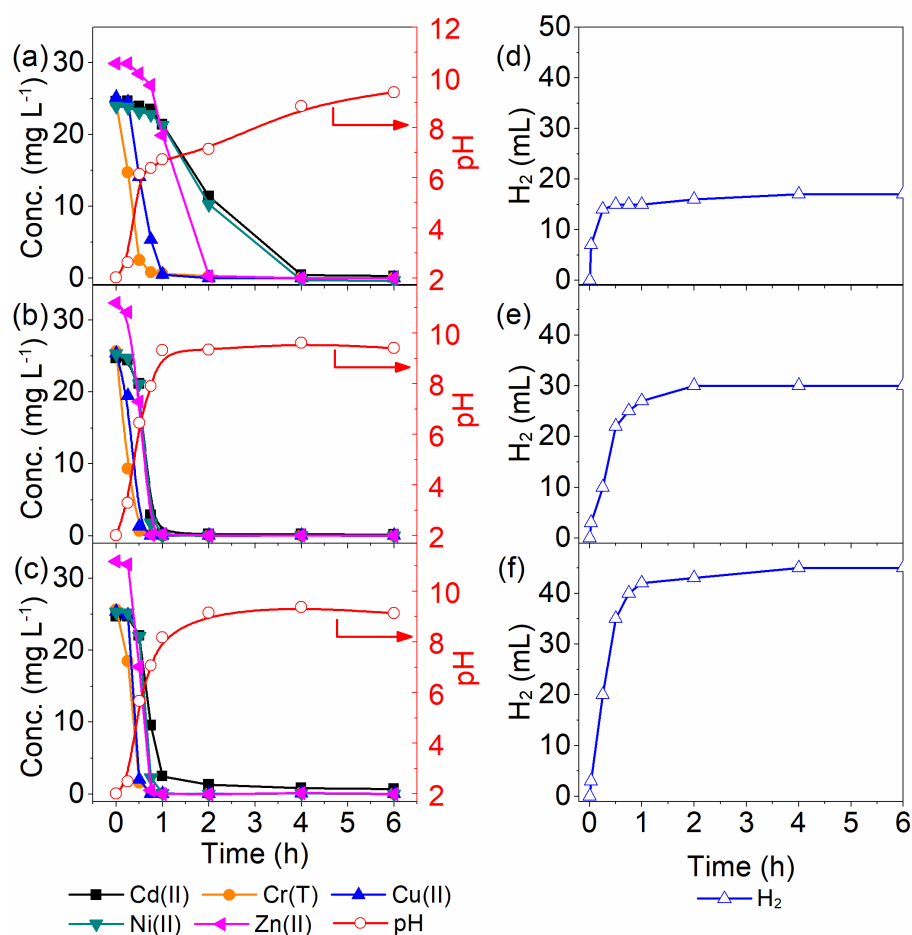


Figure S5. Effect of reaction temperature on removal of heavy metals and solution pH by MgAl40 alloy. (a, d) 18 °C, (b, e) 35 °C, (c, f) 45 °C. 300 mL, pH 2 (HCl), 3g alloy (-200 mesh), stirring speed 300 rpm.

