



Zinc and Chromium elimination from complex aqueous matrices using a unique aminopropyl-modified MCM-41 sorbent: Temperature, kinetics and selectivity studies



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ARTICLE INFO

Article history:

Received 6 November 2016
Received in revised form 31 December 2016
Accepted 2 February 2017
Available online 3 February 2017

Keywords:

Water treatment
MCM-41 sorbents
Chromium
Zinc
River waters
Selectivity

ABSTRACT

An aminopropyl-modified MCM-41 sorbent obtained by grafting amino groups on the surface of a previously synthesized MCM-41, was used for the removal of Cr(VI) and Zn(II) from different aqueous matrices: solutions of Zn(II) and Cr(VI) in distilled water, in distilled water with high-salt content, and in a natural river water sample. The sorbent particles are spherical with a mean diameter of ≈ 500 nm, surface area >600 m² g⁻¹ and uniform aminopropyl function distribution. Single component adsorption batch experiments, fitted with the Langmuir model, show that MCM-41-NH₂ has high removal capacity for Cr(VI) and for Zn(II), 87.5 and 58.9 mg g⁻¹, respectively. Binary component adsorption experiments show that the selectivity toward chromium oxyanions or zinc cations could be adjusted by changing the pH of the solution to be treated. When pH was fixed at acidic conditions chromium was preferentially removed, while the MCM-41-NH₂ sorbent retained selectively zinc species when pH was increased up to 7. The presence of salts, either added (i.e. KCl) or natural as those present in river water, resulted in an improvement in the selectivity for both metals removal reaching values of up to 97%. The obtained results indicate that MCM-41-NH₂ is an efficient and selective sorbent capable of removing Cr(VI) oxyanions and/or Zn(II) cations from complex polluted water matrices.

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1. Introduction

The pollution of water supplies due to heavy metals is one of the main environmental concerns, because it represents a potential health risk to humankind. Cadmium, copper, chromium, lead and zinc are listed as priority pollutants in the U.S. Environmental Protection Agency (USEPA) [1], because they are considered the most hazardous and harmful ones to biological species. Amongst them, hexavalent chromium (Cr(VI)) presents high carcinogenic and mutagenic activity to living organisms even at very low concentrations [2]. Despite its high toxicity, Cr(VI) is widely employed in different industrial processes such as metal finishing, electroplating, leather tanning, textiles, fungicide production and pigments synthesis and dyeing [3,4]. On the other hand, zinc cations are commonly found in waste effluents from steel manufacturing, metallurgy industries and several mining

activities. Its presence in aqueous environments promotes the generation of reactive oxygen species (ROS), which causes cellular damages due to oxidation of several biological molecules [5].

Anticipating an increase in the anthropogenic activities associated with the generation of wastewaters containing these metals, several techniques such as ion-exchange, chemical precipitation, reverse osmosis, membrane separation and adsorption have been applied to remove and recover these metals, thus minimizing the negative impact on natural environments [6,7]. Most of these processes require either high energy or large quantities of chemicals and the subsequent disposal of the residual metal sludge. In contrast, adsorption-based technologies seem to be a more appropriate and environmentally friendly method because of their easy scaling and low cost of operation. Due to the fact that the sorbent material is key of the process, several efforts have been dedicated to develop new sorbents materials having

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high durability, selectivity and versatility to remove a wide variety of pollutants. Thus, the same sorbent could be applied several times. It could adsorb specifically a desired target, and, at the same time be used to remove species with different chemical properties.

The mesoporous ordered silicas of the M41S family are currently being applied for the separation/elimination of biological substances, organic and inorganic compounds from aqueous matrices, with promising results [8–11]. These materials are silica-based networks with large-size and well organized monodisperse mesopores structures, high specific surface areas and the capability to be chemically functionalized with a variety of organic groups [12]. One of the most studied M41S family members is the MCM-41, which, after a modification of the pore walls with organic functionalities, presents high stability and regeneration capacity for its use in the removal of heavy metals from water [12,13]. When amino functions are incorporated into the 2D structure of the MCM-41, a hybrid organic-inorganic material with a modulable surface and pH environment-responsive behavior is obtained [14]. Besides, the pK_a value of the MCM-41-NH₂ hybrid material is in the range of 9–10 [15]. Thus, the quantities of NH₃⁺ species at the surface increase when pH decreases, reaching 100% at pH values below 3. Moreover, the non-reacted superficial Si-OH are transformed into silanolates (Si-O⁻) when pH increases, which together with the free electrons of NH₂ generate negatives surface sites [16,17]. Thus, depending on the pH of the water solution to be treated, the amino-modified MCM-41-based sorbents are able to interact via electrostatic forces to remove both, cations and anions. However, most of the hitherto reported work deals with adsorption experiments of aqueous solutions toward the elimination of only one of these species: anions or cations [18–21]. Fewer efforts have been devoted to employing these hybrid materials to the treatment of complex and more realistic aqueous matrices that contain anion and cations species as pollutants to be removed at the same time, and with the same sorbent. Lam and coworkers [22] have performed batch experiments with a MCM-41-NH₂ as sorbent in order to remove Cr(VI) at pH 2 from an aqueous solution containing not only chromium anions but also Cu(II) cations; the authors reported high selectivity for Cr(VI) adsorption but no significant removal for Cu(II) cations.

Taking into account these considerations, the aim of this work is to demonstrate that a unique silica-based sorbent (MCM-41-NH₂) could eliminate selectively Zn(II) cations or Cr(VI) anions present in the same aqueous solution. The selectivity towards one or the other species could be regulated by only varying the pH of the solution to be treated. Besides, the influence of temperature and ionic strength in the adsorption performance of an aminopropyl-modified MCM-41 toward zinc and chromium were evaluated. The maximum adsorption capacity at 25, 35 and 45 °C at pH 2 for Cr(VI) and pH 7 for Zn(II) were evaluated using the Langmuir model. Finally, the sorbent performance of the sample MCM-41-NH₂ was tested at room temperature for the decontamination of a real river water sample containing high levels of Cr(VI) and Zn(II).

