



STUDY OF HEXAVALENT CHROMIUM SORPTION BY HYDROTALCITES SYNTHESIZED USING ULTRASOUND VS MICROWAVE IRRADIATION

ESTUDIO DE LA SORCIÓN DE CROMO HEXAVALENTE MEDIANTE HIDROTALCITAS SINTETIZADAS UTILIZANDO IRRADIACIÓN DE ULTRASONIDO VS MICROONDAS

S.P. Paredes-Carrera^{1*}, R.F. Valencia-Martínez², M.A. Valenzuela-Zapata¹, J.C. Sánchez-Ochoa¹ and L.V. Castro-Sotelo¹

¹Lab. Catálisis y Materiales. SEPI ESIQIE, Instituto Politécnico Nacional, UPALM Zacatenco 07738, México D.F., México.

²SEPI ESIA, Instituto Politécnico Nacional, UPALM Zacatenco 07738, México D.F., México.

Received November 14, 2014; Accepted June 9, 2015

Abstract

The increase of water contamination caused by toxic compounds is a matter of primary concern, the case in point is the state of Guanajuato in Mexico, where one of the main contaminants found in wastewater is Cr(VI), a widely used compound in the tanning process. The development of an efficient technology to remove this substance from water is absolutely necessary. In this work a comparative study of different anionic clays and activated carbon as a reference, was proposed to eliminate this pollutant. Hydrotalcites were prepared by the coprecipitation method using ultrasound or microwave irradiation during the crystallization step. The interlayer compounds were: sulfates, nitrates, chlorides and etoxide-acetylacetonate. The solids were characterized by X-ray diffraction, nitrogen physisorption and scanning electron microscopy with EDS microanalysis. The amount of sorbed Cr(VI) was determined by UV-vis spectrometry. The best option for Cr(VI) removal was the hydrotalcite with chloride as anion in the interlayer. It was found that the sorption was mainly dependent of the interlayer anion and the preparation method and it was not a function of the specific area. On the other hand the activated carbon is rapidly saturated and its sorptive capacity is practically null.

Keywords: hexavalent chromium, hydrotalcites, sorption, synthesis by microwave, synthesis by ultrasound.

Resumen

El aumento en la contaminación del agua es un asunto de gran relevancia; en Guanajuato México, uno de los principales contaminantes encontrados en aguas residuales es el Cr(VI), ya que este compuesto es ampliamente utilizado en el proceso de curtido; de ahí que el desarrollo de tecnologías eficaces para eliminar este tipo de contaminantes es absolutamente necesario. En este trabajo se realizó un estudio comparativo con diferentes arcillas aniónicas, empleando como referencia al carbón activado, el cual permitió proponer un sistema eficaz de eliminación. Las hidrotalcitas se prepararon por coprecipitación mediante irradiación de ultrasonido y microondas durante la etapa de cristalización. Se utilizaron como aniones de compensación: sulfatos, nitratos, cloruros y una combinación de etóxido-acetilacetato. Los sólidos se caracterizaron por difracción de rayos-X, fisisorción de nitrógeno y microscopía electrónica de barrido con microanálisis EDS. La cantidad de Cr(VI) sorbida se determinó por espectrometría UV-vis. La hidrotalcita clorada resultó en la mejor opción para la eliminación del Cr(VI). Se encontró que la sorción es dependiente principalmente del tipo de anión interlamina seguida por el método de preparación e independiente del área específica. Por otro lado el carbón activado se satura rápidamente y su capacidad de sorción es prácticamente nula.

Palabras clave: cromo hexavalente, hidrotalcitas, sorción, síntesis por microondas y síntesis por ultrasonido.