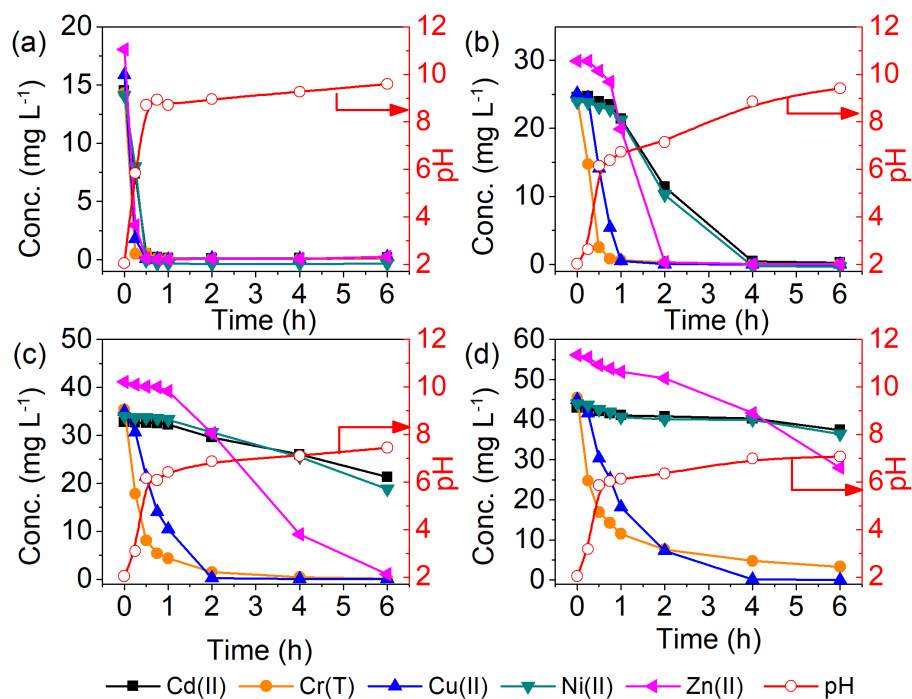


Figure S6. Effect of initial concentrations of heavy metals on . Each metal concentration in mg L⁻¹ (a) 15, (b) 25, (c) 35, (d) 45. Solution 300 mL, pH 2 (HCl), 3 g MgAl40 alloy (-200 mesh), stirring speed 300 rpm, temperature 18±2 °C.

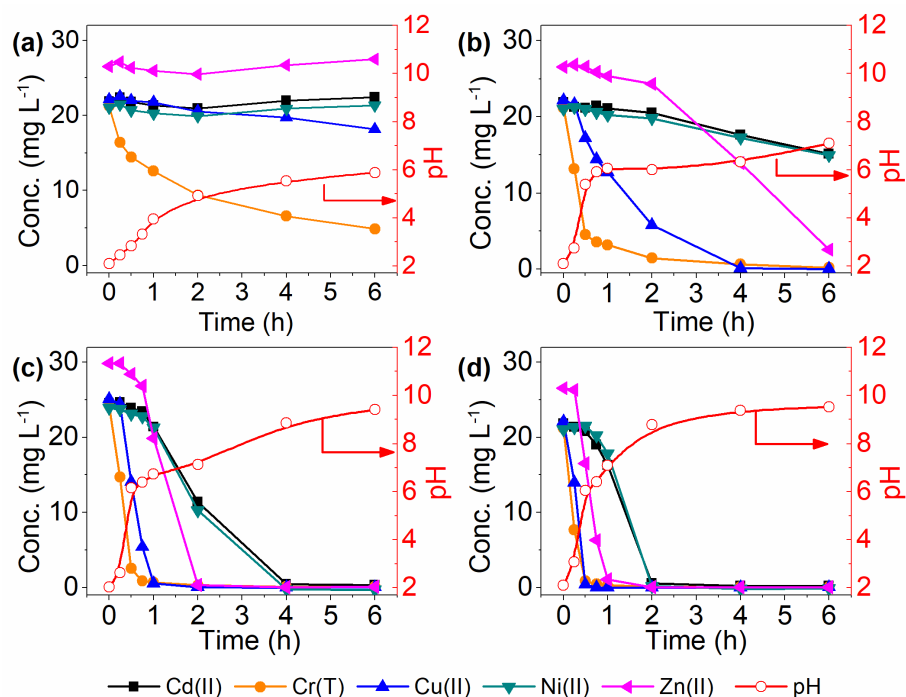


Figure S7. Effect of MgAl40 alloy dosage on the removal of heavy metals and solution pH. (a) 1 g, (b) 2 g, (c) 3 g, (d) 4 g. 300 mL, pH 2 (HCl), alloy (-200 mesh), stirring speed 300 rpm, temperature 18 ± 2 °C.