2. Materials and methods

2.1. Reactants

All the reactants were used as received without any further purification step. The synthesis of the hybrid sorbent was carried out using Tetraethyl orthosilicate (TEOS, 99%, Aldrich) as silica source, *n*-hexadecyltrimethylammonium bromide (CTMABr, 98%, Sigma) as structural directing agent, distilled water, absolute ethanol (Cicarelli, 99.5%), NH₄OH (Cicarelli, 28% p/p), toluene (Biopack) and 3-aminopropyltriethoxysilane (APTES, 98%, Sigma). The water samples to be treated used for the adsorption

experiments were prepared using K₂Cr₂O₇ (Merk) and ZnSO₄·7H₂O (Merk) as chromium and zinc sources, respectively.

2.2. Synthesis of MCM-41 and MCM-41-NH₂

The parent MCM-41 sample with spherical morphology was synthesized according to the recipe described by Grün et al. [23]. Briefly, 50 mL of distilled water, 30 mL of NH₄OH, 2.5 g of CTMABr, 75 mL of absolute ethanol and 5 mL of TEOS were mixed under vigorous magnetic stirring at room temperature (RT). The synthesis gel had the following molar composition: 1 TEOS: 0.3 CTMABr: 11 NH₄OH: 58 ethanol: 144H₂O, and was kept under stirring at 30 °C for 2 h. The final white powder product was separated by filtration, washed with water and ethanol several times and dried at RT. Finally, the sample was calcined up to 550 °C in air atmosphere for 3 h, with a heating rate of 5 °C min⁻¹. The aminopropyl functions were grafted onto the pores of the parent MCM-41 by utilizing a toluene-APTES solution as grafting agent. This post-synthetic surface modification procedure was carried out at 80 °C under magnetic stirring for 6 h. Details can be found in a previous work [13]. The final aminopropyl-modified product was named MCM-41-NH₂.

2.3. Samples characterization

The samples were characterized by nitrogen adsorption-desorption at -196 °C (BET), infrared spectroscopy (FT-IR), X-ray diffraction (XRD) at low angles, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

The morphology and the particle sizes distribution were obtained using SEM micrograph considering 150 particles for each sample; the obtained data were fitted using Gauss functions. The textural properties, specific surface area (S_g), specific pore volume (V_p) and average pore diameter (D_p) were measured in a Micromeritics equipment ASAP 2020 V1.02 E. Pore diameter distributions were determined using the Barret-Joyner-Halenda/Kruk-Jaroniec-Sayari (BJH-KJS) method. Infrared spectra of dried samples, before and after APTES treatment, were acquired with a Bruker IFS66 spectrometer with 1 cm⁻¹ resolution by co-addition of 32 scans. The samples were prepared by mixing with potassium bromide, in a 1:100 proportion, to obtain the corresponding pellets. The ordered mesoporous structure was evaluated by X-ray diffraction at low angles using a Philips PW 1710 with graphite monochromator, Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation in the range $2\theta = 1.5\text{--}8^\circ$ with steps of 0.02° and counting time of 2 s/step. A Philips 505 microscope was used for SEM analysis. TGA analysis was performed on a ShimadzuTGA-50 apparatus, heating the samples from room temperature to 750 °C at a heating rate of 5 °C min⁻¹ under air flow (20 mL min⁻¹).

2.4. Adsorption experiments

All the adsorption tests described in this work were carried out using 25 mL of aqueous solution of the desired composition and 25 mg of fresh sorbent with mechanical stirring at 450 rpm. In all experiments, after the desired time, the sorbent was separated by centrifugation (5 min, 9000 rpm). The initial and final metal concentrations in the supernatant were determined by UV-vis spectroscopy using the method of 1,5 diphenylcarbazide for Cr(VI) [24] and the dithizone method for Zn(II) [25]. All experiments were performed twice and the reported data are the average value.

2.4.1. Single metal adsorption tests

The single component adsorption isotherms for Zn(II) and Cr(VI) were performed in order to obtain the maximum elimination capacity (q_m) of MCM-41 and MCM-41-NH₂ toward each metal. In

the case of Zn(II) the pH was fixed at 7 using tris/HCl buffer; for chromium the pH was adjusted to 2 using HCl (8M). Batch experiments at $25 \pm 2^\circ\text{C}$ with metal concentration values of 10, 20, 40, 70, 100 and 130 ppm were carried out for 24 h. The Langmuir monolayer model was used to fit the experimental data of the isotherms. The Langmuir isotherm can be linearized as shown in Eq. (1):

$$C_e/q_e = 1/K_L q_m + C_e/q_m \quad (1)$$

where q_m is the maximum adsorption capacity of the adsorbent in mg of adsorbate per g of adsorbent, $K_L(\text{L mg}^{-1})$ is the Langmuir constant which is related to the intensity of adsorbent/adsorbate interaction, q_e is the adsorbed amount in mg g^{-1} and C_e is the concentration of adsorbate in equilibrium in the solution expressed in mg L^{-1} .

The batch experimental conditions, pH and time were selected in order to obtain the maximum performance of the sorbent according to previous bibliographic reports [16,26,27]. Several authors have reported a pH dependent performance when organically modified silicas are used as sorbents to remove heavy metals. Han et al. [16] determined that the optimal pH to get the higher Zn adsorption capacity for an amino-functionalized MCM-48 sorbent was 7, an experimental condition that also avoids the precipitation of zinc hydroxides. In the case of Cr(VI), the higher adsorption capacity for amino-modified sorbents is achieved at

low pH values since under this condition the surface amino groups are protonated, and the electrostatic interactions with chromium anions is favored [13,15,26]. To evaluate the effect of temperature, single metal adsorption isotherms at 35 ± 2 and $45 \pm 2^\circ\text{C}$ were obtained under the same experimental conditions described previously. In order to study the effect of the ionic strength of the water solution in the adsorption efficiency parameters, fully single metal isotherms at $25 \pm 2^\circ\text{C}$ were determined on aqueous solutions containing 0.01 and 0.1 M KCl.

