Bifunctionalized Mesoporous Silicas for Cr(VI) Reduction and Concomitant Cr(III) Immobilization

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Chromium(VI) removal via reduction–sorption on bi-functional silica adsorbents

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HIGHLIGHTS

► SH-functionalized silica is able to reduce Cr(VI) into less toxic Cr(III) species.
► Cr(III) can bind to ethylenediaminetriacetate groups in bi-functionalized sorbent.
► The reduction–sorption process is very fast and pH dependent (optimum: pH 1–3).
► Cr(III) binding is stronger than with sulfonate groups (possible column sorption).
► Good chromium sorption performance was observed in the presence of interference.

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ABSTRACT

Organically-modified silica gels bearing mercaptopropyl and ethylenediaminetriacetate groups (SiO_2–SH/ED3A) have been used for reduction and subsequent sequestration of Cr(VI) species. The uptake mechanism involves Cr(VI) reduction by thiol groups (SH) and further immobilization of the so-generated Cr(III) species via complexation to the ethylenediaminetriacetate moieties (ED3A). The most appropriate pH range (1–3) for complete Cr(VI) reduction–sorption by SiO_2–SH/ED3A originates from the balance between full reduction of Cr(VI) by SH, requiring low pH values, and quantitative complexation of Cr(III) by ED3A, which is favored in less acidic media. Such bi-functional adsorbents are considerably more effective at removal of Cr(VI) than those simply modified with thiol groups alone. The whole reduction–sorption process was characterized by fast kinetics, thus permitting efficient use of the SiO_2–SH/ED3A adsorbent in dynamic conditions (column experiments). Monitoring the amount of immobilized chromium species on the solid was achieved using X-ray fluorescence spectroscopy and UV–vis spectroscopy. Studying the influence of ionic strength and presence of heavy metals revealed few interference on Cr(VI) removal.

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1. Introduction

Chromium is widely used in diverse industrial processes, including alloys and steel manufacturing, metal finishing, electroplating, leather tanning, cooling tower blowdown, or pigments synthesis and dyeing [1–3]. In spite of considerable reduction of industrial disposal of chromium observed today, chromium contamination of soil and groundwater remains a significant environmental problem [2,4,5], and there still exists a need to control the occupational exposure and emission limit values of anthropogenic chromium as well as to find appropriate treatments likely to lower chromium pollution. Considering the difference in biological activity of the various forms of chromium, the present-day regulations and quality guidelines call for distinction between Cr(VI) and Cr(III)

species, the former being considered as more toxic than the latter [4,6–8].

Several well-documented reviews or monographs are available dealing with chromium removal from wastewaters [9–16]. It came out that firstly proposed remediation schemes were directed to reduce the carcinogenic, soluble, and mobile Cr(VI) (i.e., in acidic medium, pH ~2) to the less toxic and less mobile Cr(III), which forms insoluble or sparingly soluble precipitates (i.e., in alkaline medium, above pH ~9–10). Such methods are only applicable for concentrated industrial wastewater and produce large amounts of chemical sludge [17], generating thereby the search for other approaches. Nowadays existing technologies (see details in Supplementary Data) are mainly based on immobilization on solid supports, or separation and filtration processes, associated or not to reduction/precipitation. All these methods exhibit advantages and disadvantages and are most often applied to the removal of chromium from solutions containing relatively high initial chromium concentrations (i.e., >100 mg L^{-1}). Adsorption, though likely to generate non negligible amounts of sludge with associated disposal problems, merged recently among the most promising

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approaches for simple, efficient, and selective chromium removal [11,12]. A variety of natural and synthetic adsorbents [11] and biosorbents materials [18] have been used for tri- and hexavalent chromium removal from water and wastewaters. Among them, functionalized or bio-doped silica-based materials started to be proposed for that purpose in recent years [19–25].

A breakthrough in the field is the resort to adsorbents with both reductive and sorption properties in a single solid (chromium immobilization according to a reduction–sorption process). In doing so, one part of the adsorbent is reducing the most toxic Cr(VI) species while another part is likely to immobilize the generated Cr(III) moieties. Examples of such materials with reduction–sorption capabilities include mainly sludge and/or sulfur-containing biomass and other biosorbents [26–32], but also bacteria immobilized in sol–gel materials [22,23], organic–inorganic hybrids [33,34], inorganic iron metal or sulfides [35,36], or zero-valent iron immobilized on silica supports [24,25]. Even if some redox active centers (for Cr(VI) reduction) and/or complexing groups (for Cr(III) binding) can be identified [26,28,31,33], the intrinsic complexity of these materials often made difficult the deep understanding of the main chemical parameters affecting the overall uptake process.

In a previous report [34], we investigated the reduction–sorption properties of thiol- and sulfonic acid-functionalized mesoporous silica materials, showing that in an appropriate pH range (yet narrow, i.e., pH 2–3) Cr(VI) can be reduced by the thiol groups and the resulting Cr(III) species were retained in the material via favorable electrostatic interactions with the sulfonate moieties. The process worked quite well but suffered from at least two limitations: the stoichiometry of the redox process (limiting the scavenging properties of the material), and the rather weak interaction between Cr(III) cations and sulfonate groups. In attempting to circumvent these limitations, we have now designed a novel bi-functional adsorbent offering the advantage of bearing two distinct organofunctional groups, each one with its own properties, the first one (mercaptopropyl) being selected for its ability to reduce Cr(VI) and the second one (ethylenediaminetriacetate) for its scavenging behavior toward Cr(III) species via complex formation. The performance of such bi-functional adsorbent was evaluated with respect to various experimental parameters likely to affect the reduction–sorption process (pH, solid-to-solution ratio, concentration) in order to determine the uptake mechanism and to compare it with the mono-functional adsorbent. Such adsorbent also offers the advantage of being usable in flowing conditions (column experiments).

