

Efficient sequestration and reduction of hexavalent chromium with organosilica sol–gels

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Received 4th October 2004, Accepted 20th April 2005

First published as an Advance Article on the web 31st May 2005

DOI: 10.1039/b415365k

Sol–gel materials prepared from organically-modified silanes are used for sequestration and reduction of Cr(VI). These sol–gels act as matrices for sequestration and reduction of Cr(VI) as well as binding of Cr(III) ions in the porous structure. Acid treated sol–gels obtained from bis[3-(trimethoxysilyl)propyl]ethylenediamine (EnTMOS) and 3-mercaptopropyltrimethoxysilane (SHTMOS) sequester and reduce Cr(VI) from an external solution. The removal of Cr(VI) from solution was monitored spectrophotometrically and the sol–gels were characterized with FTIR and TEM. The amino and thiol groups in the hybrid sol–gels play a critical role and the gels containing both these functional groups are considerably more effective at removal of Cr(VI) than those containing just one of these functional groups. Finally, the pH of the medium is also found to be an important parameter in kinetics and efficiency of removal of Cr(VI).

Introduction

Chromium contamination of soil and groundwater is one of the significant environmental problems today. Chromium is believed to be the third most common pollutant at hazardous waste sites as well as the second common inorganic contaminant after lead.¹ Chromium compounds are routinely used in several industrial processes such as leather tanning, textile coloring processes, metal plating and alloying, wood treatment. Improper waste disposal techniques have contributed appreciably to chromium pollution. Consequently, development of new strategies or methods of converting toxic chromium wastes into nontoxic or less toxic compounds is critical in chromium remediation.

Among the different oxidation states of chromium, Cr(VI), which exists as CrO_4^{2-} ion in solution, is acutely toxic and a proven mutagen and carcinogen.² The structural similarity of CrO_4^{2-} to SO_4^{2-} makes it overcome the cellular permeability barrier, and oxidatively damage DNA due to production of more reactive transient Cr(V) and Cr(IV) species. The Cr(III) ion on the other hand has a high tendency to form strong complexes with soil minerals, which makes it less mobile and less available for biological intake, thereby making it less toxic. Hence, reduction of toxic Cr(VI) to less toxic Cr(III) is considered to be an important step towards overcoming chromium pollution.

There have been several studies on the methods and possible mechanisms of reduction of hexavalent chromium. It is generally known that Cr(III) forms various $\text{Cr}(\text{OH})_x$ species in the pH range from 3.8 to 11.5.³ Rajeshwar *et al.*,⁴ based on their studies on photocatalytic reduction of Cr(VI) on titania, suggest that in acidic pH, Cr(III) is more likely to occur as an ion and in basic pH as a neutral hydroxide species. Various reductants have been used so far for the reduction of Cr(VI)

including iron,⁵ H_2O_2 ,^{6,7} H_2S ⁸ and thiols.⁹ The process has also been studied with iron reducing bacteria.¹⁰

Another environmental cleanup approach has been to adsorb and thereby immobilize the toxic, heavy metal ions in porous materials. The materials used for such processes include activated carbon,¹¹ composite chitosan,¹² polypeptide biopolymers,¹³ surfactant-modified montmorillonite¹⁴ and silica.^{15–17} The process of selective adsorption of the metal ions can be brought about by introducing suitable functional groups in the adsorbing matrix. Mercury(II) ions are known to undergo preferential chelation with the thiol group¹⁶ while other metal ions like Cu^{2+} , Zn^{2+} , Cr^{3+} and Ni^{2+} show exceptional binding ability with the amino functionality.¹⁷

The present investigation involves developing thiol-/amino-functionalized porous hybrid sol–gels for efficient sequestration and reduction of toxic Cr(VI) to less toxic Cr(III). Sol–gel materials are porous silicates obtained by hydrolysis and condensation of alkoxy silanes. This route of preparing material is attractive because of the ease with which the matrix can be tailored for an application. The properties of the parent glass can be easily modified by judicious use of the functionally modified precursors. By using a combination of precursors with the required functional groups, it is possible to prepare porous materials with tunable chemical and/or physical properties. The porosity of the gels can be manipulated by the suitable choice of precursors and gels obtained from alkoxydisilane precursors containing long chain spacer unit possess large pores.¹⁸ Furthermore, these materials can also be designed to possess an optimum balance of hydrophobicity and hydrophilicity.¹⁹ Our earlier investigations on a highly porous and elastic sol–gel matrix, obtained by hydrolysis of bis[3-(trimethoxysilyl)propyl]ethylenediamine (EnTMOS) as precursor, show that the matrix is dynamically responsive to various stimuli including pH, surrounding ions in the medium, and temperature.^{19–22} The present study was carried out on the sol–gels obtained by hydrolysis of the EnTMOS precursor. The matrix was further modified by introducing thiol

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functionality through the use of 3-mercaptopropyltrimethoxysilane (SHTMOS) as precursor. The amino ligands from the EnTMOS precursor help in sequestration of dichromate ions at low pH while the thiol moieties help reduce Cr(VI) to Cr(III) ions which are in turn trapped into the matrix through chelation with amino ligands in the materials. As such, these hybrid sol–gels exhibit high affinity towards chromate sequestration, reduction, and localization of the Cr(III) ions within the matrix.

