



## Fast reduction of Cr(VI) from aqueous solutions using alumina



Fabiola Glorias-García<sup>a</sup>, José Miguel Arriaga-Merced<sup>a</sup>, Gabriela Roa-Morales<sup>a</sup>,  
Víctor Varela-Guerrero<sup>a,\*</sup>, Carlos Eduardo Barrera-Díaz<sup>a,\*</sup>, Bryan Bilyeu<sup>b</sup>

<sup>a</sup> Universidad Autónoma del Estado de México, UAEM, Centro Conjunto de Investigación en Química Sustentable CCIQS, UAEM-UNAM, Carretera Toluca-Atlaconulco, km 14.5, C.P. 50200 Toluca, Estado de México, Mexico

<sup>b</sup> Department of Chemistry, Xavier University of Louisiana, 1 Drexel Drive, New Orleans, LA 70125, United States

### ARTICLE INFO

#### Article history:

Received 22 April 2013

Accepted 14 October 2013

Available online 21 October 2013

#### Keywords:

Hexavalent Chromium

Adsorption

Reduction

Aqueous solutions

Alumina

### ABSTRACT

Hexavalent chromium is challenging to remove from industrial wastewater due to the solubility and anionic nature of the chromates. Cr(VI) is typically removed by reduction to Cr(III), then precipitation or adsorption, which requires multiple steps and bulk reagents and generates sludge. In this project, we have evaluated a sintered alumina disk as a single step sorbent for Cr(VI). The disk was porous enough that 20 mL samples passed through in about 3 s using light suction. A single pass through the disk only reduced the [Cr(VI)] by 10–20%, but by passing the solution through the disk five times up to 80% was removed in samples up to 130 mg/L and up to around 50% for much higher concentrations. The five passes through the filter disk took less than a minute. On each pass through the disk the characteristic chromate UV–vis absorbance decreased, the Cr(VI) concentration (by the diphenylcarbazide method) decreased, and the pH rose slightly. The XRD pattern showed no change in the crystal structure of the alumina, but the SEM/EDS identified chromium on the surface. In addition to confirming chromium on the surface of the alumina, the XPS spectra showed a change in the binding energy of the aluminum, which is consistent with complexation. The system was fast and effective (in series), so should be applicable to industrial wastewater treatment.

© 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Cr(VI) is a strong oxidizing agent which is extremely mobile in soil and aquatic environments and readily absorbed through skin [1,2]. It is both a known carcinogen and an irritant to plant and animal tissues. Due to the health and environmental dangers, hexavalent chromium in industrial wastewater is strictly regulated. Unlike most heavy metal ions and Cr(III), Cr(VI) is typically present as an anionic chromate which is difficult to remove through conventional means [3].

The removal of Cr(VI) from industrial effluent typically involves the reduction of the Cr(VI) to Cr(III) followed by either precipitation or adsorption [4]. The reduction can be done by a chemical reducing agent or by electrolysis, but is usually most effective at low pH. Once the chromates are reduced to Cr(III) cations, they can be precipitated as insoluble hydroxides by raising the pH or removed by adsorption. Although this multistep process is straightforward and the reagents are practical and accessible, it

does require large quantities of reagents and results in excessive amounts of hazardous sludge. Thus, a single step process would be highly advantageous.

The development of inexpensive adsorbents for the treatment of wastewaters is an important area in environmental science [5,6]. Although there are a wide variety of effective sorbents for metal cations, most are ineffective for anions like chromate. Sorbents which have proven effective include synthetic resins [7,8], inorganic materials [9], activated carbon [10], alumina [11], and composites [12].

Sorbents are usually evaluated in both batch and continuous modes. Batch mode evaluation involves mixing a certain amount of sorbent and a quantity of aqueous Cr(VI) solution, while monitoring the change in [Cr(VI)] in time for different conditions (pH, [Cr(VI)], etc.) to determine the kinetics, mechanism, and capacity of the sorbent. Batch study results are very important, but most industrial treatment processes are continuous rather than batch processes, so column studies are also necessary. In continuous mode studies, aqueous Cr(VI) solutions are passed through a column of sorbent and the concentration in the eluate is monitored [13,14]. In the case of a porous solid, like the alumina disk we are using, the solution may be passed through the solid rather than a packed column.

\* Corresponding authors. Tel.: +52 7222766610.

E-mail addresses: [vvgvic@hotmail.com](mailto:vvgvic@hotmail.com) (V. Varela-Guerrero), [cd0044@yahoo.com](mailto:cd0044@yahoo.com) (C.E. Barrera-Díaz).

