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Removal of chromium (VI) from aqueous solutions by hydrotalcite-like compounds: kinetic and equilibrium studies

N. Gutiérrez, E. Ramos*, and C. Contreras
Centro de Investigaciones en Química Inorgánica de la Universidad de Guanajuato,
Noria Alta s/n, Col. Noria Alta, 36050, Guanajuato, Gto., México,
**e-mail: ramosre@quijote.ugto.mx*

M. Olguín
Instituto Nacional de Investigaciones Nucleares,
Carretera México-Toluca s/n, km 36.5, La Marquesa, Coyoacan México, 52750, México.

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Wastewaters containing chromium (VI) generated by different industrial processes are considered dangerous residues, since chromium (VI) is a powerful epithelial irritant and a human carcinogen. Thus, it is necessary to develop new materials that can be used in the remediation of contaminated water. In the present work hydrotalcite-like compounds with Mg/Al =2 were synthesized by the sol-gel method. The hydrotalcite-like compounds were characterized and used as sorbents for removal of chromium (VI) from aqueous solutions. The maximum chromium (VI) uptake by hydrotalcite-like compounds and its heated product were 100 and 125 mg of Cr (VI)/g, respectively.

Keywords: Hydrotalcite like compounds; layered double hydroxides (LDH); chromium (VI); equilibrium studies; adsorption isotherms.

El agua residual que contiene cromo (VI) generado por diferentes procesos industriales, es considerada un residuo peligroso, debido a que el cromo (VI) produce daños a la salud. Por consiguiente, es necesario el desarrollo de nuevos materiales que se puedan utilizar en la remediación de agua contaminada. En el presente trabajo se sintetizaron, por el método sol-gel, materiales tipo hidrotalcita con relación Mg/Al=2. Los materiales tipo hidrotalcita fueron caracterizados y utilizados como sorbentes para la remoción de cromo (VI) de soluciones acuosas. La máxima capacidad de remoción de cromo (VI) del material tipo hidrotalcita fresco y del material tratado térmicamente a 350°C, fue de 100 y 125 mg de cromo (VI) /g, respectivamente.

Descriptores: Materiales tipo hidrotalcita; hidróxidos dobles laminares (HDL); cromo (VI); estudios de equilibrio; isotermas de adsorción.

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1. Introduction

Chromium is a common contaminant present in wastewaters. A wide range of industries use chromium in their processes. As a result, their effluents contain significant amounts of this metal [1]. Chromium exhibits two oxidation states: Chromium (VI) and Chromium (III). At high levels, Chromium (VI) is more toxic than chromium (III) and is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties [2].

Different techniques have been employed for Chromium (VI) removal from wastewaters. Physicochemical treatments are commonly used because these techniques are more economical than the electrochemical ones [3]. Sorption process is one of the most effective physical processes that may be used to remove Cr (VI) from wastewaters. It has been reported the use of activated carbon [4], zeolites [5], minerals [6], cationic [7] and anionic [8] clays, etc., as sorbent materials for Cr (VI). The anionic clays, witch are also known as hydrotalcite-like compounds (HLC), are commonly used has sorbent materials.

Hydrotalcite-like compounds are also known layered double hydroxides. The general formula of HLC can be expressed as $[\mathrm{M(II)}_{1-x}\mathrm{M(II)}_x(\mathrm{OH})_2]^{x+}\ \mathrm{A}^{n-}_{x/n}$; where M(II) is a divalent metal ion, M(III) is a trivalent metal and A is an anion that occupy the interlayer region of these crystalline materials. These anions can be exchange according to the affinity scale reported by Miyata. The hydrotalcite-like compounds are commonly prepared by coprecipitation of metallic salts in alkaline medium at constant pH [9]. With the purpose of modifying the textural properties of the HLC, these substances can be synthesized by the sol - gel method [10].

In the present study, HLC with Mg/Al =2 were synthesized by the sol-gel method, with the purpose of modifying their thermal and textural properties and determine their sorption capacity for Cr (VI). Additionally, the HLC was heated at 350°C and the product was also used as a sorbent for Chromium (VI).

