SPECIATION OF CHROMIUM IN WATERS VIA SOL-GEL PRECONCENTRATION PRIOR TO ATOMIC SPECTROMETRIC DETERMINATION

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ABSTRACT

SPECIATION OF CHROMIUM IN WATERS VIA SOL-GEL PRECONCENTRATION PRIOR TO ATOMIC SPECTROMETRIC DETERMINATION

Chromium occurs in natural samples in two relatively stable valence states, i.e. in the form of Cr(III) and Cr(VI) species. Their concentration in natural waters is usually very low, in the order of a few µg/L. This low concentration necessitates either the use of very sensitive analytical techniques or the application of suitable preconcentration methods prior to instrumental determination.

In the present study, a resin having immobilized mercapto or amino functional groups was prepared by reacting silica gel with 3-mercaptopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, L-glutamic acid dimethyl ester, aminophenol, aminothiophenol and aminobenzothiazol for the preconcentration of Cr(III) and Cr(VI) species in waters prior to their determination by flame atomic absorption spectrometry (FAAS). Characterization of the novel sorbents were performed using scanning electron microscopy (SEM/EDS), thermo gravimetric analysis (TGA) and elemental analysis. Among the sorbents synthesized, amino sol-gel and silica amino have been shown to be efficient in terms of sorption capacity. The applicability of the new sorbents for the preconcentration of Cr(III) and Cr(VI) species in waters was examined by batch method. After pH 4, silica amino could quantitatively sorb both Cr(III) and Cr(VI) whereas amino sol-gel sorbed only Cr(III). Effect of the amount of silica amino and amino sol-gel was examined at the optimum pH. The optimum amount of silica amino for quantitative sorption was found to be 0.1 g for 20.0 mL of 1.0 mg/L Cr(III) and Cr(VI) solutions whereas that of amino sol-gel was 0.05 g for 20.0 mL of 1.0 mg/L for both species. The effect of Cr(III) and Cr(VI) concentrations on amino sol-gel and silica amino were investigated at the initial concentrations of 1.0, 10.0, 25.0 and 50.0 mg/L. Elution was realized with 2.0 M HCl, and the percent recovery values changed between 60 and 80%.

ÖZET

ATOMİK SPEKTROMETRİK TAYİN ÖNCESİ
SOL-JEL ÖNDERİŞTİRME YARDIMIYLA
SULARDAKİ KROMUN TÜRLENMESİ

Krom doğal örneklerde iki kararlı yapıda, Cr(III) ve Cr(VI) formlarında, bulunur. Doğal sulardaki krom derişimi genellikle birkaç µg/L seviyesindedir. Bu düşük derişim ya yüksek duyarlığa sahip analitik teknikler kullanımını ya da enstrümental tayin basamağından önce uygun ön-deriştirme metotlarına başvurmayı gerektirir.

Bu çalışmada alevli atomik absorpsiyon spektrometri (FAAS) tayini öncesi silika jel ile 3-merkaptopropiltrimetoksisilan, 3-aminopropiltrimetoksisilan, L-glutamic asit dimetil ester, aminofenol, aminotiofenol ve aminobenzotiazol tepkimeye sokularak, yüzeyinde merkapto veya amino fonksiyonel grupları bulunan bir reçine hazırlanmıştır. Sentezlenen tutucu yüzeyin karakterizasyonu taramalı elektron mikroskobu (SEM/EDS), termal gravimetrik analiz (TGA) ve elemental analiz metotları ile yapılmıştır. Sentezlenen sorbentler arasında silika amino ve amino sol-jelin en yüksek tutma kapasitesine sahip olduğu gözlenmiştir. Adsorbanın çeşitli çözeltilerdeki Cr(III) and Cr(VI) türlerinin ön-deriştirilmesi çalışmalarına uygunluğu kesikli (batch) metot tutturma deneyleri ile test edilmiştir. pH 4'ten sonra silika aminonun Cr(III) ve Cr(VI) formlarının her ikisini, amino sol-jelin ise sadece Cr(III)'ü tuttuğu gözlenmiştir. Silika amino ve amino sol-jel miktarının tutunmaya etkisi optimum pH'de incelendi ve 0.05 g. amino sol-jelin 20 mL 1.0 mg/L Cr(III) ve Cr(VI) çözeltisi için % 100 tutunma sağladığı belirlendi. Aynı deney silika amino ile tekrarlandı ve gerekli miktar 0.1 g. olarak bulundu. Amino sol-jel ve silika aminonun Cr(III) ve Cr(VI)'nın başlangıç derişimlerinden ne şekilde etkilendiği, 1.0, 10.0, 25.0 and 50.0 mg/L standart çözeltilerle incelendi. Eluent olarak 2.0 M HCl kullanıldı ve geri kazanım değerlerinin % 60 ile 80 arasında değiştiği saptandı.

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CHAPTER 1

INTRODUCTION

Speciation analysis can be described as a measurement process, which gives quantitative and qualitative information on the chemical forms of an element in various samples. Speciation analysis mostly involves two steps; separation and determination. Differentiation is realized between oxidation states, simple and coordinated ions, cationic, neutral and anionic forms, protonated and unprotonated, monomeric and polymeric species.

Chromium speciation has been an important task in recent decades due to extensive use of this metal in various industries such as metallurgical (steel, ferro- and nonferrous alloys), refractories (chrome and chrome-magnesite) and chemical (pigments, electroplating, tanning and other). Chromium compounds are discharged in liquid, solid, and gaseous wastes into the environment and can have adverse biological and ecological effects (Kotas and Stasicka 2000).

There are two common oxidation states of chromium present in the environment, Cr(III) and Cr(VI). These two forms show different chemical, physicochemical and biochemical reactivity. Cr(VI) compounds are known to be more soluble, mobile and bioavailable than Cr(III) species. Because of these differences in chemistry, biochemistry, physicochemistry of Cr(III) and Cr(VI) species, determination of total Cr concentrations in a variety of samples does not give the necessary information to evaluate the effects of species.

When the concentration of Cr species is very low, they may undergo alteration during sample handling and analysis, especially in preconcentration procedures. Atomic spectrometric detection, both alone or coupled with other techniques to preconcentrate and separate the two main chromium species, Cr(III) and Cr(VI), is the most widely employed methodology reported in the literature (De la Guardia and Morales-Rubio 2003). Although the determination of chromium is directly possible with sufficient sensitivity by analytical techniques such as ICP-MS etc., separation/preconcentration methods may still be needed for matrix removal.

In this context, the aim of this thesis is to develop a suitable sorbent for the matrix separation/preconcentration purposes in the speciation and determination of chromium by atomic spectrometric techniques.

1.1. Chromium Chemistry

Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek chroma, "color"). Because its compounds are found in many different colors. Chromium is the Earth's 21st most abundant element and the sixth most abundant transition metal (Mohan and Pittman 2006). It has four stable isotopes: ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr with relative abundance of 4.31, 83.76, 9.55 and 2.38%, respectively (De la Guardia and Morales-Rubio 2003).

Chromium can exist in several chemical forms displaying oxidation numbers from 0 to 6. Metallic chromium (chromium 0) can mainly be found in alloys, such as stainless steel and in chrome-plated objects. It is used as materials with new properties, such as a resistance to corrosion, wear, temperature and decay, strength, hardness, permanence, hygiene and color.

Cr(III) in natural waters is in hydrolyzed $Cr(H_2O)_4OH^+_2$ form and complexes, and even adsorbed on colloidal matter. Cr(III) is an essential element in mammalian metabolism. In addition to insulin, it is used to reduce blood glucose levels and control certain cases of diabetes. It is also responsible for reducing blood cholesterol levels by diminishing the concentration of low density lipoproteins "LDLs" in the blood. (Anderson 1989, Mohan and Pittman 2006). Nieboer and Jusys developed an hypothesis that supports the tolerance factor (CrGTF) containing Cr(III), nicotinic acid, glycine, glutamic acid, and cysteine. Cr(III) is also used in a number of commercial products, including dyes, paint pigments and salts for leather tanning.

Cr(VI) is a strong oxidizing agent and shows chronic toxic effects including carcinogenic property and it induces dermatitis. Occupational exposure to Cr(VI) compounds leads to a variety of clinical problems. Inhalation and retention of Cr(VI)-containing materials has been reported to cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion (Gad 1989, Lee et al. 1989). A

significant concentration of Cr(III) can cause adverse effects, because its high capability to coordinate various organic compounds results in inhibition of some metallo-enzyme systems. Cr(III) is used in textile (printing, dying), tannery and industrial processes (chrome plating) (Gomez and Callao 2006). Cr(VI) dominates in wastewater from the metallurgical industry, metal finishing industry (Cr hard plating), refractory industry and production or application of pigments (chromate colour pigments and corrosion inhibition pigments) (Nriagu 1988).