This paper describes the evaluation of a sintered alumina disk as a Cr(VI) sorbent in a continuous flow column. The experimental results show success in reducing the concentration of Cr(VI), but the speed and the capacity are the unique aspects of the sorbent. The material appears to be a practical Cr(VI) sorbent for industrial treatment.

## 2. Materials and methods

### 2.1. Preparation of the supporting disk

The alumina disk was prepared by compacting 1.75 g of powder (98.0%, Aldrich) in a 22 mm diameter stainless steel holder applying 8 tons/cm<sup>2</sup> of pressure. The resulting disk was calcinated by heating to 1100 °C at 20 °C/min and holding for 48 h [15,16].

### 2.2. Cr(VI) solutions

The Cr(VI) solutions were prepared using potassium dichromate and deionized water.

### 2.3. Chromium detection in aqueous solution

The concentration of Cr(VI) was measured using the diphenylcarbazide colorimetric test method (NMX-AA-044-SCFI-2001). A solution of 1–5 diphenylcarbazide in acid forms a pink complex with Cr(VI), which is spectrophotometrically analyzed at 540 nm in a single wavelength HACH DR/4000U spectrophotometer. Total chromium concentration was measured using Atomic Absorption using the standard methods.

### 2.4. Batch experiments

In order to evaluate the Cr(VI) removal capacity of the powdered alumina, batch equilibrium tests were conducted. The alumina was put in contact with the aqueous Cr(VI) solutions at room temperature. All solutions were prepared with analytical grade reagents, using potassium dichromate (Merck, 99.5%) and deionized water. The mixtures were stirred at 8 rpm, and then the phases were separated by filtration and the Cr(VI) in solution was evaluated.

### 2.5. Continuous flow column

The alumina disk was placed into a sealed cell with an inlet and an outlet. A 5 cm diameter funnel was connected to the inlet as the reservoir for the 20 mL samples. The outlet of the cell was connected to a filter flask, so that a vacuum of approx. 0.6 psi could be applied. The 20 mL fractions were collected and analyzed separately. Under these conditions, the contact time was about 3 s for each pass.

### 2.6. Scanning electronic microscopy (SEM)

Images were obtained in a JEOL JSM 6510LV at 15 kV and 10 mm WD, using both secondary and backscattered electron signals. Samples were sputtered with about 20 nm of gold using a Denton Vacuum DESK IV.

### 2.7. Energy dispersive X-ray spectroscopy (EDS)

EDS analysis was performed with an Oxford PentaFetx5 probe attached to the SEM detailed above, the probe was calibrated prior to the analysis with a copper standard.

### 2.8. X-ray diffraction (XRD)

XRD was done on the alumina disk materials before and after the Cr(VI) reduction using a SIEMENS D-5000 diffractometer.

### 2.9. X-ray photoelectron spectroscopy (XPS)

The XPS wide and narrow spectra were acquired using a JEOL JPS-9200, equipped with a Mg X-ray source (1253.6 eV) at 200 W, over an analysis area of 1 mm<sup>2</sup>, under vacuum on the order of 10<sup>-8</sup> Torr for all samples. The spectra were analyzed using the Specs surf<sup>TM</sup> software included with the instrument and all spectra were charge corrected by means of the advantageous carbon signal (C1s) at 284.5 eV. The Shirley method was used for the background subtraction, whereas the curve fitting was done with the Gauss–Lorentz method.

## 3. Results and discussion

### 3.1. Reduction of Cr(VI) by alumina disk: effect of initial concentration and number of passes and comparison with a batch system

To determine the effect of the initial concentration of Cr(VI) on the reduction of [Cr(VI)] for each pass through the alumina disk cell, four different concentrations were evaluated. The concentration of each solution after passing through the disk 1 through 5 times is shown in Table 1. After 5 passes, the [Cr(VI)] of the low concentration solutions (up to 130 mg/L) was reduced by about 80%, whereas the high concentration (700 mg/L) solution was only reduced by about 50%.

As the Cr(VI) interacts with the alumina and as the concentration and species of Cr(VI) change, there is an expected change in the solution pH, which can give insight into the mechanism of the process. The pH of the solutions were monitored as a function of number of filtrations as shown in Table 2. In all cases, the pH becomes less acidic. This reduction in the [H<sup>+</sup>] implies both a complexation between the chromates and the alumina and a shift in the chromate–dichromate equilibrium.

As a comparison to the continuous treatment Fig. 1 shows the Cr(VI) concentration as a function of contact time with powdered alumina. Note, that the Cr(VI) removal is ca 40% in 60 min of contact time.