*Corresponding author. E-mail: : siviappcar@gmail.com
Tel. 57-29-60-00 ext 54224 Fax 57-29-60-00

1 Introduction

1.1 Toxicity and problems caused by the hexavalent chromium

One of the main problems in the tanning industry is the environmental pollution. Among the principal contaminants is hexavalent chromium, in this state of oxidation the chromium has negative effects on living creatures, it can be a mutagenic agent, carcinogen and extremely reactive with others chemical compounds; although there have been attempts to replace chromium in the tanning process with substances that generate less aggressive waste into the environment, 80% of the tanning process still uses it, by giving the skin the properties such as softness, impermeability and elasticity; unfortunately no substitute has been found (Reyes-Gutiérrez *et al.*, 2009; Suarez *et al.*, 2013). In Mexico the main problem focuses on the state of Guanajuato, as the leather tanning and processing of leather goods is one of the main economic activities in this state (Armienta *et al.*, 1997). The discharges apparently exceed limits established by the Mexican norms (NOM-127-SSA1-1994, 1994 and NMX-AA-044-SCFI-2001, 2001) and the Environmental Protection Agency of the United States (EP(NOM-127-SSA1-1994, 1994 and NMX-AA-044-SCFI-2001, 2001)A/600/ R-96/084, 2000), which should have a maximum value of 0.05 mg of Cr(VI) per liter. In the seventies activated carbon was used to remove Cr(VI) in anion form (chromate) from water; this material which is abundant and inexpensive, is widely used for this purpose and for removal of cations of polluted effluents (Dermatas *et al.*, 2006 and Wilkin *et al.*, 2005) In the case of Cr(VI) in activated carbon, it has been reported a retention of 6% in concentrations of 100 ppm (Wilkin *et al.*, 2005). Other materials have also been tested such as cationic and anionic clays; the latter have been reported retention values of 15%, using calcined layered double hydroxides (LDH) prepared with conventional coprecipitation method in autoclave. These rare compounds are important considering that they retain anions like chromium: it is for these reasons the important to develop new techniques to synthesize this type of material with microwave and ultrasound assisted methods. These methods optimize textural properties like volume, type, size and distribution of porosity as well as the surface area. It has been found that the last properties are dependent on time, power and frequency of irradiation (microwave or ultrasound). In addition

they decrease reaction time from hours to minutes. To understand how these materials efficiently exchanged anionic species such as Cr(VI), it is necessary to know the structure and properties of LDH.

1.2 Layered double hydroxides (LDH)

The LDH structure may be easily visualized from brucite as hexagonal closed packing of hydroxyls ions and magnesium ions occupying all the octahedral positions. If Mg^{2+} ions are substituted by Al^{3+} ions during the synthesis process, the LDH in brucite-type structure is obtained. The brucite-type layer (HO-Mg-O-Al-OH) is then positively charged. To maintain the electrical neutrality, anions are required and they are located in the interlayer spaces (Cavani *et al.* 1991; Châtelet *et al.*, 1996; Vaccari 1998; Faour *et al.* 2010). Fig. 1 represents the LDH structure. The LDH can be represented by the general formula: $[(M^{II})_{1-x}(M^{III})_x(OH)_2]^{x+}[A_{x/m}^{m-}] \cdot nH_2O$, where M^{II} is a divalent metal, M^{III} is a trivalent metal and A is a compensating anion ($CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-, \dots$), where charge m and n is the number of water molecules. The most common LDH, known as hydrotalcite, is constituted by magnesium and aluminum as M^{II} and M^{III} metals and the positive charges are compensated by carbonate anions.

The structure of this kind of compounds, based on the stacking of positively charged layers with anions and water, confers relatively high mobility to the anions. It has been observed, that the anions are easily exchanged in the following order (Bellotto *et al.* 1996):

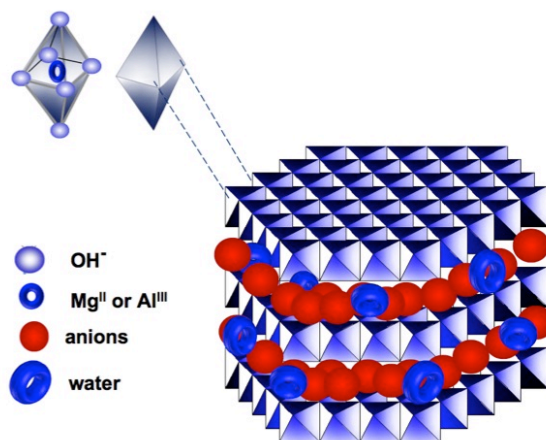


Fig. 1. Structure of a Mg-Al LDH compound.

