Post-Print: Synergistic Removal Effect of Magnesium-Aluminum Metal Oxide on Coexisting Cu2+/Cr(VI)

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Abstract

Using the calcined product of MgAl-CO_3^{2-} hydrotalcite (LDH), designated as LDO, as a heavy metal ion adsorbent, the removal performance of LDO toward heavy metal ions was investigated in single Cu^{2+}, Cr(VI) systems and Cu^{2+}/Cr(VI) coexisting systems. Combined with XRD, FT-IR, and SEM characterization of the metal-LDO composites, the removal mechanism of the dual metals (Cr(VI) anion + Cu^{2+} cation) on LDO was elucidated. The results demonstrate that the adsorption of Cr(VI) and Cu^{2+} on LDO manifests as a synergistic adsorption effect involving multiple interactions. In addition to the Jahn-Teller effect of Cu^{2+} and the hydrogen bond synergistic many-body effect, the Cu^{2+}-CrO_4^{2-}-LDO system also experiences electrostatic interactions, hydration, coordination, as well as coprecipitation and subsequent precipitation, forming a Mg-Al-Cu ternary composite.

Full Text

Synergistic Effect of Mg/Al Metal Oxides on Removal of Mixed Cu^{2+} and Cr(VI)

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ABSTRACT

Layered double oxide (LDO) as a heavy metal ions removal agent was acquired by calcining Mg-Al containing layered double hydroxide (LDH) and then the performance of the LDO for removal heavy metal ions was assessed in solutions with single Cu^{2+} or Cr(VI) and with mixture of Cu^{2+} and Cr(VI). The spent adsorbents were characterized by XRD, FT-IR and SEM to clarify the co-adsorption mechanism of Cr(VI) and Cu^{2+} on the LDO. The results show that the co-adsorption of Cu^{2+} and Cr(VI) on the LDO can be ascribed to a synergistic effect of multiple interactions: apart from the "Jahn-Teller" effect of Cu^{2+} and many-body terms to hydrogen bonds interaction, there may exist effects such as hydration, electrostatic interaction and coordination etc in the system Cu^{2+}-CrO_4^{2-}-LDO, which enhanced the co-precipitation and subsequent precipitation on the adsorbent surface, therewith, the synergistic effect promoted the formation of Cu^{2+}-CrO_4^{2-}-LDO hybrids.

KEY WORDS inorganic non-metallic materials, hydrotalcites, heavy metal ions, Cu^{2+}/Cr(VI), Jahn-Teller effect

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Introduction

Layered double hydroxide compounds (anionic clays, LDHs) represent a novel class of inorganic functional materials with layered structures. Their host layer composition is tunable, interlayer anions are exchangeable, and they possess large specific surface areas that readily accommodate guest ions, enabling the removal of anionic heavy metals [1]. Calcined hydrotalcite metal oxides (LDOs) exhibit even greater anion adsorption capacity and specific surface area, attracting considerable attention for their strong anion removal capabilities [2]. In recent years, Mg-Al-LDHs have demonstrated remarkable effectiveness in treating wastewater containing chromium anions (Cr(VI)), though their removal efficiency for heavy metal cations remains unsatisfactory. Consequently, researchers have intercalated complexing agents into LDH interlayers or employed anionic surface modification to enhance cation removal capacity. Industrial wastewater typically contains multiple heavy metal pollutants, making it critically important to investigate the interaction mechanisms between multiple metal ions and heavy metal removal agents. To date, research on heavy metal removal by hydrotalcites has primarily focused on single metal ion systems, while studies on heavy metal ion removal in binary metal systems, particularly the interaction between coexisting anionic-cationic heavy metal ions (Cr(VI)+Cu^{2+}) and hydrotalcite adsorbents, are rarely reported. Therefore, it is necessary to elucidate the interaction characteristics of metal-hydrotalcite complexes under conditions where heavy metals and their oxyanions coexist. This study investi-

gates the adsorption performance of LDOs for single metal ions (Cr(VI), Cu^{2+}) and binary metal ions (Cr(VI)+Cu^{2+}), explores the interactions between Cr(VI), Cu^{2+} and LDOs, and elaborates on the interaction mechanism to understand LDO adsorption behavior, improve heavy metal removal performance, and provide a theoretical foundation for expanding hydrotalcite applications in water treatment.