### 3.2. UV–vis spectra

The UV–vis spectra (200–900 nm) of the original 130 mg/L Cr(VI) solution and each of the passes through the disk is shown in Fig. 2. The original Cr(VI) solution has two well defined peaks at 256 and 350 nm and a smaller one at 440 nm which indicate the presence of Cr(VI). As expected, the intensity of the absorbance decreases with each pass through the disk, indicating a decrease in the Cr(VI) in solution. There is also a small shift in the wavelength of each peak, likely due to the chromate interacting with the alumina and a change in the Cr(VI) species itself.

To determine if the alumina itself was contributing to the UV–vis absorbance, distilled water was run through the filter and analyzed. As shown in Fig. 3, the water does develop a pronounced absorbance at around 225 nm from passing through the alumina. A small component also develops around 273 nm.

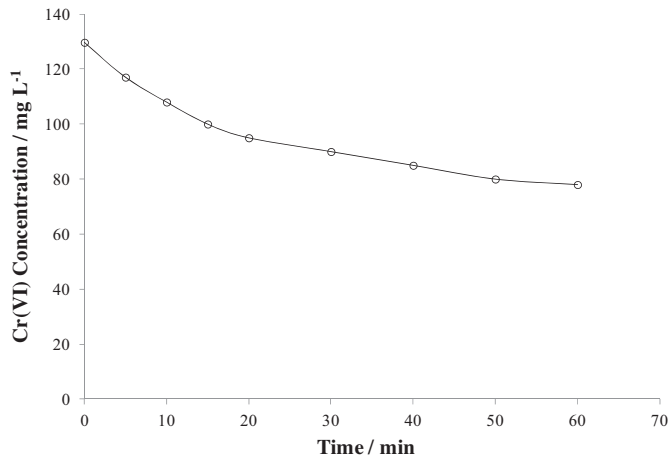
As shown in Fig. 4, dichromate ion has two distinctive peaks in the UV–vis range, but also reacts with diphenyl carbazide to

**Table 1**  
Cr(VI) concentration as a function of filtrations.

Initial[Cr] (mg/L)	Number of filtrations					% Reduction
	1	2	3	4	5	
700	690	630	520	486	370	47
130	115	93	87	69	25	80
30	27	25	20	11	7	76
10	7	5	4	3	2	80

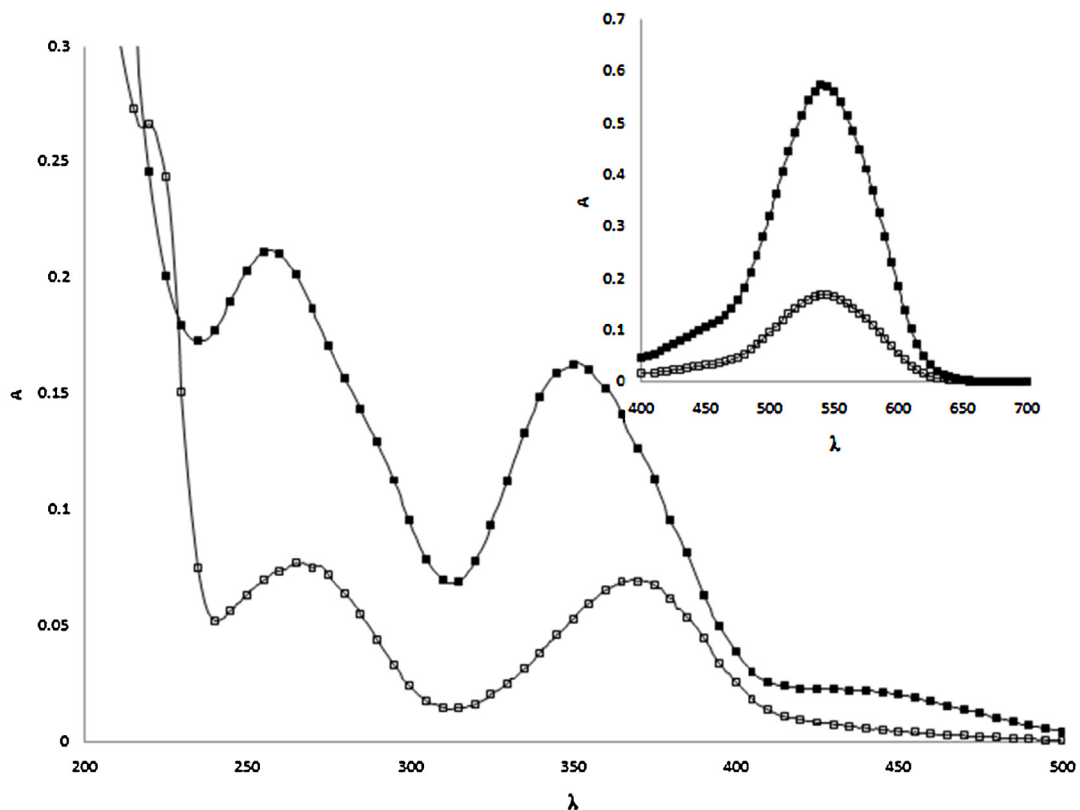
**Table 2**  
pH variations in solution as a function of filtrations.