Experimental

Chemicals used in this study include bis[3-(trimethoxysilyl)propyl]ethylenediamine (EnTMOS) 62% in methanol (purchased from Gelest), 3-mercaptopropyltrimethoxysilane (SHTMOS) (purchased from Gelest), tetramethoxysilane (TMOS) (purchased from Acros, 99%), and potassium dichromate (purchased from Acros).

Preparation of gels

EnTMOS gel was prepared by mixing 1.44 ml of EnTMOS and 2.5 ml of H₂O. The sol obtained was clear and gave a gel in 2–3 minutes. EnTMOS-SH gel was prepared with 1.44 ml of EnTMOS, 0.75 ml of SHTMOS and 2.5 ml of H₂O. The sol resulted in a gel in 3 minutes. EnTMOS and EnTMOS-SH gels were aged for a day under ambient conditions. The aged gels were powdered using a mortar and pestle and treated with 25 ml of 0.5 M HCl for an hour. The acid treated gels were washed with large amounts of water to remove excess acid and used for dichromate sequestration and reduction. The acid treated gels in this study are referred to as EnTMOS/H⁺ and EnTMOS-SH/H⁺. The gels which no longer converted dichromate solution were partially reactivated by repeating the acid treatment with 25 ml of 0.5 M HCl for an hour (EnTMOS-SH/H⁺_{reactivated}). TMOS sol was prepared by sonicating a mixture of 3 ml TMOS, 0.8 ml H₂O, and 0.044 ml of 0.04 M HCl for 30 minutes. Acid treated TMOS-SH (TMOS-SH/H⁺) gels were prepared by mixing 1.75 ml of TMOS sol, 0.75 ml of SHTMOS, and 0.3 ml H₂O. The compositions of different sol–gel samples studied in this work are given in Table 1.

Analysis and characterization

Optical absorption spectra were measured on a Hewlett Packard model 8453 spectrophotometer. The wavelength at which the UV-Vis absorption peak of the dichromate appears

is very much dependent on both the concentration and the pH of the solution. Around pH 9, the peak is observed at 373 nm and, in the pH range 5–3, the peak appears around 350 nm.²³ The concentration of Cr(VI) was calculated using a calibration curve constructed with absorbance of standard solutions of concentrations in the range 2×10^{-4} M to 5×10^{-4} M. Prior to the spectral analysis, a blank spectrum was taken with a polystyrene cuvette filled with water. Depending on the activity of the sol–gels and the corresponding change in the absorbance, a measured aliquot of the test dichromate solution (from 0.225 to 1 ml) (0.01 M, 35 ml) was taken in the cuvette and diluted to 3.5 ml with water. However, the test solution was not diluted when the dichromate solution turned colorless and peak intensity was diminished. The number of moles of Cr(VI) removed was calculated as the difference in the number of moles of dichromate before and after treatment with the gel until the gel caused no further change in the dichromate solution. FTIR spectra of a weighed amount of thiol containing gels (5 mg) dispersed in KBr were taken on a Nicolet Magna IR 560 spectrophotometer. Weighed amounts (0.1 g) of powdered sol–gels were degassed at 200 °C and the multipoint BET surface area and pore size analysis were carried out on a Quantachrome Nova unit at 77 K.

Treatment of dichromate solution with sol–gels

For monitoring the sequestration and reduction, 35 ml of potassium dichromate (0.01 M) solution was taken in a beaker and the powdered gel (3.8 g) was added to it. The mixture was stirred with a stir bar on a magnetic stirrer. The pH of the dichromate solution was noted before and after addition of the gel with a Thermo Orion (model 230) pH meter. The filtrate was analyzed spectrophotometrically for Cr(VI) ions at regular intervals. The treatment was carried out with sequential treatment with 35 ml of dichromate solution batches until no further change in the absorbance was observed in the UV-Vis spectrum. The total amount of Cr(VI) was calculated based on the total combined Cr(VI) removed due to the sequential treatment. The various color changes during the sequestration and reduction of the Cr(VI) ions were also recorded photographically.

Results and discussion

Preparation of gels

The gels used in this study were selected so as to maximize sequestration and reduction of dichromate ions. The EnTMOS

Table 1 Sol–gel compositions, the precursors and the number of moles of the precursors and the post treatment of the sol–gels

Sol–gel	Precursors used	No. of mmoles of the precursor	Acid treatment of the sol–gels
EnTMOS	EnTMOS	2.1	—
EnTMOS/H ⁺	EnTMOS	2.1	HCl (0.5 M), 1 h
EnTMOS-SH	EnTMOS + SHTMOS	2.1 4.0	—
EnTMOS-SH/H ⁺	EnTMOS + SHTMOS	2.1 4.0	HCl (0.5 M), 1 h
EnTMOS-SH/H ⁺ _{reactivated}	EnTMOS + SHTMOS	2.1 4.0	HCl (0.5 M), 1 h
TMOS-SH/H ⁺	TMOS + SHTMOS	9.2 4.0	HCl (0.5 M), 1 h