Table 1. Identification name, precursors and irradiation time of synthesized materials

Name	Precursors		Irradiation time 10 min
CTHCl10U	AlCl ₃ ·6H ₂ O	MgCl ₂ ·6H ₂ O	Ultrasound
CTHCl10M	AlCl ₃ ·6H ₂ O	MgCl ₂ ·6H ₂ O	Microwave
CTHSO410U	Al ₂ (SO ₄) ₃ ·18H ₂ O	MgSO ₄	Ultrasound
CTHSO410M	Al ₂ (SO ₄) ₃ ·18H ₂ O	MgSO ₄	Microwave
CTHNO310U	Al(NO ₃) ₃ ·9 H ₂ O	Mg(NO ₃) ₂ ·6 H ₂ O	Ultrasound
CTHNO310M	Al(NO ₃) ₃ ·9 H ₂ O	Mg(NO ₃) ₂ ·6 H ₂ O	Microwave
CTHEA10U	Al(CH ₃ COCHCOCH ₃) ₃	Mg(CH ₃ CH ₂ O) ₂	Ultrasound
CTHEA10M	Al(CH ₃ COCHCOCH ₃) ₃	Mg(CH ₃ CH ₂ O) ₂	Microwave

The LDH can be obtained by direct or indirect synthesis (Vaccari 1999). Indirect synthesis can traditionally be conducted using three main techniques: a) direct anion exchange, b) anion exchange by elimination of the interlayer precursor species susceptible to acid attack and c) regeneration of the calcined LDH. The calcined LDH which is composed by metal oxides, may be rehydrated again contacting the solid with an anionic aqueous solution; the hydrocalcite structure is, then recovered incorporating the solution anions.

Employing ultrasound and microwave irradiation methods which depend on the power, time and frequency of irradiation, improves exchange capacity and there is an increment of the specific surface area and crystallinity. We therefore propose the use of LDH Mg/Al with interlayer components: nitrates, chlorides, sulfates and the combination of ethoxide-acetylacetonate with activated carbon as a reference. Such compounds are proposed in order to generate different textural properties and find out whether the interlayer components interfere in the texture.

Additionally the microwave and ultrasound irradiation methods allow larger specific areas than LDH prepared with conventional methods in autoclave (Fetter *et al.*, 1997). This is expected to have more Cr(VI) sorption (Gutiérrez *et al.*, 2008; Solis *et al.*, 2013).

It is worth mentioning the use of Cr(VI) in acid medium that has been reduced photocatalytically as chromate or dichromate to Cr (III) at low concentrations, with successful results by using TiO₂ as a catalyst (Koch *et al.* 2007; Soto-Borbón *et al.* 2014). In this case we did not use synthesized LDH because these materials strongly adsorb the Cr(VI) and retards or inhibits the photocatalytic reduction process (Paredes *et al.*, 2006).

2 Experimental

2.1 Synthesis of LDH by ultrasound and microwave methods

LDH compounds with an Al/(Mg+Al) molar ratio of 0.25 were synthesized according to the following procedure. A 1.86 N aqueous solution of NaOH was added to a 2.5 M aqueous solution, which contains the precursors to maintain a pH value of 10.5 under a nitrogen inert atmosphere. The obtained gel was treated with ultrasound or microwave irradiation. In the case of materials prepared by microwave irradiation, the experimental conditions were as follow: in an LG microwave model MS1147G operating at 120 W and 2.5 GHz.