Initial[Cr] (mg/L)	Number of filtrations					
	0	1	2	3	4	5
700	3.22	4.99	5.09	5.14	5.21	5.32
130	5.09	5.18	5.24	5.45	5.65	5.89
30	6.12	6.31	6.53	6.63	6.79	6.90
10	6.65	6.85	6.89	6.93	6.95	6.99

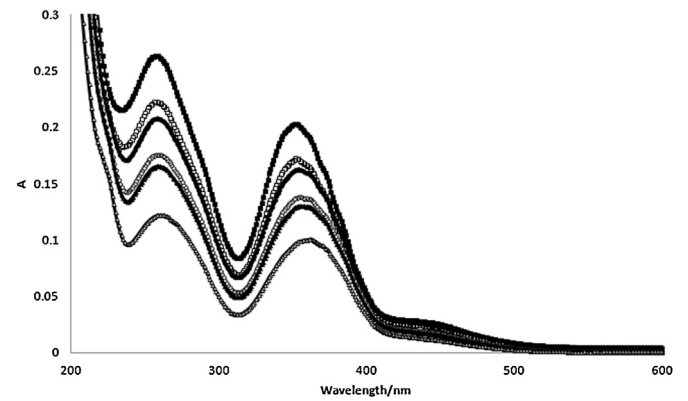


**Fig. 1.** Cr(VI) concentration as a function of contact time. Initial Cr(V) concentration of 130 mg L<sup>-1</sup>.

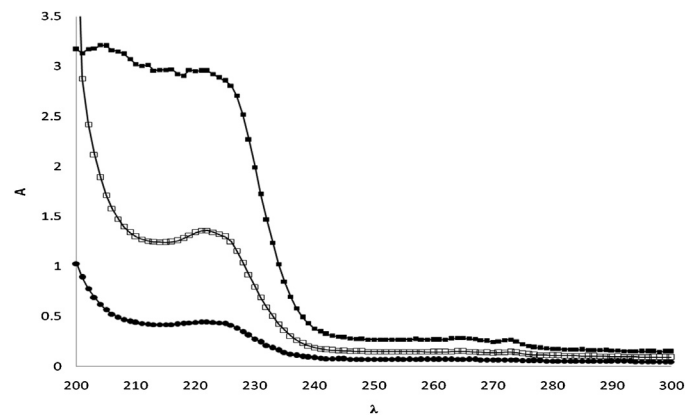
produce a distinctive peak. The original solution with 130 mg L<sup>-1</sup> of Cr(VI) exhibits two distinctive peaks at 256 and 350 nm. These peaks both decrease in absorbance and shift in wavelength after 15 passes through the alumina filter. This is an indication of the



**Fig. 4.** UV-vis spectra of the initial Cr(VI) solution with an initial concentration of 130 mg L<sup>-1</sup> (■) and the solution after 15 passes through the alumina filter (□). The DPC results at 540 nm for the initial 130 mg L<sup>-1</sup> Cr(VI) solution (■) and that after 15 passes through the filter (□).



**Fig. 2.** UV-vis spectra of a 130 mg/L Cr(VI) solution (■) and after one (□), two (●), three (○), four (▲), and five (△) passes through the alumina disk.