2. Experimental

2.1. Reagents and solutions

All reagents were analytical grade and solutions were prepared with high-purity water (18 MΩ cm) from a Millipore Milli-Q water purification system. Stock solutions of Cr(VI) were prepared by dissolving accurate weighed portions of a $K_2Cr_2O_7$ powder (Prolabo) in deionized water, from which working solutions were prepared by dilution and pH adjustment using nitric acid. Other solutions were prepared by dissolving the appropriate analytical-grade reagents, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 10H_2O$, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, or NaCl (from Fluka or Sigma-Aldrich), in deionized water.

2.2. Preparation of bi-functional silica samples

The chromatographic grade silica Kieselgel 60 was obtained from Merck (average particle size: 125 25 μm; specific surface area: 425 25 m2 g^{-1}; average pore size: ~7 nm; surface hydroxyl content: 3.6 mmol OH g^{-1}). Grafting agents were mercaptopropyltrimethoxysilane (MPTMS, 95%, Lancaster) and N-[(3-trimethoxysilyl)-propyl]-ethylenediamine triacetate (ED3A, 50% (w/w) aqueous solution of sodium salt of ED3A–silane coupler, Petrarch Systems Inc.). Solvents were toluene (95%, Merck), ethanol and methanol (Merck).

2.2.1. Silica gel with covalently attached mercaptopropyl groups

Thiol-functionalized silica samples (SiO$_2$–SH) were synthesized according to a grafting procedure described in the literature [37,38]. Silica gel was first washed with 1 M H_2SO_4 and then with distilled water till neutral pH, and dried at 100 °C. Before silylation, the silica powder was dried in an oven at 210 °C for 3 h, put into a flask, which was then filled with toluene (100-mL) and left for blending for several minutes. Then a selected aliquot of MPTMS solution in toluene was added to the slurry to reach a final content of 1 mmol of organosilane for 1 g of silica gel. The grafting reaction was conducted at 100 °C for 6 h. The resulting precipitate was then washed in Soxhlet's apparatus with toluene (1 h) and then with methanol for 24 h. The final material contained about 0.4 mmol of covalently immobilized thiol groups per gram of adsorbent.

2.2.2. Silica gel with covalently attached mercaptopropyl and ethylenediaminetriacetate groups

Thiol- and ethylenediaminetriacetate-functionalized silica samples (SiO$_2$–SH/ED3A) have been prepared according to a similar procedure as that reported for getting ethylenediaminetriacetate-bonded silica gel [39]. Briefly, 5.0 g of SiO$_2$–SH was placed into 20 mL of water–methanol solution (1:1 in volume) and left blended for 30 min. Then 4.0 ml of ED3A–silane coupler solution was added to SiO$_2$–SH slurry and blended for 3 days at the room temperature. The adsorbent was filtered, washed with distilled water and dried at 100 °C under reduced pressure. It contained about 0.4 mmol of immobilized ED3A groups per gram of material, i.e., the same amount as SH groups. Such optimal conditions for functionalization of SiO$_2$–SH with ED3A groups have been defined after investigating the binding of the ED3A–silane coupler to pure silica gel (1 g mixed with 4 ml of a 1:1 water–methanol solution containing the ED3A–silane coupler at concentrations varying from 13 to 290 g L^{-1}).

2.3. Instrumentation–materials characterization

Solution-phase analysis of total chromium was performed by inductively-coupled plasma with detection by atomic emission spectroscopy (ICP-AES, Plasma 2000, Perkin-Elmer). Distinction between Cr(VI) and Cr(III) species was made using the conventional diphenylcarbazide (DPC)-UV/Vis spectrometric method [40]. Other metal ions were analyzed by atomic absorption spectrometry (AAS) using a flame atomization "Saturn" apparatus and a propane-butane-air flame. Several physico-chemical techniques were used to characterize the solid phases, including Fourier-transform infra red (FTIR), X-ray photoelectron (XPS) and X-ray fluorescence (XRF) (see details in Supplementary Data).

Composition of the adsorbents was determined by elemental analysis (CHONS) using a Thermofinnigan FlashEA 1112 analyzer. The thiol group content was also analyzed by back potentiometric titration. The sample (typically 0.5–1.0 g) was equilibrated with a mixture of 10 ml of 0.040 M AgNO$_3$ and 20 mL of deionised water. The suspension was kept without light access for 12 h and then titrated potentiometrically using a standardized KCl solution.

2.4. Equilibration procedures

2.4.1. Static mode

Batch equilibration (24 h) involved aqueous suspensions of Cr(III) or Cr(VI) containing selected amounts of SiO_2–SH/ED3A in the pH range 1–7 (adjusted using 0.1 M HNO_3 or NaOH). Mono-functionalized SiO_2–SH or SiO_2–ED3A materials were also used for comparison purposes. Equilibrations were performed at room temperature, under magnetic stirring, typically in 25 or 50 mL solution with solid-to-solution ratios varying between 0.2 and 10 g L^{-1}. Ionic strength was adjusted with NaCl (from 0.01 to 1 M) and final pH was always measured at the end of the reaction. Solid and liquid phases were separated by filtration and the amount of Cr(VI) and Cr(III) species in solution was determined. Interference studies were performed by adding metal ions (Fe, Cu, Ni, at concentrations ranging from 0.004 to 0.48 mmol L^{-1}) in the suspension (0.05 g adsorbent in 25 ml solution containing 0.23 mmol L^{-1} Cr(VI)). The residual metal concentrations were analyzed by ICP-AES. It was confirmed from three independent replicates that the Cr(VI) removal experiments were reproducible within at most 5% error.