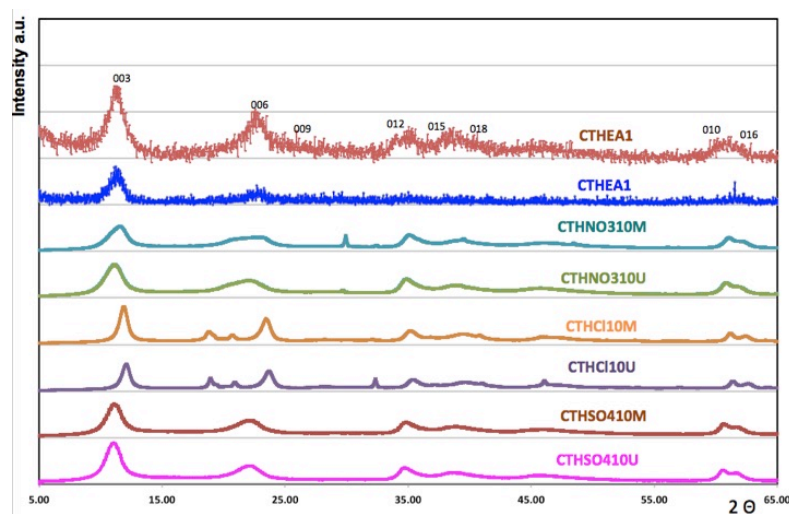


Fig. 2. XRD diffraction patterns of synthesized LDH according to Table 1

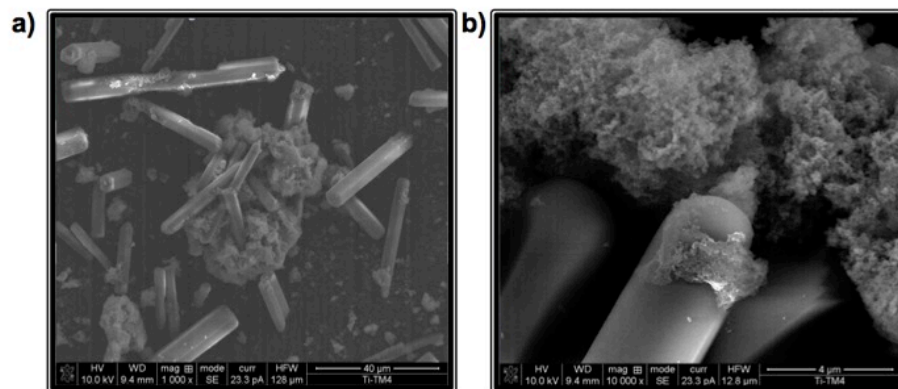


Fig. 3. Scanning electron micrographs at different magnifications a) 1000X and b) 10000X, of sample CTHEA10U synthesized by ultrasonic irradiation.

In the case of ultrasound irradiation the gel was irradiated in an Elma D-78224 cleaner container operating at 2.4 kW and 25 kHz. In both methods the irradiation time was 10 minutes. The samples were washed with deionized water and dried at 70 °C. These samples were labeled according to Table 1.

2.1.1 Characterization of sorbents

All the sorbents were characterized by X-ray diffraction (XRD) and nitrogen physisorption at 74 K. X-ray diffraction patterns were obtained in a Siemens D-500 diffractometer coupled to a copper anode X-ray tube. A diffracted beam monochromator selected the $K\alpha$ radiation. The BET surface areas, pore volume and mean pore diameter were determined by standard multipoint techniques using a Micromeritics ASAP 2010 instrument. A Jeol 1020 Scanning Electron Microscope coupled to an EDS detector provided the sample micrographs and the corresponding elemental composition.

2.2 Cr(VI) sorption using LDH and activated carbon as a reference

2.2.1 Sorbent materials

The sorption process was evaluated for Cr(VI), and two sorbent materials were tested: i) activated carbon as a reference, ii) LDH with compensating anion SO_4^{2-} , NO_3^- , Cl^- and $(CH_3CH_2O)_2 - (CH_2COCHCOCH_3)_3$. The activated carbon was commercial sample provided by Aldrich (99.2 %), while layered double hydroxides (LDH) were synthesized by ultrasound and microwave techniques.

2.2.2 Experimental procedure

The sorption of the anionic component Cr(VI) was carried out using synthesized LDH. The evaluation of the sorption process was performed by UV-vis spectroscopy using a GCB Cintra 20 equipment. A series of aqueous Cr(VI) solutions at different concentrations (100, 200 y 300 ppm) were prepared using potassium dichromate (Aldrich, 98 %), and concentration was measured by UV-VIS spectrophotometry in order to obtain the calibration curve.

The sorption process was conducted in a glass vial (10 ml), in which 0.1 g of sorbent was weighed, then, 10 ml of the polluted solution was added, the vial was stirred for periods of 0.25, 0.5, 0.75, 1.0, 1.5 and 2 hours. Later, the vials were centrifuged for 5 min to separate the sorbent of the purified solution. After that, the solutions were analyzed spectrophotometrically at λ_{max} 265 nm in order to determine their concentrations; finally the amount of Cr(VI) sorbed ions was determined by comparison with the blank.