Cr(III) and Cr(VI) are stable enough to occur in the environment. Cr(IV) and Cr(V) form only unstable intermediates in reactions of trivalent and hexavalent oxidation states with oxidizing and reducing agents, respectively. The Cr(III) oxidation state is the most stable (Figure 1.1). Energy would be required to convert it to lower or higher states. The negative standard potential (E^o) of the Cr(III)/Cr(II) metal ion couple signifies that Cr(II) is readily oxidized to Cr(III), and Cr(II) species are stable only in the absence of any oxidant (Kotas and Stasicka 2000). The reduction potential of Cr(II) is -0.91V and that of Cr(III) is -0.74 V (De la Guardia and Morales-Rubio 2003).
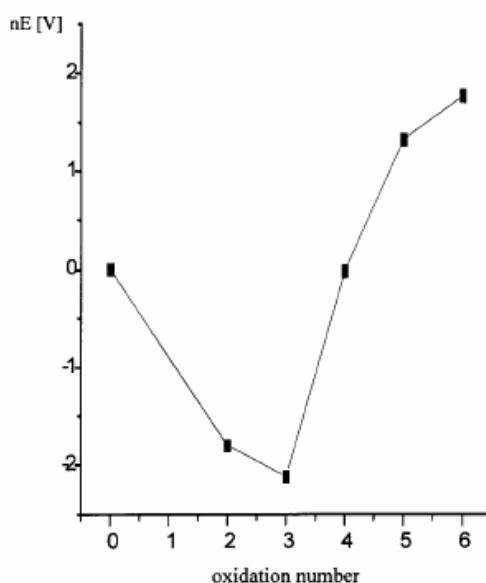
Figure 1.1. The Frost diagram for chromium species in acidic solution
(Source: Shriver et al. 1994).

In acidic solution Cr(VI) demonstrates a very high positive redox potential (E^o within 1.33 and 1.38 V, Figure 1.2) (Greenwood and Earnshaw 1984, Shriver et al.

1994, Ball and Nordstrom 1998) which denotes that it is strongly oxidizing and unstable in the presence of electron donors. As the $HCrO_4^-$ reduction is accompanied by the H^+ consumption (Reaction 1), decrease in acidity decreases the formal potential (Figure 1.2). The reduction potential of hydrogen chromate ion to Cr(III) is 1.35 V in strong oxidizer acidic medium. In more basic solution the reduction of CrO_4^{2-} (Reaction 2), generates OH^- against a gradient (Nieboer and Jusys 1988). The reduction potential of chromate to Cr(III) hydroxide is -0.13 V in basic medium.

$$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad (1)$$

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3 + 5OH^- \qquad (2)$$
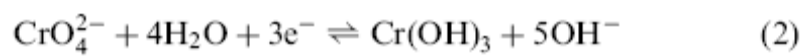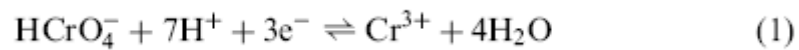
The equlibrium data, different oxidation states and chemical forms have been showed in specified Eh and pH ranges by Pourbaix diagram (Figure 1.2.). The solid and dissolved species is associated with the dissolution of chromium in water. All of the known species containing Cr, O and H exist in equilibrium with water at atmospheric pressure. The +2 ,+3, +4 and +6 valence states of chromium are known to exist at equilibrium in water. The concentration of total chromium is 10^{-8} M.
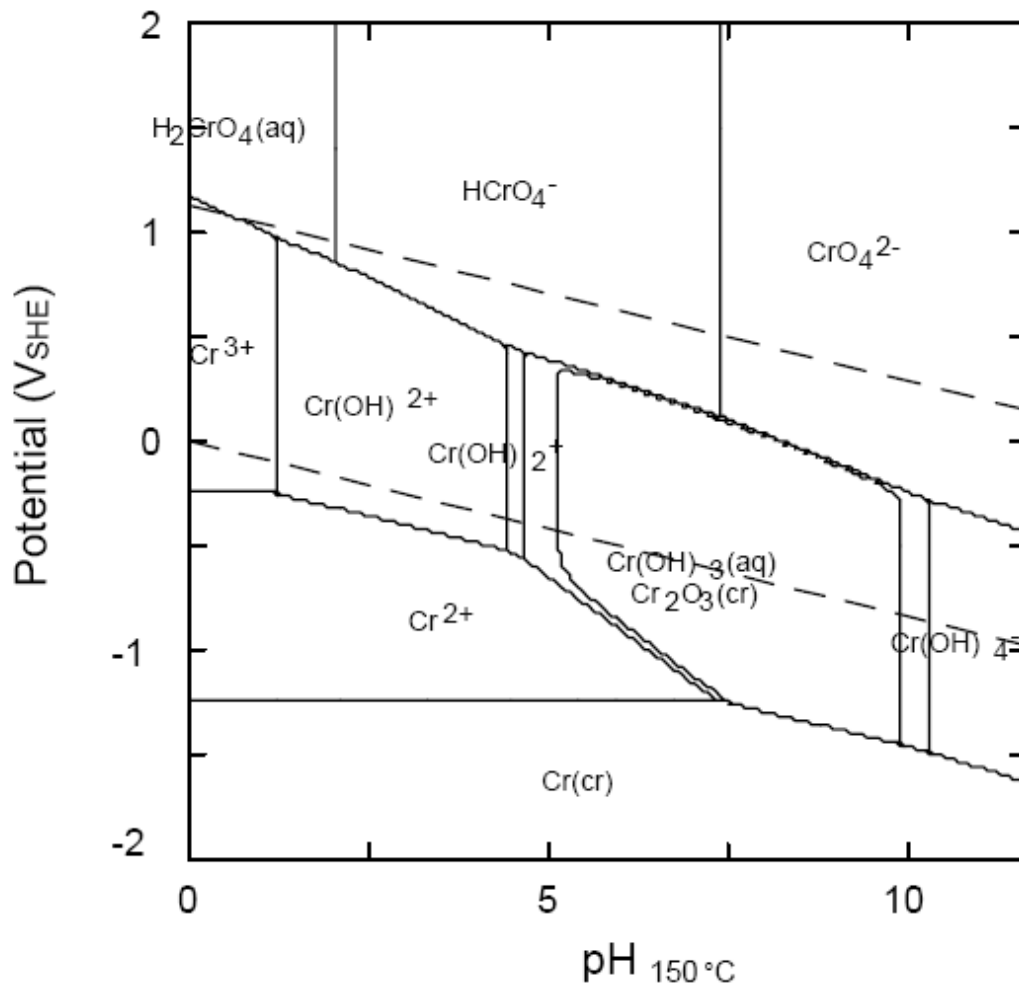
Figure 1.2. A simplified Pourbaix diagram for chromium species at 150 °C and $[Cr(aq)]_{tot}=10^{-8}$ (Source: Ball and Nordstrom 1998, Richard and Bourg 1991, Nieboer and Jusys 1988).

1.1.1. Chromium Speciation

1.1.1.1. Cr(III)

Cr(III) presence, concentration and forms in the environment depend on different chemical and physical processes, such as hydrolysis, complexation, redox reactions and adsorption. In the absence of complexing agents, Cr(III) was suggested to exist as hexa-aquachromium (3+) and its hydrolysis products (Figure 1.3).

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(OH)(H_2O)_5^{2+} + H_3O^+ \qquad (3)$$

$$Cr(OH)(H_2O)_5^{2+} + H_2O \rightleftharpoons Cr(OH)_2(H_2O)_4^+ + H_3O^+$$

$$(4)$$

$$Cr(OH)_2(H_2O)_4^+ + H_2O \rightleftharpoons Cr(OH)_3 \cdot aq + H_3O^+ \qquad (5)$$
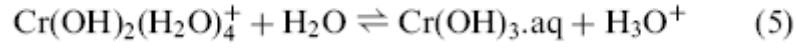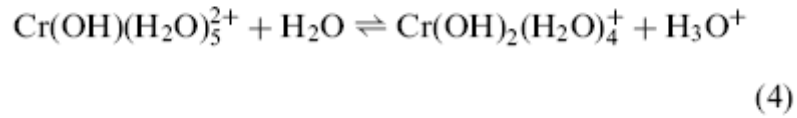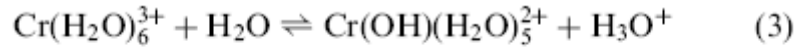
$Cr(H_2O)_6^{3+}$ is a moderately strong acid (pK ~4) (Reaction 3) and its deprotonated forms formulated shortly as $CrOH^{2+}aq$, $Cr(OH)_2^+aq$ and $Cr(OH)_3aq$ are dominating successively within pH 4-10. Trihydroxochromium is sparingly soluble within a pH range of 5.5-12 (minimum between pH 6.5 and 11.5; Richard and Bourg 1991, Ball and Nordstrom 1998), and overlaps considerably the pH range of natural waters (Figure 1.3.). Dominant forms of Cr(III) are the hydroxo complexes, $Cr(OH)_2^+aq$ and $Cr(OH)_3aq$ in the environment.

$Cr(OH)_3aq$ shows amphoteric behaviour. At higher pH, it is transformed into the soluble tetrahydroxo complex, $Cr(OH)_4^-$ [pK=15.4 or 18.3].

$$Cr(OH)_3(s) + 2H_2O \rightleftharpoons Cr(OH)_4^- + H_3O^+ \qquad (6)$$
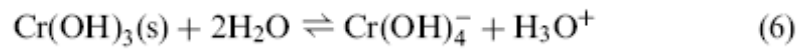
At more concentrated Cr(III) solutions ($>10^{-6}$ M) the polynuclear hydrolytic products, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, $Cr_4(OH)_6^{6+}$, could also be expected (Kotas and Stasicka 2000).
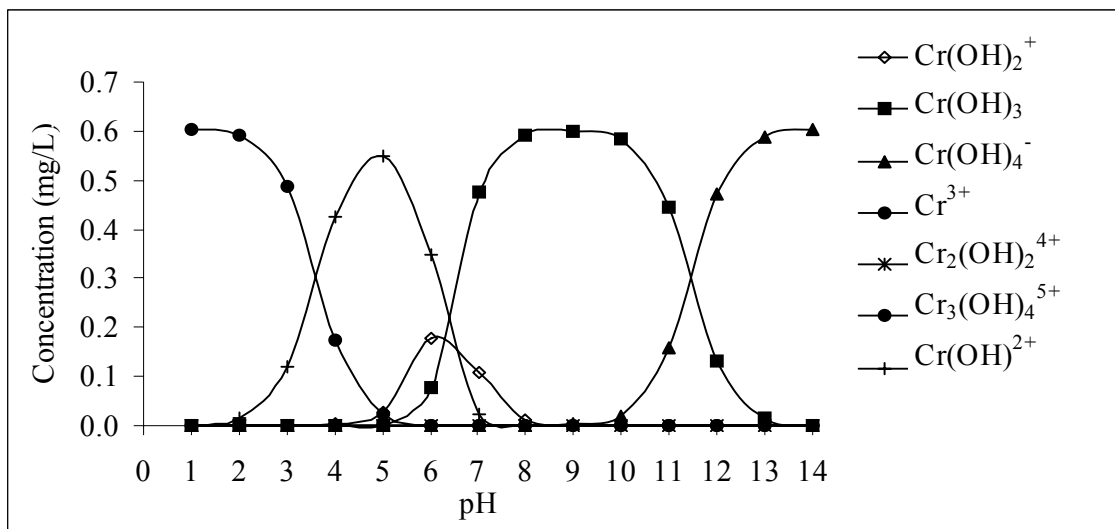
Figure 1.3. Cr(III) speciation as a function of pH (ionic strength of about 0.01 M and Cr(III)$_{conc.}$= 1.0 mg/L) (Source: visual MINTEQ program).