2.4.2. Dynamic mode

Sorption reactions have been also performed in dynamic mode, using a glass column filled with 100 mg of the adsorbent, with pH of chromium solutions adjusted to 2.5 (optimum value observed from batch experiments), and details on the various experiments can be found in Supplementary Data.

3. Results and discussion

3.1. Adsorbent preparation and characteristics

Attachment of mercaptopropyl groups (SH), on one hand, and ethylenediaminetriacetate moieties (ED3A), on the other hand, onto the silica surface requires two distinct grafting procedures. The first one is the "classical" grafting reaction of MPTMS on silica in refluxing toluene [37] but special care should be taken to avoid complete coverage of the whole silica surface to enable further immobilization of ED3A groups, which can be easily made by adjusting the MPTMS/silica ratio [41]. Then, ED3A groups were attached to the SiO_2–SH material by reaction with the ED3A–silane coupler in water–methanol medium, in a similar way as previously described [39]. Again, it was possible to adjust the amount of immobilized groups by tuning the ED3A–silane coupler-to-silica ratio (see Fig. S1 in Supplementary Data for N-[(3-trimethoxysilyl)-propyl]-ethylenediamine triacetate binding to silica gel, for which a maximum ED3A content of *ca.* 0.7 mmol g^{-1} was achieved). When using the SiO_2–SH material instead of bare silica, the amount of immobilized ED3A groups was lower due to the presence of SH groups occupying a significant portion of the silica surface. This is confirmed by chemical analysis, indicating the presence in the final bi-functional adsorbent (SiO_2–SH/ED3A) of SH groups (0.38 ± 0.02 mmol g^{-1} from elemental analysis; 0.40 ± 0.03 mmol g^{-1} from silver titration), and ED3A groups (0.39 ± 0.02 mmol g^{-1}, from elemental analysis).

The presence and the integrity of the organo-functional groups were further checked by FTIR (see Fig. S2 in Supplementary Data). The spectra of thiol-bearing samples were characterized by C-H stretching vibrations of the propyl chains at 2855 and 2960 cm^{-1} and a weak vibration corresponding to the -SH group at 2578 cm^{-1} [42]. The ED3A-groups can be identified via the vibration of their carboxylate/carboxylic acid moieties, leading to a band at 1728 cm^{-1} (COOH) and two others (COO$^-$) at 1631 cm^{-1} (this latter being superimposed to that of weakly physisorbed water [43]) and 1405 cm^{-1}, in agreement with previous observations [44], whereas
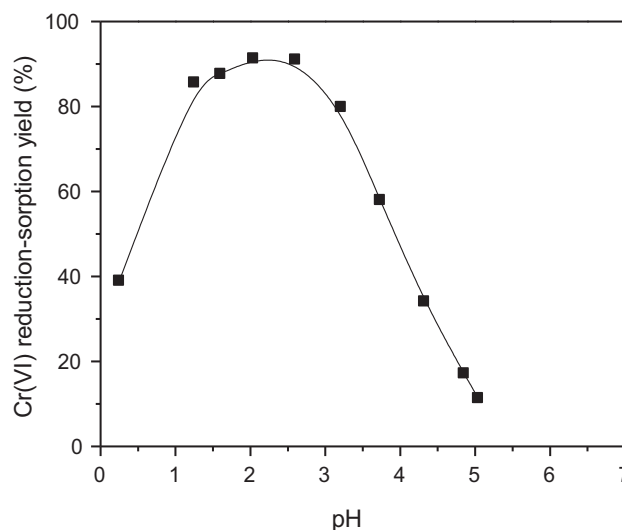

Fig. 1. Variation of Cr(VI) reduction–sorption yields as a function of pH, using the SiO_2–SH/ED3A adsorbent; experimental conditions: solid-to-solution ratio of 2.0 g L^{-1}, starting Cr(VI) concentration in solution equal to 100 μM (25 mL solution).

the characteristic band of ED3A at 1332 cm^{-1} [45] was almost invisible because it was located too close to the huge signal corresponding to siloxane moieties in the 1000–1300 cm^{-1} range [42].
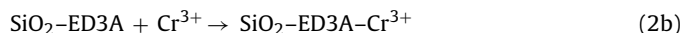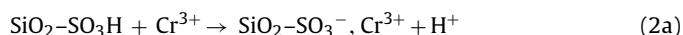
3.2. Batch sorption experiments

3.2.1. Cr(VI) reduction–sorption on SiO_2–SH/ED3A

The bi-functional SiO_2–SH/ED3A adsorbent led to significant chromium uptake, especially between pH 1 and 3 (Fig. 1). One already knows that thiol-functionalized silica (i.e., SiO_2–SH) is likely to reduce Cr(VI) species [34], in agreement with observations made with other thiol-containing solids [33,46]. The reaction can be described by Eq. (1) [34]:

$$SiO_2-SH + 2HCrO_4^- + 8H^+ \rightarrow SiO_2-SO_3H + 2Cr^{3+} + 5H_2O \qquad (1)$$

This equation indicates that Cr(VI) reduction is favored at lower pH values (consistent with thermodynamic predictions [47]). This explains the right part of the curve (Fig. 1), indicating dramatic decrease in sorption yields above pH 3 (to reach almost zero at pH 5), because the medium was not acidic enough for thiol groups to reduce Cr(VI) species. This is also confirmed by solution-phase analyses, revealing that all the remaining chromium species in solution are in the Cr(VI) form.