2.4.2. Binary metal adsorption tests

Water solutions containing 40 and 130 ppm of Cr(VI) and Zn(II) were prepared and batch adsorption experiments were conducted for 24 hs at $25 \pm 2^\circ\text{C}$, at pH values equal to 2 and 7. In the case of 130 ppm the adsorption experiments were repeated with the addition of KCl (0.01 M). The concentration of 130 ppm was selected because in the single metal adsorption tests it was determined that this is the optimal experimental value to evaluate the maximum adsorption capacity of the sorbent.

2.4.3. River water sample adsorption tests

The simulated contaminated natural river water was prepared by adding chromium and/or zinc, to water samples from the Black river (*río Negro, Patagonia, Argentina*). Three river water samples were prepared: one of them with 130 ppm of Cr(VI), another one

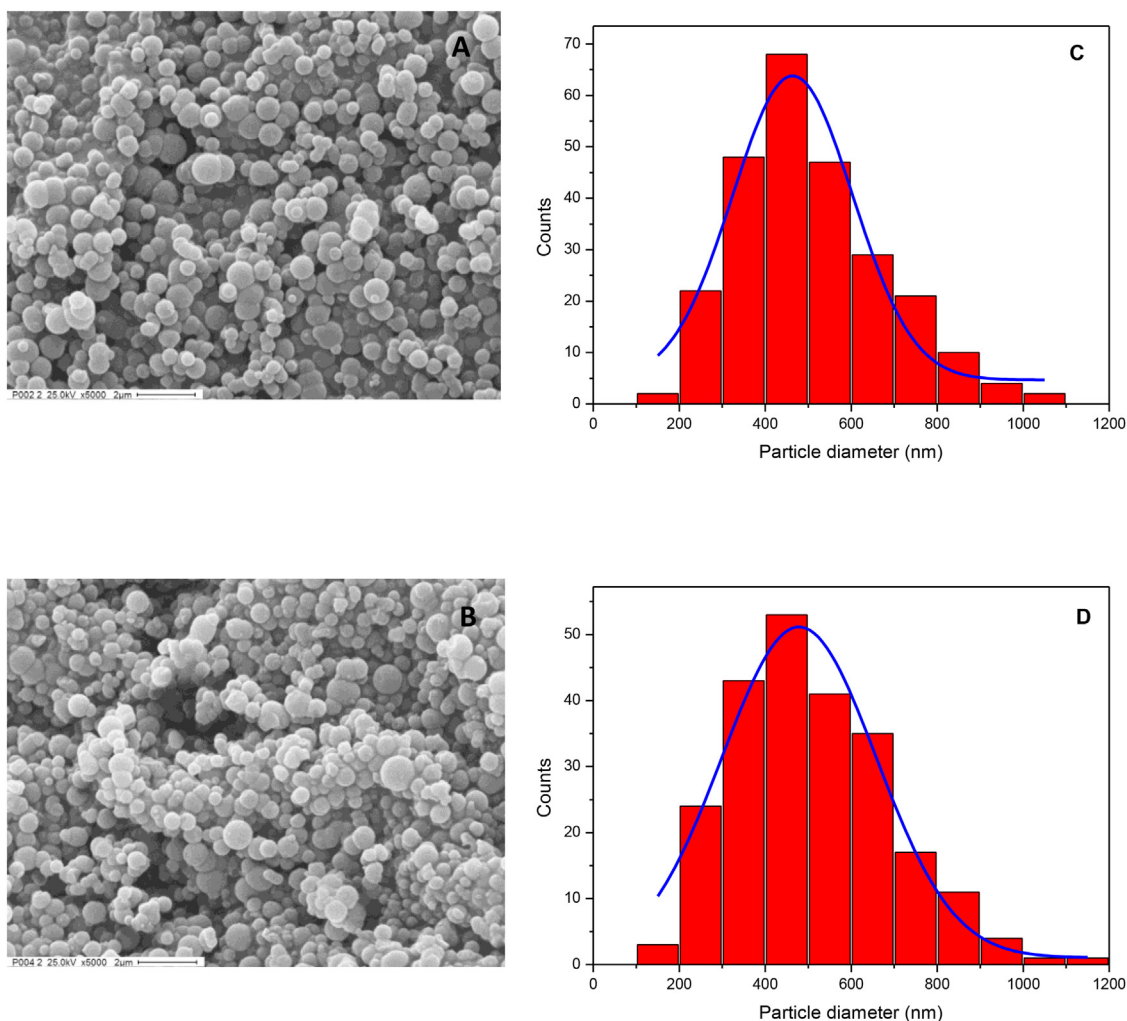


Fig. 1. SEM images and particle sizes distribution of MCM-41 (A and C) and MCM-41-NH₂ (B and D) obtained from SEM measurements (blue lines: fitting by assuming Gaussian distribution). The bar scale corresponds to 2 μm .

with 130 ppm of Zn(II), and the last one containing 130 ppm of both metals. The batch-like adsorption experiments with these real water matrices were realized at 25 ± 2 °C at constant pH values of 2 and 7.

3. Results and discussion

3.1. Sample characterization

The external morphology and the particle size distribution of the samples were evaluated by SEM (Fig. 1). It can be seen that both, the pristine and MCM-41-NH₂ samples, present spherical shape and very similar average particle diameters (Table 1). Therefore, the post-synthesis method employed for the surface modification with APTES did not induce morphological changes in the original sample.

The pore structure was evaluated through low angle X-ray diffraction patterns, in the 2θ range of 1.5 – 8° (Fig. 2). Both samples display an intense main peak at 2.1° . In the case of pristine MCM-41 two broad peaks are displayed in the 2θ region of 4 – 6° . The peaks are associated with the highly 2D hexagonal $p6m$ mesopores arrangement typical of MCM-41 mesophase [28]. A decrease in the intensity of the entire diffractogram of MCM-41-NH₂ sample is observed and the widest peaks in the 4 – 6° region are almost undetectable. This phenomenon can be attributed to the presence of the aminopropyl functions inside the mesopores, which produces a decrease in electron density difference between pores and walls, and thus a decrease in the XRD signal [13]. Therefore the diffraction patterns similitude allows concluding that the post-grafting treatment with APTES does not change the internal pores structure of the parent sample.