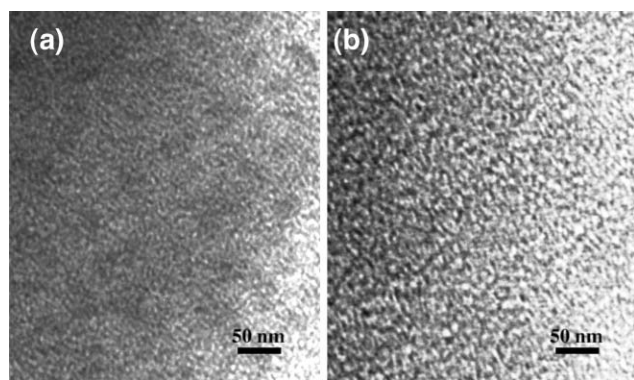


Fig. 1 TEM micrographs of (a) TMOS-SH, (b) EnTMOS-SH gels.

gels are characterized by enlarged porosity, increased diffusion of small molecules and sensitivity to pH. Additionally, the amino groups in the network provide a ligating environment for binding and chelation of the metal ions. The formation of the hybrid gels results in altered porosity as compared to pristine gels which is likely to facilitate diffusion of exogenous molecules. The hybrid gels are characterized by the presence of both thiol and amino functionalities which play a critical role in sequestration and reduction of dichromate ions. The gels were characterized by TEM (Fig. 1) which shows enlarged porosity for EnTMOS-SH gels as compared to TMOS-SH gels. In general, the pores of the TMOS-SH gels are on the order of 2.5–3.3 nm while the pores in EnTMOS-SH gels have diameters in the range 5.0–6.6 nm. Thus, the pores in EnTMOS-SH gels are roughly twice the size of those in TMOS-SH gels.

Sequestration of Cr(VI) ions

Addition of powdered EnTMOS gel (2.6 g) to the Cr(VI) solution (0.01 M, 35 ml) resulted in a change of pH of the medium from 4.5 to 10 (Table 2). This increase in pH is possibly due to the basic nature of EnTMOS sol–gels. The optical absorption spectra of the sample showed only a minimal change in the absorbance peak of Cr(VI). On the other hand, addition of EnTMOS/H⁺ gel to the Cr(VI) solution results in sequestration of the dichromate by the gels and a clear colorless filtrate was obtained within 7 minutes (Fig. 2).

The sequestration of the Cr(VI) is evident from the color change of the gel which turned from white to yellow in color. The sequestration of the negatively charged dichromate ions

when the EnTMOS gels are acidified indicates a mechanism based upon ion-exchange. The as-prepared EnTMOS gels are basic and protonation of amino groups makes the overall network positively charged which facilitates sequestration of the negatively charged dichromate ions. However, the absence of any changes in the optical absorption spectra indicates that the Cr(VI) ions retain their original identity and are not reduced. The rapid decay of the peak in optical absorption spectrum of the dichromate solution taken 7 minutes after the addition of the EnTMOS/H⁺ sol–gel indicates disappearance of the Cr(VI) species from the solution (Fig. 2d). The developed yellow coloration in the EnTMOS/H⁺ gel suggests simply sequestration of the chromate ions in the sol–gel matrix without reduction of the Cr(VI) species.

In order to confirm that the precursors formed a stable gel network and that there was no leaching of the EnTMOS or SHTMOS precursors from the gels under conditions of acidification and/or treatment with Cr(VI) solutions, the gels were treated with Co(II) ions. The changes in absorption spectra of the Co(II) ions can be effectively used to provide an estimate of whether there was any leaching of the amino- or thiol-functionalized sol–gel precursors. As shown in Fig. 3, the solution of Co(II) ions is characterized by an absorption peak at 510 nm. However, as shown in Fig. 3(a), when treated with EnTMOS precursor, a new peak appears at 647 nm and when treated with SHTMOS a new peak appears at 420 nm. These peaks can be used to confirm the absence of leaching under the experimental conditions employed in this study. The standard spectra (Fig. 3a) were obtained from a solution of CoCl₂ (1 ml) and 0.05 ml of EnTMOS (0.166 mmol) in 0.95 ml H₂O and a solution of CoCl₂ (1 ml) and 0.05 ml of SHTMOS (0.27 mmol) in 0.95 ml H₂O. As mentioned in the Experimental section, Preparation of gels, the powdered EnTMOS-SH gel was treated with 25 ml of 0.5 M HCl for an hour. After the treatment, the gel was filtered from the suspension and the filtrate was used for analysis of amine and thiol. The pH of the obtained filtrate was measured and was observed to be 6.7. The obtained EnTMOS-SH/H⁺ gel was further treated with the potassium dichromate solution (35 ml, 0.01 M). The colorless filtrate obtained after treatment of dichromate solution was also analyzed for the amine- and thiol-containing precursors.