On the other hand, Cr(III) species (generated by Cr(VI) reduction by thiol groups) are immobilized on the adsorbent, as ascertained by XPS analysis (via Cr2p$_{3/2}$ and Cr2p$_{1/2}$ signals located respectively at binding energies of 577.3 eV and 586.7 eV, which are characteristics of Cr(III) [48]). This confirms that Cr(VI) species have been really reduced by thiol groups and that the adsorbed species are in the form of Cr(III) on the material. Actually, the generated Cr(III) species are likely to interact with either ED3A groups (via complex formation) or sulfonic acid moieties (via ion exchange/electrostatic interactions), as illustrated in the following equations:

$$SiO_2-SO_3H + Cr^{3+} \rightarrow SiO_2-SO_3^-, Cr^{3+} + H^+ \qquad (2a)$$

$$SiO_2-ED3A + Cr^{3+} \rightarrow SiO_2-ED3A-Cr^{3+} \qquad (2b)$$

At this stage it is difficult to distinguish unambiguously between these 2 processes but several features tend to indicate that the ED3A chelate plays an important role. First, the stoichiometry of the redox reaction (Eq. (1)) shows that 2 Cr(III) species are formed when only one SO$_3$H is generated whereas sorption yields as high as 90% have
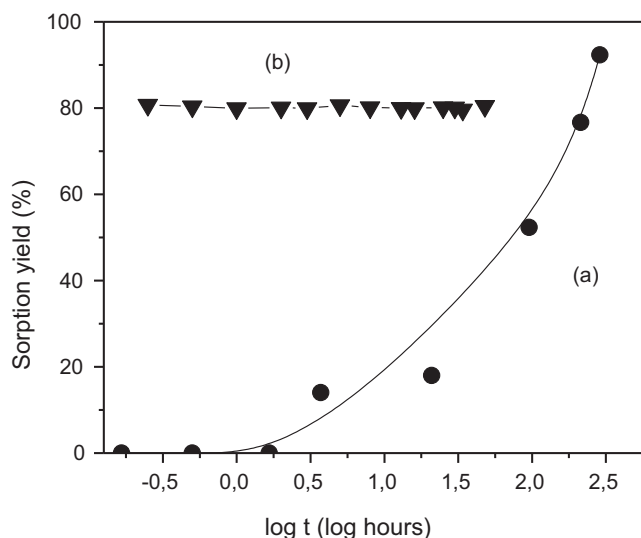
Fig. 2. Effect of contact time between (a) a Cr(III) solution and the SiO$_2$–ED3A adsorbent, or (b) a Cr(VI) solution and the SiO$_2$–SH/ED3A adsorbent, on the chromium sorption yields; experimental conditions: solid-to-solution ratios of 4.0 g L^{-1} (a) or 2.0 g L^{-1} (b), starting Cr(III) and Cr(VI) concentrations in solution equal to 192 μM and 100 μM, respectively (25 mL solution), and pH in the medium equal to 5.0 (a) or 2.5 (b).

been observed (Fig. 1), demonstrating that ion exchange (Eq. (2)a) cannot be the only process explaining Cr(III) immobilization and, therefore, complex formation with ED3A should occur. Secondly the pH range for effective reduction–sorption using SiO$_2$–SH/ED3A (i.e., in the 1–3 range, see Fig. 1) is significantly larger than for SiO$_2$–SH (i.e., between pH 2 and 3 [34]), indicating more efficient Cr^{3+} binding in acidic medium for the SiO$_2$–SH/ED3A sorbent, which can be explained by complex formation with ED3A (even at pH values as low as 0.5–1, consistent with highly stable Cr(III) complexes with HEDTA [49] or EDTA [50] in strongly acidic media).

Kinetics associated to Cr(VI) reduction and subsequent Cr(III) immobilization onto SiO$_2$–SH/ED3A are very fast (see curve b in Fig. 2), showing steady state values for maximum sorption yields in less than 15 min (i.e., the first measured data). This supports the idea of fast binding of freshly generated Cr(III) in the form of Cr^{3+} species, which are formed close to ED3A groups in the porous material and thereby likely to undergo rapid complexation, contrary to as-prepared solutions of Cr(III) in which chromium is in the form of Cr(H$_2$O)$_6{}^{3+}$ which requires slow ligand exchange before being complexed with the ED3A chelate [49,51] (as supported by curve a in Fig. 2).