1.1.1.2. Cr(VI)

Cr(VI) can form several species, namely Cr(VI) is found as CrO_4^{2-}, $HCrO_4^-$ or $Cr_2O_7^{2-}$, depending on both pH of the medium and total Cr(VI) concentration. The dependence on pH is illustrated in Figure 1.4. H_2CrO_4 is the strong acid (Sperling et al. 1992a). At pH>1 deprotonated forms of Cr(VI) is seen. Above pH 7 only CrO_4^{2-} ions exist in solution through out the concentration range. In the pH between 1 and 6, $HCrO_4^-$ is predominant (Cotton and Wilkinson 1980, Greenwood and Earnshaw 1984, Nieboer and Jusys 1988).

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K_7 = 10^{-0.75} \qquad (7)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad K_8 = 10^{-6.45} \qquad (8)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K = 10^{2.2} \qquad (9)$$
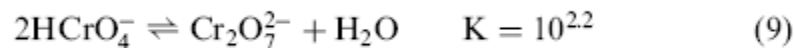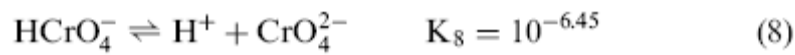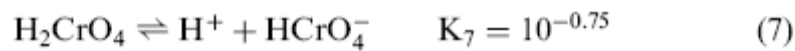
Cr(VI) compounds are quite soluble, and thus, mobile in the environment. However, Cr(VI) oxyanions are readily reduced to trivalent forms by electron donors such as organic matter or reduced inorganic species, which are ubiquitous in soil, water and atmospheric systems (Stollenwerk and Grove 1985).
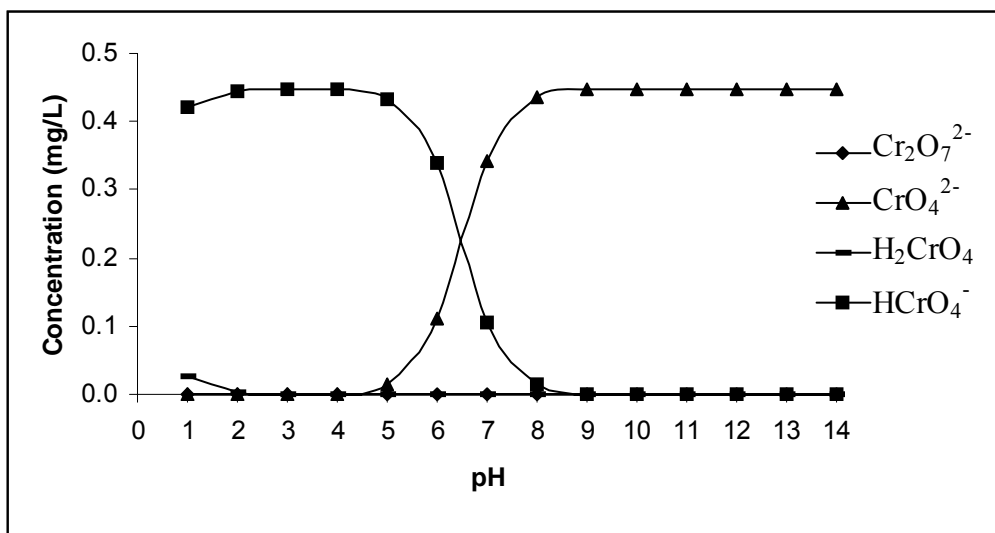
Figure 1.4. Cr(VI) speciation as a function of pH (ionic strength of about 0.01 M and Cr(VI)$_{conc.}$= 1.0 mg/L) (Source: visual MINTEQ program).

1.2. Environmental Distribution of Chromium

1.2.1 Water

As mentioned before, chromium exists in its two stable oxidation states including Cr(III) and Cr(VI) in natural waters. The presence and ratio between these two forms is dependent on chemical and photochemical redox transformation, precipitation/dissolution and adsorption/desorption reactions.

Cr(III) should be the only form under anoxic or suboxic conditions. Cr(III) species are stable at pH$\leq$6, whereas at pH$\geq$7 the CrO_4^{2-} ions should predominate in oxygenated aqueous solutions (Campanella 1996). At intermediate pH values, the Cr(III)/Cr(VI) ratio depends on O_2 concentration. In oxygenated surface waters, pH, O_2 concentration, the presence and concentration of reducers and complexing agents is important for the occurrence of significant Cr(III) quantities (Pettine et al. 1991, Kieber and Helz 1992). The predominant species is sometimes important for it. At the same time, Cr(III) is easily oxidized to Cr(VI) in the presence of manganese oxides under the conditions prevalent in natural waters (Pettine and Millero 1990, Johnson and Xyla 1991, Richard and Bourg 1991).

Cr(III) forms many different complexes with naturally occurring organic compounds, such as amino, fulvic, humic and other acids. Aqua/hydroxo complexes of Cr(III) speciation are dominant in surface waters (Kaczynski and Kieber 1994, Masscheleyn et al. 1992). In natural waters, the complexation decreases commonly the Cr(OH)$_3$aq precipitation in the pH conditions (Figure 1.2). But Cr(III) is immobilized by macromolecular compounds and thus removed from the solution in most of these complexes. Moreover, aqua/hydroxo Cr(III) complexes is strongly adsorbed by solids (Masscheleyn et al. 1992). It decreases Cr(III) mobility and bioavailability in waters.

Aqua/hydroxo complexes of Cr(III) speciation are so easily oxidized than Cr(III) complexes with organic ligands. Therefore Cr(III) is better stabilized by ligands other than H_2O and/or OH$^-$. Cr(VI) species are only weakly sorbed to inorganic surfaces. It is also the most mobile form of Cr in the environment.

Cr forms in wastewater have quite different nature and behaviour from those present in natural waters. Because physicochemical conditions of the wastes vary about various industrial sources. The presence and concentration of Cr forms depend mainly

on the Cr compounds applied in the technological process, on pH and on organic and/or inorganic wastes coming from the material processing. Cr forms with various inorganic and organic ligands is determined by effecting their pH value, solubility, sorption and redox reactions. The poorly soluble $Cr(OH)_3aq$ should be predominant under acidic or neutral pH conditions in wastewater. However, a high content of organic matter is effected in soluble organic Cr(III) complexes (Stein and Schwedt 1994, Walsh and O'Holloran 1996a, b).

1.2.2. Soil

In natural soils, chromium is the main source. The average amount of chromium in various kinds of soils ranges from 0.02 to 58 μmol/g (Coleman 1988, Richard and Bourg 1991).

In soils, chromium is present mostly as insoluble $Cr(OH)_3aq$ or as Cr(III). The dominant chromium form is dependent strongly on pH; in acidic soils (pH<4) it is $Cr(H_2O)_6^{3+}$, whereas at pH<5.5 it is its hydrolysis products, mainly $Cr(OH)^{2+}aq$ (Ritchie and Sposito 1995). Macromolecular clay compounds can easily adsorb both of these forms.

Cr(VI) is present mostly in soluble such as Na_2CrO_4 in neutral to alkaline soils. $CaCrO_4$, $BaCrO_4$ and $PbCrO_4$ are examples of moderately soluble chromates (James 1996). A dominant form of Cr(VI) in more acidic soils (pH<6) is suggested to be $HCrO_4^-$.

The most mobile forms of chromium in soils are CrO_4^{2-} and $HCrO_4^-$ ions. They can be taken up by plants and easily leached out into the deeper soil layers, thus, leading to ground and surface water pollution (Calder 1988 and Handa 1988).