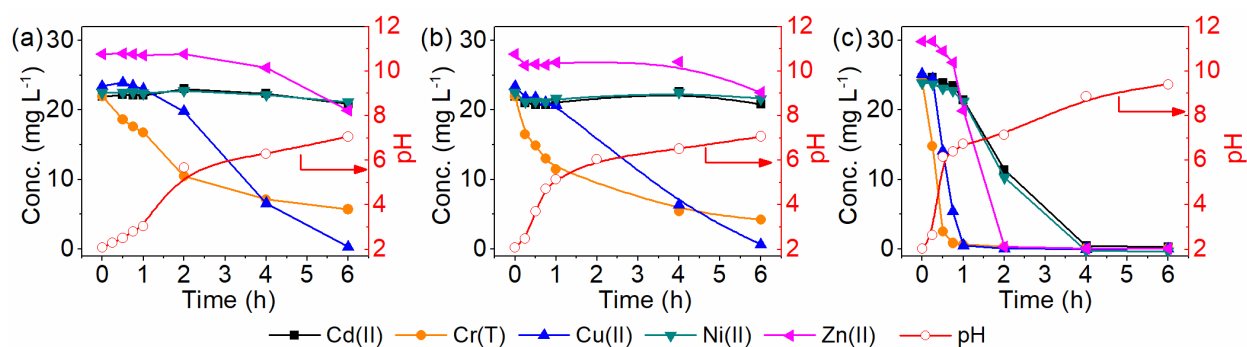


Figure S8. Effect of MgAl40 alloy particle size on the removal of heavy metals and solution pH. (a) -50 mesh, (b) -80 mesh and (c) -200 mesh. 300 mL, pH 2 (HCl), 3 g alloy (-200 mesh), stirring speed 300 rpm, temperature 18 ± 2 °C.