3.2.2. Performance of the adsorbents: sorption isotherms-residual concentrations

Fig. 3A shows the variation of SiO$_2$–SH/ED3A (curve a) and SiO$_2$–SH (curve b) sorbent capacities as a function of the initial Cr(VI) concentration in solution. The data demonstrate clear advantage of the bi-functional adsorbent: while the sorption capacity for SiO$_2$–SH rapidly leveled off at about 0.15 mmol g^{-1}, that of SiO$_2$–SH/ED3A rapidly grew up to 0.4–0.5 mmol g^{-1} in the same conditions. A maximum value of 0.69 mmol g^{-1} (SiO$_2$–SH/ED3A) is even reached in the presence of a large excess of Cr(VI) in solution. Even more overwhelming is the comparison of adsorption isotherms (see inset in Fig. 3A), showing that negligible amounts of remaining chromium in solution were observed with SiO$_2$–SH/ED3A up to a capacity of about 0.4 mmol g^{-1} (with a Langmuir H-type isotherm), contrary to SiO$_2$–SH for which significant chromium uptake was only visible with non negligible equilibrium chromium concentrations in solution (type S isotherm). This
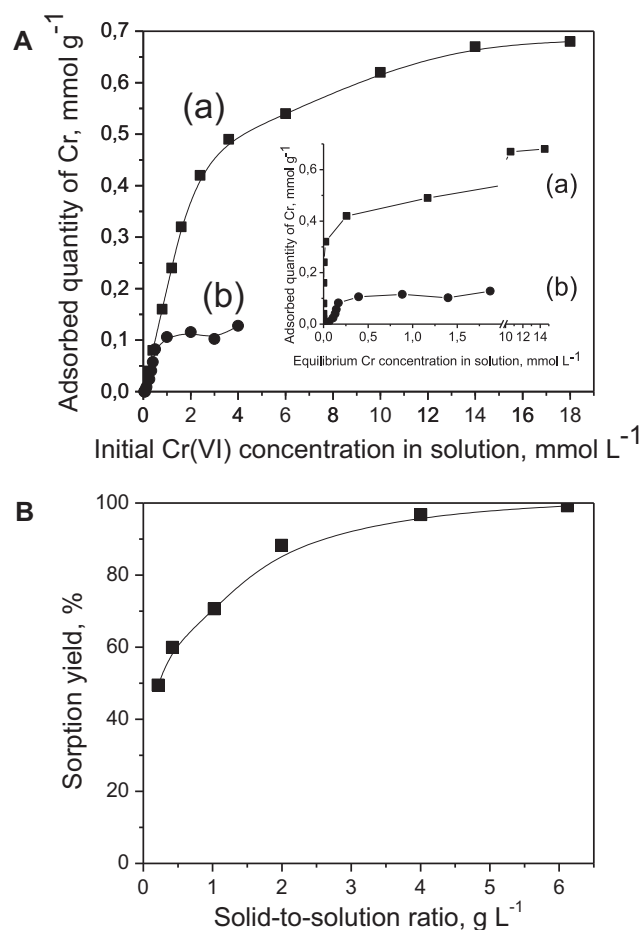

Fig. 3. (A) Variation of the amount of adsorbed chromium on (a) SiO$_2$–SH/ED3A and (b) SiO$_2$–SH, as a function of the initial Cr(VI) concentration in solution (25 mL solution at pH 2.5, containing 125 mg of adsorbent); the corresponding isotherms (i.e., same variations given versus the equilibrium chromium concentrations in solution) are given in the inset. (B) Variation of chromium sorption yields, as a function of the solid-to-solution ratio, using SiO$_2$–SH/ED3A particles suspended in 50 mL of 100 μM Cr(VI) solution at pH 3.0.

further confirms the above hypotheses of Cr(III) immobilization onto SiO$_2$–SH/ED3A (Eq. (2)a & b): a strong binding to ED3A chelates (which are indeed present in the material at a content of 0.4 mmol g^{-1}) via complex formation (Eq. (2)a) and then a weaker binding to the generated sulfonic acid species via ion exchange/electrostatic interactions (Eq. (2)b). Only this second (weak interaction) binding process was likely to occur with the mono-functionalized SiO$_2$–SH material. These results also suggest the formation of a 1:1 complex between Cr(III) and ED3A on silica, consistent with the stoichiometry of the corresponding Cr(III)-HEDTA complex in solution [49].

Due to the particular sorption mechanism (reduction + adsorption), it appears intricate to quantitatively characterize the parameters that could be derived from classical adsorption models (i.e., Langmuir, Freundlich). Anyway, attempts were made to do so from the isotherms presented in Fig. 3A. While non linear fits were observed on the basis of the Freundlich model, quite good fitting was obtained using the Langmuir model for Cr(VI) on both SiO$_2$–SH/ED3A and SiO$_2$–SH adsorbents. The sorption parameters calculated from these fits are respectively $K_a = 5.8$ L mg^{-1} and $q_m = 34.7$ mg g^{-1} ($r^2 = 0.997$) for SiO$_2$–SH/ED3A, and $K_a = 27.1$ L mg^{-1} and $q_m = 7.2$ mg g^{-1} ($r^2 = 0.947$) for SiO$_2$–SH. Performance in capacity for SiO$_2$–SH/ED3A is comparable to other silica-based adsorbents applied to Cr(VI) removal via either

Table 1
Comparison of silica-based materials used for Cr(VI) removal.

Adsorbent	pH	Sorption capacity (mg/g)	Time window	Ref.
Direct immobilization				
Mesoporous aluminosilicate from microcline	5.5	112	20 min	[21]
2-mercaptopyridine-functionalized silica gel	9	45	30 min	[20]
2-mercaptopyridine-functionalized SBA-1	9	95	30 min	[20]
mono-	7–9	94		
di- amino ligands functionalized SBA-1	7–9	178	5 min–5 h	[19]
tri-	7–9	211		
mono-	7–9	53		
di- amino ligands functionalized MCM-41	7–9	92	5 min–5 h	[19]
tri-	7–9	115		
Reduction–sorption				
Thiol-functionalized mesoporous silica	2.5	32	not available	[34]
Zn(0) on silica gel	6	20	not available	[52]
Core-shell Fe@SiO$_2$ nanocomposite	6	467	180 min	[53]
Bacteria *Burkholderia* sp. in sol–gel material	7.4	0.028	days	[23]
Bi-functionalized SiO$_2$–SH/ED3A sorbent	1.5–3	35	< 5 min	This work

direct adsorption [19–21] or reduction–sorption [23,34,52,53] (Table 1). They are also in agreement with values reported for a wide range of adsorbents (see extensive Table in a comprehensive review [11] or some more recent works [18,32,54,55]). The main interest of the present approach with respect to these previous works is the ultra-fast sorption process, enabling column experiments (see Section 3.3), and the possibility to operate in acidic media, *i.e.*, in conditions close to those relevant for industrial wastewaters.

