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Effect of particle size on copper removal by layered double hydroxides

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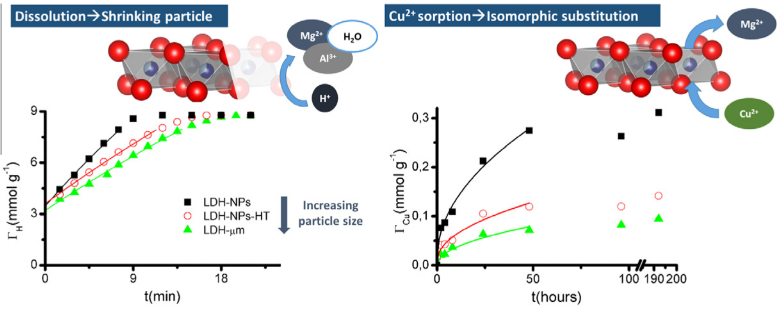
HIGHLIGHTS

- Mg^{2+} leaching in neutral media and congruent dissolution rate in acid boosted in nanoLDHs.
- At low Cu^{2+} concentrations, the pH buffering capacity of LDHs produce $Cu(OH)_2$ precipitation.
- In these conditions, nanoLDHs presented higher affinity for Cu^{2+} ions than microLDHs.
- At large Cu^{2+} concentrations, the sorption mechanism is isomorphic substitution of Mg^{2+} ions.
- NanoLDHs, due to their higher exposed surface, exhibited larger sorption capacities than microLDHs.

GRAPHICAL ABSTRACT



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ABSTRACT

Layered double hydroxides are increasingly studied as heavy metal scavengers but the effect of particle size in their removal behavior has not been explored yet. Here, these aspects were studied in three solids with similar structure and composition but different in size and morphology. Nano-sized LDHs were synthesized by a coprecipitation method with separate nucleation and aging steps and compared to a micro-sized LDH. Proton and Cu^{2+} uptake were studied using both kinetics and isotherms, which were fitted using different models. Decreasing particle size caused an increasing Mg^{2+} leaching in neutral and basic media and an increased dissolution speed in acid media, both of them due to the larger exposed surface of smaller particles. Depending on the Cu^{2+} concentration and LDH buffering capacity, Cu^{2+} removal was produced by $Cu(OH)_2$ precipitation at the particle surface or by isomorphic substitution of Mg^{2+} ions at the octahedral sites of LDH layers (diadochy). The uptake rate of the latter was controlled by the intraparticle diffusion of Mg^{2+} ions and, consequently, it was quite independent of the particle size. On the other hand, the uptake capacity decreased with increasing particle size due to the site availability diminution with increasing diffusion path, which led to a decreasing volume of the layer available for Cu^{2+} uptake for increasing particle size values.

1. Introduction

Heavy metal ions, such as Cu^{2+}, Ni^{2+}, Pb^{2+} or Cd^{2+} represent a serious hazard due to their mobility, persistency and increasingly mobilization due to mining, plating and tanning activities [1]. These pollutants are remediated mainly by precipitation, ion exchange and adsorption processes [2,3] and materials such as activated carbon, zeolites, ion exchange resins, clays or layered double hydroxides (LDHs) are investigated as sorbents [4]. Also, the use of micro and nanomaterials generates an great attention due to the surface area increase, and the consequent improved availability of active sites [5].

LDHs are extensively studied as sorbents due to their ion exchange capacity, reconstruction reactions and acid-base

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buffering capacity (due to the dissolution reactions of LDH layers at low pH values) [6]. LDHs structure is derived from that of brucite ($Mg(OH)_2$) and it is described as layers of edge-sharing octahedra, where divalent metal ions are partially substituted by trivalent ones. Consequently, the layers present a positive charge excess that is compensated by the introduction of anions between them [7]. The general formula of these compounds can be written as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot y\ H_2O$, where M^{II} and M^{III} are the metal ions that constitute the layers and A^{n-} is the interlayer anion.

Although LDHs are mainly studied as scavengers of anionic pollutants, either organic [8] or inorganic [9], numerous studies on the heavy metal remediation capacity of LDHs have also been performed [10–14]. Heavy metal ions are eliminated by two main mechanisms: precipitation and chelation. In the first case, the dissolution reactions of LDH layers buffer the pH of the contaminated media, which induce the precipitation of the corresponding heavy metal hydroxides, either as part of an LDH phase or not [12]. In the case of chelation, the LDH sorbent is intercalated with a functional ligand that interacts with the heavy metal ion, which is incorporated to the interlayer of LDHs [11,15,16]. In addition to these main mechanisms, adsorption/surface complexation processes have also been proposed for heavy metal adsorption by these solids [17].

In the case of the precipitation mechanism, the uptake capacity and kinetics are mainly controlled by the dissolution behavior of LDHs [12,13], which, as a surface controlled reaction, is expected to be determined by their particle size [6]. LDHs are obtained in a wide size range, from a few tens nanometers [18] to several micrometers [19]. Nevertheless, the effect of particle size on the solubility of LDHs remains unexplored, as well as the consequences on the heavy metal scavenging capacity of these solids.

