



# Evaluation of layered zinc hydroxide nitrate and zinc/nickel double hydroxide salts in the removal of chromate ions from solutions



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## ABSTRACT

Layered zinc hydroxide nitrate (ZnHN) and Zn/Ni layered double hydroxide salts were synthesized and used to remove chromate ions from solutions at pH 8.0. The materials were characterized by many instrumental techniques before and after chromate ion removal. ZnHN decomposed after contact with the chromate solution, whereas the layered structure of Zn/Ni hydroxide nitrate (Zn/NiHN) and Zn/Ni hydroxide acetate (Zn/NiHA) remained their layers intact after the topotactic anionic exchange reaction, only changing the basal distances. ZnHN, Zn/NiHN, and Zn/NiHA removed 210.1, 144.8, and 170.1 mg of  $\text{CrO}_4^{2-}$ /g of material, respectively. Although the removal values obtained for Zn/NiHN and Zn/NiHA were smaller than the values predicted for the ideal formulas of the solids (194.3 and 192.4 mg of  $\text{CrO}_4^{2-}$ /g of material, respectively), the measured capacities were higher than the values achieved with many materials reported in the literature. Kinetic experiments showed the removal reaction was fast. To facilitate the solid/liquid separation process after chromium removal, Zn/Ni layered double hydroxide salts with magnetic supports were also synthesized, and their ability to remove chromate was evaluated.

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## 1. Introduction

Environmental concerns have made contamination of water bodies with heavy metals like  $\text{Cr}^{6+}$  become a hot topic. Chromium in the hexavalent state is a soluble harmful species that can negatively affect the human health; it is also toxic to animals and the aquatic environment. Hence, removing  $\text{Cr}^{6+}$  from water bodies or treating the potential sources of this species before their release into the environment is crucial [1]. Researchers have attempted to produce alternative, inexpensive, and active materials that could replace expensive wastewater and water treatments like solvent extraction, chemical precipitation, ultrafiltration, reverse osmosis, and ionic exchange [2–4]. Adsorption is a physicochemical process that can employ inorganic, organic, or biological/natural materials to remove heavy metals from contaminated waters successfully [4,5]. In this context, layered hydroxide salts (LHS) and layered double hydroxide salts (LDHS), which are easy to synthesize and display high anionic exchange capacity (AEC), have received increasing attention from the scientific community [6–8]. Moreover, LHS and LDHS can function as catalysts, fillers in functional polymers, and key materials to obtain intelligent systems for controlled drug delivery, just to name a few of their applications [8,9].

The LHS structure derives from the brucite structure ( $\text{Mg}(\text{OH})_2$ ), where water molecules or other anions partially replace the hydroxyls

octahedrally coordinated to divalent metals, to give materials with the general formula  $\text{M}^{2+}(\text{OH})_{2-x}(\text{A}^{-m})_{x/m} \cdot n\text{H}_2\text{O}$  [10,11]. The LHS structure contains only one divalent metal, but two divalent metals can simultaneously occupy the octahedral sites of the structure, resulting in LDHS with general formula  $\text{M}_1^a_{1-y}\text{M}_2^b_y(\text{OH})_{2-x}(\text{A}^{-m})_{x/m} \cdot n\text{H}_2\text{O}$ . The present work focuses on the high AEC of LHS and LDHS [12].

Many industrial processes, including oil refinement, production of fertilizers, and galvanization, generate chromate anions ( $\text{CrO}_4^{2-}$ ) [13,14], which are highly toxic to animals and plants [14]. The CONAMA (National Environmental Council) resolution number 430/11, a Brazilian law regarding effluent disposal, allows maximum  $\text{Cr}^{6+}$  value of 0.1 mg/L in wastewaters [15], which justifies the importance of finding new alternative ways to remove chromate from industrial discharges.

This study aimed to synthesize zinc hydroxide nitrate (ZnHN) and two LDHS (Zn/Ni hydroxide nitrate – Zn/NiHN and Zn/Ni hydroxide acetate – Zn/NiHA) and verify their ability to remove chromate from solutions. Zn/NiHN and Zn/NiHA containing a magnetic support (magnetite) were also synthesized to facilitate the solid-liquid separation process.