Fig. 3A shows the FTIR spectra of MCM-41 and MCM-41-NH₂ samples. The Si—O—Si vibrational modes can be observed for both in the 1000 – 1300 region, this band is associated to the inorganic SiO₂ framework of the MCM-41 structure [29]. A widening in the 3000 – 3500 cm⁻¹ region is observed for MCM-41-NH₂ in comparison with the parent material. This observation indicates an overlaying of the bands of superficial adsorbed water (O—H stretching band) and amino/ammonium functionalities [29]. Additional bands are observed in the hybrid sample at the 2800 – 3000 cm⁻¹ region and 1560 cm⁻¹ assigned to C—H and N—H vibrations modes, respectively [30,31]. An important change in the band at 960 cm⁻¹ is observed after APTES treatment, this band is assigned to the surface Si-OH vibrations and which clearly became into a shoulder as a consequence of amino-groups attachment to the SiO₂ network. This fact indicates that the organic functions are covalently attached to the surface by replacing silanols of the MCM-41 network [32].

The nitrogen adsorption-desorption isotherms at -196 °C of both samples show the characteristic type IV curves, according to the IUPAC classification, associated with mesoporous materials, besides, no hysteresis loops were observed (Fig. 4a). The latter is

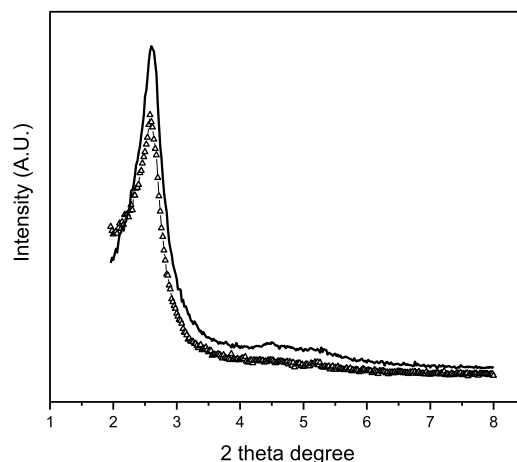


Fig. 2. X-ray diffraction profiles at low angles of MCM-41 (line) and MCM-41-NH₂ (triangles) samples.

associated with a reversible adsorption–desorption process suggesting the presence of pores with diameters smaller than 4 nm [33]. These results are in agreement with data reported for MCM-41 based samples with pore diameters smaller than 4 nm [33]. The pore size distributions obtained by applying the BJH-KJS method are presented in Fig. 4B showing average pore diameters values of 3.3 nm for MCM-41 and 2.8 nm for MCM-41-NH₂ samples. It can be observed that upon addition of amino function, both the BET surface area and the total pore volume decrease (Table 1). The reported variations in the textural properties jointly with the aminopropyl group loading determined by TGA (Table 1), the FTIR results and decrease in the XRD signal, allow concluding that the amino functions were incorporated within the pores of the MCM-41 structure. According to previous reported data [17,34], all these changes indicate a good aminopropyl distribution over the entire pore network. The density of surface functional groups (d) calculated by applying Eq. (2) (Table 1) indicates a high functionalization degree and reinforces the idea that aminopropyl functions on MCM-41-NH₂ are well dispersed in the mesoporous structure [38].

$$d = N_A L_0 / S_{\text{BET}} \quad (2)$$

where L_0 represents the quantity of molecules attached to the mesoporous silica surface measured by TGA, and S_{BET} is the specific surface area obtained from the nitrogen sorption experiments.

In a previous work, we demonstrated that the organic function distribution is a very important issue that must be addressed in the field of sorbents design. A poor distribution of the active sites results in low capacity for the removal of the selected target, while a uniform distribution of functional groups over the entire particle ensures high efficiency sorption behavior [34].

Table 1

Textural and surface properties of MCM-41 and MCM-41-NH₂.

Sample/Parameter	Particles Diameter (nm) ^a	Surface area (m ² g ⁻¹) ^b	Pore volume (cm ³ g ⁻¹) ^b	Pore diameter (nm) ^c	Functional group loading (mmol g ⁻¹) ^d	d (molecules nm ⁻²)
MCM 41	463 ± 13	1002	0.7	3.3	–	–
MCM 41-NH ₂	478 ± 15	605	0.4	2.8	1.8	1.1

^a By SEM.

^b By nitrogen sorption (BET).

^c BJH-KJS method.

^d By TGA analysis.

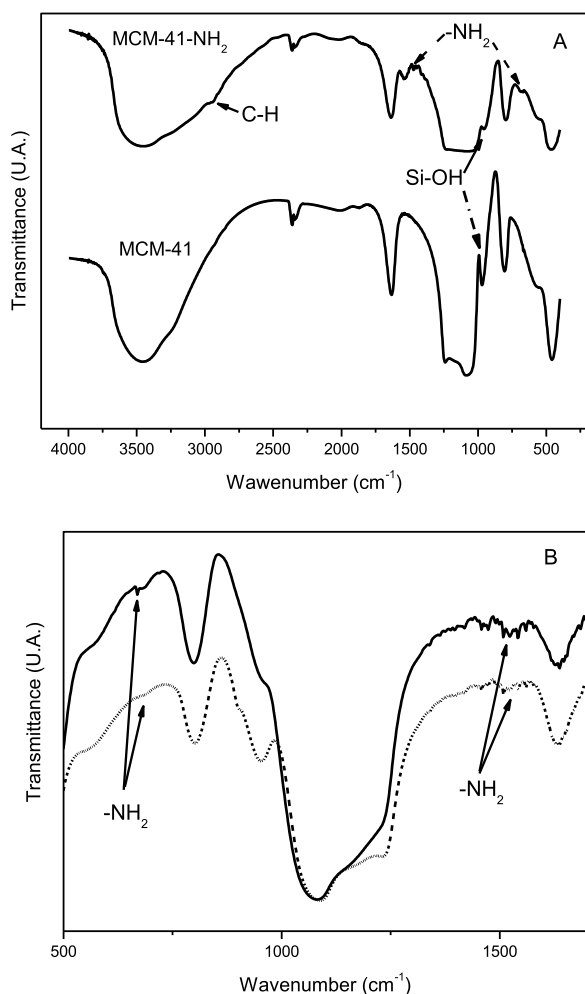


Fig. 3. FT-IR spectra of (A): pristine MCM-41 and fresh MCM-41-NH₂, (B): MCM-41-NH₂ after chromium adsorption at pH 2 (dash line) and zinc adsorption at pH 7 (solid line). Relevant frequency bands are indicated with narrows.