Fig. 3B shows that SiO$_2$–SH/ED3A is likely to decrease the residual chromium concentration below low threshold values, but this requires the use of solid/solution ratios high enough. For instance, working in a solution containing initially 0.1 mM Cr(VI), the use of SiO$_2$–SH/ED3A contents increasing from 2 to 4 and then to 6 g L^{-1} resulted in sorption yields of 88, 97, and 99%, respectively. The adsorbent is thus likely to reduce chromium concentration under the μM concentration level. In view of the importance of the solid-to-solution ratio (Fig. 3B) and considering the fast sorption kinetics (Fig. 2b), flow-through experiments could be even more effective for chromium removal via reduction–sorption on such bi-functional porous material (see Section 3.3).

3.2.3. Solid phase analysis after reduction–sorption experiments

An additional feature to support the existence of two forms of adsorbed Cr(III), and the best performance of SiO$_2$–SH/ED3A compared to SiO$_2$–SH, is provided by the optical analysis of adsorbent samples treated with Cr(VI) solutions of increasing concentration. The reduction–sorption of chromium started earlier using the bi-functional SiO$_2$–SH/ED3A adsorbent and led to the observation of much intense color as a result of higher contents of adsorbed species (see Fig. S3 in Supplementary Data). One can distinguish the characteristic blue/violet color of the Cr(III)–ED3A complex [49] on SiO$_2$–SH/ED3A, the intensity of which increasing as high was the chromium loading. This is more quantitatively evidenced from recording UV–vis diffuse spectra (see Fig. S4 in Supplementary Data) for which the main peak at 565 nm [49] was found to increase linearly up to a chromium loading of 0.4 mmol g^{-1} (corresponding to the content of ED3A groups in the material) and then tended to level off. At higher chromium loadings, an additional colored contribution appeared (see the three last spots on the right of Fig. S3A), which corresponds to the greenish-yellow color typical of the SiO$_2$–SO$_3$$^-$,Cr^{3+} ion pair formed when using the mono-functionalized SiO$_2$–SH adsorbent (see Fig. S3B). This confirms the two forms of adsorbed Cr(III) on SiO$_2$–SH/ED3A and that the firstly formed one corresponds to the more stable SiO$_2$–ED3A–Cr(III) complex.

From the analytical point of view, adsorbed Cr(III) on SiO$_2$–SH/ED3A can be quantitatively determined by XRF, showing a linear relation of the signal intensity and chromium content in the adsorbent in the whole range up to 0.6 mmol g^{-1} (or 30 mg g^{-1}, as shown on Fig. S5 in Supplementary Data). These values correspond well to those calculated from solution-phase analyses (by difference with respect to starting chromium concentrations in solution), checking thereby that mass balance was maintained during the reduction–sorption process.

3.3. Column sorption experiments

The potential for SiO$_2$–SH/ED3A to remove Cr(VI) from wastewaters in dynamic conditions was evaluated in model experiments using toxic metal concentrations in the mM range. Typical results are illustrated on Fig. 4, for two chromium concentrations and three distinct flow rates. Both the variations of the remaining chromium concentrations in the eluate and the adsorbed chromium on the material have been plotted, respectively on parts A and B of figure, as a function of the solution volume passed through the column.

Several conclusions can be drawn from these results. First, if the maximum sorption yields are independent on the solution flow rate (in the 0.1–1.0 mL min^{-1} range), this parameter has some effects on the overall speed of the reduction–sorption process, especially more marked at 4 mM Cr(VI) than at 2 mM. This can be evidenced from the breakthrough data (Fig. 4A) in which the S-shaped curves were more well-defined at lower flow rates, as expected from longer contact times for reaching steady-state. This is also evident from adsorbent capacity variations (Fig. 4B), showing that higher flow rates required larger solution volumes to fill the column. Secondly, the maximum uptake capacity was *ca.* 0.37 mmol g^{-1} (i.e., near the content of ED3A groups in the material), suggesting that only the strong chelating ED3A groups are likely to retain Cr(III) species that have been reduced by thiol groups. In such dynamic conditions (column sorption experiments), the lability of the SiO$_2$–SO$_3$$^-$,Cr^{3+} ion pair does not allow the durable immobilization of Cr(III) species via electrostatic interactions with sulfonic acid moieties. This confers definite advantage to the SiO$_2$–SH/ED3A adsorbent over the previously reported SiO$_2$–SH/SO$_3$H one, which cannot be used in column (no measurable Cr(III) retention). Thirdly, under optimal conditions (i.e., low flow rates), there exists an inverse relationship between the breakthrough volume and the chromium solution concentration (i.e., 0.02 L for [Cr(VI)] = 2 mM, and 0.01 L for [Cr(VI)] = 4 mM, see Fig. 4A), suggesting that the chromium concentration does not affect the kinetics of the reduction–sorption process.
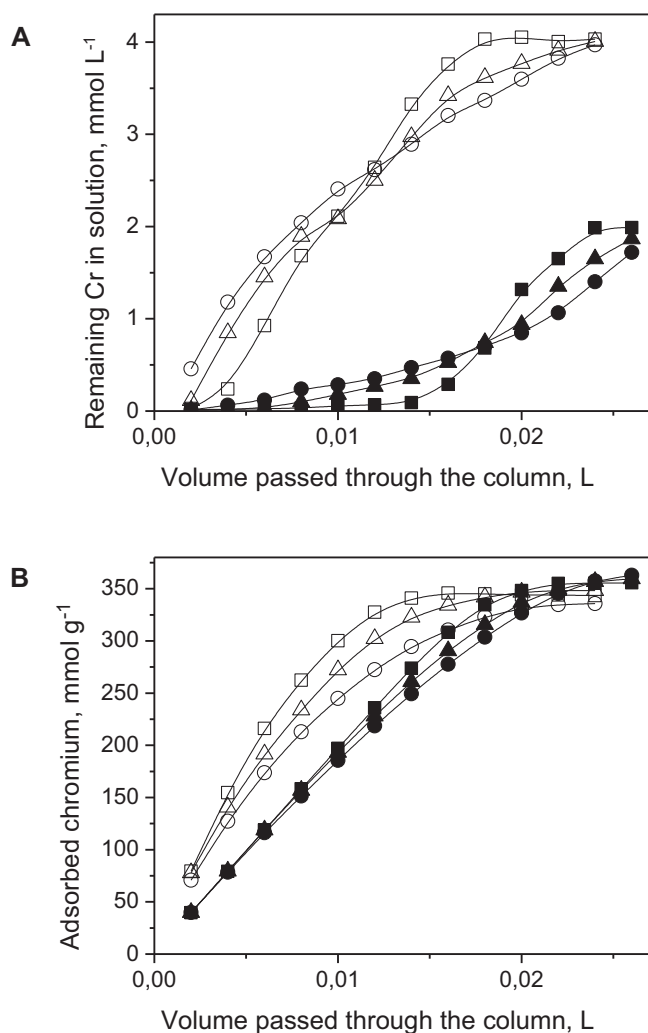
Fig. 4. Cr(VI) reduction–sorption onto SiO$_2$–SH/ED3A in dynamic mode. Variation of (A) the concentration of remaining (non adsorbed) chromium in solution at the output of the column, and (B) the amount of adsorbed chromium onto the solid phase, as a function of the solution volume passed through the column; the experiments have been performed at two Cr(VI) concentrations (2 mM (■,▲,●) and 4 mM (□,△,○), at pH 2.5, and three different flow rates (0.1 mL min^{-1} (■,□), 0.4 mL min^{-1} (▲,△), and 1.0 mL min^{-1} (●,○)); other experimental condition: 100 mg adsorbent in the column (Ø 6 mm).