**Fig. 3.** UV-vis spectra after passing it through the alumina disk for one (●), five (□), and fifteen (■) times.

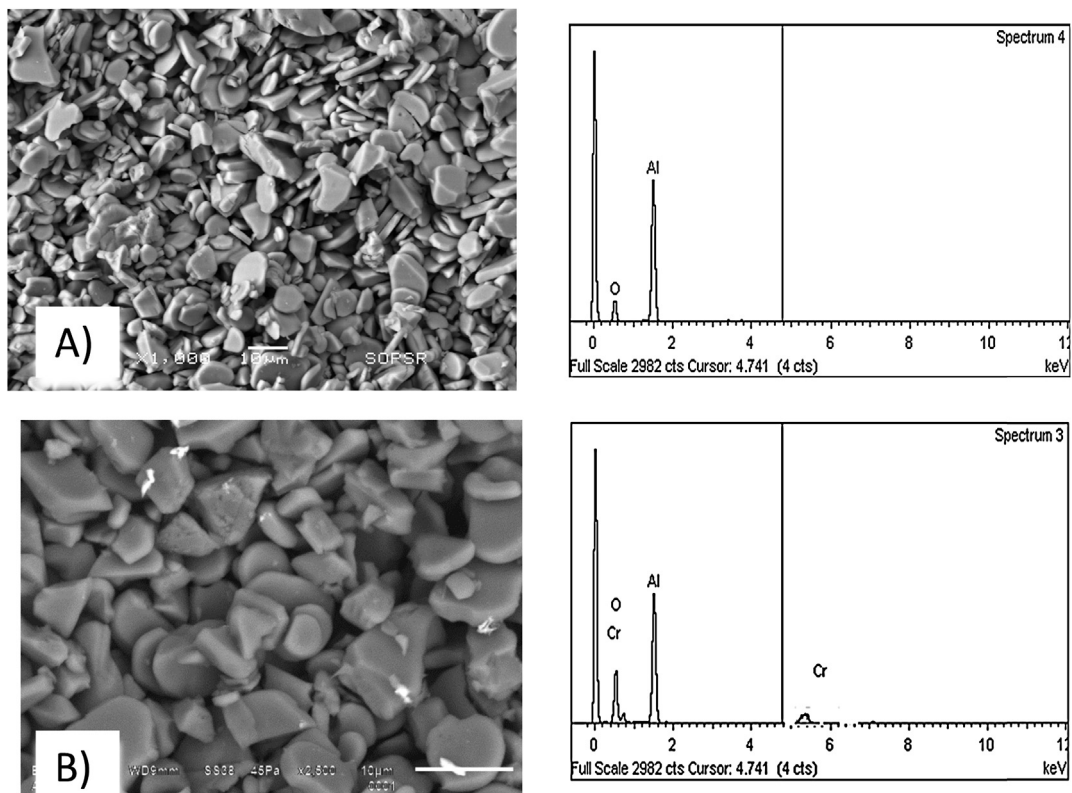


Fig. 5. SEM images and EDS spectra of alumina disk before (a) and after (b) contact with a solution of  $700 \text{ mg L}^{-1}$  of Cr(VI).

