

Contribution to Copper Elimination Study by Adsorption on Double-Layered Hydroxides HDL

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The present work is a contribution to copper removal study by adsorption on Double-Layered Hydroxides Co-Cr-HDL prepared by co-precipitation method at pH of 10. Characterization of the solid was performed by both FTIR and DRX techniques. The kinetic study and the determination of adsorption isotherms were carried out in a batch system at room temperature to evaluate the effect of the adsorbent-adsorbate contact time, the adsorbate initial concentration, the solution pH and the adsorbent mass on the retention of copper and the adsorption capacity of the synthesized HDL. Retention of copper reached 50 % on 0.05 g of HDL during 6 hours of contact at the pH of synthesized aqueous solution. Experimental kinetic data have been well described by the pseudo-second-order model and adsorption equilibrium can be represented by the Langmuir model which gives us information on the nature and the texture of the solid surface which would be homogeneous, with sites energetically identical, able to receive the copper ions in monolayer, without interaction between the adsorbed chemical species.

1. Introduction

Discharges of organic and metallic pollutants into environment remain a serious problem in many countries, facing many industries such as mining, hydrometallurgy, pulp and paper, petrochemicals, refining, fertilizers, electroplating, surface treatments, etc. The main liquid waste from surface treatments baths such as baths of pickling, of degreasing, of treatment and of rinsing contain surface treatment metals such as Copper, Nickel, Chromium, Cadmium, Zinc, ... (Beaux, 1997) which can cause accidental pollution into the environment.

Different disorders have been described as a consequence of copper accumulation in animals and humans. Acute copper intoxication causes severe gastroenteritis. Prolonged exposure to copper can cause irritation of the nose, mouth, and eyes and causes headaches, upset stomach, dizziness, vomiting, and diarrhea.

For the elimination of the potential for environmental disturbance in a perspective of sustainable development, depollution of water and recovery of industrial waste are important objectives for both industrialized and developing countries. To achieve this, treatment technologies must be developed, permitting thus to preserve the environment. Many techniques of depollution are developed in recent years including chemical precipitation processes, flocculation, ion exchange, electrolysis, membrane processes and adsorption.

In this study, the adsorption process was applied to the retention of copper from effluents of surface treatment discharges using the Layered Double Hydroxides LDH (or HDL) as adsorbent prepared by the co-precipitation method at constant pH. LDH have been of great interest since a few years due to their electrochemical properties (Deroy and Besse, 1989; Guerlou-Demourgues and Delmas, 1994) or anion exchange and their use in heterogeneous catalysis. HDL, also called anionic clays, (Vaysse, 2011) are little abundant materials in the natural state, but easily synthesizable in the laboratory which requires a simple titration assembly, with an inexpensive and available material, and also allows us better control of the composition of the reaction medium and gives well crystallized products (Taoualit et al., 2015). The structure is constituted by a stack of brucite-type sheets $[M_{1-y}^{II} L_y^{III} (OH)_2]^{y+} [X^n]_{y/n} [H_2O]_z$ with common stops, as shown in figure 1. The partial substitution of the trivalent cations M (III) for the divalent cations L (II) generates an excess of positive charge

on the sheets. The charge density being proportional to the ratio $y = \frac{n(M^{III})}{n(M^{III} + L^{II})}$. In order to ensure the overall electrical neutrality, anionic species (X^{n-}) are then intercalated in the interlayer space in conjunction with water molecules, the cohesion of the structure results, on the one hand, from electrostatic interactions between the oxygenated metal sheets and the anions and on the other hand from a hydrogen bonding network established between the water molecule and the interlamellar anions hydroxides of the sheets (Géraud, 2006).

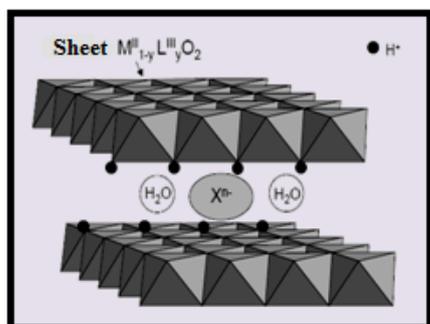


Figure.1: Schematic representation of a LDH phase structure ((Géraud, 2006)