Cr(VI) is reduced to Cr(III) in reduction reactions, or Cr(III) is oxidized to Cr(VI) in oxidation reactions. The pH, oxygen concentration, the presence and concentration of reducers are important in these processes (Figure 1.5). James and Bartlett suggested that Cr(VI) mobile forms that are $HCrO_4^-$ and CrO_4^{2-}, can be reduced by different inorganic reducers such as Fe(II) or S^{2-} (James and Bartlett 1998) This process called `dechromification' is quite important. In the absence of such a process, all atmospheric oxygen could be converted into chromate(VI) which would pose a threat to life on earth (James and Bartlett 1988).
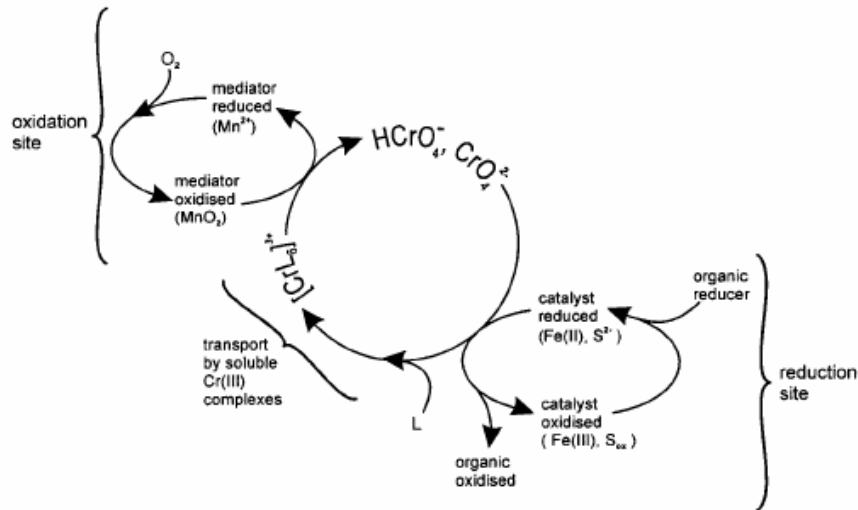
Figure 1.5. The chromium oxidation-reduction cycle in soils
(Source: James and Bartlett 1988, James 1996).

1.2.3. Atmosphere

Chromium in the atmosphere has been reviewed by Seigneur and Constantinou (1995). According to the authors, most of it originates from anthropogenic sources which account to 60-70% of its total abundance. Chromium also originates from natural sources which account for the remaining 30-40%. The main human activities involving chromium include metallurgical industries, refractory brick production, electroplating, combustion of fuels and production of chromium chemicals, mainly chromates and dichromates, pigments, chromium trioxide and chromium salts. The other potential sources of atmospheric chromium are of less importance such as the cement industry, production of phosphoric acid in a thermal process and combustion of refuse and sludge (Nriagu et al. 1988). The main natural sources are volcanic eruptions and erosion of soils and rocks. Other less important natural sources of chromium include airborne sea salt particles and smoke from forest wildfires (Pacyna and Nriagu 1988).

The concentrations of chromium (5-13 pg/m^3) are observed as the lowest over the South Pole. Average atmospheric concentrations of this metal are higher. The range of chromium is observed from 1 ng/m^3 in rural to 10 ng/m^3 in polluted urban areas (Nriagu et al. 1988). The amount of chromium is dependent on the intensity of industrial processes, proximity to the sources, the amount of chromium released and meteorological factors.

1.3. Methods for Chromium Determination

Chromium speciation is very important in different branches of natural sciences. Therefore, total chromium measurements alone cannot determine the actual environmental impact. This requires speciation techniques with sufficient selectivity and high sensitivity.

The determination of chromium at trace level usually requires separation and/or preconcentration stages prior to instrumental determinations (Balarama Krishna et al. 2005). Although chromium ions can be directly determined in water using sensitive analytical techniques, such as ETAAS or ICP-MS; flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are preferred for their low cost and economic use (Duran et al. 2007).

Figure 1.6. shows the mostly used pretreatments for speciation of chromium. The most frequent pretreatments used are complex formation (about 38%) and preconcentration by column/ionic exchange (about 23%). About 14% of the pretreatments are based on oxidation-reduction reactions that can convert Cr(III) to Cr(VI) and vice versa to determine the total chromium in one of these forms. In some cases, one species and total chromium are determined together and the other species is calculated by the difference between the two. Only 3% of the pretreatments are determined by digestion and separation processes, because in liquid samples the species are usually solubilized.
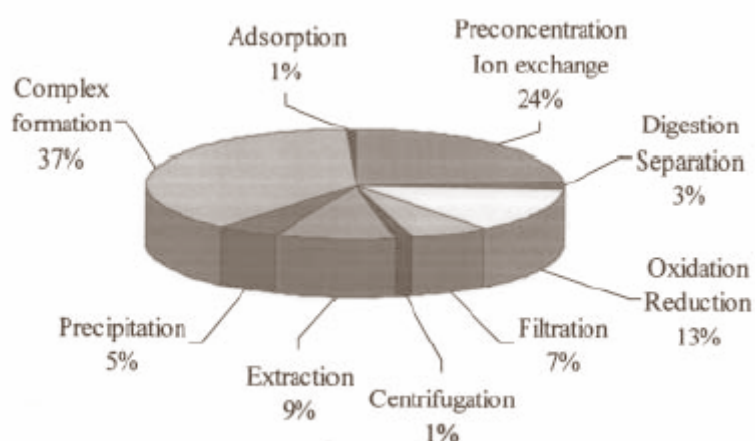
Figure 1.6. Pretreatment methods used for the speciation of chromium
(Source: Marqués et al. 2000).

All the techniques employed to determine Cr(VI) and/or Cr(III) are summarized in Figure 1.7. The most frequently used techniques are atomic spectrometric techniques in the form of either flame or furnace AAS (23%), inductively coupled plasma atomic emission spectrometry (2.5%) or different hyphenated techniques (9%). Other techniques such as UV-VIS spectrometry (33%) or chromatographic techniques (11%) have also often been used to determine these chromium species. Each technique has its limitations, but inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the well-established technique with good sensitivity, low detection limits and rapid sample analysis. Inductively coupled plasma mass spectrometry (ICP-MS) is used when more sensitive determinations are required.
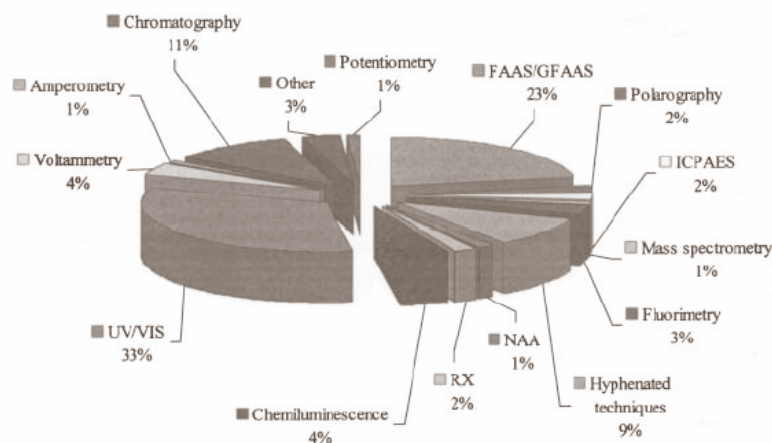
Figure 1.7. Techniques employed in the determination of Cr(VI) and/or Cr(III)
(Source: Marqués et al. 2000).

1.3.1. Spectrophotometric Methods

Spectrophotometric methods can be used for routine determination of the different chromium species using reagents in order to form absorbing species that present selectivity in the response. The most common method for determining Cr(VI) in aqueous solutions is based on the reaction of diphenylcarbazide (DPC) with Cr(VI) at a pH of 1.0 ± 0.3. As stated by many researchers, diphenylcarbazide (DPC) is an inexpensive and very sensitive color reaction with Cr(VI) in acid solution and Cr(III)-

diphenylcarbozone complex presents (Tunçeli and Türker 2002, Gomez 2006, Andersen 1998).

1.3.2. Atomic Spectrometric Methods

FAAS or ETAAS are the most commonly used techniques in the determination of chromium traces, the low level of chromium concentration in parenteral solutions is not compatible with the detection limit of FAAS. The LODs can range from ng/L to µg/L. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of analyte elements in the sample are too low to be determined directly by FAAS. On the other hand, FAAS is widely applied in routine laboratories due to its lower cost and greater simplicity as compared with ETAAS. LOD value range is 0.8-200 ng/mL for Cr(VI) and 0.2-80 ng/mL for Cr(III) in FAAS.

1.3.3. Plasma–Source Methods

Most commercial plasma source instruments use an argon ICP as in inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). In plasma source instruments, liquid samples are employed. Solid samples are decomposed and solubilized prior to introduction to the plasma by a proper nebulization device. ICP-MS achieves more lower LOD value than ICP-OES. LOD value range is 0.06 and 5.5 ng/mL for Cr(VI) and 0.06 and 0.3 ng/mL in ICP-MS. It is 0.2 and 61 ng/mL for Cr(VI) and 1.4 and 45 ng/mL for Cr(III) in ICP-OES (De la Guardia and Morales-Rubio 2003).

1.4. Synthesis of New Sorbent for Chromium Speciation

There are studies on chromium determination using various sorbents like 5-palmitoyl oxine-functionalized XAD-2 resin (Filik et al. 2003), Amberlite XAD-7 resin impregnated with Aliquat 336 (Saha et al. 2004), a XAD sorbent derivatized with shellac (Yalçın and Apak 2006), 4-(2-Thiazolylazo)-resorcinol (TAR) and Amberlite

XAD-16 (Wuilloud et al. 2006), 1,5-diphenylcarbazone complex on amberlite XAD-16 resin (Tunçeli and Türker 2002), Amberlite XAD-2010 (Bulut et al. 2006), a maleic acid-functionalized XAD sorbent (Yalçın and Apak 2004), Means of Melamine-Urea-Formaldehyde Resin (Demirata 2001), on Chromotrope 2R coated Amberlite XAD-1180 (2R-1180) resin (Saracoğlu et al. 2002), Ambersorb 563 resin (Narin et al. 2006), Dowex 50W-X8 resin loaded with 2-amino-benzenethiol (Veni et al. 2006), *Saccharomyces cerevisiae* immobilized on sepiolite (Bag et al. 2000), on *Bacillus sphaericus* loaded diaion SP-850 resin (Tüzen et al. 2006), and chitin, chitosan, ion exchanger; Purolite CT-275 (Purolite I), Purolite MN-500 (Purolite II) and Amberlite XAD-7 (Baran et al. 2003).