2. Experimental procedures

2.1. Preparation of the hydrotalcite-like compound

HLC with Mg/Al=2 were prepared by the sol-gel method. Magnesium ethoxide (0.66 mol) and aluminium acetylacetonate (0.33 mol) were dissolved in ethanol containing a small amount of HCl. The solution was refluxed at 70°C with constant stirring. The pH of the mixture was adjusted at 11.5 with NH_4OH. Then, 0.5 mol of water was added. The mixture was stirred and refluxed until the gel was formed. Finally, the samples were dried at 70°C for 24 hours. Their heated products were prepared by heating the dried samples at 350°C in air for 5 hours. The HLC and it heated product were characterized by X-ray Diffraction, porosity, BET surface area and thermogravimetric and deferential thermal analysis.

2.2. Equilibrium study

The adsorption capacity of HLC and its thermally treated products was determined in a batch procedure, using chromate concentrations of 500, 1000 and 2000 mgL^{-1} (expressed in Cr). The samples were stirred in a shaker/rotator, at 25°C. The Cr (VI) concentrations were determined by the atomic absorption, using a spectrophotometer Perkin Elmer 100 series. The absorbance was measured at 371.6 nm.

The experimental adsorption data were fitted with the Langmuir, Freundlich and Dubinin-Radushkevich equations. Adsorption parameters and the correlation coefficients of the curves were calculated from the adsorption isotherm data.

2.3. Kinetic study

The kinetic study of the Chromium (VI) sorption process was performed in a batch procedure. The chromium concentration was 1000 mgL^{-1}. Chromium concentrations: 1000 mgL^{-1}. The sample was stirred in shaker/rotator at 25°C. Several samples of the liquid were taken after: 1, 2, 4, 8, 16, 32, 64, 128, 256 and 512 minutes.

3. Results and discussions

3.1. Chemical structure

The diffraction pattern of HLC is shown in Fig. 1. The diffraction pattern of the sample confirms that the solid has a double layered structure, corresponding to hydrotalcite type material (card JCPDS 22-0700).

3.2. Thermal study

The TGA curve exhibits a three-step decomposition process as shown in Fig. 2. In the first step ranging from 24 to 189°C, the sample losses physically adsorbed water (14.47%). This endothermic effect is reflected as a peak on the DTA curve with a minimum at 100°C. In the second step, in the range of 189 - 358°C, the sample losses a further 14.49% of its mass, corresponding to the interlayer water. This weight loss is associated with an endothermic effect with a minimum at 260°C. Finally, the weight loss occurring between 358 - 510°C is due to the dehydroxylation of the hydrotalcite layers and to carbonate decomposition (17.67%). This weight loss is associated with an endothermic peak centered at 400°C.

TABLE I. Surface area and porosity of hydrotalcite-like compound and its heated product.

sample	surface area (m^2/g)	micropore volume (cm^3/g)	micropore size (Å)
HLC	222.50	0.237	39.144
Heated product	356.78	0.526	54.948

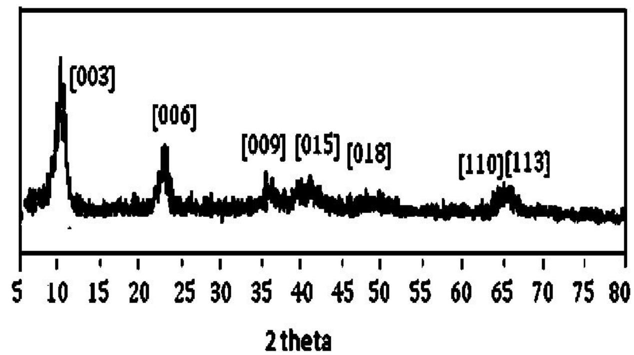

FIGURE 1. XRD spectrum of hydrotalcite-like compound.

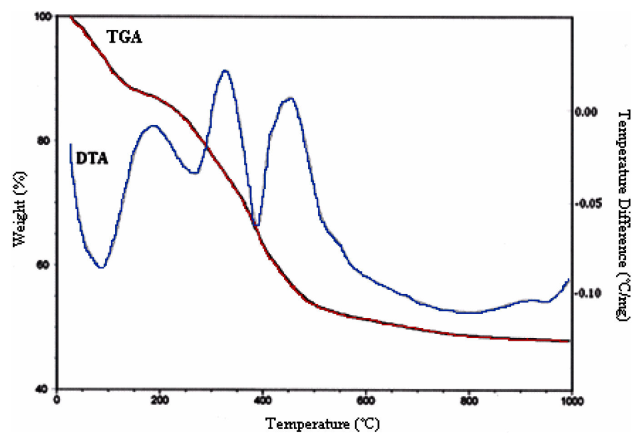

FIGURE 2. Thermal analysis (DTA and TGA) of hydrotalcite-like compound.