Supplementary Information

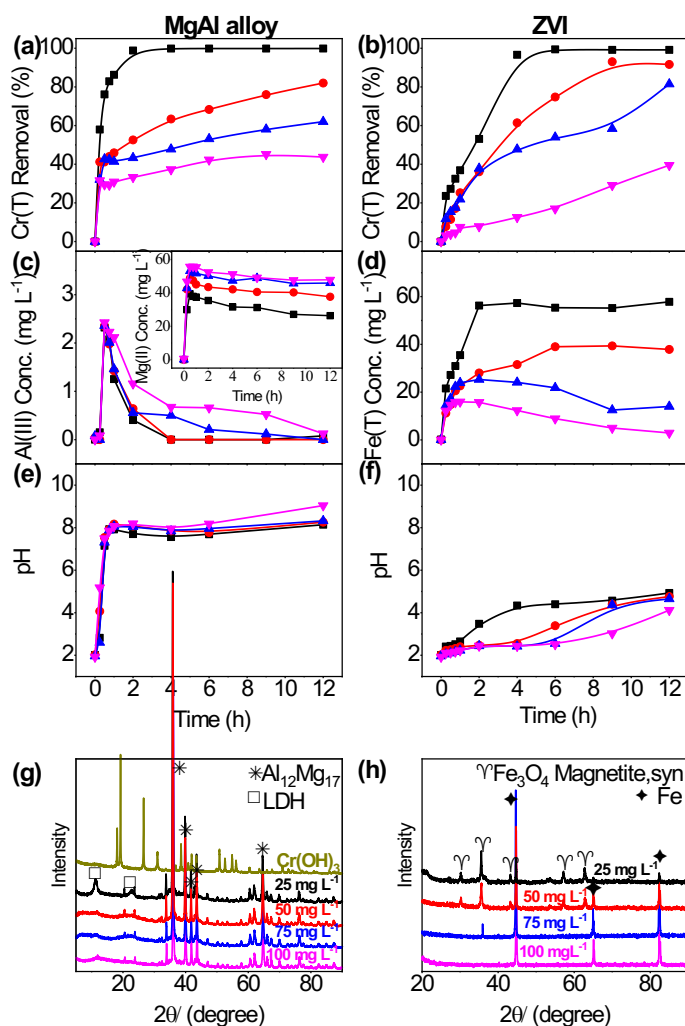


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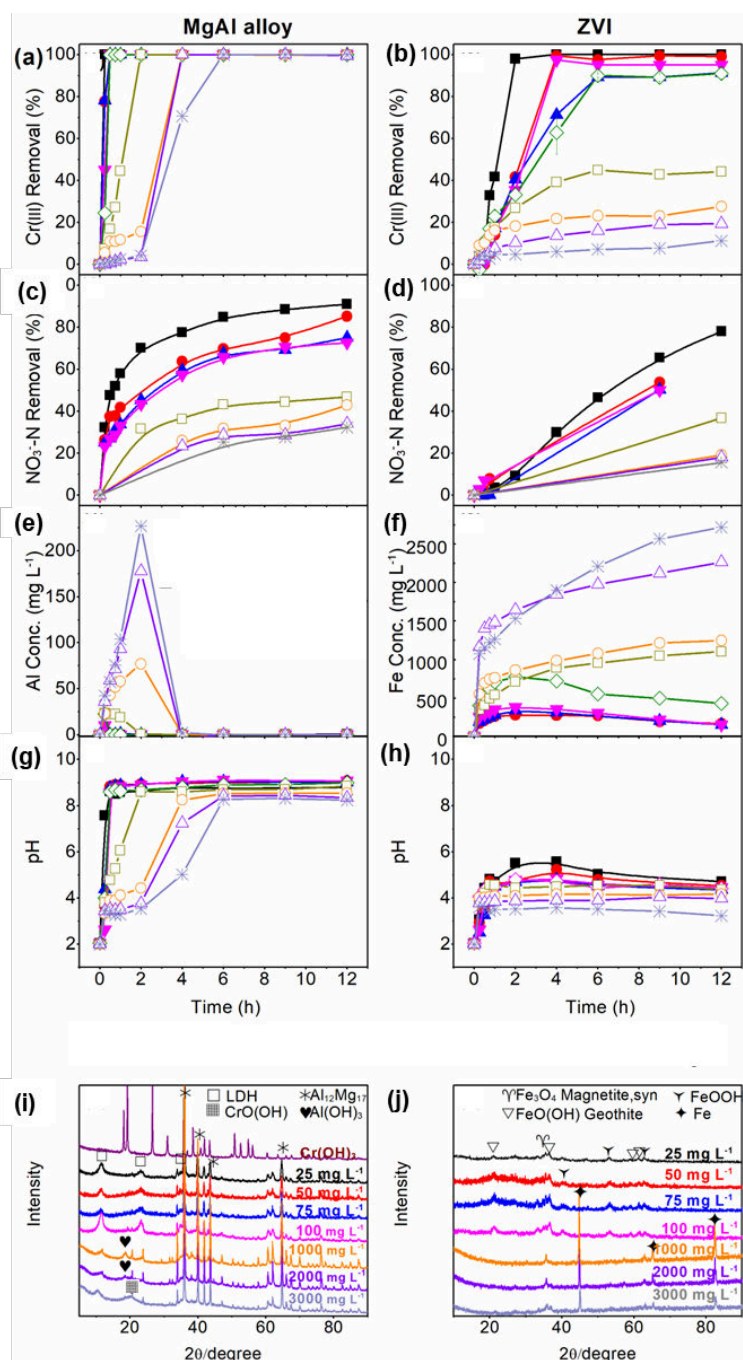


Figure S2. Reaction of different $\text{Cr}(\text{NO}_3)_3$ concentrations with MgAl alloy (left panel and ZVI (right panel). (a) Cr(III) removal, (b) NO_3^- removal, (c) Concentration of Al, Mg or Fe ions, (d) pH of solution, (e) XRD characterization of reaction product. $\text{Cr}(\text{NO}_3)_3$ solution 300 mL, pH 2 (HCl); 3 g alloy (-200 mesh), stirring speed 300 rpm, temperature 22 ± 2 °C. The initial concentration of Cr(III): ■=25, ●=50, ▲=75, ▼=100, ◇=300, □=500, ○=1000, △=2000, ※=3000 mg L^{-1} .