3.2. Single metal adsorption tests

Fig. 5 shows the results of the kinetic experiments performed on single metal aqueous solution containing Cr(VI) or Zn(II) at 10 and 100 ppm. For both metals, at low metal concentration (10 ppm), the adsorption kinetics is very fast, reaching more than 90% of metal elimination from water within the first 30 min. When the initial concentration was increased up to 100 ppm, more time (≈ 120 min) was needed to get a steady state in both cases. However, for Zn(II) lower values of metal elimination were reached, 40% versus 66% for Cr(VI). The obtained data were fitted using the pseudo-first and pseudo-second order kinetic models (Figs. S1, S2 and Table S1). The pseudo-second order model fit the experimental kinetic data the best, with correlation coefficient (r^2) for both metals at both initial concentrations very close to 1, in accordance with the vast existing literature on this topic [7,35]. Thus, the global adsorption process would be a contribution of different adsorption paths, i.e. a first and quick step that involves the interaction between ions and the external surface of the sorbent particles, followed by ion diffusion inside the pores. As expected, the intraparticle diffusion step becomes important when ion concentration increases, as revealed by the different times needed to reach steady state.

Fig. 6 presents the fully adsorption isotherms at 25, 35 and 45 °C for single metal aqueous solution of Cr(VI) at pH 2 and for Zn(II) at pH 7 for MCM-41-NH₂. The resulting parameters obtained applying the Langmuir isotherm model are listed in Table 2. The

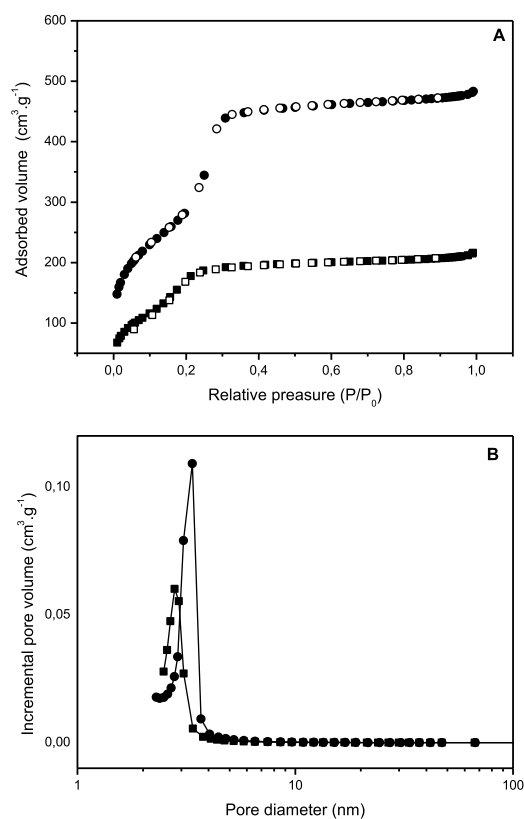


Fig. 4. (A) Nitrogen adsorption (full symbols)-desorption (empty symbols) isotherms for pristine MCM-41 (circles) and MCM-41-NH₂ (squares) samples. (B) BJH-KJS pore sizes distribution: pristine MCM-41 (circles) and MCM-41-NH₂ (squares).

estimated maximum elimination capacities (q_m) toward Cr(VI) from an aqueous single metal solution at pH 2 reported in Table 2, are significantly higher than those previously reported for traditional adsorbents. Typical values reported for modified carbon sorbents [26] and N-incorporated MCM-41 [36] samples are in the range of 20–60 mg g⁻¹. Other sorbents such as coconut shell charcoal and commercial activated carbon modified with nitric acid showed quite lower Cr(VI) removal capabilities (average values of 15 mg g⁻¹) [37] in comparison with the MCM-41-NH₂ system studied in this work. In the case of Zn(II), the q_m values

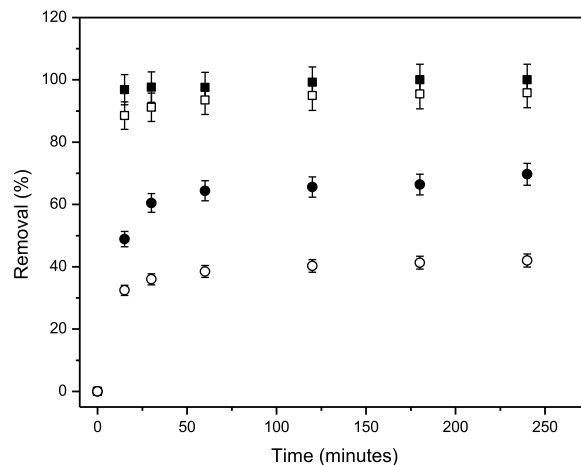


Fig. 5. Kinetic experimental curves for batch adsorption experiments for chromium (full symbols) and zinc (empty symbols). Initial concentration: squares (10 ppm), circles (100 ppm).