3 Results

3.1 Characterization of synthesized LDH

In all cases the XRD diffraction patterns show the characteristic signals of the LDH according to the Joint Committee on Power Diffract and Standards (JCPDS) library card 22-0700, which were obtained free of impurities after 10 minutes of ultrasound or microwave irradiation. Except for CTHCI10U and CTHCI10M samples, unidentified impurities can be observed between 18, 20 and 34°.

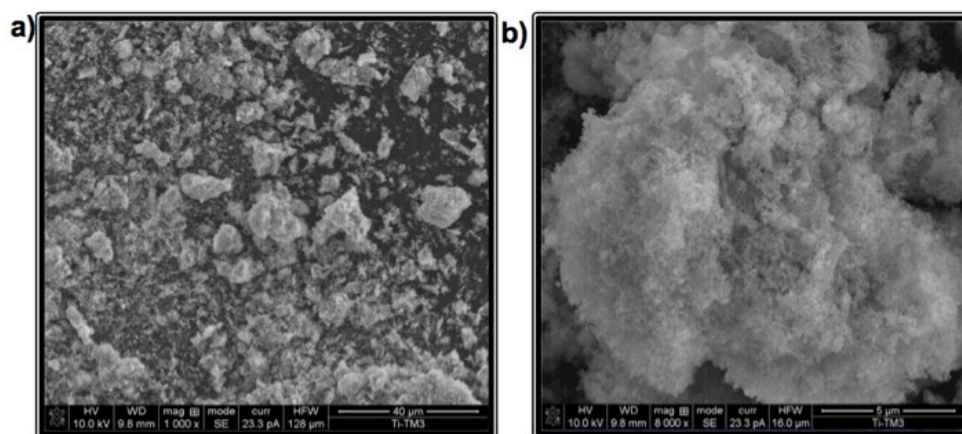


Fig. 4. Scanning electron micrographs at different magnifications a) 1000X and b) 8000X, for sample CTHEA10M, synthesized by microwave irradiation at $x=0.25$.

It can be observed a shift in the intensity 003 which is attributed to the different size of the interlayer anions. CTHEA10U and CTHEA10M samples were obtained from a different diffractometer and that is why the signals are different from the rest, nevertheless they can be easily compared with the other samples.

When comparing samples with sulfates like interlayer anions (CTHSO410M and CTHSO410U) based on the intensity 003, it can be seen that the sample synthesized by ultrasound is more ordered than the one synthesized by microwave. Same behavior was observed for samples with nitrate compensation anions CTHNO310U and CTHNO310M, in both cases the crystallinity is favored by the ultrasound irradiation method.

In the case of samples CTHCl10U and CTHCl10M with chloride compensation anions and ethoxide-acetylacetonate anions (samples CTHEA10U and CTHEA10M) the contrary effect is observed, i.e. the samples obtained by microwaves are more crystalline than the ultrasound ones and with a larger crystal size.

Based on Bragg's law, interlayer spacing was determined with an average value of 3 Å, with the exception of chlorinated species with a value of 2.5 Å.

When comparing synthesis methods, it was observed that samples obtained by ultrasound, resulted in materials with larger crystal size than those obtained by microwaves. It is established from the above that the crystallinity depends on the interlayer components, rather than the synthesis method (microwaves or ultrasound). Being CTHEA10M the most ordered sample, it is followed by CTHSO410U and CTHCl10M respectively.

Fig. 3 shows, the scanning electron micrographs at two different magnifications of CTHEA10U sample which was synthesized by ultrasonic irradiation with interlayer components ethoxy-acetylacetonate and metal molar ratio (x) of 0.25.

An overview of CTHEA10U sample at 1000 X (a), shows two morphologies, one formed by cylindrical materials with different thicknesses, and the other integrated by irregular agglomerated particles. Details at 10000 magnifications in b), it can be appreciated that the agglomerated particles have a porous appearance and the cylindrical structures apparently have no porosity. EDS microanalysis in both morphologies presented the same chemical composition of Al and Mg and equal to $x = 0.252$.

Fig. 4 shows the scanning electron micrographs at different magnifications (1000 and 8000) of CTHEA10M sample, which was synthesized by microwave irradiation method at the same conditions and composition as the CTHEA10U sample.