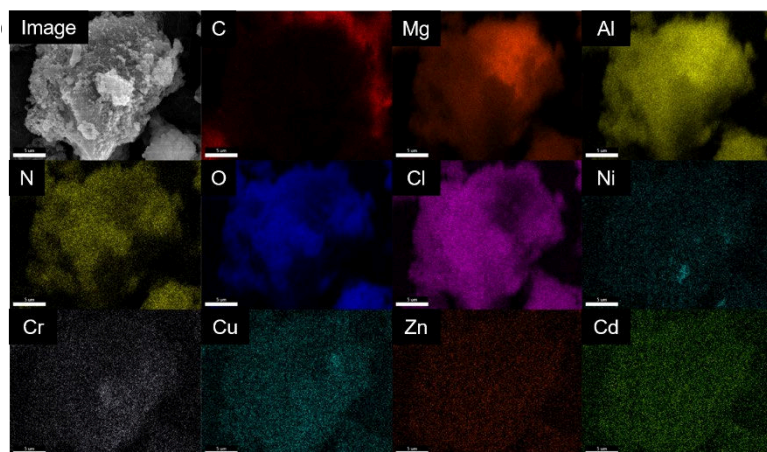


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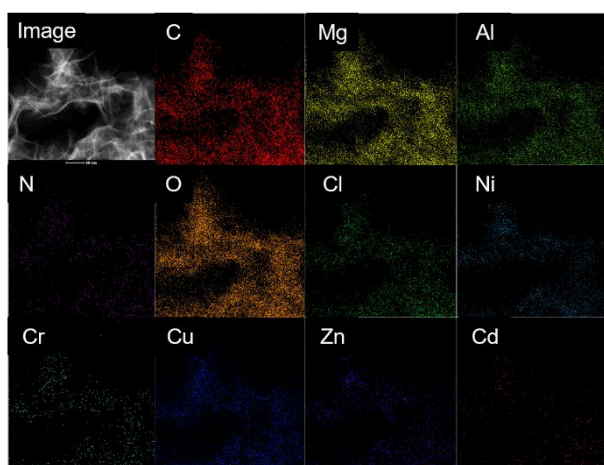