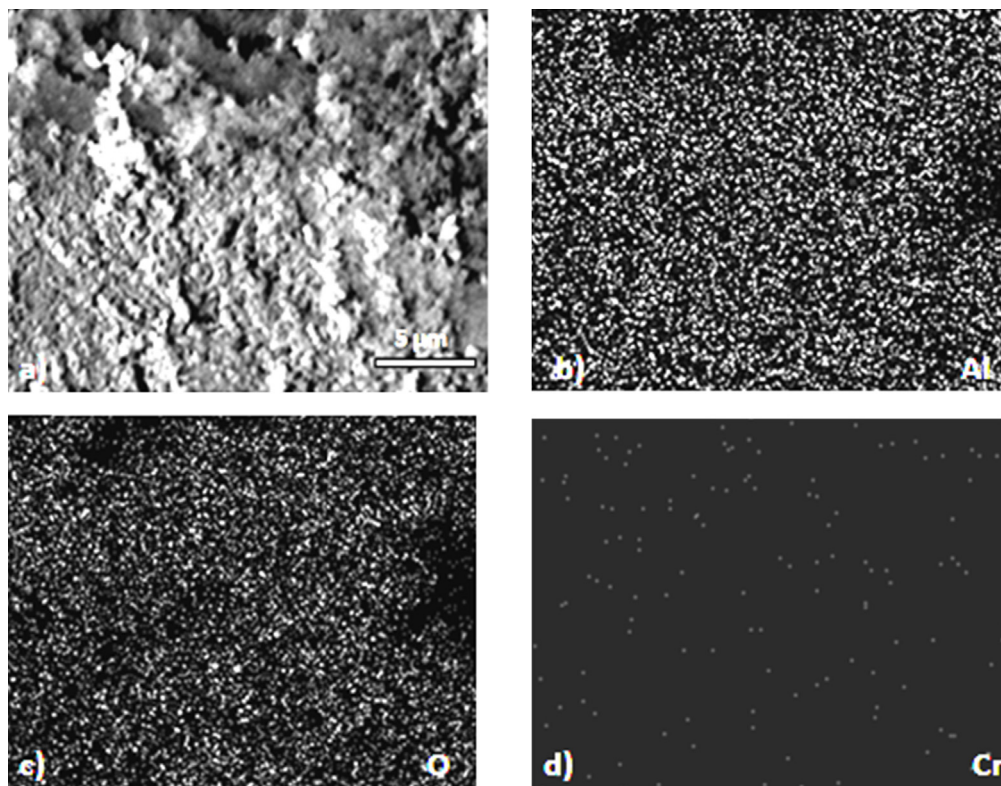
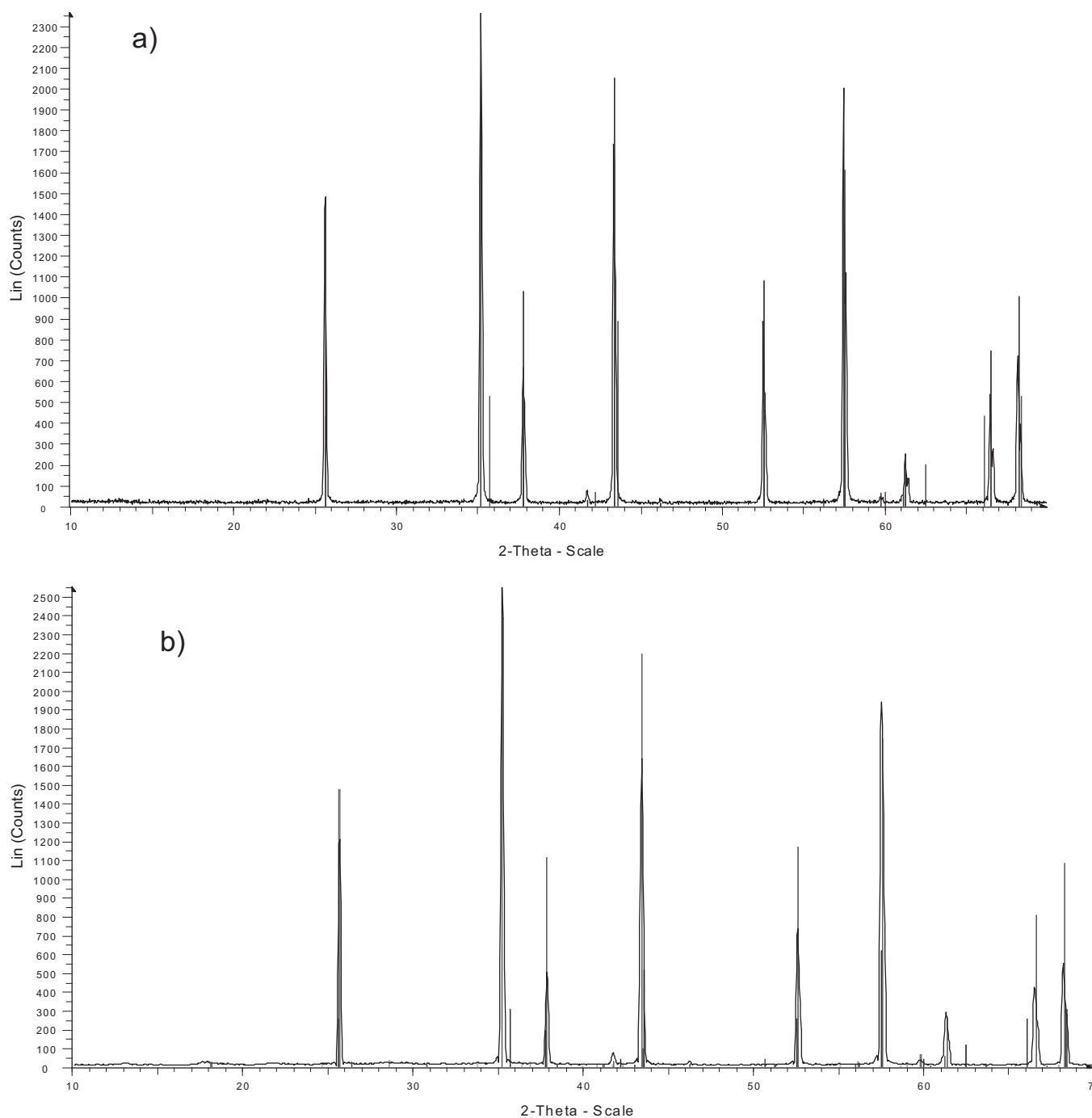


Fig. 6. The SEM image of the alumina surface after exposure to a  $700 \text{ mg L}^{-1}$  solution of Cr(VI) (a) and EDS element maps of the (a) aluminum (b), oxygen (c), and chromium (d) in the sample.