The micrograph shows at 1000X (Fig. 4 (a)) that the microwave irradiation method produces only one irregular agglomerated morphology similar to one of the morphologies found by the ultrasound method. This morphology is also manifested in X-ray diffractions patterns. It can be seen in Fig. 2, based on the width of the diffraction signals for CTHEA10M sample, that the crystal size are smaller than those obtained from the CTHEA10U sample. Additionally the CTHEA10M structure presents higher crystallinity

Based on the above results, the morphology of a specific material, in this case LDH with compensating anions ethoxide-acetylacetonate is dependent on the irradiation method (microwave or ultrasound) during

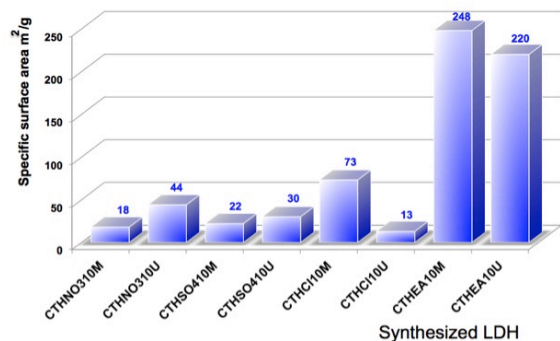


Fig. 5. Specific surface area of synthesized LDH by the BET method.

the crystallization step.

EDS microanalysis of synthesized samples by microwave or ultrasound irradiation, showed values close to $X = 0.25$, indicating that the composition of the brucite-type layer remains unaltered by the synthesis method.

The specific surface area of the synthesized materials was determined by the BET method; the values are presented in Fig 5.

It is observed that CTHEA10U and CTHEA10M compounds present the highest specific surface area, this is attributed to being an organic material (4.8 Å) (Paredes *et al.*, 2006) that generates higher average pore size (28 Å) and thus higher surface area (248 m²/g for CTHEA10M and 220 m²/g for CTHEA10U). Followed in size by CTHCl10M sample with a specific surface area of 73 m²/g and porosity of 8 Å. Is important to note that in almost all synthesized samples, the interlayer spacing formed was almost the same (3 Å), with the exception of chlorinated species with a value of 2.5 Å.

Based on Fig. 5 we observe that specific surface area is independent of the irradiation method. We can not predict which irradiation method produces the highest specific surface areas. It is considered that the specific surface area, crystallinity and the interlayer distance are dependent on the compensation anion more than the irradiation technique. Other advantages of microwave or ultrasound irradiation methods techniques in comparison with autoclave, are the reduction of the synthesis time from hours (24 hours) to minutes and the control of textural properties, which are a function of time, power and type of irradiation.

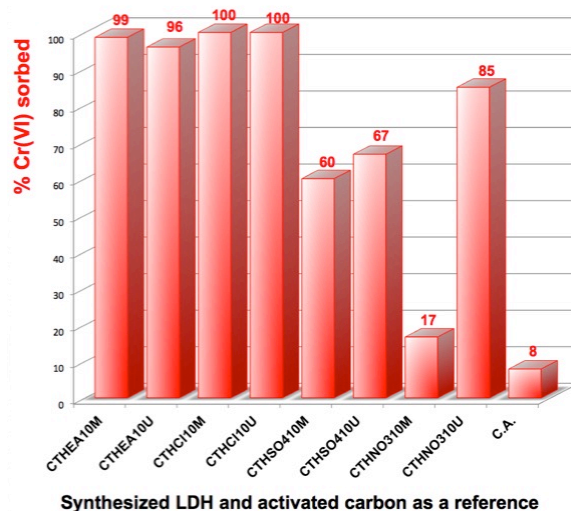


Fig. 6. Percentage of sorbed Cr(VI) as a function of equilibrium time (200 minutes) using synthesized LDH and activated carbon as a reference at 300 ppm of Cr(VI).

3.2 Sorption of Cr(VI) using synthesized LDH and activated carbon as a reference

Fig. 6 presents the final sorption values of Cr(VI) in percentage using synthesized LDH and activated carbon as a reference at 300 ppm and equilibrium time (200 minutes). The experiments were also performed at 100 and 200 ppm of Cr(VI) at different times, but for lack of space we only report the highest concentration of 300 ppm.