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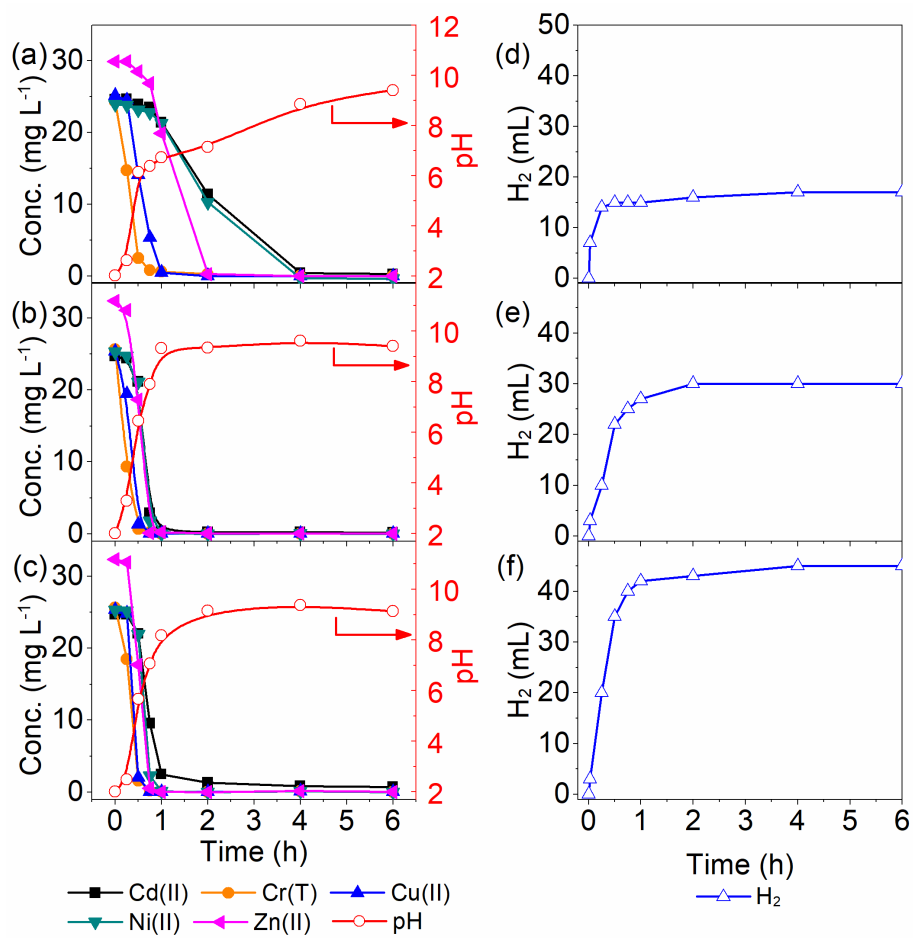


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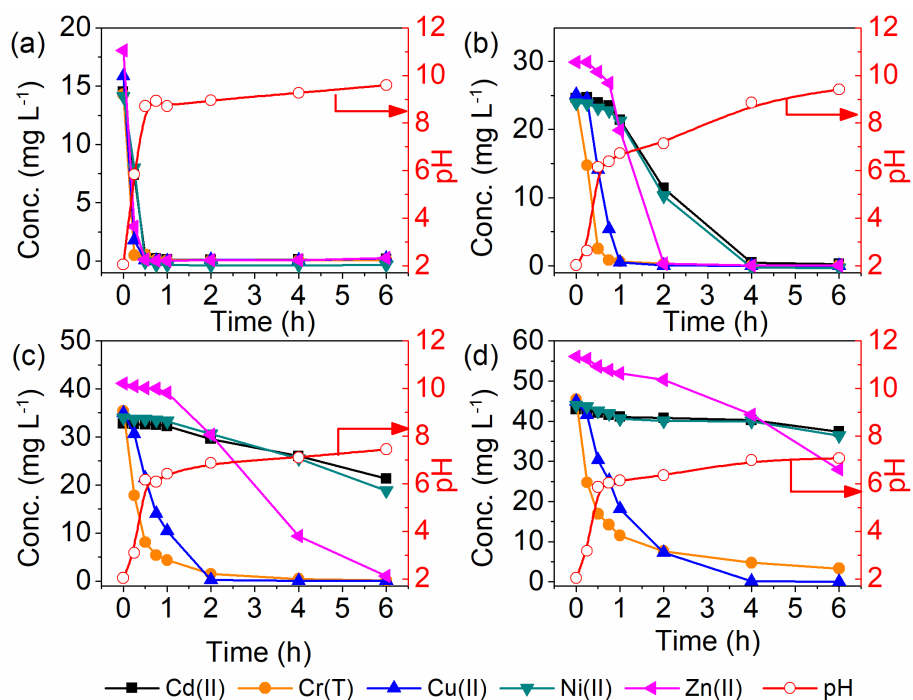