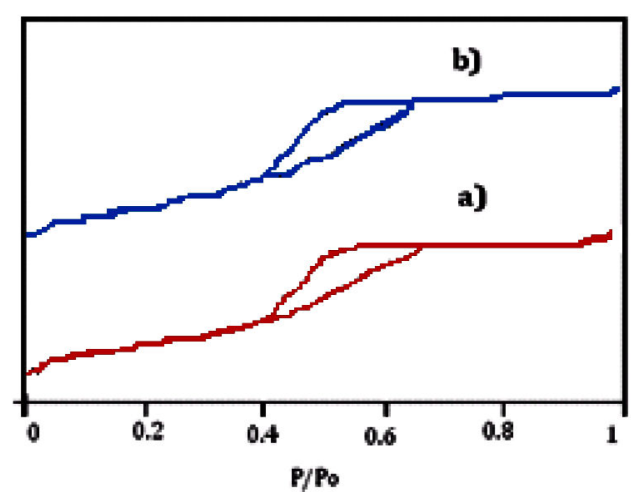

FIGURE 3. (a) Adsorption isotherm of hydrotalcite-like compound and (b) its heated product.

TABLE II. Calculated Langmuir, Freundlich and Dubinin-Radushkevish isotherm parameters for Cr (VI) adsorption onto hydrotalcite-like compound (HLC) and its heated product at 350°C (HLC-350).

Sample	Langmuir isotherm			Freundlich isotherm			Dubinin-Radushkevish isotherm			
	R^2	Q_{max} (mg/g)	K (L/mg)	R^2	K (mg/g)	n	R^2	Q_D (mg/g)	B_D (mol^2/kJ^2)	E (kJ/mol)
HLC	0.999	111.11	0.080	0.971	76.11	7.50	0.999	138.8	0.337	1.20
HLC-350	1.000	138.88	0.150	0.850	13.62	0.26	0.961	154.3	0.338	1.21

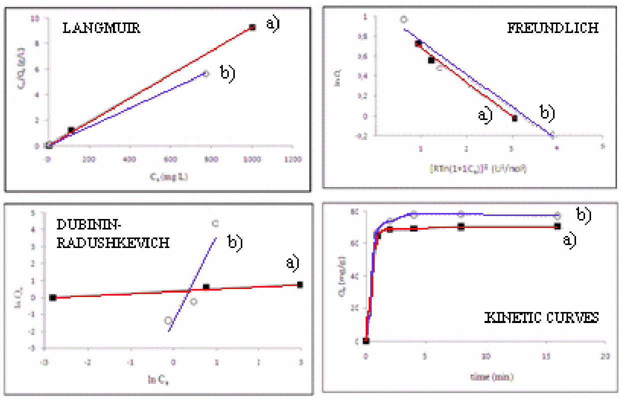

FIGURE 4. Langmuir, Freundlich, Dubinin-Radushkevish (D-R.) isotherms and sorption kinetic plots for adsorption of Cr (VI) on: (a) hydrotalcite-like compound; (b) its heated product at 350°C.

3.3. Textural properties

The N_2adsorption-desorption isotherms of the HLC and its thermally treated product are shown in Fig. 3. The two solids exhibit a type IV isotherm, witch is typical of mesoporous materials. In Table I the surface area and porosity of the HLC and its heated product is presented. It can be observed that the thermal treatment of the HLC at 350°C caused the surface area and the porosity of the solid to increase.

3.4. Adsorption equilibrium studies

Langmuir isotherm represents equilibrium distribution of metal ions between the solid and liquid phases and are often expressed as: $C_e/Q_e = 1/(Q_{max}K) + C_e/Q_{max}$ [11]. The linear plots obtained after graphing C_e/Q_e vs C_e indicates that the adsorption of Cr (VI) by HLC and its heated product fit the Langmuir adsortion equation, as shown in Fig. 4. The values of Q_{max} and K are presented in Table II. As can be seen, the uptake capacity of the heated product is higher than that of the HLC. This can be attributed to the high surface area of the heated product.