From Fig. 6, we have the final order of Cr(VI) sorption by synthesized LDH and activated carbon as a reference, from highest to lowest values is as follows: CTHCl10M=CTHCl10U > CTHEA10M > CTHEA10U > CTHNO310U > CTHSO410U > CTHSO410M > CTHNO310U > CA

CTHCl10M and CTHCl10U samples with chloride as interlayer anion at 15 minutes of contact time resulted the best option to remove Cr(VI) at different concentrations (100, 200 and 300 ppm). Activated carbon was the least suitable material for the sorption of Cr(VI), it presented an average maximum sorption of 8% in the concentration of 100, 200 and 300 ppm at 200 minutes, even though this material has a very high specific surface area.

It can be observed that the specific surface area is not a determining factor in the sorption of Cr(VI), therefore a study of Cr(VI) sorption based on the specific surface area was performed and the results are shown in Fig. 7.

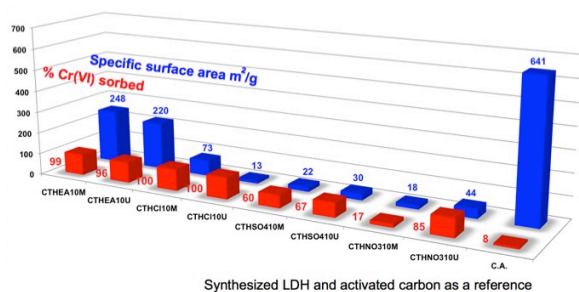


Fig. 7. Results of Cr(VI) sorption based on the specific surface area at 300 ppm, for synthesized LDH and activated carbon as a reference.

It can be observed from samples with nitrate compensation anion (CTHNO310M and CTHNO310U), that there apparently is a relationship between the specific surface area and the sorption capacity, i.e. the sample synthesized by ultrasonic irradiation (CTHNO310U) with higher specific surface area (44 m²/g, Fig. 7) has a mayor sorption capacity than the one synthesized by microwave irradiation (18 m²/g). In samples CTHEA10M-CTHEA10U, CTHSO410U-CTHSO410M and CTHCI10U-CTHCI10M, we do not observed any relationship between specific surface area and sorption capacity, since the samples with chloride interlayer anion with less specific surface area (CTHCI10U and CTHCI10M), showed the highest sorption capacity. Based on the observed details, the sorption of Cr(VI) is mainly due to an anion exchange process more than textural properties (specific surface area, type-size-distribution of porosity) produced by the synthesis technique (microwave or ultrasound), finally from Fig. 7 the activated carbon which has a high specific surface area (641 m²/g) the sorption capacity is only 8%.

Conclusions

It was obtained LDH, free of impurities with interlayer compounds: sulfates, nitrates, chlorides and etoxide-acetylacetonate by the coprecipitation method using ultrasound or microwave irradiation during the crystallization step, with a irradiation time of 10 minutes.

When comparing the ultrasound and microwave methods, in samples with nitrates and sulfates as interlayer components, crystallinity is increased by the ultrasonic irradiation method, the contrary case occurs for samples with chloride and etoxide-acetylacetonate as interlayer compounds. Although ultrasound-synthesized LDH materials in all cases

have a larger crystal size than those synthesized by microwave.

Based on the SEM micrographs CTHEA10U and CTHEA10M samples presented two morphologies when irradiated with microwaves, one in the form of agglomerates and the other with cylindrical form, the latter in greater amounts. The ultrasound method only produced the agglomerate morphology, therefore the morphology is dependent on the synthesis method (microwave or ultrasound).

The Cr(VI) sorption process of the synthesized LDH, is dependent of the interlayer anion, less of the textural properties and independent of the specific surface area.

It was found that the best material for Cr(VI) sorption is the synthesized CTH with chloride anion (CTHCI10U and CTHCI10M), regardless of the synthesis method. It has the advantage that the substitution of chromium by chlorine helps as a sanitizing agent in the treatment of effluents.

Acknowledgements

The authors gratefully acknowledge SECITI-PICSO12-151 and SIP IPN- SIP2014 13 75 projects for financial support.