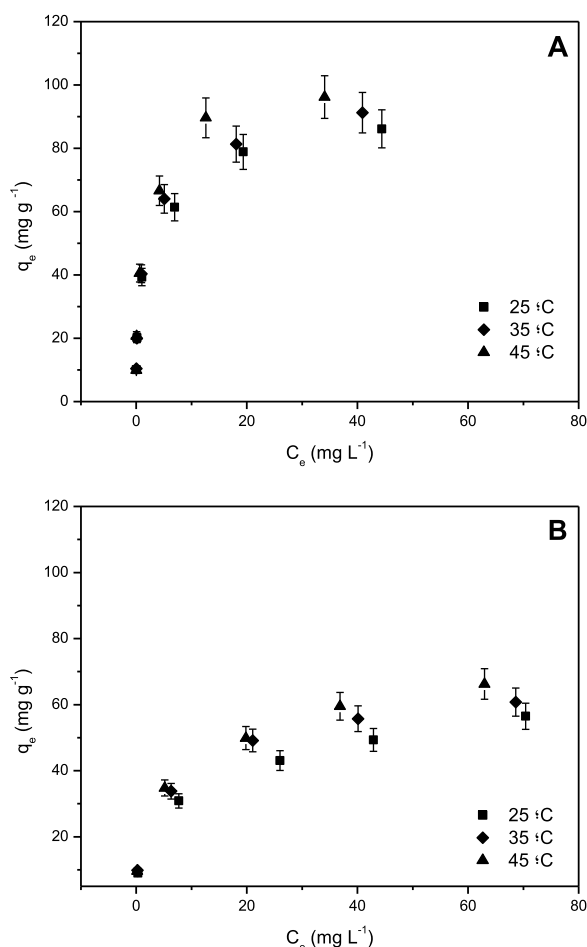


Fig. 6. Single component adsorption isotherms at different temperatures obtained from 24 h batch experiments with MCM-41-NH₂ (A) for Cr(VI) at pH=2 and (B) for Zn(II) at pH=7.

Table 2

Adsorption parameters of the Langmuir isotherms model at 25, 35 and 45 °C for the adsorption of Cr(VI) and Zn(II) on MCM-41-NH₂ at different ionic strength.

		Without KCl			0.01 M KCl	0.1 M KCl
		25 °C	35 °C	45 °C	25 °C	25 °C
Cr(VI)	q _m	87.5 ± 6	92.3 ± 6	97.8 ± 7	80.6 ± 6	72.1 ± 5
	K _L	0.765	0.857	1.200	0.359	0.193
	r ²	0.9965	0.9955	0.9976	0.9967	0.9896
Zn(II)	q _m	58.9 ± 4	68.4 ± 5	73.8 ± 5	51.4 ± 4	47.2 ± 3
	K _L	0.158	0.163	0.170	0.152	0.145
	r ²	0.9937	0.9926	0.9924	0.9952	0.9923

obtained for MCM-41-NH₂ are slightly lower or similar to the reported values by other authors for another silica based sorbents systems [38,39]. Radi and coworkers applied a ketoenol-Furan substituted silica for Zn(II) removal with a maximum metal uptake

Table 3

Thermodynamics parameters at different temperatures for the sorbent-sorbate systems MCM-41-NH₂-Cr(VI) and MCM-41-NH₂-Zn(II).

Temperature (°C)	Cr (VI)			Zn (II)		
	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹)	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹)
25	-26.2	17.8	147.5	-22.9	2.6	85.5
35	-27.4			-23.8		
45	-29.2			-24.6		

at pH ≈ 5 of 23.4 mg g⁻¹ [20]. Thus, comparing the adsorption capacity of the MCM-41-NH₂ sample with those of other adsorbents, it can be concluded that this material shows a very good performance for Cr(VI) and Zn(II) adsorption. Besides, it is important to remark that the FT-IR spectra of the Zn and Cr adsorbed MCM-41-NH₂ samples (Fig. 3B) still showed the characteristic bands of aminopropyl groups. This indicates that the sorbent still possesses, after 24 h of use, amino functions on its surface.

Batch adsorption experiments conducted with the pristine MCM-41 sample (Fig. S3), indicate that at pH=2 adsorption of Cr(VI) is negligible. However, this adsorbent is able to adsorb more Zn than the functionalized one (86.2 vs 58.9 mg g⁻¹ at 25 °C). Thus, the great advantage of the functionalized material is the capability for the extraction of both pollutants.

The performance of MCM-41-NH₂ as sorbent must be analyzed taking into account its surface composition and its pH environment-responsive behavior. When the working pH was fixed at 2, the sample's surface is composed of ammonium (-NH₃⁺) and silanols (Si-OH) species [22,31]. Considering that the chromium principal species is HCrO₄⁻, an electrostatic interaction is likely to take place [34,40], leading to the adsorption of the anions onto the positively charged surface of the adsorbent, without impediments or any repulsion. In the case of Zn isotherms, at a pH value of 7, the MCM-41-NH₂ surface presents a more complex pore surface composition. At this pH the silanols are partially deprotonated (pK_a ≈ 7) creating negative silanol/silanolate entities which provide a surface with negative places. Meanwhile, with a pK_a of ≈ 9–10, the N-containing groups are as ammonium and amino groups. Therefore, the surface at neutral pH presents negative, neutral and positive sites [31]. Thus, the interaction between zinc cations and the MCM-41-NH₂ surface would have, in some extend, electrostatic impediments. This could justify the slightly lower values of q_m found for our sample compared with those reported by other authors when mercapto-modified MCM-41 samples were used for zinc adsorption (q_m values of ≈ 62 mg g⁻¹) [39]. This explanation can also be used to understand the differences observed in Fig. 5, where it can be seen that the slope of the zinc kinetic experiments is lower than that for the chromium ones.