For analysis, 1 ml of the filtrate was mixed with 1 ml of CoCl₂ (0.1 M). UV-Vis spectra of the as-prepared solutions were taken and compared to establish that the precursors were not leaching during treatment with Cr(VI). As shown in Fig. 3(b), the spectrum of Co(II) is unaltered when mixed in

Table 2 Characteristics of different sol–gel compositions for Cr(VI) sequestration and reduction

Sol–gel	Initial pH	pH after addition of sol–gel	Cr(VI) removed ^a / μmol	Rate of Cr(VI) removal/ (μmol min ⁻¹) ^b	Percentage Cr(VI) removed	Percentage efficiency ^c of sol–gel	Relative efficiency of sol–gels
EnTMOS	4.5	10	3.25	0.03	0.23	0.08	5.2 × 10 ⁻³
EnTMOS/H ⁺	4.5	2.8	100	3.75	7	2.5	0.16
EnTMOS-SH	4.5	9.9	37.7	0.3	2.69	0.9	0.03
EnTMOS-SH/H ⁺	4.5	4.2	1240	30	88.6	29.52	1
EnTMOS-SH/H ⁺ reactivated	4.5	4.7	770	29	55	18.33	0.62
TMOS-SH/H ⁺	4.5	4.38	5	0.03	0.36	0	8.4 × 10 ⁻³

^a Calculated until there was no further change in the Cr(VI) concentration. ^b Calculated for initial 30 minutes of the treatment. ^c Percent efficiency = [μmol of Cr(VI) removed/(μmol of NH)] × 100.

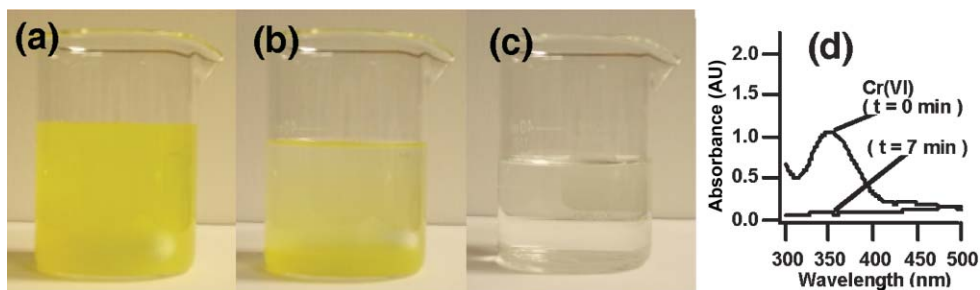


Fig. 2 Treatment of Cr(VI) (26.25 μmol) solution with EnTMOS/H⁺ gel: (a) immediately after addition of the gel (0 min), (b) after 7 min, (c) colorless filtrate after 7 min, (d) optical spectra showing changes in intensity of Cr(VI) peak, spectrum at $t = 0$ min taken with 4.82×10^{-5} M and at $t = 7$ min with 1×10^{-2} M Cr(VI) solution.

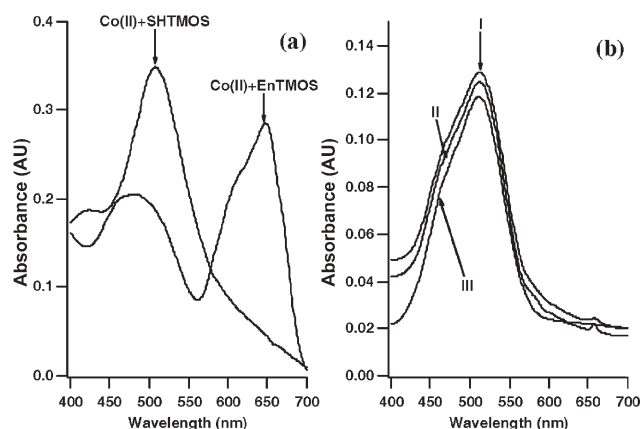


Fig. 3 Absorption spectra of Co(II) ions in the presence of precursors and filtrates. (a) Standard spectra of CoCl₂ (0.1 mmol) with EnTMOS (0.166 mmol) and with SHTMOS (0.27 mmol) in water. (b) Absorption spectra of CoCl₂ (0.1 mmol) in water (spectrum I), with filtrate after acid treatment (spectrum II), and with filtrate after dichromate treatment (spectrum III).

with the filtrate obtained after acidification as well as after treatment with Cr(VI). The results indicate that the precursors are forming a robust network and there is no leaching of the precursors. Furthermore, no leaching is observed from as-prepared, acid-treated and Cr(VI)-treated gels. Thus, it can be inferred that the functional groups are localized in the sol-gel matrix and the free diffusion of the precursors to the external environment is not possible.

Sequestration and reduction of Cr(VI) ions

The use of EnTMOS-SH gels results in sequestration as well as reduction of the Cr(VI) ions. The photographs of various stages in the treatment of Cr(VI) solution with EnTMOS-SH gel are shown in Fig. 4. The gels change their color from white to light olive green indicating formation of Cr(III) species. The gels completely absorb the dichromate ions and a clear filtrate of the external contact solution was obtained in about 38 minutes.