References

- Armienta M.A., Rodríguez R., Cenicerros N., Juárez F., Cruz O. (1996). Distribution, origin and fate of chromium in soils in Guanajuato, México. *Environmental Pollution* 91, 391-397.
- Bellotto M., Rebours B., Clause O., Lynch J., Bain D., Elkaïm E. (1996). A reexamination of hydrotalcite cristal chemistry. *The Journal of Physical Chemistry* 100, 8527-8534.
- Cavani F., Trifiró F., and Vaccari A. (1991). Hydrotalcite-type anionic clays: preparation, properties and applications. *Catalysis Today* 11, 173-301.
- Châtelet L., Bottero J.Y., Yvon J. and Bouchelaghem A. (1996). Competition between monovalent and divalent anions for calcined and uncalcined hydrotalcite: anion exchange and adsorption sites. *Colloids and Surface A* 111, 167-175.
- EPA/600/R-96/084. United States Environmental Protection Agency. (2000). Guidance for Data Quality Assessment: Practical Methods for Data

- Analysis (QA/G-9): Washington, DC, United States Environmental Protection Agency. *Office of Research and Development*, 219.
- Dermatas D., Moon D.H. (2006). Chromium leaching and immobilization in treated soils. *Environmental Engineering Science* 23, 77-87.
- Faour A., Prévot V., Taviot-Gueho C. (2010). Microstructural study of different LDH morphologies obtained via different synthesis routes. *Journal of Physics and Chemistry of Solids* 71, 487-490.
- Fetter G., Ramos E., Olguin M.T., Bosch P., Lopez T., Bulbulian S. (1997). Sorption of I^{131} by hydrotalcites, *Journal of Radionalytical and Nuclear Chemistry* 221, 63-66.
- Koch C., Ovid'ko I.A., Seal S., Veprek S. (2007). *Structural nanocrystalline materials: fundamentals and applications*. Cambridge University Press, Cambridge, New York, 95-97.
- Gutiérrez N., Ramos E., Contreras C. (2008). Removal of chromium (VI) from aqueous solutions by hydrotalcite-like compounds: kinetic and equilibrium studies. *Revista Mexicana de Física* 55, 135-138.
- NOM-127-SSA1-1994. Norma Oficial Mexicana (1994). *Salud ambiental*. Agua para uso y consumo humano. Límites permisibles de calidad y tratamientos a que debe someterse el agua para su potabilización: México. Secretaría de Salud.
- NMX-AA-044-SCFI-2001. Norma Oficial Mexicana (2001). *Análisis de aguas - Determinación de cromo hexavalente en aguas naturales, potables, residuales y residuales tratadas - Método de prueba: México*. Secretaría de Economía.
- Paredes S.P., Fetter G., Bosch P., Bulbulian S. (2006). Sol-gel synthesis of hydrotalcite-like compounds. *Journal of Materials Science* 41, 3377-3382.
- Reyes-Gutiérrez L.R., Romero-Guzmán E.T., Olmos-Salinas M.G., Rodríguez-Castillo R. (2009). Chemical species of chromatite of an industrial landfill in the León valley, Guanajuato. *Revista Mexicana de Ciencias Geológicas* 26, 104-116.
- Solís M., Gil J.L., Solís A., Pérez H.I., Manjarrez N., Perdomo M. (2013). The sedimentation process a simple method to diminish contaminants in textile effluents. *Revista Mexicana de Ingeniería Química* 12, 585-594.
- Soto-Borbón M.A., Sánchez-Corrales V.M., Trujillo-Camacho M.E. (2014). Characterization of TiO_2 /alginate screenprinting films. *Revista Mexicana de Ingeniería Química* 13, 227-236.
- Suarez O.J., Olaya J.J., Rodil S. (2013). The effect of operating conditions during plating on the electrochemical behavior and morphology of trivalent solution derived chromium coatings. *Revista Mexicana de Ingeniería Química* 12, 129-141.
- Vaccari A. (1998). Preparation and catalytic properties of cationic and anionic clays. *Catalysis Today* 41, 53-71.
- Vaccari A. (1999). Clays and catalysis: a promising future. *Applied Clay Science* 14, 161-198.
- Wilkin R.T., Su C., Ford R.G., Paul C.J. (2005). Chromium removal processes during groundwater remediation by a zerovalent iron permeable reactive barrier. *Environmental Science and Technology* 39, 4599-4605.