The adsorption of trace elements onto stationary phase has proved to be a valuable separation preconcentration techniques because of very high concentration factors compraed to other techniques. Silica-gel is used as an adsorbent and as a supporting material various chelating agents. Because of its ion-exchange property, the low acidity of silanol groups and the less pronounced donor properties of the surface oxygen, interaction between most of the metal ions and the silica-gel surface is rather weak. Therefore, the use of unmodified silica for this purpose is not popular. Instead, silica-gel is modified with organofunctional groups.

There are several organic functional groups modified silica gel surface in preconcentration studies. For example, Ekinci and Köklü used 3-aminopropyltriethoxy-silane modified silica-gel for the separation and preconcentration of V, Ag, Mn and Pb prior to their determination by GFAAS. Hassanien et al. functionalised with aminopropyltrimethoxysilane obtaining the aminopropyl silica gel (APSG). The APSG was reacted subsequently with morin yielding morin-bonded silica gel (morin-APSG) for separation and preconcentration of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) from aqueous medium. The obtained silica was subjected to surface modification using N-2-(aminoethyl)-3-aminopropyltrimethoxysilane in order to increase adsorptive properties of the silica surface (Jesionowski 2003). Volkan and Ataman developed a mercapto modified silica-gel for pre-concentration of arsenite from natural waters. Körez et al. developed speciation and preconcentration method utilising a mercapto modified silica microcolumn for determination of trace amounts of inorganic tellerium in waters by hydride generation atomic absorption spectrometry. Göktürk et al. determined ultra-trace amounts of germanium on mercapto modified silica-gel by using hydride generation flame atomic absorption spectrometry (HGAAS). Alcântara et al. used 2-

mercaptobenzimidazole (MBI) modified a silica gel surface by homogeneous and heterogeneous routes in removing Hg(II) from aqueous media. P´erez-Quintanilla et al. used 2-mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media. Shiraishi et al. investigated the extraction and separation of transition metals using several inorganic adsorbents modified with ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) as chelating ligands. Pu et al. prepared 2-mercaptobenzothiazole modified silica-gel for flow injection on-line preconcentration separation of silver by flame atomic absorption spectrometry. Safavi et al. used directly silica bonded analytical reagents: synthesis of 2-mercaptobenzo-thiazole silica gel and its application as a new sorbent for preconcentration and determination of silver ion using solid-phase extraction method. Evangelista et al. described hexagonal mesoporous silica modified with 2-mercaptothiazoline for removing mercury from water solution. Jamali et al. prepared thiophene-2-carbaldehyde modified mesoporous silica as a new sorbent for separation and preconcentration of palladium prior to inductively coupled plasma atomic emission spectrometric determination. In other work, chemically modified silica gel with aminothioamido-anthraquinone was used for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II) (Ngeontae et al. 2007). Macarovscha et al. applied silica modified with zirconium oxide for on-line determination of inorganic arsenic using a hydride generation-atomic absorption system. Maltez and Carasek used zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silica surface using a flow system for chromium speciation and preconcentration.

1.4.1. Surface Modificiation of Silica Surface

Modification of silica surface relates to all the processes that change in chemical composition of the surface. Surface can be modified either by physical treatment that leads to change in ratio of silanol and siloxane concentration of the silica surface or by chemical treatment that leads to change in chemical characteristics of silica surface. The adsorption properties are significantly affected by the modification.

The systematic use of immobilization of organofunctional groups has increased in recent years, mainly on silica, because this support offers pronounced advantages over other organic/inorganic supports, such as high surface area, a narrow average pore size distribution, mechanical resistance, and rigidity.

Silica gel surface can be modified by two distinct processes organo-functionalization, where the modifying agent is an organic group, and inorgano-functionalization, in which the group anchored on the surface can be an organometallic composite or a metallic oxide (Jal et al. 2004).

1.4.2. Amino/Mercapto Modified Sol-gel

The chemical modification of the silica gel surface is a well-known and convenient method for combining silica gel with an organic molecule. Among the more promising highly developed surfaces are the silica attached organosilanes which are widely used in various technologies. Amino/mercapto functional group attached to silica is used in order to increase the chemical (mainly adsorptive) reactivity of the silica. Speciation and preconcentration of chromium with amino/mercapto modified silica gel surface (Sil-NH$_2$)/(Sil-SH) in aqueous solutions was investigated prior to their determination by flame atomic absorption spectrometry.

1.5. The Aim of this Work

One of the goals of this study was to investigate speciation of Cr(III) and Cr(VI) in waters via sol-gel preconcentration prior to Atomic Spectrometric determination. Firstly, a suitable sorbent surface for preconcentration of Cr(III) and Cr(VI) is investigated.

The other goal was to develop a suitable sorbent surface for pre-concentration of Cr(III) and Cr(VI) containing water samples. For this purpose an inorganic support material, like our synthesized sol-gel and commercial silica-gel, was functionalized with 3-mercaptopropyltriethoxysilane, 3-aminopropyltriethoxysilane, L-glutamic acid dimethyl ester, 2-aminobenzothiazole, 2-aminothiophenol and 2-aminophenol. The newly synthesized materials were characterized by SEM/EDS, TGA, and elemental analysis.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Reagents

All reagents were of analytical grade. Ultra pure water (18 MΩ) was used throughout the study. Glassware and plasticware were cleaned by soaking in 10% (v/v) nitric acid and rinsed with distilled water prior to use.

1. Standard Cr(III) stock solution (1000 mg/L): Prepared by dissolving 1.924 g of chromium nitrate ($Cr(NO_3)_3.9H_2O$) (Merck, Germany) in 250 mL ultra pure water and acidified with 1% (v/v) HNO_3 (Merck, Germany).

2. Standard Cr(VI) stock solution (1000 mg/L): Prepared by dissolving 0.7072 g of potassium dichromate ($K_2Cr_2O_7$) (Merck, Germany) in 250 mL ultra pure water and acidified with 1% (v/v) HNO_3 (Merck, Germany).

3. Calibration standards: Lower concentration standards were prepared daily from their stock standard solutions.

4. pH adjustment: NH_3 (Merck) (0.1-1.0 M) and HNO_3 (Merck) (0.1-1.0 M) were used.

5. Silica-gel: (60 mesh; Merck) was used in the preparation of functional group modified silica.

6. 3-mercaptopropyltrimethoxysilane (Fluka) and 3-aminopropyltrimethoxysilane (Fluka) were used as the functional groups modified silica-gel.

7. 3-Chloropropyltriethoxysilane 97% (Alfa Aesar) was used for chloro functionalization of silica-gel.

8. Dry Toluene (Merck, Germany), Diethyl ether (Merck, Germany), extra pure Toluene (Merck, Germany) were used as solvents

2.2. Instrumentation and Apparatus

2.2.1. Apparatus

In sorption studies with batch method, Yellowline OS 10 basic orbital shaker was used to provide efficient mixing. The pH values were measured with InoLab Level 1 pH meter supplied with a combined electrode.

2.2.2. Flame Atomic Absorption Spectrometry (FAAS)

An atomic absorption spectrometer, Thermo Elemental Solaar M6 Series with air acetylene/nitrous oxide burner was applied for the measurements throughout the study using chromium hollow cathode lamp with a maximum current of 10 mA at the wavelengths of 357.9 nm. A deuterium (D_2) hollow cathode lamp was used for background correction and the monochromator slit was kept at 0.5 nm.

2.2.3. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

A Varian Liberty Series II Axial view ICP-OES instrument was operated with plasma gas flow rate of 15 L/min, incident power of 1.2 kW and auxiliary gas flow rate of 1.5 L/min. Continuous nebulization was realized by means of a concentric glass nebulizer with cyclonic chamber. The sampling flow rate was 1.0 mL/min. The wavelengths, namely, 267.716 and 357.869 nm were employed in the measurements.

2.2.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Chromium determination was made with Agilent 7500 ICP-MS. The data were collected by monitoring m/z 53, and m/z 54 using peak jump mode. The instrument was operated with coolant gas flow rate of 15 L/min, auxiliary gas flow rate of 0.90 L/min forward power of 1.2 kW, reflected power of 1W, sample uptake time of 25 sec. and integration time of 100 msec.

2.3. Synthesis of the New Sorbents for Chromium Speciation

2.3.1. Synthesis of Sol-gel

25.0 mL TEOS, 27.0 mL ethanol and 8.0 mL H_2O were mixed immediately. After adjusting the pH to 4.5 with 2.10^{-4} M HCl, the mixture was stirred 30 minutes. Then, it was allowed to gel at room temperature for 3 days in a closed container. It was dried to constant weight at 60 °C for approximately one week. After drying, the glasses were crushed in a porcelain cup (Eroğlu T. 1996).

2.3.2. Synthesis of Amino Sol-Gel Resin

25.0 mL TEOS, 27.0 mL ethanol and 8.0 mL H_2O was mixed immediately. After adjusting the pH 4.5 with 2.10^{-4} M HCl, 2750 µL 3-aminopropyltrimethoxysilane was added drop by drop. The rest was the same as described in section 2.3.1.