## 2. Experimental

### 2.1. Synthesis of the materials

Zinc hydroxide nitrate (ZnHN) was synthesized by the co-

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precipitation method. To this end, 100 mL of  $\text{Zn}(\text{NO}_3)_2$  (LAB Synth) at 0.25 mol/L was mixed with 100 mL of NaOH (VETEC Química) at 0.1 mol/L. The reaction was performed by simultaneously adding these two solutions to a beaker containing 200 mL of distilled water, dropwise. The reaction was magnetically stirred at 500 rpm, and the final pH was adjusted to between 6.5 and 7.0. After precipitation, the white milky dispersion was left in contact with the mother solution for 24 h. Then, the material was separated by centrifugation (4000 rpm for 6 min), washed with distilled water five times, and dispersed after each washing. The white solid was dried at 65 °C for two days.

The oxide/salt reaction method was used to obtain Zn/NiHN. Briefly, 2.06 g of ZnO (LAB Synth) was added to 200 mL of  $\text{Ni}(\text{NO}_3)_2$  solution (LAB Synth) at 0.25 mol/L, which corresponded to a Ni/Zn molar ratio of 2:1. The reaction was magnetically stirred at 500 rpm and 65 °C for seven days. After that, the green material was separated by centrifugation (4000 rpm for 4 min), washed with distilled water four times, and dried at 65 °C for two days.

An anionic exchange reaction was chosen to prepare Zn/NiHA. For this purpose, 2.00 g of the previously prepared Zn/NiHN was added to 200 mL of  $\text{Ni}(\text{CH}_3\text{COO})_2$  (VETEC Química) at 0.25 mol/L, and the reaction was magnetically stirred at 500 rpm and 65 °C for four days. The green material was separated by centrifugation (4000 rpm for 4 min), washed with distilled water four times, and dried at 65 °C for two days.

To facilitate the separation of the solid layered material dispersion from the solution after chromium removal, LDHS containing a magnetic support were also synthesized (Zn/NiHN-mag and Zn/NiHA-mag). In the presence of magnetite, the materials were separated by application of a magnetic field instead of using filtration or centrifugation steps.

The magnetite used as support for Zn/NiHN and Zn/NiHA was synthesized by mixing 100 mL of  $\text{FeSO}_4$  at 0.25 mol/L with 100 mL of  $\text{Fe}_2(\text{SO}_4)_3$  at 0.5 mol/L; the pH was increased with slow addition of 50 mL of NaOH at 1 mol/L. After pH 11 was achieved, the black precipitate was separated by centrifugation (4000 rpm for 3 min), washed with distilled water four times, and dried in a desiccators containing freshly activated amorphous silica for four days. Zn/NiHN-mag was achieved by following the same method used to obtain Zn/NiHN, except that 0.10 g of magnetite powder was also added to the reaction medium.

The oxide/salt reaction method was used to synthesize Zn/NiHA-mag. In this reaction, 4.07 g of ZnO (LAB Synth) and 0.10 g of magnetite were added to 200 mL of  $\text{Ni}(\text{CH}_3\text{COO})_2$  (VETEC Química) at 0.5 mol/L, which gave a Ni/Zn molar ratio of 2:1. The reaction was magnetically stirred at 750 rpm and 65 °C for seven days. The green material was separated by application of a magnetic field, washed with distilled water four times, and dried at 65 °C for two days.

## 2.2. Characterization methods

To study the physical and chemical characteristics of the synthesized materials, they were characterized by various instrumental techniques. The X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 diffractometer operating with  $\text{CuK}\alpha$  radiation (1.5418 Å) at 30 mA and 40 kV; the dwell time was 2°/min. The materials in the powder form were placed in an aluminum or glass sample holder and gently pressed to avoid peaks shifting from the real positions.