In this work, these aspects were studied in three solids with similar structure (studied by X-ray diffraction, infrared spectra and thermal analysis) and composition, but different size and morphology (determined by dynamic light scattering and scanning electronic microscopy). Their dissolution and Cu^{2+} uptake behavior was studied by kinetics and isotherms. The obtained results were modeled to determine the mechanism involved in these processes and compare the uptake capacity and affinity of LDHs with different size.

2. Materials and methods

Reagent grade chemicals (Baker, Anedra) were used with no previous purification. All solutions were prepared with purified water (18 MΩ Milli Q, Millipore System). Unless otherwise stated, all experiments were performed at room temperature. Synthetic hydrotalcite (DHT-6) was gently provided by Kyowa Kagaku Kogyo Co., Ltd., Japan.

2.1. Synthesis of LDH nanoparticles

LDH nanoparticles intercalated with carbonate were obtained by a method involving separate nucleation and aging steps, similar to that described by Xu and coworkers [20]. Briefly, a solution containing the metal salts (50 mL) was poured into an alkaline solution containing Na_2CO_3 (0.2 L) under vigorous stirring induced by an Ultraturrax T18 BASIC agitator at 25,000 rpm. The Mg/Al ratio in the initial metal ions solution was 3:1 ($[Al^{3+}] = 0.2\ mol\ L^{-1}$), while the $[OH^-]/[Mg^{2+} + Al^{3+}]$ was 2.2 and the $[CO_3^{2-}]/Al$ ratio was 1 in the alkaline solution. The obtained solid was immediately separated from the supernatants by centrifugation, washed 3 times with water and dispersed into 0.2 L of water by magnetic stirring for 24 h. The sample thus obtained was named LDH-NPs. Another sample was obtained as previously described but an additional step of aging by hydrothermal treatment (HT) at 80 °C for 4 h was added (LDH-NPs-HT). The synthesized samples and microsized LDH provided by Kyowa (DHT-6, from here on named LDH-μm) were stored as dispersions ($10\ g\ L^{-1}$) in closed bottles.

2.2. Particle size and morphology

The hydrodynamic apparent diameter (d) and zeta potential (ζ) of the samples were determined by dynamic light scattering (DLS) and electrophoretic light scattering (ELS) measurements, respectively, using a Delsa Nano C instrument (Beckman Coulter). The measurements were performed in $1\ g\ L^{-1}$ dispersions of the corresponding samples in $5\ mmol\ L^{-1}$ NaCl solution, ultrasonically dispersed for 30 min. d values were obtained from the autocorrelation function ($g^{(2)}$) using the cumulants method and the size distributions were obtained by the CONTIN method, while electrophoretic mobilities were converted to ζ using the Smoluchowski equation. Scanning electron microscopy (SEM) images were obtained in a FE-SEM Σigma instrument on samples covered with a Cr layer. The samples were prepared placing 0.05 mL of $0.1\ g\ L^{-1}$ dispersions of the samples on the holder, which was dried at 50 °C without further manipulation.

2.3. Structural characterization

50 mL of each dispersion were lyophilized in order to perform the structural characterization of the samples. Mg and Al contents were determined by atomic absorption spectrometry in a Varian AA240 instrument. The samples were dissolved in HNO_3 and afterwards diluted to meet the calibration range. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out in a Shimadzu DTG 60 instrument in flowing air and at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) patterns were recorded in a Phillips X'pert Pro instrument using a CuKα lamp ($\lambda = 1.5408$ Å) at 40 kV and 40 mA in step mode (0.05°, 1.2 s). FT-IR spectra were measured in a Bruker IFS28 instrument using KBr pellets (1:100 sample:KBr ratio).

2.4. LDHs dissolution

LDH dissolution at equilibrium was studied in $1\ g\ L^{-1}$ LDH dispersions in $5\ mmol\ L^{-1}$ NaCl (to fix the ionic strength) with increasing [HCl] (up to $35.2\ mmol\ L^{-1}$). The dispersions thus obtained were agitated for 48 h in an orbital shaker and pH was determined as previously described.

The kinetics of LDH dissolution was studied in $1\ g\ L^{-1}$ LDH dispersions in $5\ mmol\ L^{-1}$ NaCl at two [HCl] (0.88 and $8.80\ mmol\ L^{-1}$). Once the LDH particles were added, the dispersion was continuously agitated and the pH was measured every 90 s using a Titrando 905 automatic titrator (Metrohm) controlled by Tiamo software and coupled to a Metrohm 9.0262.100 combined pH electrode. The pH values were converted to proton uptake, $\Gamma_H = ([H^+]_0 - [H^+]_t) * V/m$, where $[H^+]_0$ and $[H^+]_t$ are proton concentration at t = 0 and at a given time t, V is the dispersion volume and m is the sample mass.

The Γ_H vs. t curves were fitted with the following equations [6,11,21,22]

$$\text{Zero order}: \Gamma_H = \Gamma_{H,0} + k_0 \cdot t \tag{1}$$

$$\text{Diffusion}: \Gamma_H = \Gamma_{H,0} + k_D \cdot t^{0.5} \tag{2}$$

$$\text{First order}: \ln \Gamma_H = n\Gamma_{H,0} + k_1 \cdot t \tag{3}$$

$$\text{Second order}: \frac{1}{\Gamma_H} = \frac{1}{\Gamma_{H,0}} + k_1 \cdot t \tag{4}$$