Experimental

All reagents used were analytically pure grade, and deionized water was used throughout. MgAl hydrotalcite was prepared following the method described in reference [3]. $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with a Mg/Al molar ratio of 4 (total metal ions 0.5 mol) were dissolved in deionized water to prepare a mixed salt solution. Urea (urea/NO_3^- molar ratio of 4) was weighed and mixed thoroughly in a three-neck flask, then vigorously stirred at 105°C for 10 h. After crystallization at 80°C for 10 h, the product was filtered, washed, and dried to obtain MgAl hydrotalcite, designated as LDH. A portion of the sample was calcined at 500°C for 4 h, and the resulting metal oxide was designated as LDO. The LDO was placed in an appropriate amount of 0.3 mol/L Na_2CO_3 solution at room temperature, shaken at constant temperature for 4 h, then filtered and dried to obtain the "memory" LDH sample, designated as RLDH.

Heavy Metal Ion Removal **Single metal ion removal:** 0.10 g of LDO was added to 100 mL of $K_2Cr_2O_7$ solution with various initial Cr(VI) concentrations (C_0Cr: 0–400 mg/L) at initial pH 4.5. The mixture was shaken at 50°C (200 rpm) for 6 h to reach equilibrium (data not shown), then centrifuged at 8000 rpm. The remaining Cr(VI) concentration in the supernatant (C Cr) was measured to evaluate LDO removal performance. The precipitate was washed with deionized water to neutrality, dried, and used for XRD, FT-IR, and SEM characterization. The same procedure was applied to evaluate LDO performance in $CuCl_2$ solution for Cu^{2+} removal, with the remaining Cu^{2+} concentration in the supernatant designated as C Cu.

Binary metal ion removal: Based on single metal ion experimental results, 0.10 g of LDO was added to mixed metal solutions with a constant initial Cr(VI) concentration of 200 mg/L and varying initial Cu^{2+} concentrations (C_0Cu: 0–102.4 mg/L). The same procedure as the single metal ion equilibrium removal method was followed: the supernatant was analyzed for C Cr, C Cu, and pH to investigate LDO removal performance for Cr(VI) and Cu^{2+}. Similarly, in mixed metal solutions with a constant initial Cu^{2+} concentration of 76.8 mg/L and varying initial Cr(VI) concentrations (C_0Cr: 0–400 mg/L), LDO removal performance for Cr(VI) and Cu^{2+} was studied. The equilibrium adsorption capacity of Cr(VI) and Cu^{2+} (q Cu,Cr) was calculated using the formula q Cu,Cr = (C_0Cr,Cu -C Cr,Cu) × V/m, where m is the adsorbent mass (g) and V is the reaction solution volume (L).

Characterization X-ray diffraction (XRD) was performed using a Japanese Rigaku D/MAX-3C powder diffractometer (CuKα radiation, 40 kV, 30 mA, scanning speed 2°/min). Field emission scanning electron microscopy (SEM) was conducted using a JEOL JSM-6700F instrument. Fourier transform infrared spectroscopy (FT-IR) was performed using a PE Spectrum One B spectrometer (resolution 4 cm^{-1}). Mg^{2+} and Cu^{2+} concentrations were determined using a PE 5100-PC atomic absorption spectrometer. Cr(VI) concentration was measured using a Hitachi UV-3400 spectrophotometer with the diphenylcarbazide spectrophotometric method (GB7467-87).

Results and Discussion

2.1 Equilibrium Adsorption Capacity and pH Values

2.1.1 LDO Removal of Cu^{2+} and Cr(VI) at Constant Initial Cr(VI) Concentration The adsorption performance of LDO for single Cu^{2+} was investigated in solutions with varying C_0Cu, as shown in [Figure 1: see original paper]. The equilibrium adsorption capacity of LDO for Cu^{2+} increased rapidly with increasing C_0Cu, reaching 63.1 mg/g at C_0Cu = 76.8 mg/L. Further increasing C_0Cu led to a plateau in equilibrium adsorption capacity. At a constant C_0Cr of 200 mg/L, the effect of varying C_0Cu on LDO removal of Cr(VI) and Cu^{2+} was examined. When C_0Cu was below 76.8 mg/L, the equilibrium adsorption capacities for both Cu^{2+} and Cr(VI) (q Cu and q Cr) increased rapidly with C_0Cu. At C_0Cu = 76.8 mg/L, q Cu reached 73.4 mg/g while q Cr reached 181.1 mg/g. Further increasing C_0Cu resulted in gradual leveling off of both q Cu and q Cr ([Figure 1: see original paper]). Compared with the single Cu^{2+} system, the q Cu for Cu^{2+} in the Cr(VI)/Cu^{2+} coexistence system at C_0Cu = 76.8 mg/L increased by 16.3%.