The variations of q_m with increasing temperature reported in Table 2 indicate that both sorption processes are endothermic. The changes in maximum sorption capacities with increasing temperature are higher for Zn than for Cr, the change is about 25% for zinc while for chromium an increase of only 12% was. Table 3 shows the thermodynamics parameters of the adsorption process, namely changes in standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) which were calculated using the following equations:

$$\Delta G^{\circ} = -RT \ln K_L \quad (3)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad (4)$$

where K_L is the Langmuir constant where concentration terms are expressed in L mol⁻¹, R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T

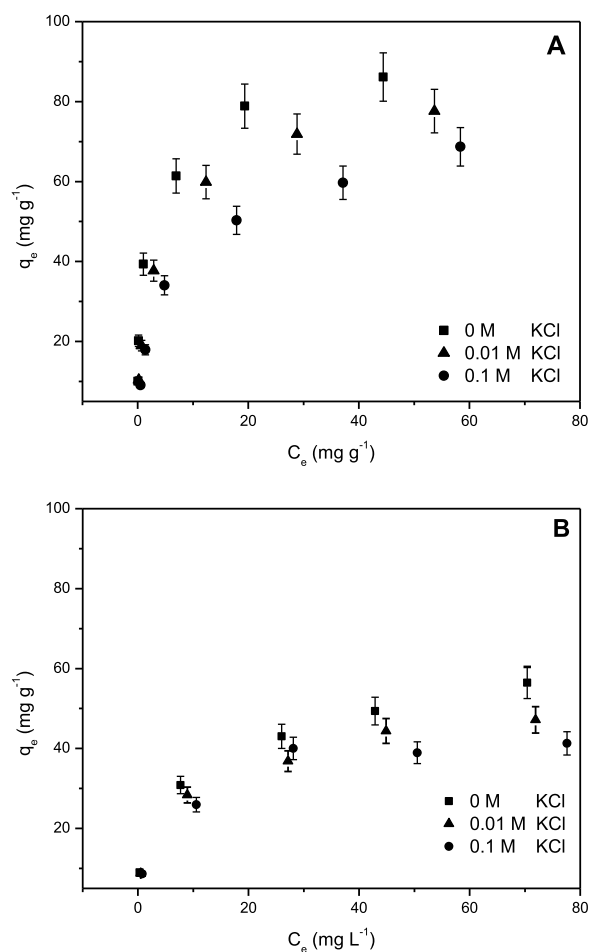


Fig. 7. Single component adsorption isotherms at different ionic strength and 25 °C: (A) adsorption experiments at pH = 2 for Cr(VI) removal, (B) experiments at pH = 7 for Zn(II) removal.

Table 4

Selectivity values for Cr(VI) and Zn(II) obtained in batch adsorption tests at pH values of 2 and 7 with initial metals concentration equal to 40 and 130 ppm using distilled water.

	40 ppm		130 ppm	
	pH = 2	pH = 7	pH = 2	pH = 7
Cr(VI)	0.98	0.02	0.76	0.06
Zn(II)	0.02	0.98	0.24	0.94

is the temperature expressed in Kelvin. The fact that the ΔG^0 value becomes more negative with increasing temperature, suggests that chromium and zinc adsorption onto MCM-41-NH₂ is favored by the temperature increase, according to the q_m increment reported in Table 2.

3.3. Single metal adsorption tests at different ionic strength

Wastewaters with heavy metals as pollutants as a result of textile dyeing, leather tanning, and electroplating industries often contain significant quantities of salts. Thus, in order to evaluate the performance of the MCM-41-NH₂ system as sorbent under more realistic conditions, the q_m Langmuir parameter for single metal solutions containing Cr(VI) or Zn(II) was also evaluated under different ionic strengths (0.01 and 0.1 M KCl) at 25 °C. The fully adsorption isotherms under these experimental conditions are showed in Fig. 7, and the fitting Langmuir parameters are listed in

Table 2. The isotherm without KCl aggregates was added in Fig. 7 in order to facilitate the comparison and to improve the understanding of the influence of ionic strength. When KCl concentration rises, a slight decrease in q_m for Cr(VI) and Zn(II) was registered. These results suggest that, in the case of chromium, the chloride anions interact to some extent with the positive surface sites of the sorbent, thus competing with chromium anions. Moreover, the interaction between HCrO_4^- and K^+ reduces the activity of chromium ions due to increasing non-ideality of solution. The obtained results are similar to those reported by Wang et al. for the adsorption of Cr(VI) under different NaCl concentrations, where an increase in sodium chloride concentration led to the linear decrease in numerical values of q_{max} [41].

In the case of Zn(II), the q_m variations suggest a competition between zinc cations and K^+ for the silanolate sites (SiO^-) existing on the surface of the sample at neutral pH together with a decrease in the zinc activity due to interactions with chloride anions.

It can be concluded that all results of single metal adsorption tests indicate that the aminopropyl-modified MCM-41 sample is able to eliminate Cr(VI) anions or Zn(II) cations with good performance by varying the pH of the solution to be treated.

3.4. Binary metal adsorption tests

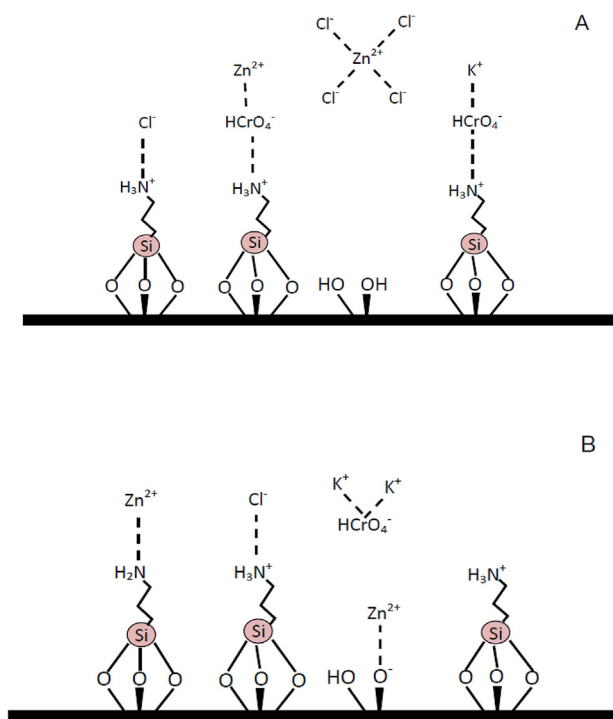
Table 4 shown the results for the adsorption assays in distilled water using 40 and 130 ppm of Cr(VI) and Zn(II). The experimental results are showed as selectivity (S), which was calculated using the following expression:

$$S_{M1} = \frac{\text{ppm of } M_1 \text{ eliminated from solution}}{\text{total ppm } (M_1 + M_2) \text{ eliminated from solution}}$$

Where M_1 and M_2 refer to Cr(VI) and Zn(II) respectively.