**Fig. 7.** XRD spectra of alumina before (a) and after (b) contact with a  $700 \text{ mg L}^{-1}$  solution of Cr(VI).

decrease in concentration and likely a change in Cr(VI) species (dichromate ion to chromate ion). The change in concentration is confirmed in the diphenyl carbazide results.

### 3.3. SEM/EDS

The surface morphology of the  $\alpha$ -alumina disk before and after contact with chromium was evaluated by SEM, while EDS was used to determine the elemental composition. The SEM image of the surface of the alumina disk is shown in Fig. 5a. The surface appears homogeneous with circular features of 5 to  $20 \mu\text{m}$ . As expected, EDS detect only aluminum and oxygen. The proportions of aluminum and oxygen correspond to a weight %

of 59.2 and 40.8 and an atomic % of 46.21 and 53.79, respectively (Fig. 5b).

As shown in Fig. 5b, the SEM image of the alumina disk after exposure to a  $700 \text{ mg L}^{-1}$  Cr(VI) solution does not change significantly, but there appear to be some bright areas on the surface that could be due to adsorbed Cr(VI). However, the EDS spectra clearly detects Cr(VI) on the surface. The EDS spectrum of the surface indicates the presence of aluminum (58.71 weight % or 45.74 atomic %), oxygen (39.9 weight % or 53.49 atomic %), and chromium (1.36 weight % or 0.57 atomic %). The presence of chromium on the surface is small compared with the concentration of Cr(VI) in solution, but the distribution of chromium across the surface is uniform, as shown in the elemental map in Fig. 6.



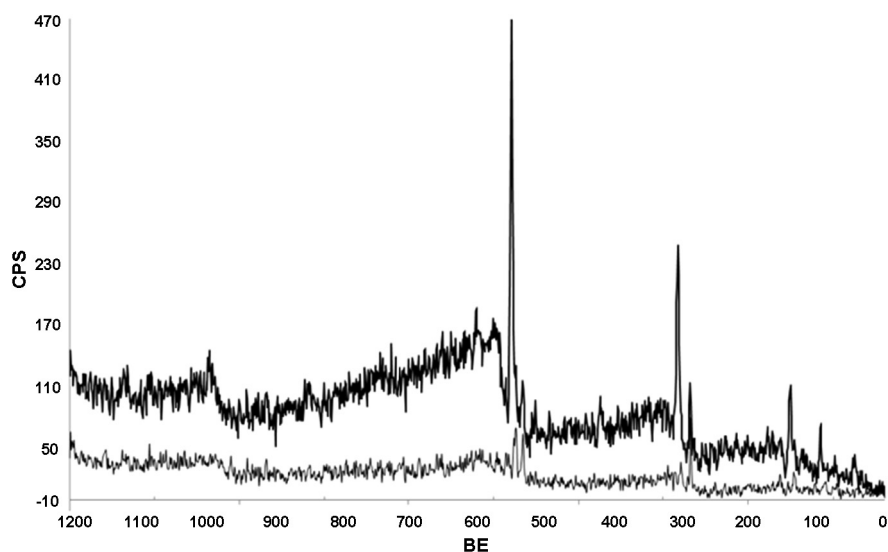


Fig. 8. XPS of alumina before (top) and after (bottom) exposure to a Cr(VI) solution.

**Table 3**  
Comparative study of Cr(VI) sorption among different alumina presentations.

Sorbent	[Cr(VI)] (mg L <sup>-1</sup> )	Experiment conditions	Cr(VI) removal (%)	References
Granular activated alumina particle size spherical 150 mesh	100	2 g of activated alumina mechanically agitated for 90 min	50	[18]
γ-Alumina (20–50 nm)	.01 M	2 g of alumina in a slurry reactor initial pH 3.0	50	[19]
α-Alumina powder	130	1.72 g	40	Present study
α-Alumina disk	130	1.75 g compacted in a disk and the treatment time is less than 1 min	80	Present study

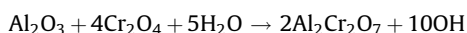
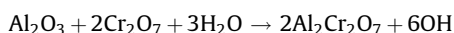
### 3.4. XRD

The X-ray diffraction (XRD) spectra of the alumina before and after exposure to the Cr(VI) solution are shown in Fig. 7. The diffraction peaks are the same before and after the exposure, so the chromium binding does not change the crystal structure of the alumina.