In the single Cu^{2+} system, the pH at equilibrium remained approximately 4.5 across different C_0Cu conditions (no Mg detected in equilibrium solution), whereas the pH of pure water containing 1 g/L LDO was 11.5, indicating that Cu^{2+} significantly reduced the reaction system pH (data not shown). In the Cr(VI)/Cu^{2+} coexistence system, the equilibrium pH (eq-pH) was 11.5 when no Cu^{2+} was added. However, upon addition of Cu^{2+} (C_0Cu = 12.8 mg/L), eq-pH rapidly decreased to 6.8. Continued increase in C_0Cu led to a gradual decrease in eq-pH, which dropped to 4.6 at C_0Cu = 102.4 mg/L (Mg detected in equilibrium solution) ([Figure 1: see original paper]).

2.1.2 LDO Removal of Cu^{2+} and Cr(VI) at Constant Initial Cu^{2+} Concentration In both single Cr(VI) and Cu^{2+}/Cr(VI) coexistence systems (C_0Cu constant at 76.8 mg/L), the equilibrium adsorption capacities of LDO for Cr(VI) and Cu^{2+} increased with increasing C_0Cr, reaching saturation adsorption at C_0Cr = 200 mg/L ([Figure 2: see original paper]). In the single Cr(VI) system, the Cr(VI) equilibrium adsorption capacity (q ’ Cr) was 111.0 mg/g at C_0Cr = 200 mg/L. In the Cu^{2+}/Cr(VI) coexistence system, the Cr(VI)

equilibrium adsorption capacity (q' Cr) increased to 181.1 mg/g, representing a 63.2% enhancement compared to q ' Cr, while the Cu^{2+} equilibrium adsorption capacity (q' Cu) was 73.4 mg/g.

In the single Cr(VI) system, eq-pH' remained approximately 11.5 across different C_0Cr conditions, indicating that Cr(VI) had negligible effect on solution pH (data not shown). In the Cr(VI)/Cu^{2+} coexistence system, eq-pH' was 4.2 when no Cr(VI) was added, but increased rapidly with increasing C_0Cr, reaching 5.6 at C_0Cr = 400 mg/L ([Figure 2: see original paper]).

In summary, the simultaneous presence of Cu^{2+} and Cr(VI) significantly increased the removal amounts of both Cr(VI) and Cu^{2+} by LDO, demonstrating a synergistic removal effect. The addition of Cu^{2+} notably reduced the pH of the coexistence equilibrium adsorption system. Compared with single-component removal, multi-component coexistence removal introduces additional interactions among adsorbates, making the removal patterns more complex. To further investigate the synergistic removal mechanism of Cr(VI) and Cu^{2+}, adsorption products from LDO in single Cr(VI) and Cu^{2+} systems and in the Cr(VI)/Cu^{2+} coexistence system at C_0Cr = 200 mg/L and C_0Cu = 76.8 mg/L were designated as Cr-LDH, Cu-LDH, and Cu-Cr-LDH, respectively, with RLDH as a reference, for structural characterization to explore the interaction mechanism between the anionic-cationic metal ions Cr(VI), Cu^{2+} and LDO.

2.2 Characterization

2.2.1 XRD Spectral Analysis [Figure 3: see original paper] presents the XRD patterns of Cu-Cr-LDH, Cr-LDH, Cu-LDH, and RLDH. All samples exhibited typical hydrotalcite crystal diffraction peaks, indicating that LDO recovered its original hydrotalcite crystal structure through the "memory effect." Both Cu-LDH and RLDH showed d_{003} 0.770 nm, confirming these samples as CO_3^{2-}-pillared hydrotalcites [4]. The Cu-Cr-LDH adsorption equilibrium occurred at pH 5.2 ([Figure 1: see original paper] and [Figure 2: see original paper]), while Cr-LDH was at pH 11.5, indicating that Cr(VI) existed primarily as the anionic CrO_4^{2-} species. The d_{003} spacing of Cr-LDH was 0.903 nm, demonstrating that CrO_4^{2-} intercalation increased the interlayer spacing [5], while Cu-Cr-LDH showed d_{003} = 0.924 nm, slightly larger than Cr-LDH. This increase resulted from the "Jahn-Teller" effect of Cu^{2+} entering the layers, which caused distortion of octahedra within the layers and increased layer thickness [6]. The (110) and (113) diffraction peaks of Cu-LDH and Cr-LDH were clearly distinguishable, indicating well-maintained structural regularity. Cu-LDH exhibited a hydrotalcite crystal structure but contained substantial $Cu_2(OH)_3Cl$ impurity phases, consistent with previous research [7]. The (110) and (113) peaks of Cu-Cr-LDH were barely discernible, indicating poor structural regularity in Cu-Cr-LDH, though some $Cu_2(OH)_3Cl$ impurity phases were also present. The (009) diffraction peak showed splitting, presenting two distinct peaks, possibly because the "Jahn-Teller" effect of Cu^{2+} rendered the layer distortion un-