When the initial metals concentration was 40 ppm, the selectivity values for both Cr(VI) and Zn(II) were close to unity at pH 2 and 7, respectively. In high concentration tests (130 ppm), at pH 2, the selectivity was 0.76 and 0.24 toward Cr(VI) and Zn(II), respectively. These selectivity values indicate that some zinc ions are adsorbed over the sample surface. However, the zinc adsorption at acidic conditions with amino-modified silica sorbents should not happen due to the surface composition, as previously described. However, this experimental observation can be understood taking into account the mechanism proposed by Wu et al. [42] to explain the simultaneous removal of Cu(II) and sulfates anions. According to this model Zn(II) would interact with the protonated amine groups through previously adsorbed HCrO_4^- species. This mechanism was also employed by Lam et al. [22] to explain the adsorption of $\text{Cr}_2\text{O}_7^{2-}$ by previously multivalent cations adsorbed on MCM-41-NH₂, which provide adsorption sites for the anions by building up alternating ad-layers of positive cations and negative anions. Scheme 1 depicts a representation of the possible interactions between the metals ions with the sample surface entities, at the different experimental conditions used in the bath assays.

When KCl was added at pH 2 (Table 5), the selectivity toward chromium elimination increased up to 0.97. Thus, the presence of salt inhibits the adsorption of Zn almost completely as evidenced by the changes in selectivity values reported in Tables 4 and 5. This reinforces the idea that there is a competition between zinc cations and K^+ plus a decrease in the zinc activity due to interactions with chloride anions. When the pH was fixed at 7, Zn(II) is adsorbed preferentially against chromium with and without added salt; selectivity values are higher than 0.94 in both experiments. These results are in agreement with other reported data, indicating that no chromium interaction occurs with amino-modified sorbents at pH values higher than 6 [13,36].



Scheme 1. Sorbent surface composition and main sorbent-sorbate interactions A: pH = 2, B: pH = 7.

Table 5

Selectivity values for Cr(VI) and Zn(II) obtained in batch adsorption tests at pH values of 2 and 7 with initial metals concentration equal to 130 ppm dissolved in distilled water with 0.01 M KCl and river water.

	0.01 M KCl		river water	
	pH = 2	pH = 7	pH = 2	pH = 7
Cr(VI)	0.97	0.04	0.95	0.14
Zn(II)	0.03	0.96	0.05	0.86

3.5. River water matrix adsorption tests

Simulated polluted waters contaminated with 130 ppm of chromate and/or 130 ppm of zinc ions were prepared using river water from the *río Negro*, located in the coastal area of Viedma city, Patagonia, Argentina. To evaluate the influence of a real matrix in the q_m parameter, single metal adsorption batch assays and a binary metal adsorption test were carried out.

In the case of Cr(VI), compared with assay carried out in distilled water, the maximum adsorption capacity measured decreased from 87.5 to 54.8 mg g⁻¹, whereas a reduction from 58.9 to 43.6 mg g⁻¹ was observed for Zn(II).

Table 5 shows the selectivity values for the elimination of chromium and zinc when the two metals were incorporated at the same time to the river water sample. In accordance with the selectivity values discussed previously for the 0.01 M KCl solution at pH 2 (Table 5), the presence of salt inhibits the zinc adsorption almost completely, and the selectivity toward Cr(VI) reach 95%. When pH was fixed at 7, the selectivity values were similar to those measured at this pH in the 0.01 M KCl solution, indicating that Zn (II) is adsorbed preferentially against chromium. All the adsorption results using this natural aqueous matrix can be understood considering its chemical composition (Table S2), where the presence of chlorine, sulfate, carbonate and calcium ions would be playing the same role as the added KCl as discussed in previous paragraphs. Thus, the adsorption studies here undertaken show

that it is possible to separate selectively Cr(VI) anions from a natural water matrix containing high levels of Zn(II) cations, or vice versa, when MCM-41-NH₂ is used.

4. Conclusions

This work demonstrates that it is possible to achieve high adsorption selectivity for Cr(VI) and Zn(II) by using a unique silica mesoporous adsorbent obtained by post-grafting of aminopropyl functions on MCM-41. The metals ions were adsorbed fast and with high adsorption capacities through an endothermic process. The selectivity toward chromium oxyanions or zinc cations could be modulated by changing the pH of the water solution to be treated; this was possible due to the pH environment-responsive behavior of the MCM-41-NH₂ surface. In distilled water at acidic conditions the MCM-41-NH₂ preferentially adsorbed Cr(VI) against Zn(II) with a selectivity of 76% which increased up to 97% after addition of KCl due to a competition between zinc cations and K⁺ and a decrease in zinc activity due to interactions with chloride anions. Conversely, at neutral pH the MCM-41-NH₂ adsorbed zinc with and without added salt, reaching selectivity values always greater than 94%. The presence of natural salts (e.g. Cl⁻, K⁺, SO₄²⁻, Ca²⁺) in the river water matrices, helped to avoid the building up of alternating layers of zinc cations and negative chromium oxyanions, and vice versa, resulting in high selectivity values for Cr(VI) and Zn(II) pollutants. The good performance of MCM-41-NH₂ as sorbent in binary polluted complex water matrices demonstrates that this silica-based sorbents are promising materials for environment protection and remediation.

Acknowledgments

This work was funded by Universidad Nacional de Río Negro (UNRN) (PI-40-C-392 and PI-40-C-481). PPM thanks Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for his graduate student fellowship. Authors would like to thank Ms. Graciela Valle for FTIR measurements and to Dr. Leandro N. Bengoa for his collaboration in the preparation of the manuscript. The authors are grateful to María Cecilia Moreno, CICPBA translator, for checking the English version. We also thank to Lic. Mariela Teller and Lic. Pablo Fetsis for the assistance in the SEM and nitrogen sorption measurements, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2017.02.003>.

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