2.3.3. Synthesis of 3-Aminopropyltrimethoxysilane Modified Silica-Gel (Silica-amino)

A 5.0 g of silica-gel was washed in 100 mL of 0.01 M acetic acid under vacuum for 10 min. to wet its pores. After washing, the silica-gel was filtered from a suction pump and placed into 25.0 mL of toluene solution. Then 3.0 mL of 3-aminopropyltrimethoxysilane was added dropwise by vigorous magnetic stirring to prevent self polymerization (Göktürk et al. 2000). About 0.15 mL of concentrated acetic acid was added dropwise such that a 0.1 M solution was obtained in toluene. The mixture was stirred overnight. Then, 0.15 mL portion of acetic acid was added dropwise and mixture was refluxed at approximately 60 °C for 2 h with magnetic stirring. Finally, samples were filtered using a vacuum pump and washed well with toluene before being left overnight in an oven at 80 °C. The proposed functionalization reaction way is illustrated in Figure 2.1.

Figure 2.1. Schematic illustration of modification on the silica-gel with 3-aminopropyl-trimethoxysilane.

2.3.4. Synthesis of 3-Mercaptopropyltrimethoxysilane Modified Silica –Gel (Silica-mercapto)

A 5.0 g of silica-gel was washed in 100 mL of 0.01 M acetic acid under vacuum for 10 min. to wet the pores of it. After washing, the silica-gel was filtered through a suction pump and placed into 25.0 mL of toluene solution. Then 3.0 mL of 3-mercapto-propyltrimethoxysilane was added dropwise to prevent self polymerization by vigorous magnetic stirring (Göktürk et al. 2000). The rest was the same as describe in section 2.3.3. The proposed functionalization reaction way is illustrated in Figure 2.2.
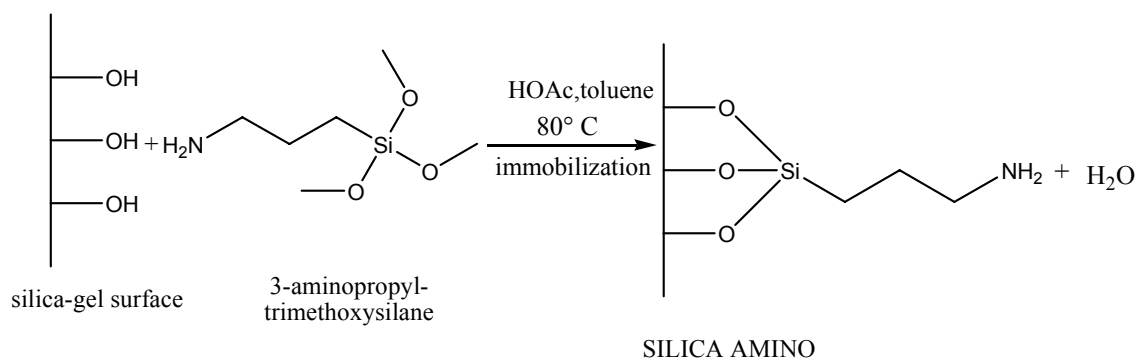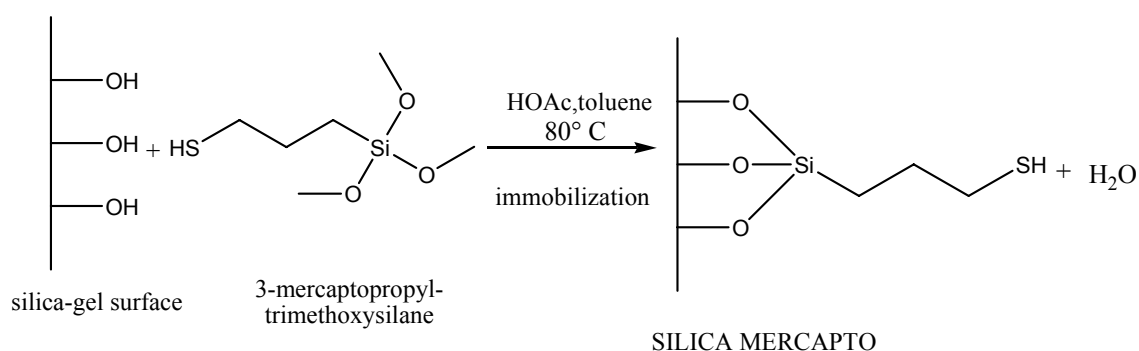

Figure 2.2. Schematic illustration of modification on the silica-gel with 3-mercapto-propyltrimethoxysilane.

2.3.5. Synthesis of 3-Mercaptopropyltrimethoxysilane Modified Sol-Gel (Sol-gel mercapto)

A 5.0 g of synthesized sol-gel was washed in 100 mL of 0.01 M acetic acid under vacuum for 10 min. to wet its pores. After washing, the synthesized sol-gel was filtered through a suction pump and placed into 25.0 mL of toluene solution. Then 3.0 mL of 3-mercaptopropyltrimethoxysilane was added dropwise by vigorous magnetic stirring to prevent self polymerization (Göktürk et al. 2000). The rest was the same as described in section 2.3.3.

2.3.6. Synthesis of L-glutamic Acid Dimethyl Ester Modified Silica-Gel (Silica-aminoacid)

A 5.0 g of silica-gel was activated at 160 °C under vacuum for 5 h. The activated mesoporous silica was suspended in 50.0 mL of dry toluene and 5.0 mL (20.76 mmol) of 3-chloropropyltriethoxysilane (CPTS) were added. The mixture was stirred for 48 h at about 100 °C under reflux and in N_2 atmosphere. The resulting product (Si-Cl) was filtered off and washed with ethanol (2×30 mL), diethyl ether (2×30 mL) and dry toluene (2×30 mL). The product was evaporated for 4 h at 70 °C in 150 mbar, and then immersed in 50 mL of dry toluene. After dissolving L-glutamic acid dimethyl ester, it was added to the mixture.

To dissolve L-glutamic acid dimethyl ester, 4.83 g (22.84 mmol) of L-glutamic acid dimethyl ester hydrochloride and 4.25 g of Na_2CO_3 were dissolved in 40 mL water. Then the mixture was extracted for three times with 30 mL ethylacetate to separate organic phase. The organic phase was washed with 40 mL of brine solution (NaCl). It was dried with $MgSO_4$. The solvent (EtOAc) was removed under vacuum. Thus L-glutamic acid dimethyl ester was prepared from its HCl salt.

The mixture of chloride functionalized silica with dissolved L-glutamic acid dimethyl ester was stirred for 11 h at room temperature under a nitrogen atmosphere and then at 80 °C for an additional 18 h. The resulting modified silica (silica-aminoacid) was filtered off and washed with toluene (2×30 mL), ethanol (2×30 mL) and diethyl

ether (2×30 mL). Finally, the resulting product was concentrated under vacuum. (Pérez-Quintanilla et al. 2006). The proposed functionalization reaction way is illustrated in Figure 2.3.
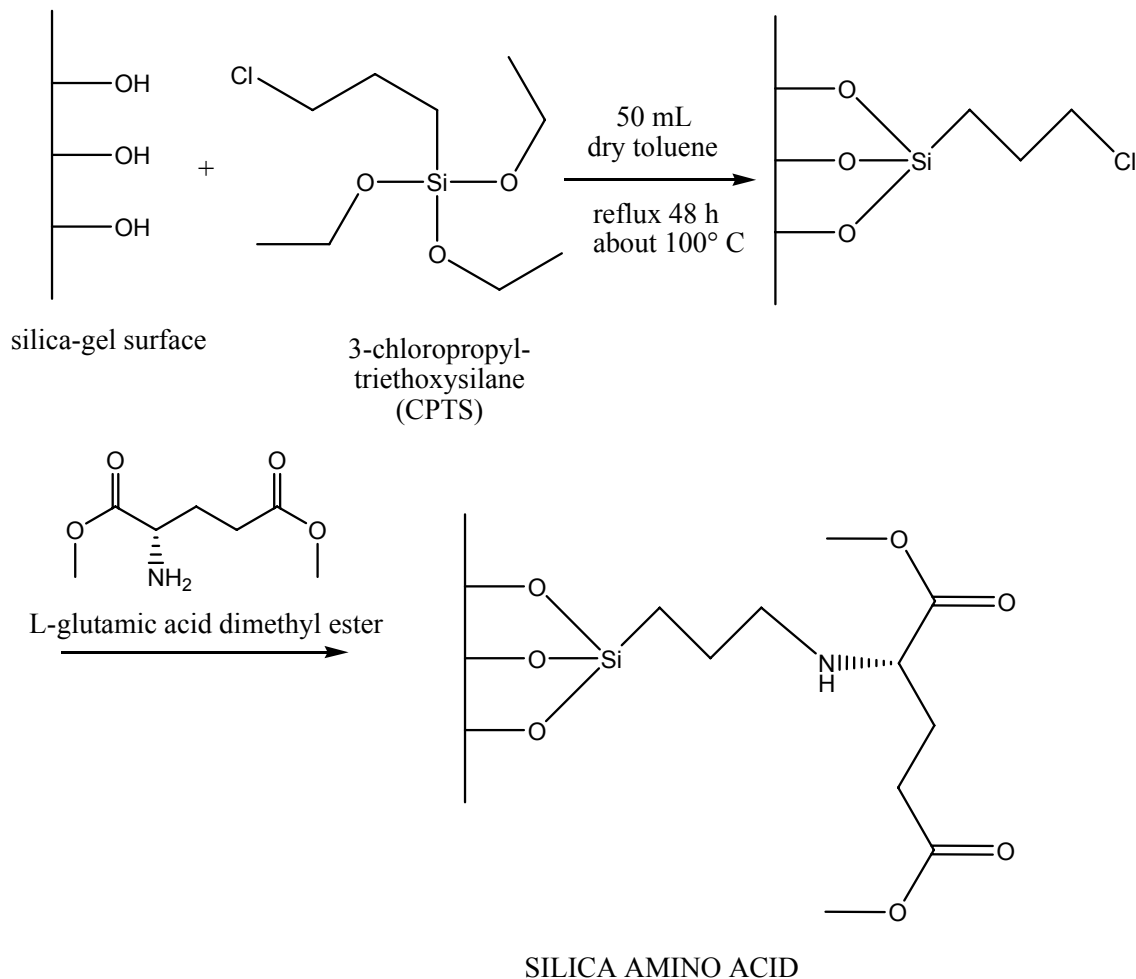
Figure 2.3. Schematic illustration of modification on the silica-gel with dissolved L-glutamic acid dimethyl ester.