Freundlich equation is used to describe heterogeneous surface energies and is expressed using the linear equation: $\ln Q_e = \ln K_f + 1/n \ln C_e$ [11]. The linear plots of $\ln C_e$ vs $\ln Q_e$ for HLC and its heated product indicate that the adsorption Cr (VI) fit reasonably well to the Freundlich adsorption equation (Fig. 4). The K_f and n values are shown in Table II. According to the Freundlich adsorption model, the n value is related to the distribution of bonded ions on the adsorbent surface. Furthermore, n values between 1 and 10 represent beneficial adsorption [12]. According to the n values obtained for HLC and its heated product, it can be stated that the adsorption of Cr (VI) on HLC is more favorable than that of its heated product.

The *Dubinin-Radushkevish* equation was chosen to estimate the adsorption energy. The model is often expressed as: $\ln Q_e = \ln Q_D - B_D\,[RT \ln (1+1/C_e)]^2$. The plots of $\ln Q_e$ against $[RT \ln (1+1/C_e)]^2$ for HLC and its heated product gives a straight line as shown in Fig. 4. The linear regression values (R^2), presented in Table III, indicate that the experimental data fit well to the Dubinin-Radushkevich equation. The calculated values of Q_D and B_D are shown in Table II. The higher the Q_D values, the higher the adsorption capacity. The Q_D values of HLC and its heated product indicate that these solids exhibit high adsorption capacity. The apparent adsorption energy values (E) are presented in Table II. These values were calculated from the Dubinin-Radushkevich isotherms using the equation:

$$E = \frac{1}{(2B_D)^{1/2}}.$$

These adsorption energy values suggest that adsorption occurs through a complex mechanism that probably includes physisorption and internal diffusion processes [13]. In Table II the correlation coefficient values (R^2) obtained from three adsorption values are shown. From the R^2 values, it can be inferred that the Langmuir equation is appropriate for describing the adsorption behavior of Cr (VI) on HLC and its heated product.

3.5. Kinetic studies

In Fig. 4, the sorption kinetic curves of HLC and its heated product are shown. The adsorption velocity of Cr (VI) on both solids is a very rapid one, since the equilibrium concentration of Cr (VI) is attained after eight minutes of contact time.

4. Conclusions

Hydrotalcite like compound with Al/Mg=2 was synthesized by the sol-gel method. This compound and its heated product at 350°C were used for removing chromium (VI) from aqueous solution. The sorption capacity of the solids was improved by thermal treatment of the hydrotalcite like compound. The maximum chromium (VI) uptake by hydrotalcite-like compounds and its heated product were 100 and 125 mg of Cr (VI)/g, respectively. The experimental chromium (VI) adsorption data for hydrotalcite-like compounds and its heated products fitted well to the Langmuir model. For both solids the equilibrium concentration of chromium (VI) was reached after eight minutes of contact time.

1. L.F. de Filipps and C.K. Pallaghy, *Alg. Wat. Pollut.* (1994) 31.
2. M. Cieslak, *Polyhedron* **15** (1996)3667.
3. W.J. McLay and F.P. Reinhard,*Wast. Minim.Recov.Tech. Met. Finish*. **98** (2000) 817.
4. S.B. Lalvani, T. Wiltowski, A. Hubner, and A. Weston, *Carbon* **36** (1998) 1219.
5. E. Chmielewska, *Turk J Chem* **27** (2003) 639.
6. D.K. Sing, D.N. Saksena, and G. Prasad, *J. Chem. Thech Biotechnol*. **87** (2001) 273.
7. N.K. Lazaridis and D.D. Asouhidou, *Chemosphere* **42** (2001) 373.
8. M. del Arco, D. Carriazo, C. Martin, A.M. Perez-Grueso, and V. Rives, *Mat. Sci. Forum* **514-516** (2006) 1541.
9. F. Trifiro and A. Vaccari, *Comp. Supra Chem* **7** (1996) 251.
10. E. Ramos , T. Lopez, and P. Bosch, *J. of Sol-Gel Sci. and Tech.* **8** (1997) 437.
11. T Casey, J. Unit Treatment Processes in water and wastewater engineering (John Wiley and Sons Ltd., 1997) p.113.
12. K. Kadirvelu and C. Namasivayam, *J. of Memb. Sc.* **165** (2000) 159.
13. M. Horsfall, J.A.I. Spiff, and A.A. Abia, *Bull Korean Chem Soc* **25** (2004) 969.