Addition of EnTMOS-SH gel caused a basic pH of 9.9 in the Cr(VI) solution (Table 2). The increase in pH is consistent with the basic nature of the gel and exchange of hydroxide ions with chromate anions. The absorption spectra of the sample taken at various time intervals show a gradual decrease in the peak corresponding to Cr(VI) at 370 nm (Fig. 4d). The greenish coloration developed in the sol-gel indicates the presence of Cr(III) in the gel matrix. EnTMOS-SH differs from the EnTMOS gel matrix by the presence of thiol functionality in the former. The introduction of the thiol groups in the EnTMOS gel matrix apparently brings about reduction of Cr(VI) to Cr(III).

Upon addition of the EnTMOS-SH/H⁺ gel, the pH of the Cr(VI) solution (4.5) remained almost unaltered (4.2). The acidification of the amino groups is expected to make the gels positively charged resulting in effective sequestration of dichromate ions. Fig. 5 shows the changes that take place in the Cr(VI) solution after the addition of the EnTMOS-SH/H⁺ gel. The gel turned red-brown on addition to the Cr(VI) solution within 3 minutes. The brown coloration slowly changed to green indicating formation of Cr(III) species. The

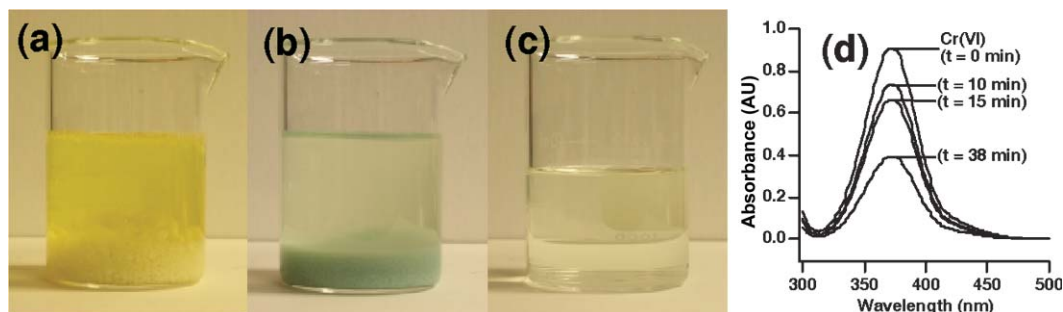


Fig. 4 Sequestration and reduction of Cr(VI) (26.25 μmoles) using EnTMOS-SH gel. (a) Cr(VI) solution immediately after addition of gel (0 min), (b) after 38 min, (c) filtrate after 38 min, (d) optical spectra showing changes in intensity of Cr(VI) peak, [Cr(VI)] = 1.75×10^{-4} M.

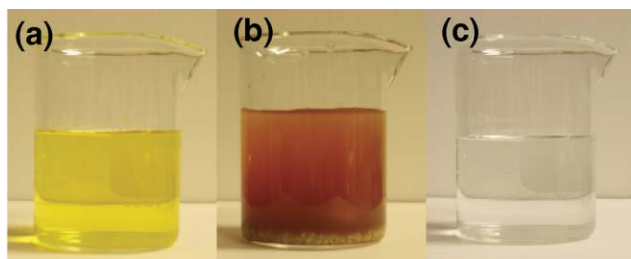


Fig. 5 Reduction of Cr(VI) (100 μ moles) using EnTMOS-SH/H⁺ gel: (a) dichromate solution, (b) after addition of gel (3 min), (c) colorless filtrate obtained after 3 min.

absorption spectra of the dichromate solution treated with EnTMOS-SH/H⁺ are shown in Fig. 6.

Table 2 gives the percentage of Cr(VI) removed from solution due to the treatment with the sol-gels. Sol-gels obtained with tetramethoxysilane (TMOS) precursor are known to possess smaller pores and as a result exhibit limited diffusion of external molecules. Low sequestration of the dichromate ions in the TMOS based sol-gels is possibly due to combined effects of the overall negative charge of the matrix as well as the restricted flow of the dichromate ions through the matrix due to the smaller pores. The sol-gels obtained with silanes containing a spacer group (such as EnTMOS) are known to yield matrices with bigger pores. Our earlier investigations on sol-gels obtained from EnTMOS precursor have shown them to be responsive to various stimuli like pH, other ions, temperature and solvents in the surrounding medium.^{19–22} In acidic medium, the amino groups of the ethylenediamine spacer group undergo protonation. The reduction of dichromate at basic pH is known to be a much slower process as compared to that in acidic pH.^{4,6} So the basic pH caused by the addition of EnTMOS and EnTMOS-SH gels to Cr(VI) solution may be a possible reason for the low conversion in EnTMOS and EnTMOS-SH gels. Additionally, the smaller pores of the TMOS-SH gels are also likely to contribute to the slower rate and low overall reduction.