3.4. Influence of the presence of concomitant foreign species

The effect of high ionic strength on the adsorbent capacity was first considered in static conditions, by working in excess Cr(VI), for which a decrease in the reduction–sorption capacity by about 40% was observed at high ionic strength (>0.5 M, see Fig. S6 in Supplementary Data). At the same time, distribution coefficients (K_d values) were found to decrease by a factor of about 2 (see inset in Fig. S6), but remained rather high, even at high ionic strength (e.g., 435 mL g^{-1} in the presence of 1 M NaCl). This behavior can be rationalized by considering the reduction–sorption mechanism discussed above. Indeed, only Cr(III) species weakly bonded to -SO$_3$$^-$ moieties contribute to the loss in capacity (i.e., from 0.69 to 0.43 mmol g^{-1}). This confirms again the major importance of the strong ED3A chelates in maintaining the immobilization properties of the bi-functional adsorbent.

Because ED3A-functionalized materials are likely to adsorb other metal ions [39], we have then investigated the possible effect of the presence of such species which can be present along with chromium in typical acidic wastewaters (e.g., from
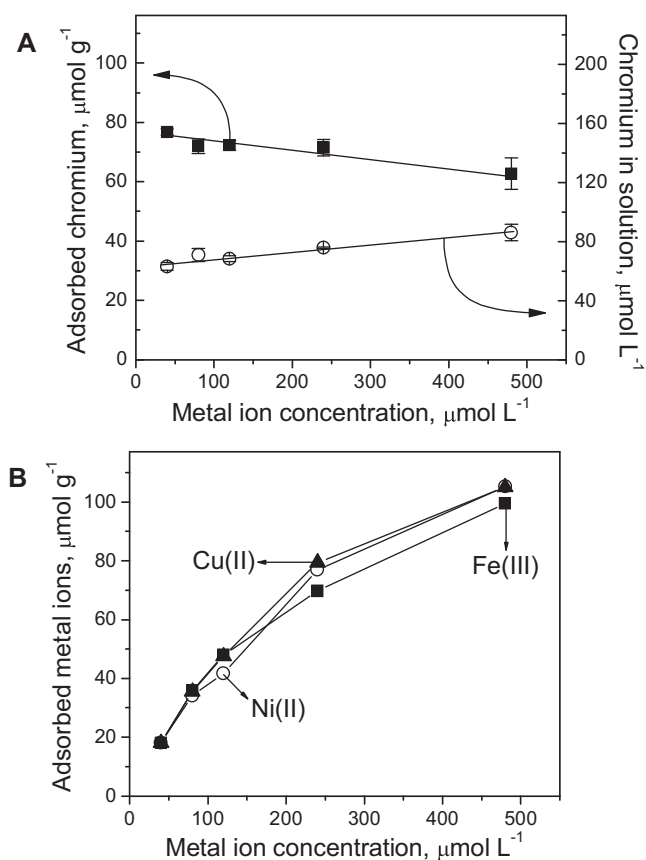

Fig. 5. (A) Influence of the presence of metal species (Cu(II), Ni(II), and Fe(III), in mixture) at increasing concentrations, on Cr(VI) reduction–sorption yields using the SiO$_2$–SH/ED3A adsorbent (2.0 g L^{-1}; starting Cr(VI) concentration in solution equal to 233 μM; pH 2.5), expressed as both the amount of adsorbed chromium and the remaining quantity of chromium in solution, as a function of the foreign metal species concentration. (B) Variation of the amounts of Cu(II) (▲), Ni(II) (○), and Fe(III) (■), adsorbed on the SiO$_2$–SH/ED3A material, as a function of their initial concentration in solution, as measured from experiments performed in the same conditions as in (A).