2.3.7. Synthesis of 2-aminobenzothiazole, 2-aminothiophenol and 2-aminophenol Modified Silica-Gel

As described in section 2.3.6., silica-gel was chlorinated by using 10.0 g of silica-gel and 10 mL of CPTS. Then, obtained silica chloride is divided to three parts. 3.5 g of the obtained silica chloride was taken and then immersed in 35.0 mL of dry toluene. 2.40 g of 2-aminobenzothiazole was added and the mixture stirred for 39 h

under reflux conditions under N_2 atmosphere (about 110 °C). The resulting product (Silica 2-aminobenzothiazole) with a white colour was filtered off and washed with toluene, ethanol and diethyl ether until a colourless washing solution was obtained. Finally, the resulting product was dried for 4 h at 70 ^{0}C in 150 mbar.

The other two parts of obtained silica chloride was used for modification of silica gel with 2-aminothiophenol and 2-aminophenol. In each case 3.5 g of silica chloride was taken and the same procedure was followed as described above. (1.71 mL (15.99 mmol) of 2-aminothiophenol or 1.74 g of 2-aminophenol was added instead of 2-aminobenzothiazole) The resulting product obtained with 2-aminothiophenol (Silica 2-aminothiophenol) was yellow whereas the other product with 2-aminophenol (Silica 2-aminophenol) had a red colour. The proposed functionalization reaction ways are illustrated in Figure 2.4-2.6.

SILICA 2-AMINOBENZOTHIAZOLE
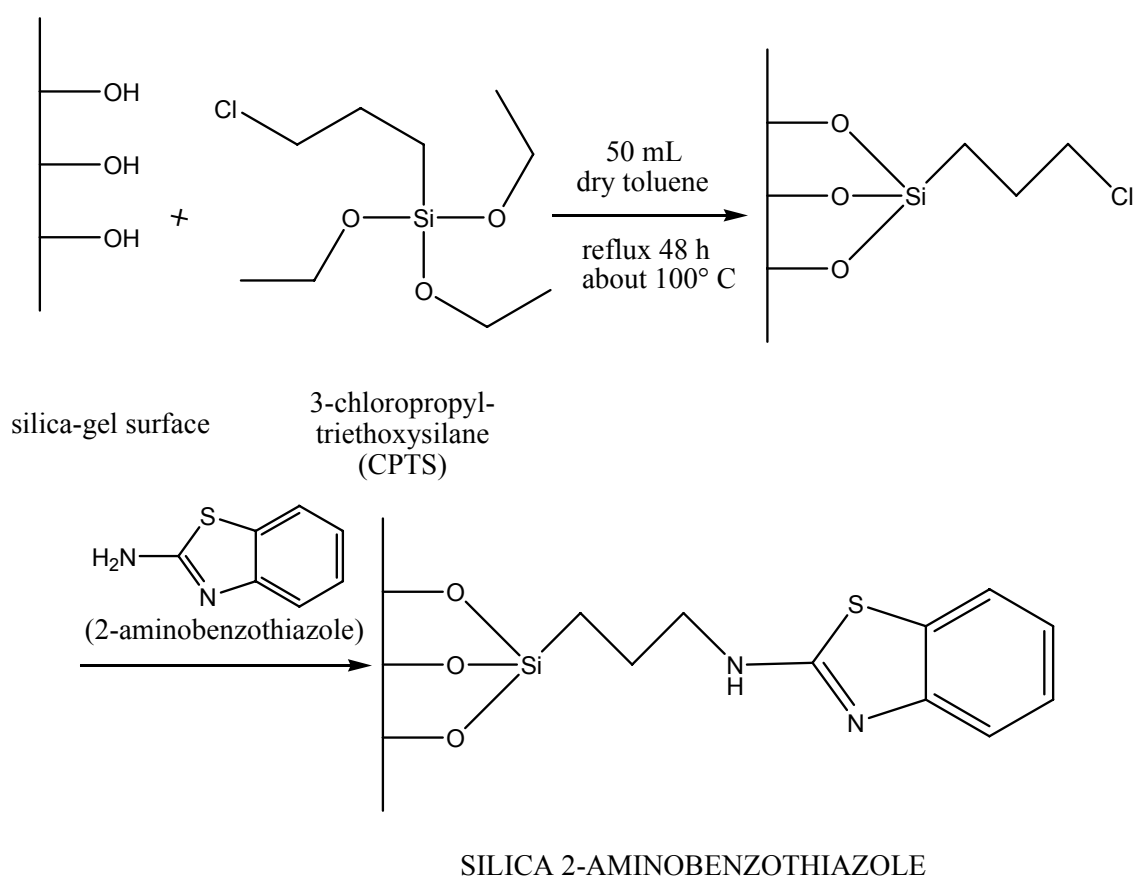
Figure 2.4. Schematic illustration of modification on the silica-gel with 2-amino-
benzothiazole.
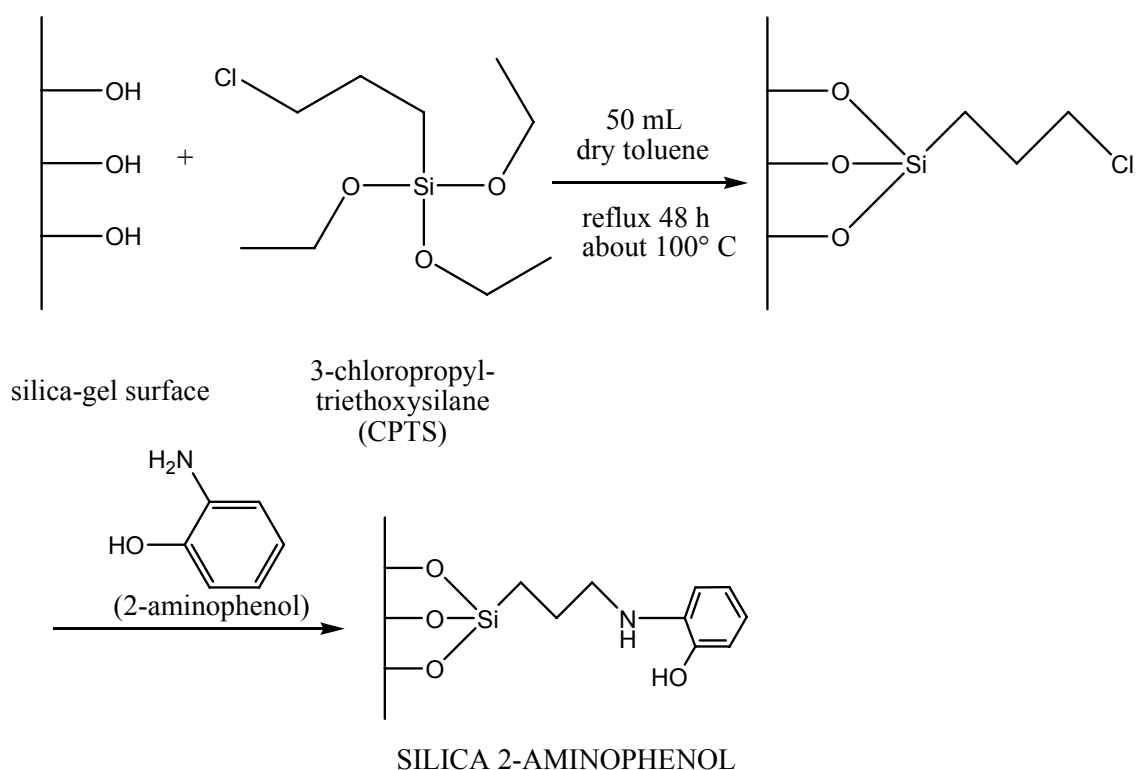
Figure 2.5. Schematic illustration of modification on the silica-gel with 2-aminophenol.

2.4. Characterization of the Synthesized Sorbent

Firstly, a number of characterization experiments were performed to test the success of modification procedure; that is whether the functional groups were attached to the sol-gel produced. Characterization of the sorbents was carried out by using Scanning Electron Microscopy (SEM/EDS), Thermo Gravimetric Analysis (TGA) and elemental analysis.