In the case of EnTMOS-SH/H⁺ and EnTMOS/H⁺ gels a prior treatment with acid results in the protonation of the matrices. These gels are characterized by enlarged porosity as shown in Fig. 7 which shows TEM images of EnTMOS-SH/H⁺ gels before and after treatment with dichromate solution. The

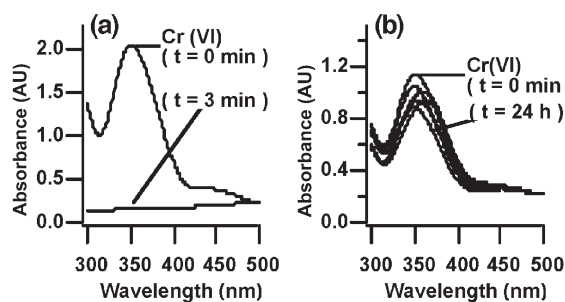


Fig. 6 Optical absorption spectra of dichromate solution taken at different time intervals containing (a) EnTMOS-SH/H⁺, spectrum at $t = 0$ min taken with solution 4.1×10^{-4} M and at $t = 3$ min with 1×10^{-2} M Cr(VI) solution, (b) TMOS-SH/H⁺, [Cr(VI)] = 4.82×10^{-5} M.

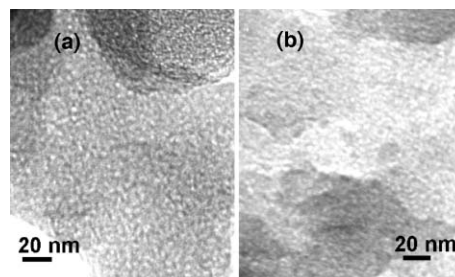


Fig. 7 TEM micrographs of (a) EnTMOS-SH/H⁺ gels, (b) after treatment with Cr(VI).

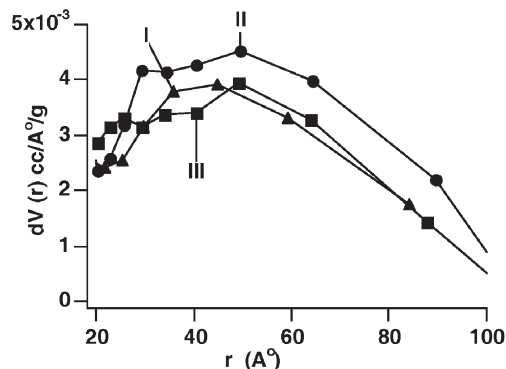


Fig. 8 Pore size distribution calculated by BJH method from desorption isotherms for EnTMOS-SH (trace I), EnTMOS-SH/H⁺ (trace II), and EnTMOS-SH/H⁺ after treatment with Cr(VI) (trace III).

results are further confirmed by BET surface area measurements (Fig. 8 and Table 3) which show increase in pore volume and surface area upon protonation of the matrix. When these sol-gels are added to the dichromate solution, they do not affect the pH of the solution. As a result, the pH of the dichromate solution is maintained at around 4, resulting in reduction of dichromate under acidic conditions. Further, the enlarged pores due to acid treatment, aid in easy inflow of the dichromate ions into the silica matrix increasing the accessibility to the thiol groups. EnTMOS-SH/H⁺ gel system brings about 30 times more change in the total Cr(VI) content at 100 times faster rate than EnTMOS-SH (Table 2). The chelation of the amino groups in the gel with the Cr(III) ions is likely to be an important factor in stabilization of Cr(III). Liu *et al*¹⁷ have reported exceptional binding ability of Cr(III) with the N moiety in the amino functionalized materials.

Interactions of organosilica sol-gels with Cr(VI) ions

The hybrid organosilica sol-gels exhibit electrostatic, redox, and acid–base interactions with Cr(VI) species thereby causing

Table 3 Multipoint BET surface areas, pore volumes and pore radii of organosilica sol-gels

Sample	Pore volume/cm ³ g _{N₂} ⁻¹ (STP)	Surface area/m ² g ⁻¹
EnTMOS-SH	0.25	111.34
EnTMOS-SH/H ⁺	0.31	155.22
EnTMOS-SH/H ⁺ after Cr(VI) treatment	0.26	146.36

sequestration and reduction of Cr(VI) and binding of the Cr(III) ions. The sequestration-only effect observed with the amino-functionalized EnTMOS gel system indicates that these gels mainly act as positively charged ion-exchange materials and interact electrostatically with the negatively charged Cr(VI) ions. The interaction is most likely due to exchange of Cr(VI) ions with hydroxide ions. This is consistent with the observed increase in pH of the external contact solution. On the other hand, the thiol-functionalized gels are able to reduce the Cr(VI) species.