The Fourier transform infrared (FTIR) spectra were acquired on a Bomem apparatus model MB-100. The samples were dispersed in spectroscopic grade KBr, and the pellets were pressed at 10 t for 5 min. The spectra were obtained by accumulating 32 scans between 400 and 4000  $\text{cm}^{-1}$ , with resolution of 2  $\text{cm}^{-1}$ .

The scanning electron microscopy (SEM) images were recorded

on a Tescan VEGA3 LMU microscope. Samples dispersed in water were dropped on an aluminum sample holder. After evaporation, the images were registered at 10 kV. After imaging, energy dispersive spectroscopy (EDS) measurements were conducted by using AZ Tech (Advanced) software and detector SDD with area of 80  $\text{mm}^2$ . The scans were performed between 0 and 11 keV.

The thermal analysis curves (simultaneous thermogravimetry – TGA and differential scanning calorimetry – DSC) were obtained with Netzsch STA 449F3 equipment, in alumina crucibles, at a scan speed of 10 °C/min, under synthetic air flow (50 mL/min).

## 2.3. Chromium removal experiments

Chromium removal by ZnHN, Zn/NiHN, and ZnNiHA was assayed by adding 40 mg of one of the solids to 40 mL of  $\text{K}_2\text{Cr}_2\text{O}_7$  at 625 ppm (part per million) (chromate in excess). The pH was adjusted to 8.0 with NaOH solution. The mixtures were shaken at 23 °C for four days, and five experimental points were collected. The pH of the solution was set to 8.0 to ensure that chromate was present during equilibrium [16].

To quantify the chromate concentration in the solutions before and after the removal reactions, UV–vis absorbance spectra were collected on a UV-2401 PC (Shimadzu) apparatus. The spectra were acquired from 300 to 800 nm; the resolution was 0.1 nm. Before the experiments, a calibration curve was obtained at pH 8.0 for solutions ranging from 3.2 to 21.4 ppm; the maximum chromate absorbance occurred at 370 nm.

Batch experiments were performed for the kinetic assays. Each experimental point (time) was collected in independent experiments. For Zn/NiHN and Zn/NiHA (intercalation reactions), each experimental point was collected by adding 30 mg of each solid into 40 mL of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at 26.3 ppm, at 26 °C. In previous experiments, equilibrium had been reached after 2 h, so all the experiments were performed for 2 h. For the kinetic assays involving ZnHN, 60 mg of the solid was added to 40 mL of  $\text{K}_2\text{Cr}_2\text{O}_7$  at 89 ppm, at 26 °C, for 6 h. In this case, the curve was not adjusted to any kinetic models because the material did not retain its structure after the reaction.

## 3. Results and discussion

The XRD patterns (Fig. 1) displayed the typical profiles of layered compounds—a sequence of basal peaks appeared in the beginning of the diffraction pattern.

All the compounds do not present diffraction peaks of expected contamination like hydroxides or oxides from the divalent metals and all the peaks were indexed according to the literature [17–19]. Mercury software or Search Match software were used to index the diffraction peaks (ZnHN – JCPDS card 72-0627). The sharp diffraction peak evidenced that ZnHN was highly crystalline and presented a higher particle size on the h00 direction, comparable to the particle size of the other two samples, which exhibited broad peaks. The basal spacing was taken from the basal peak with the highest order and was equal to 9.78, 9.17, and 13.07 Å for ZnHN (Fig. 1a), Zn/NiHN (Fig. 1b), and Zn/NiHA (Fig. 1c), respectively. As expected, the basal distance of Zn/NiHA was larger than the basal distance of the other materials because acetate is larger than nitrate. For the same structure and the same counter-ion, the basal distance can vary depending on the mode that the anions accommodate into the interlayer region of the material and on the level of hydration of said material.

The FTIR spectrum of ZnHN (Fig. 2a) presented O–H group stretching bands between 3600 and 3290  $\text{cm}^{-1}$ , attributed to structural hydroxyls and water molecules [20,21]. Three bands emerged in this region and referred to distinct structures of

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