### 3.5. XPS

The XPS spectrum of the alumina disk before and after the filtration is shown in Fig. 8. Although peaks due to the chromium are apparent, an important peak is due to aluminum at around 80 eV. The change in this aluminum peak indicates a change in binding energy, which implies the formation of a complex with the chromium [17].

Together, the XPS, EDS and DRX results indicate that the chromium is forming a complex with the aluminum in the alumina rather than being adsorbed onto the surface or trapped in the pores. A very recent report indicates that Cr(VI) sorption on γ-alumina is significant, with >50% of 10<sup>-5</sup> or 10<sup>-4</sup> M Cr(VI) adsorbed on 5 g/L γ-alumina at pH < 7–8. Sorption decreases significantly with increasing pH and increasing Cr(VI)/solid ratios. In this study the suggested mechanism for the Cr(VI) is the formation of surface and solution complexes such as:



### 3.6. Comparison of the result within previous works

Table 3 indicate Cr(VI) removal obtained by different alumina presentation.

## 4. Conclusions

Passing the solution through a sintered alumina disk can be quickly reduced the concentration of hexavalent chromium. Each pass through the filter reduces the concentration further, so using a series of filtration disks could achieve any desired concentration. The mechanism of the adsorption appears to be the formation of a complex between the alumina substrate and the aqueous chromates. Due to its speed and ease of use, this process has potential applications in industrial wastewater remediation.

## Acknowledgements

We thank Universidad Autonoma del Estado de Mexico for support in the realization of this research. Thanks to CONACYT (Project 153828) and for the financial support to Fabiola Glorias Garcia and Jose Miguel Arriaga Merced. Thanks to Dr. Fenando Urena for the XRD and SEM analysis presented in this paper. Thanks to M. C. Gustavo Lopez Tellez for the XPS analysis.

## References

- [1] M. Stoepler, *Hazardous Metals in the Environment Techniques and Instrumentation in Analytical Chemistry*, Elsevier, New York, 1992p. 373.
- [2] J. Gaulhofer, V. Biabchi, *Chromium Metals and their Compounds in the Environment*, VCH, Weinheim, 1991p. 30.
- [3] C. Barrera-Díaz, M. Palomar-Pardavé, M. Romero-Romo, S. Martínez, *J. Appl. Electrochem.* 33 (2003) 61.
- [4] C.E. Barrera-Díaz, V. Lugo-Lugo, B. Bilyeu, *J. Hazard. Mater.* 223–224 (2012) 1–12.
- [5] K. Wagner, S. Schulz, *J. Chem. Eng. Data* 46 (2001) 322.
- [6] A.K. Jain, V.K. Gupta, S. Jain, Suhas, *Environ. Sci. Technol.* 38 (2004) 1195.
- [7] A.K. Sengupta, D. Clifford, *Ind. Eng. Chem. Fundam.* 25 (2) (1986) 249.
- [8] F. Ureña-Núñez, P. Díaz-Jimenez, C. Barrera-Díaz, M. Romero-Romo, M. Palomar-Pardave, *Radiat. Phys. Chem.* 68 (2003) 819.
- [9] M. Lehmann, A.I. Zouboulis, K.A. Matis, *Chemosphere* 39 (1999) 881–892.

- [10] M. Pérez-Candela, J.M. Martínez, R. Torregrosa-Macia, *Water Res.* 29 (1995) 2174.
- [11] S. Mor, K. Ravindra, N.R. Bishnoi, *Bioresour. Technol.* 98 (2007) 954.
- [12] G. López-Téllez, C.E. Barrera-Díaz, P. Balderas-Hernández, G. Roa-Morales, B. Bilyeu, *Chem. Eng. J.* 173 (2011) 480.
- [13] M.N. Kathiravan, R.K. Rani, R. Karthick, K. Muthukumar, *Bioresour. Technol.* 101 (2010) 853.
- [14] N. Fiol, C. Escudero, J. Poch, *React. Funct. Polym.* (2006) 795.
- [15] V. Varela-Guerrero, Y. Yoo, M.C. McCarthy, H.K. Jeong, *J. Mater. Chem.* 20 (2010) 3938.
- [16] Z.P. Lai, M. Tsapatsis, J.R. Nicolich, *Adv. Funct. Mater.* 14 (2004) 716.
- [17] *Handbook of X-ray Photoelectron Spectroscopy*, JEOL, 1991, pp. 40–41.
- [18] I. Marzouk, L. Chaabane, L. Dammak, B. Hamrouni, *Am. J. Anal. Chem.* 4 (2013) 420.
- [19] T.J. Reich, C.M. Koretsky, *Geochim. Cosmochim. Acta* 75 (2011) 7006.