2. Experimental study

2.1 Preparation of the adsorbent Co-Cr-LDH

Co-Cr-HDL was prepared by co-precipitation method at constant pH by titrating 100 mL of $\text{Co}(\text{Cl}_2) \cdot 6\text{H}_2\text{O}$ (99-100%, purchased from Riedel-de-Haën) and $\text{Cr}(\text{Cl}_3) \cdot 6\text{H}_2\text{O}$ (98%, purchased from Merck) mixture solution, defined by a molar ratio y equal to 2 with 100 mL of Na_2CO_3 solution 1M (99.5 -100% from Panreac) and NaOH 2M (97% purchased from Biochem Chemopharma) at room temperature under strong agitation during about 90 minutes while the pH was maintaining constant equal to 10. When the precipitation reaction was completed, the resulting gel was refluxed at 60°C for 15 hours to allow crystal growth. Once the heat treatment achieved, the product was filtered and washed several times with distilled water until complete elimination of excess ions on the solid (Cl^- , Na^+), then dried in an oven at 70°C over one night. Obtained product was in the form of a sinterable solid then it was ground using an agate mortar to give a very fine white powder. Thereafter, the solid was calcined in a furnace at temperature of 600°C with an air inlet for 4hours, and a temperature rise of $5^\circ\text{C} \cdot \text{min}^{-1}$. Obtained solid was then characterized by different physico-chemical techniques such as X-ray diffraction, infrared spectroscopy FTIR and the point of zero charge Pzc. Several studies have shown that (López Nieto et al., 1995) calcined HDL (HDLc) have remarkable and higher adsorptions than non-calcined phases. For this reason, calcined HDL at 600° was used for copper adsorption, in this work.

2.2 Preparation and dosage of Copper solutions

Copper stock solution of $1\text{g} \cdot \text{L}^{-1}$ was prepared by dissolving a given amount of CuSO_4 in distilled water. Other solutions at different concentrations were obtained by successive dilutions. The initial pH was adjusted with dilute solutions of HCl (0.1M) and/or NaOH (0.1M).

The residual copper in the aqueous solution was analyzed by atomic absorption spectrophotometry with flame (Analytik Jena s5) at appropriate copper wavelength $\lambda = 324.8 \text{ nm}$.

The copper adsorption capacity, the adsorbed quantity and the removal efficiency ($E \%$) of copper on Co-Cr-HDL were calculated from equations 1, 2 and 3:

$$Q_t = \frac{C_0 - C_t}{m} \times V \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

$$E (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Where Q_t ($\text{mg} \cdot \text{g}^{-1}$) is the copper ions amount adsorbed at time t (min), Q_e ($\text{mg} \cdot \text{g}^{-1}$) represents the amount of adsorbed metal at equilibrium per unit mass of solid, C_0 ($\text{mg} \cdot \text{L}^{-1}$), C_t ($\text{mg} \cdot \text{L}^{-1}$) and C_e ($\text{mg} \cdot \text{L}^{-1}$) are respectively

the initial, the final concentration of copper (at time 0 and t) and at equilibrium in the aqueous solution, V is the aqueous solution volume (mL) and m (g) represents the amount of the adsorbent Co-Cr-HDL.

2.3 Adsorption kinetic studies of Copper on synthesized HDLs

The adsorption tests on Co-Cr-HDL were carried out in batch system using 250 mL glass bottles closed with a stopper and covered with aluminium paper, all, containing a known Co-Cr-HDL mass to which was added separately a volume of 100 mL of Copper aqueous solution at fixed initial concentration and a constant pH. The assembly was placed under horizontal stirring on an oscillating table at room temperature during 24 hours. Samples were thus taken at different time intervals ranging from 0 to 24 h of contact. After filtration, the adsorbates were analyzed directly by atomic absorption spectrophotometer at the wavelength $\lambda = 324.8$ nm. The effect of adsorbent mass, contact time, copper initial concentration and of aqueous solution pH on Copper adsorption were investigated.

3. Results and Discussion

3.1 Characterization

X-ray diffraction

Obtained diffractogram of Co-Cr-LDH is represented on figure 2. The general appearance of the spectrum is typical of hydrotalcite-type compounds (Bouda, 2013). Indeed, this characteristic is represented by the existence of intense and symmetrical peaks at low values of 2θ and less intense and generally asymmetric peaks at higher angular values. The first peak at $2\theta \approx 11^\circ < 30^\circ$ has been indexed as d_{003} and corresponds to $d_{003} = 5 \text{ \AA}$. This basic reflection corresponds to the inter-sheet space. It makes it possible to calculate the parameter of the mesh c with $c = 3d_{003}$. The second characteristic peak at the higher 2θ values was indexed as d_{110} and corresponds to $d_{110} = 1.82 \text{ \AA}$. This basic reflection corresponds to the intermetallic distance a, with $a = 2d_{110}$. The cell parameters are $c = 15 \text{ \AA}$ and $a = 3.64 \text{ \AA}$. These values are in agreement with those found in the literature (Benselka-Hadj Abdelkader et al., 2011; Lahkale et al., 2014; El Mouhalhal et al., 2003). Co-Cr-HDL matrix is of crystalline form.