stable, leading to the formation of $Mg_2(OH)_2CO_3$ impurity phases and lattice distortion.

2.2.2 FT-IR Analysis [Figure 4: see original paper] shows the FT-IR spectra of Cu-Cr-LDH, Cr-LDH, Cu-LDH, and RLDH samples. All samples exhibited characteristic hydrotalcite infrared absorption peaks. The Cu-LDH sample showed $_3$ vibration peaks of CO_3^{2-} at 1370 and 674 cm^{-1} with intensities essentially identical to RLDH, indicating that the CO_3^{2-} content in Cu-LDH interlayers remained largely unchanged, confirming Cu-LDH as a CO_3^{2-}-pillared hydrotalcite, consistent with XRD analysis ([Figure 3: see original paper]). In contrast, Cr-LDH and Cu-Cr-LDH samples showed significantly weakened CO_3^{2-} absorption peak intensities at 1370 cm^{-1}, indicating only trace amounts of CO_3^{2-}, while characteristic d(Cr-O) vibration peaks of CrO_4^{2-} appeared near 885 and 923 cm^{-1}, demonstrating that CrO_4^{2-} had partially replaced CO_3^{2-} in the interlayers. Additionally, the absorption peak at 557 cm^{-1} was attributed to layer M-O bond stretching vibrations (M-O-M or O-M-O, M: Mg, Al) or MOH bending deformation vibrations. The absorption peak of Cu-LDH at 557 cm^{-1} shifted to higher wavenumbers, possibly because $Cu_2(OH)_3Cl$ impurity phases increased the M(Mg, Al)-O bond energy on the layers. Compared with Cr-LDH, the CrO_4^{2-} absorption peak of Cu-Cr-LDH at 923 cm^{-1} showed a significant shift to higher wavenumbers with increased intensity, likely due to enhanced Cr-O bond energy.

2.2.3 SEM Analysis [Figure 5: see original paper] presents the characteristic morphologies of Cu-Cr-LDH, Cr-LDH, Cu-LDH, and RLDH samples observed by SEM. RLDH exhibited thin hexagonal crystal shapes with irregular grain edges, good dispersion, uniform size, and well-developed crystallinity. Cu-LDH showed an irregular layered structure with relatively compact layer stacking, possibly related to $Cu_2(OH)_3Cl$ impurity phases attached to layer surfaces. Cr-LDH displayed distinct lamellar structures with some hexagonal platelet distributions, irregular grain edges, more compact structure than RLDH, and non-uniform sizes. Cu-Cr-LDH showed good dispersion but developed a loose, worm-like special structure on the layers, likely because Cu^{2+} introduction into hydrotalcite layers caused "Jahn-Teller" distortion leading to layer twisting. These results corroborate XRD and FT-IR analyses.

2.3 Interaction Mechanism Between Anionic-Cationic Ions (Cr(VI)+Cu^{2+}) and LDO Our research group previously found that in single Cr(VI) systems, CrO_4^{2-} rapidly intercalated into LDO layers during adsorption removal, coordinating with layer metal ions to form complex hydrogen bond networks through multiple hydrogen bonding interactions, while simultaneously adsorbing onto hydrotalcite layer surfaces through electrostatic interactions, thereby enabling rapid LDO reconstruction to the LDH layer structure [9]. Clay colloid surfaces possess residual negative charges that can electrostatically adsorb positively charged Cu^{2+}. Since no electron sharing occurs with solid surface atoms