Under the reaction conditions employed in our study, the Cr(VI) oxo species that can be found predominantly in the solution include $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- in the pH range 2–6 and CrO_4^{2-} at $\text{pH} > 6$.²⁴ These negatively charged ions can interact effectively with the positively charged EnTMOS matrix. Since only the spectra of the external contact solution could be recorded, the decrease in intensity of the dichromate peak in the optical absorption spectrum corresponds to depletion of dichromate ions from the external solution due to non-reductive sequestration as well as reductive conversion of dichromate to Cr(III). Consequently, the results provide a direct estimate of the effectiveness of the sol-gels toward removal of the toxic Cr(VI) from the external environment. Table 2 shows that percentage of Cr(VI) removed by treatment with different sol-gels. Acid treated EnTMOS-SH gels are most effective at removing Cr(VI). It is important to note that the sol-gels remove more Cr(VI) ions using the combined pathways of sequestration, reduction, and chelation than would be feasible with a single mechanism. Therefore, the gels containing both thiol and amino groups are considerably more effective at removal of Cr(VI) than those containing just one functional group. The reduction of Cr(VI) is presumably facilitated by thiol groups which are well-known reductants of chromates. In the presence of thiol moieties, the redox interaction can be represented as reduction of Cr(VI) to Cr(III) coupled with oxidation of thiol to disulfide. The oxidation of thiols is an established mechanism for conversion of toxic Cr(VI) to relatively benign Cr(III).^{24,25}

In order to validate the involvement of thiols in the reduction process, we studied the changes of the thiol moiety using FTIR spectroscopy, which provides critical information about changes of the S–H group. Fig. 9 gives FTIR spectra of thiol-containing EnTMOS-SH/H⁺ and TMOS-SH/H⁺ gels. The S–H bond stretching vibrations occur at 2600–2550 cm^{-1} . The transmittance of the peak at 2575 cm^{-1} decreases on the treatment of the Cr(VI) solution with the gel powder indicating

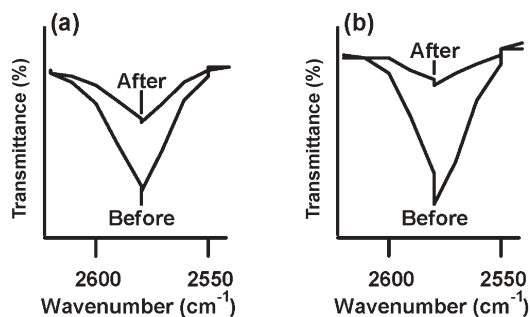


Fig. 9 FTIR spectra of (a) EnTMOS-SH/H⁺, (b) TMOS-SH/H⁺ gels before and after Cr(VI) treatment.

depletion of free S–H groups. Disappearance of the peak due to S–H protons of the sol-gels upon treatment with dichromate solution confirms the involvement of the thiol groups in the reduction process. Overall, the results are consistent with previously established mechanisms of chromate reduction by thiol containing species.^{24,25}

Taken together, the results support a mechanism for interactions of gels with Cr(VI) ions involving electrostatic sequestration followed by reductive conversion of Cr(VI) to Cr(III) and binding of the Cr(III) ions to the ligating matrix. The reduction of Cr(VI) possibly proceeds *via* formation of thioether linkage with Cr(VI) ions (or binding of thiol to oxochromium unit) as has been observed with glutathione (and cysteine) based systems. Such Cr^{VI}–SR species are relatively long-lived intermediates and are typically characterized by a reddish-brown color.²⁴ The formation of a reddish-brown intermediate in the EnTMOS-SH/H⁺ system lends some support to this mechanism. In the protonated system it is likely that the Cr^{VI} initially binds to the thiol group since the amino groups are protonated. Given the fact that Cr^{VI} is a hard acid and thiols are soft ligands such an interaction would be quite unfavorable when other ligating groups are available. Indeed, the intermediate is either very short lived or is not observed with gels which are not acid-treated and contain readily available amino groups for ligation. The oxidation/reduction reactions of thiols in porous silicate matrices have been well-characterized^{26,27} and the results suggest a possible role of thiols in reduction of Cr(VI). While the exact mechanism of participation of thiols remains to be established, the formation of green colored species upon treatment with Cr(VI) ions is a clear indication of formation of Cr(III) species as the end product. In any case, the enlarged pores of the acid-treated gels favor fast reduction of Cr(VI) ions through increased diffusion and binding of the network thiols to the Cr(VI) ions.

The Cr(III) ions formed upon reduction are chelated by the ligating amino groups in the matrix as observed by virtually no leakage of the green color to the external solution. While the gels turn completely green, there is no trace of color in the external solution. The EnTMOS-SH/H⁺ was found to be saturated after removing about 90% of Cr(VI) from the dichromate solution (Fig. 10a). This is likely due to congestion of pores due to formation of Cr(III)–amino complexes in the porous matrix, which slows diffusion and makes the thiol