electroplating [56]). Fig. 5A shows that under pure thermodynamic competition conditions (i.e., excess adsorbent over solute), the presence of foreign species (Fe(III), Cu(II), Ni(II)) at concentrations ranging from half to twice as that of chromium did not dramatically affect the sorption yields (less than 20% decrease when interfering species were two times in excess over Cr(VI)), even if these species were likely to bind to the material (Fig. 5B) but at ca. 10 times lower contents in comparison to chromium. More importantly, pH was found to play a major role on the selectivity series. This has been considered here by studying desorption of a SiO$_2$–SH/ED3A column previously loaded with chromium (as Cr(VI) for immobilization by reduction–sorption) and various other metal species, following a pH-gradient elution process (see inset in Fig. 6). The results (Fig. 6) clearly shows a selectivity series in which adsorbed Cr(III) appears to be the most stable species: Pb(II) < Co(II) < Fe(III) < Ni(II), < Cu(II) < Cr(III). In such pH-gradient desorption experiment, the pH value for half-desorption yield is commonly used to compare the stability of immobilized complexes [57]. According to data from Fig. 6, this value decreased in the following order for metal ions tested here: Pb (4.2), Co (2.3), Fe (1.8), Ni and Cu (1.6), and no measurable data was available for chromium as less than 10% Cr(III) was desorbed at pH 1.5 (the lowest pH tested here). This means that only Cu(II), Ni(II) and Fe(III) could interfere with Cr(VI) if present in solution in high excess over Cr(VI). In agreement with data presented in Fig. 1 (curve b), chromium species only
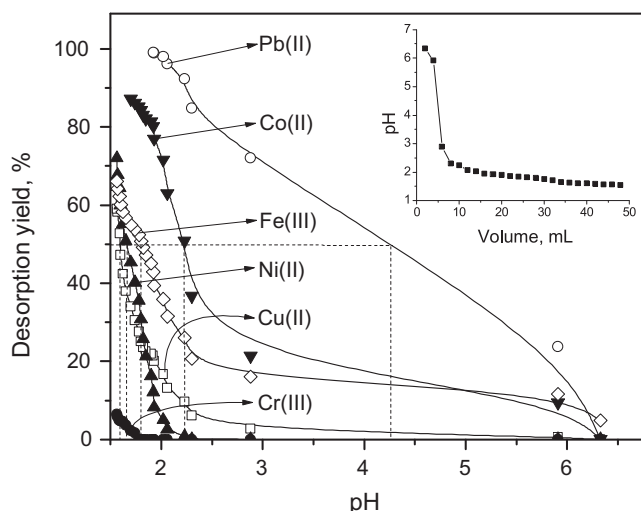
Fig. 6. Variations of the desorption yields, as a function of pH, of a column made of 100 mg of SiO$_2$–SH/ED3A material pre-treated with a solution (25 mL) containing 80 μM of various metal species; desorption was made at a flow rate of 1.0 mL min^{-1} in a pH-gradient elution mode (see variation in pH values as a function of the elution volume in the inset). Metal species were Pb(II) (○), Co(II) (▼), Fe(III) (◇), Ni(II) (▲), Cu(II) (□), and Cr(VI) (adsorbed as Cr(III) species, ●).

started to desorb at very low pH values. For instance, at pH 1.6, more than 90% of chromium is still bonded to the adsorbent, when other metal species are desorbed at yields ranging from 50 to 100% (Fig. 6).

4. Conclusion

Adequately engineered bi-functional silica adsorbents, SiO$_2$–SH/ED3A, bearing one component designed to reduce toxic Cr(VI) (thiol groups in this case) and another one specifically selected for immobilizing the so-generated, yet less toxic, Cr(III) species (i.e., ethylenediaminetriacetate moieties), have proven to offer good performance for the efficient removal of chromium from aqueous medium, according to a reduction–sorption mechanism. Actually, the produced Cr(III) species can be sequestrated in the material via either complexation with the ethylenediaminetriacetate ligand (ED3A) or ion exchange/electrostatic interactions with sulfonic acid moieties generated concomitantly to Cr(VI) reduction by thiol groups. The strong chelate properties of ED3A toward Cr(III) species, however, gave rise to significant improvement (in terms of operational pH range, durable adsorbent capacity, and low residual chromium concentration in solution) in comparison to the former SiO$_2$–SH/SO$_3$H material suffering form weak interactions between Cr(III) and the sulfonic acid groups. This has been notably exploited here in dynamic mode (column experiments) for which the presence of ED3A groups was essential to immobilize the reduced Cr(III) species on the adsorbent, which were not retained by "simple" electrostatic interactions with sulfonate moieties. Cr(VI) reduction and subsequent Cr(III) uptake was also possible in the presence of other metal species and the immobilized Cr(III) was found to be more stable at lower pH values than the other metal ions. Finally, optical (UV–vis) and spectroscopic (XRF) techniques can be used to quantify the adsorbed species and to distinguish between the strong ED3A–Cr^{3+} complex and the weaker SO$_3$$^-$,Cr^{3+} ion pair on the solid.

Supplementary data available

Introductory and experimental details; various loadings of ED3A groups on SiO$_2$–ED3A; FTIR spectra of SiO$_2$–SH, SiO$_2$–SH/ED3A, and

SiO$_2$–ED3A; color and UV–vis diffuse spectra of SiO$_2$–SH/ED3A at various chromium contents; XRF analysis of chromium content in the adsorbent; effect of ionic strength.

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.jhazmat.2013.02.019.

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