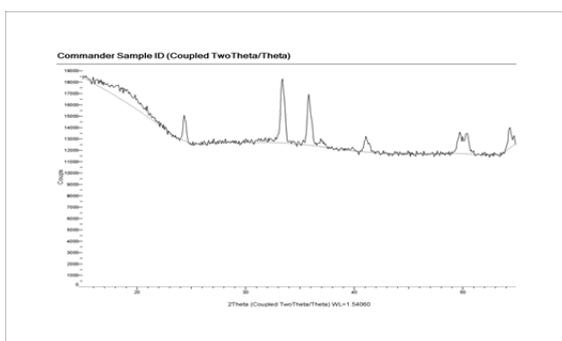


Figure 2: The X-Diffraction of Co-Cr-HDL

Spectroscopy IR

FTIR spectrum of Co-Cr-LDH sample was obtained on a Perkin Elmer apparatus in the range $4000-400 \text{ cm}^{-1}$ and represented on figure 3. The study by IR spectroscopy (Figure 3) confirms the obtention of HDL by the appearance of all the expected bands (Segni, 2005; Chebli, 2016; Ferreira et al., 2004; Lu et al., 2016).

The FTIR spectrum of Co-Cr-LDH is typical of layer double hydroxides and agrees well with the typical results obtained and found in literature (Lu et al., 2016; Ray L. Frost et al., 2005; Bouhent, 2011; Garcia-Sosa et al., 2015). Indeed, the broad band at 3463 cm^{-1} is attributed to the hydroxide groups (OH^-) present in the layer and of water molecules intercalated and /or absorbed. The vibration band in the vicinity of 2500 cm^{-1} , can be attributed to the deformation of the OH^- molecules. The band at 1637 cm^{-1} is assigned to the angular deformation of H_2O molecule, the vibration band at 1381 cm^{-1} which corresponds to the antisymmetric elongation of the inter-lamellar carbonates CO_3^{2-} . At low wave number (672 and 436 cm^{-1}) bands are respectively due to the M-O and O-M-O vibrations of prepared Co-Cr-HDL sheet (M represents the divalent or trivalent metal, here Co or Cr).

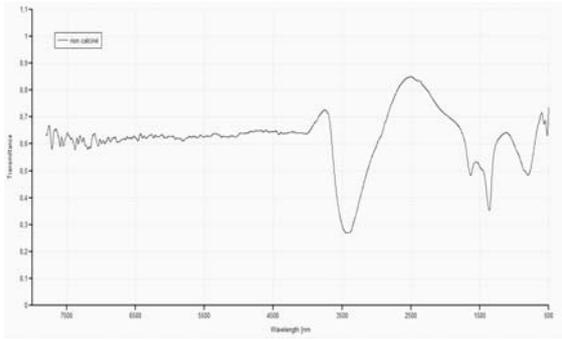


Figure 3: FTIR spectrum of Co-Cr-HDL

3.2 Parametric study of Copper adsorption on Co-Cr-HDL

Effect of Co-Cr-HDL mass

The retention of copper increases from 0 to 51% when the Co-Cr-HDL mass varies from 0 to 0.05 g. For higher masses, a state of pseudo-equilibrium is reached (Figure 4). A higher value of the solid has no influence on the retention of the copper species. This behavior results probably because the number of active sites available is all the greater as the mass is great (0.05 g), which favors the adsorption of a large quantity of copper.

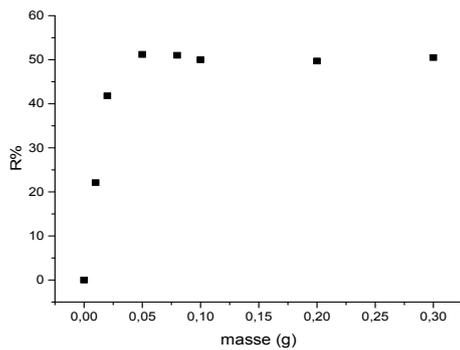


Figure 4: Effect of Co-Cr-HDL mass on Copper removal

Effect of contact time

The adsorption of copper ions consists of two steps (Figure 5). The first one being more or less rapid corresponding to the occupation of the anionic clay active sites by the copper during about 6 hours. The second step is slower, it corresponds to the equilibrium and stability of the adsorption. pH of the solution is that of the solution initially prepared.