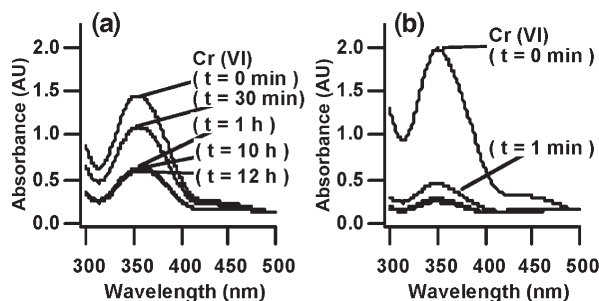


Fig. 10 Absorption spectra of dichromate solution taken at different time intervals: (a) saturated EnTMOS-SH/H⁺, spectra taken as saturation approached with $[\text{Cr(VI)}] = 4.1 \times 10^{-4} \text{ M}$, (b) reactivated EnTMOS-SH/H⁺, spectrum at $t = 0 \text{ min}$ taken with solution $4.1 \times 10^{-4} \text{ M}$ and at $t = 1 \text{ min}$ with $1 \times 10^{-2} \text{ M}$ Cr(VI) solution.

groups inaccessible. This observation to some extent is supported by the fact that such a saturated gel can be at least partially reactivated by treatment with 0.5 M HCl for an hour. During this acidification process some Cr(III) ions leach into the external solution as observed by the development of color in the contact solution. Similarly, the protonation of the amino groups possibly enlarges the pores resulting in accessibility of buried thiol sites necessary for reduction. The optical absorption spectra associated with treatment of Cr(VI) with the reactivated gel are shown in Fig. 10(b). After reactivation, the EnTMOS-SH/H⁺ gels could remove an additional 770 μmol of Cr(VI). The rate of change of Cr(VI) caused by EnTMOS-SH/H⁺ reactivated was found to be almost the same as the EnTMOS-SH/H⁺ gels (Table 2). The reactivation process refurbishes protons to the matrix thereby making the material more porous with improved accessibility to the thiol sites.

The relative efficiency of different sol–gels used in this study is listed in Table 2. The percentage efficiency of sol–gels is expressed as the ratio of moles of Cr(VI) removed to the total moles of functional groups (*i.e.* moles of NH groups) in the sol–gels. The results provide a direct estimate of the role of these groups in removal of Cr(VI). As can be seen, the acid treated EnTMOS-SH gels are the most effective at removal of Cr(VI) while as-prepared gels are not as effective. Similarly, as-prepared EnTMOS gels are not able to sequester Cr(VI) ions but upon acid-treatment these gels become moderately active at sequestration. Incorporation of thiol groups in EnTMOS-SH makes these gels slightly more effective. However, gels containing only the thiol groups (TMOS-SH) are relatively less effective due to smaller pores of the gel matrix even when acidified as well as due to the absence of amino groups in these materials necessary for electrostatic interaction with Cr(VI) ions. These gels do not exhibit sensitivity to pH and therefore the pore structure is not modified upon acid treatment. More importantly, gels containing both thiol and amino functional groups by themselves are not effective unless the pores are modified and activated through acid treatment. As such, the results suggest that the pH-regulated volume sensitivity of the EnTMOS-derived gels plays a critical role in the efficient removal of Cr(VI) ions. This is consistent with the significantly retarded ability of the TMOS-SH/H⁺ gel system toward removal of Cr(VI) ions. Thus, the combined influence of enlarged porosity, proton-dependent volume sensitivity, chelating effect due to amino groups, and the provision of redox equivalents by thiol groups confers on the hybrid EnTMOS-SH gel system particularly effective means for sequestration and reduction of Cr(VI) ions. While materials containing amino groups have been shown to be effective at adsorption of Cr(VI) anions,^{28,29} the additional incorporations of thiols in our system also provides a means for chemically transforming them to Cr(III). These gels therefore not only act as versatile materials for removal and environmental cleanup of toxic Cr(VI) species but also aid in converting it to a relatively benign and inert Cr(III) species.

Conclusions

Hybrid sol–gels containing amino and thiol groups are shown to be effective at removal of toxic Cr(VI) *via* sequestration in

the porous network followed by reduction. The Cr(III) ions formed as a result are trapped in the matrix *via* binding to the ligating groups of the matrix. Our study outlines a molecular design approach for organically-modified sol–gel matrices that can be tailored to serve as the environmental cleanup mops for Cr(VI) ions. The enlarged pores of the materials at low pH provide facile diffusion of ions from the external medium. The efficiency of the pH responsive gels can be easily modulated through variation of environmental pH. The dual action of electrostatic and redox interactions of Cr(VI) with the organosilica gels can be effectively used in environmental cleanup and remediation of toxic Cr(VI)–oxo anions. It is found that the action of sol–gels is due to a combined influence of enlarged porosity at low pH, electrostatic influence of amino groups, the reducing power of thiol groups, and the chelating effect of amino groups. These sol–gels reduce the chromate ions efficiently and trap them within the porous structure thereby providing a direct mechanism for cleanup of chromates. Finally, the approach outlined in this work provides technologically compatible and economically viable materials for removal as well as remediation of chromium-based toxic waste materials.

Acknowledgements

The authors wish to thank Dr Steve Schmitt for assistance with TEM measurements and Aniket Datar for help with taking photographs of the samples. We are also grateful to Prof. Tomasz Wiltowski, Dr Kanchan Mondal, and Debalina Dasgupta for their help and assistance with BET surface area measurements. Finally, we thank the Materials Technology Center at SIU for financial support of this work.

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