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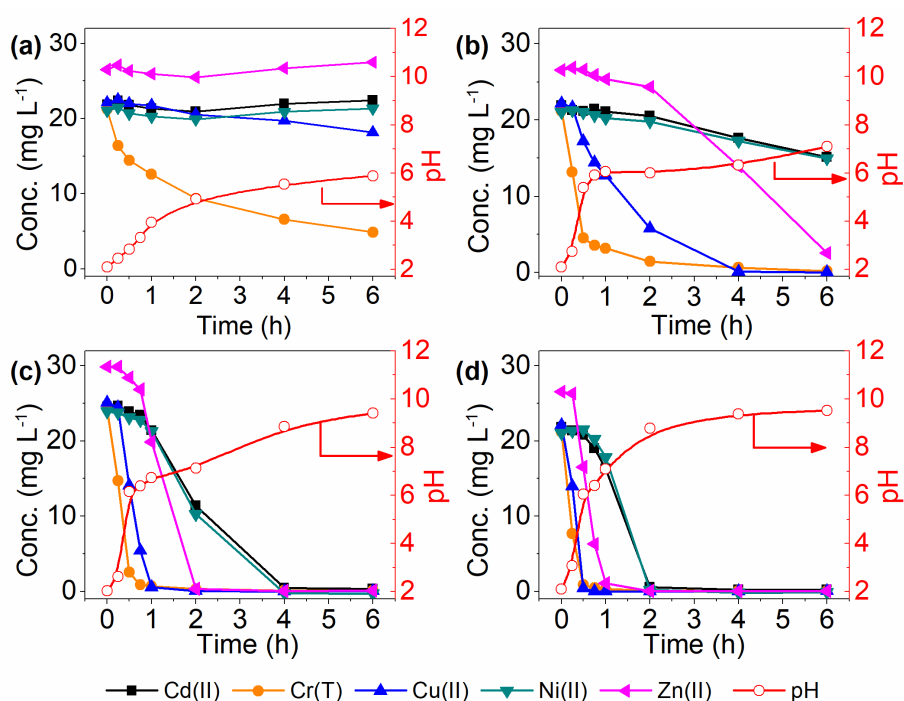


Figure S7. Effect of MgAl40 alloy dosage on the removal of heavy metals and solution pH. (a) 1 g, (b) 2 g, (c) 3 g, (d) 4 g. 300 mL, pH 2 (HCl), alloy (-200 mesh), stirring speed 300 rpm, temperature 18 ± 2 °C.

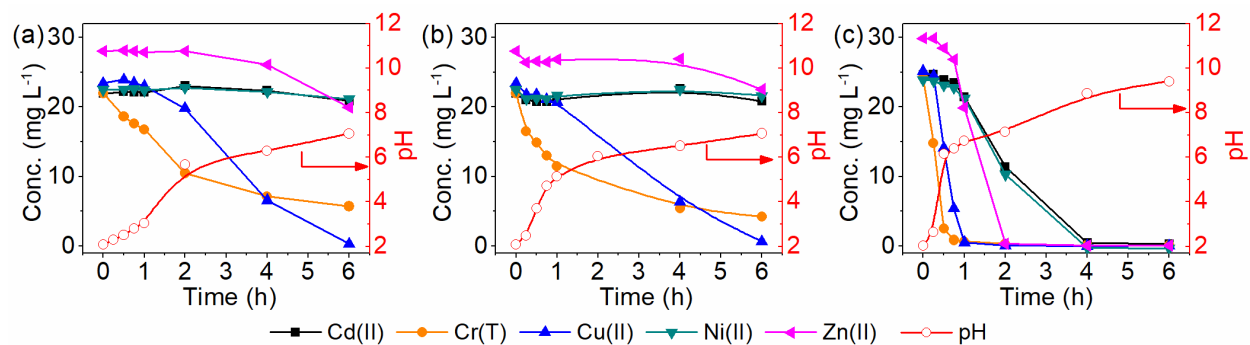


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In situ layered double hydroxide for efficient remediation of acidic water

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