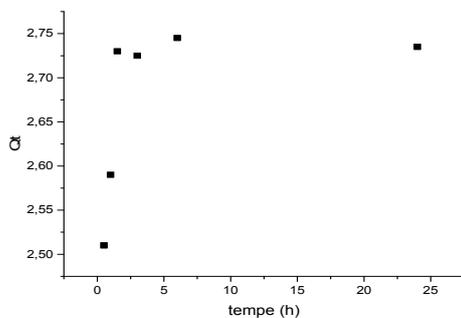


Figure 5 : Adsorption kinetic of Copper on Co-Cr-HDL according to contact time

Effect of pH

Obtained results (Figure 6) show that at pH <5, adsorbed copper regularly increases to become optimal at a pH of 5 and then decrease as the pH increases. Copper is mainly in its ionic form Cu^{2+} in such a pH. Addition of H^+ ions to lower the pH, leads to the neutralization of the OH^- ions released by the HDL structure (Ait Ichou et al., 2014; Aider, 2015), which leads us to suppose that it is probably due to electrostatic interactions between Cu^{2+} and the Co-Cr-HDL synthesized carbonate ions, which favors the adsorption of copper in an acid medium. The carbonate ions that are released due to calcination are very difficult to exchange (Bouda, 2013). A pH of 5 is then considered optimal for the adsorption of copper on the calcined Co-Cr-HDL clay.

Effect of initial concentration

Increase of initial concentration causes a decrease in the Copper adsorbed quantity. High removal efficiencies are obtained for an initial concentration of 10 mg. L⁻¹ (Figure 7).

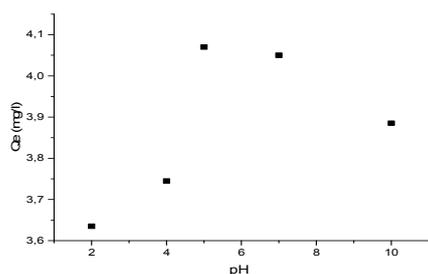


Figure 6 : Influence of pH on the adsorption quantity of Copper

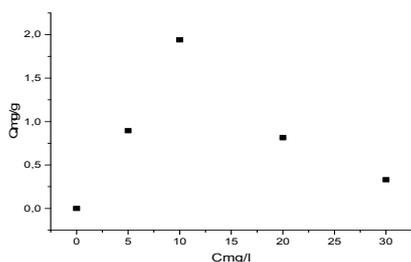


Figure 7 : Influence of Copper initial concentration on its adsorption

Modeling of isotherms and kinetics of Copper adsorption on Co-Cr-HDL

Application of the pseudo-first-model and pseudo-second-model to Copper adsorption reveals that the experimental kinetic data have been well described by the pseudo-second-order model with correlation coefficient $R^2 = 1$. On the other hand, the linear forms of Langmuir, Freundlich and Temkin equations were employed to describe the equilibrium data. The performance of each form was judged through the correlation coefficients R^2 (Table 1).

Table 1: Langmuir, Freundlich and Temkin isotherm parameters for Copper retention on Co-Cr-HDL at $T=25^\circ\text{C}$ and $\text{pH} = 5$

| Langmuir | | | Freundlich | | | Temkin | | |
|-----------------|----------------------------|-------|------------|-------|-------|--------|-------|-------|
| Q_m (mg/g) | b (L. mg^{-1}) | R^2 | $1/n$ | K_F | R^2 | A | B | R^2 |
| 9.434 | 2.23×10^{-2} | 0.987 | 12.5 | 0.883 | 0.743 | 4.7169 | 0.212 | 0.749 |

4. Conclusions

In the present work, the synthesis of the calcined clay Co-Cr-HDL by the co-precipitation method has been carried out to apply it in the adsorption of copper in aqueous solution resulting from surface treatment

discharges. The synthesized anionic clay Co-Cr-HDL corresponds to a hydrotalcite compound with good crystallinity and has the property to be able to regenerate after calcination and formation of mixed oxides. The retention of copper reached 50 % on 0.05 g of HDL during 6 hours at the pH of synthesized aqueous solution. Experimental kinetic data have been well described by the pseudo-second-order model and adsorption equilibrium can be represented by the Langmuir model which gives us information on the nature and the texture of the solid surface which would be homogeneous, with energetically identical sites, able to receive the copper ions in monolayer, without interaction between the adsorbed chemical species. Obtained results demonstrate the immense potential of HDLs as adsorbents for toxic metal ions remediation in polluted waters and wastewaters. LDH can be suitable for the treatment of charged effluents containing species that are harmful to the environment such as surface treatment baths (electroplating, metallurgy, copper plating, etc.), wastewater from olive mills which are heavily loaded with terms of organic matter, ... since the technique is economically feasible requiring a simple titration assembly, and an inexpensive and available material in the laboratory.

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