(no electron transfer), H^+ is not released; however, under certain conditions, surface hydrated groups (-OH_2) and coordinated hydroxyl groups (-OH) on clay surfaces can coordinate with Cu^{2+} and release H^+, thereby reducing solution pH [10]. In single Cu^{2+} systems, Cu^{2+} reduced the equilibrium solution pH, but this effect was independent of Cu^{2+} concentration ([Figure 1: see original paper]). This indicates that after LDO addition to the system, CO_3^{2-} rapidly intercalated into the interlayers, causing LDO reconstruction and layer structure recovery while generating abundant -OH groups. Cu^{2+} and Cl^- in solution formed $Cu_2(OH)_3Cl$ precipitates that rapidly adsorbed onto layer surfaces through electrostatic interactions. Since hydrogen bonding interactions between CO_3^{2-} and layer M-O bonds are relatively weak, CO_3^{2-} introduction hardly affected the host layer' s space group structure, and Cu could not readily replace Mg in the layers. Meanwhile, some Cu^{2+} also coordinated with layer -OH_2 and -OH groups, releasing H^+. The formation of $Cu_2(OH)_3Cl$ consumed substantial -OH groups, and Cu coordination released H^+, collectively reducing the equilibrium solution pH. However, the equilibrium pH was independent of Cu^{2+} concentration because at low Cu^{2+} concentrations, adsorption occurred primarily through Cu^{2+} coordination with solid surfaces, whereas at higher Cu^{2+} concentrations, adsorption was dominated by electrostatic interactions [10].

In Cu^{2+}/Cr(VI) coexistence systems, Cr(VI) and Cu^{2+} exhibited significant synergistic effects on LDO. Upon LDO addition, immediate surface -OH formation occurred through combination with H_2O, inducing rapid CrO_4^{2-} intercalation. Since interlayer CrO_4^{2-} hydrogen bonding with layers is much stronger than that of CO_3^{2-}, CrO_4^{2-} introduction enhanced host-guest interactions while weakening intra-layer interactions, causing Al-O and Mg-O bond energies to decrease and bond lengths to increase, thereby substantially reducing layer stability [11,12]. Cu replaced Mg in the layers (Mg detected in solution) [7], forming distorted octahedral coordination structures centered on Cu^{2+} [13]. Layer distortion occurred ("Jahn-Teller" effect), intensifying layer twisting and instability. Six Cu-O bonds formed elongated octahedra with four short and two long bonds, generating small amounts of $Mg_2(OH)_2CO_3$ crystalline phases during Mg-Al-Cu ternary composite formation. Additionally, H_2O entered the interlayers along with CrO_4^{2-} diffusion, primarily interacting with layer M-O bonds [14]. The "Jahn-Teller" effect stretched the layers vertically, increasing layer thickness while weakening interactions between M-O bonds and interlayer CrO_4^{2-} and H_2O. Reduced electrostatic and hydrogen bonding interactions between host and guests increased interlayer spacing, which in turn facilitated further CrO_4^{2-} and H_2O intercalation. Increased interlayer H_2O further decreased Cu^{2+}-CrO_4^{2-}-LDO system stability, enhanced covalent character, and gradually transformed the system from ionic to molecular crystals, forming stable Mg-Al-Cu ternary composites [15]. Furthermore, adsorption and reconstruction processes were accompanied by co-precipitation and subsequent precipitation phenomena, causing partial Cu^{2+} and Cr(VI) removal through precipitation adsorption on the adsorbent surface.

Conclusion

LDO exhibits synergistic removal effects for coexisting Cu^{2+} and Cr(VI). In Cu^{2+}/Cr(VI) coexistence systems, the equilibrium removal amounts of Cr(VI) and Cu^{2+} by LDO increased by 63.2% and 16.3%, respectively, compared with corresponding single systems. The removal of Cu^{2+} and Cr(VI) on LDO involves synergistic effects of multiple interactions directly related to host-guest interactions in hydrotalcites, ultimately attributable to layer and anion properties. Particularly, the "Jahn-Teller"effect of Cu^{2+} forms distorted octahedra that destabilize the layers. The interactions of layer metal ions with guest CrO_4^{2-}, interlayer H_2O, and -OH groups all weaken as the "Jahn-Teller" effect of Cu^{2+} on layers intensifies. The adsorption of Cr(VI) and Cu^{2+} on LDO demonstrates synergistic effects among multiple interactions, likely arising from many-body hydrogen bond cooperative effects, hydration, coordination between layer metal ions and -OH, electrostatic interactions between layers and interlayer CrO_4^{2-} and H_2O, and synergistic effects under the "Jahn-Teller" effect of Cu^{2+}, accompanied by increased co-precipitation and subsequent precipitation.

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