In addition to the characterization experiments mentioned above, the sorption behaviour of the novel sorbents gave valuable information about the modification of the silica-gel and synthesized sol-gel. If the functional groups ($-SH$ or $-NH_2$) had not been attached to the support, it would not have shown any sorption.
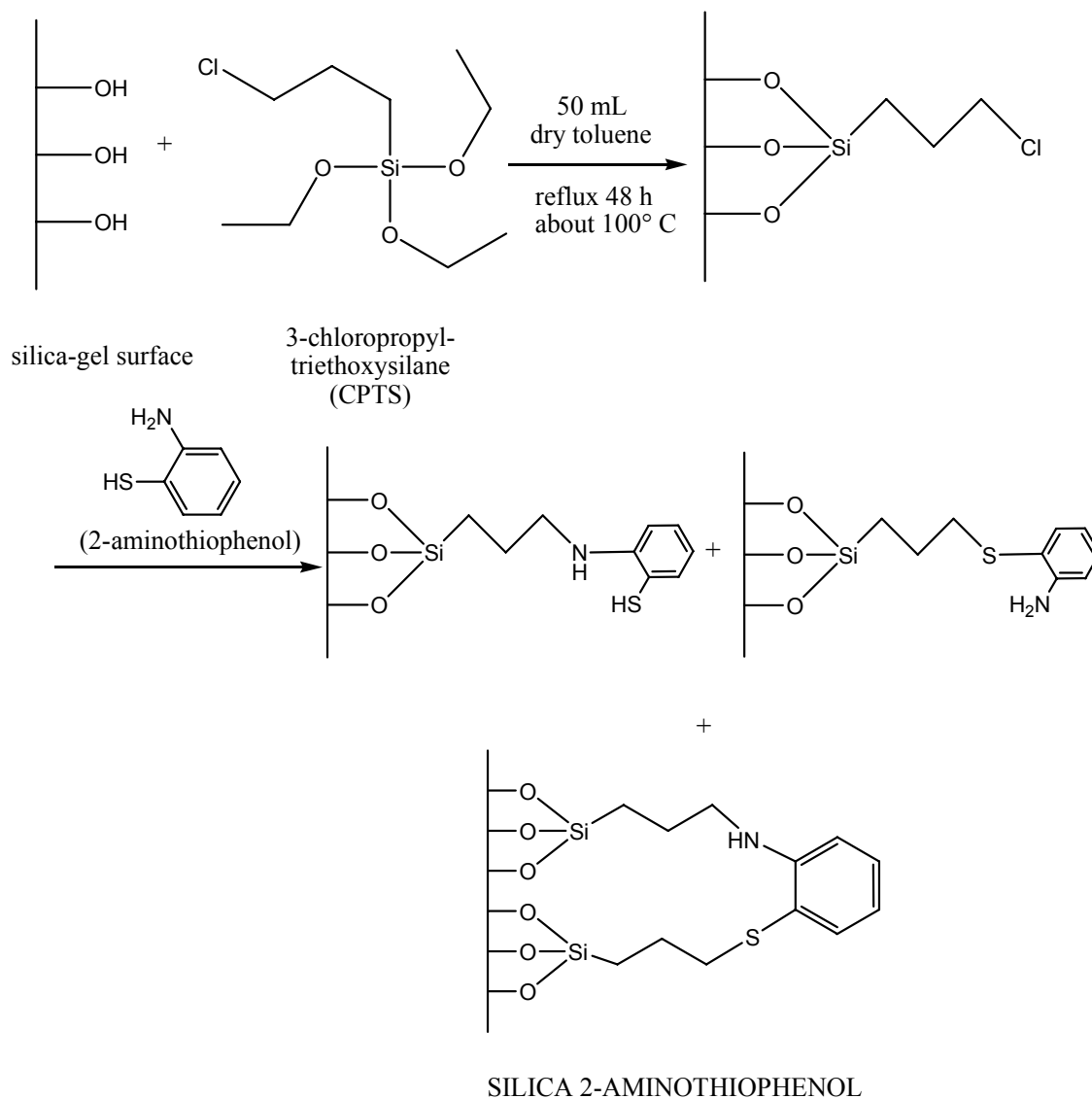
Figure 2.6. Schematic illustration of modification on the silica-gel with 2-amino-
thiophenol.

2.4.1. Scanning Electron Microscopy (SEM/EDS)

SEM/EDS characterization was performed using a Philips XL-30S FEG type instrument at the Center of Material Research at İzmir Institute of Technology. Prior to analysis, solid samples were sprinkled onto adhesive aluminium/carbon tapes supported on metallic disks. Images of the sample surfaces were then recorded at different magnifications. Energy-dispersive X-ray Spectroscopy (EDS) analysis was performed at randomly selected areas on the solid surfaces and back-scatter electron (BSE) detector

was utilized during SEM analysis. It is used for the elements having a large atomic number difference between each other. During the measurements, EDS mapping was carried out at magnification of specified values (1000x, 1200x) and applied the voltage was 18 kV under vacuum conditions of 3.5×10^{-5} mbar.

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2.4.2. Elemental Analysis

An elemental analyzer, Leco CHNS-932 was used to determine the percentage of C, H, N and S in unmodifed and modified silica-gel (silica amino, amino sol-gel, silica mercapto, sol-gel mercapto, silicaamino acid, silica 2-aminophenol, silica 2-aminothiophenol and silica 2-aminobenzothiazole).

2.4.3. Thermo Gravimetric Analysis (TGA)

The thermogravimetric analyses were carried out using a thermogravimetric analyzer from TA instruments (Model Perkin Elmer Diamond TG/DTA) at the Center of Material Research at İzmir Institute of Technology. The samples were heated from 25 °C (room temperature) to 800 °C with heating rate of 10 °Cmin^{-1} under a flux of argon gas.

2.5. Determination of Cr(III) and Cr(VI)

Cr(III) and Cr(VI) sorption behaviour of silica-gel, amino sol-gel, silica 2-aminobenzothiazole, silica 2-aminothiophenol and silica 2-aminophenol were evaluated using all three methods, namely FAAS, ICP-MS and ICP-OES for 2 days. 1.0 mg/L solutions of Cr(III) and Cr(VI) were prepared separately and the pH of the solutions was adjusted to the desired value using NH_3 (0.1 M-1.0 M) and HNO_3 (0.1 M-1.0 M). The data in ICP-MS were collected by monitoring m/z 53, and m/z 54 using peak jump mode. In ICP-OES, two wavelengths were chosen for chromium, namely 267.716 and 357.869 nm.

2.5.1. Calibration Curves for Chromium with FAAS

In order to plot the calibration curves of chromium, standard solutions from 0.1 mg/L to 2.0 mg/L were prepared from 1000 mg/L chromium standard with simple dilution. All standards contained 1% HNO_3 (v/v).

2.5.2. Speciation and Preconcentration Studies

2.5.2.1. Sorption Studies of Cr(III) and Cr(VI)

A separation/preconcentration step is necessary especially for difficult matrices to provide chromium determination at low concentrations. Using batch process, the appropriate sorbent for preconcentration/speciation of chromium, various adsorbents such as ion exchangers and chelating resins were tried. As an initial experiment, 1.0 mg/L (20.0 mL) solutions of Cr(III) and Cr(VI) was prepared from their stock solutions separately. First, sorption experiments were performed in pure water. The pH of these solutions was adjusted between 1.0 and 9.0. About 0.05 g sorbent was added to the each solutions. Each mixture was shaken manually for 1.0 minute and then placed on the shaker for 30 minutes at room temperature. At the end of the shaking period, the mixture was filtered through filter paper and the filtrate was acidified to have 1% HNO_3 (v/v) before sample introduction. Then Cr(III) and Cr(VI) concentrations were determined by FAAS using the optimum conditions.

2.5.2.1.1. Types of Sorbents

As mentioned above, to find the suitable sorbent for the speciation and preconcentration of chromium speciation were chosen by educated guess from the adsorbents that exist in our laboratory. The investigated sorbents for Cr(III) and Cr(VI) sorption are given in Table 2.1.

Table 2.1. Properties of the sorbents investigated for Cr(III) and Cr(VI) sorption.

Type	Sorbent	Functional Group
Adsorbents	Amberlite XAD-2	Polyaromatic
	Amberlite XAD-4	Polyaromatic
	Duolite-XAD-761	Methylol
	Supelite DAX-8	Acrylic ester
	Celite C-545 AW	Calcined Diatomaceous Silica
Anion Exchangers	Duolite A-7 Resin	Polyamine
Chelating Resins	Duolite C-467	Amino-phosphoric

2.5.2.2. Studies with Synthesized Sorbents

The chromium sorption studies with synthesized sorbent were performed with the same procedure as described above. The extent of chromium sorption was tested on the synthesized sol-gel, silica-gel, amino sol-gel, silica mercapto, sol-gel mercapto, silica-amino, silica amino acid, silica 2-aminobenzothiazole, silica 2-aminothiophenol and silica 2-aminophenol.

2.5.2.2.1. Effect of Solution pH

To see the change in sorption behavior of the sorbents in a wide pH range (1.0-10.0), 1.0 mg/L solutions of Cr(III) and Cr(VI) were prepared separately and the pH of the solutions was adjusted to the desired value (1.0-10.0) using NH_3 (0.1 M-1.0 M) and HNO_3 (0.1 M-1.0 M). The percent sorption of the solutions was determined by the same procedure mentioned above.

2.5.2.2.2. Effect of Shaking Time

In order to obtain quantitative sorption, the effect of shaking time was investigated. For this purpose, 20.0 mL of 50.0 mg/L Cr(III) and Cr(VI) solutions, separately were shaken with 0.05 g of silica-gel, amino sol-gel and silica amino from 1

min to 240 minutes. After filtration, the resultant solutions were made acidic with 1% HNO_3 v/v and were analyzed by FAAS using the optimum conditions.

2.5.2.2.3. Effect of Sorbent Amount

The amount of sorbent is an important factor for quantitative sorption of the analytes from a given solution. For this purpose, 20.0 mL of 50.0 mg/L Cr(III) and Cr(VI) solutions were shaken with varying amounts of silica-gel, amino sol-gel and silica-amino (0.01g to 0.10 g) for 30 minutes. After filtration, the resultant solutions were analyzed by FAAS as stated before.

2.5.2.2.4. Effect of Initial Cr(III) or Cr(VI) Concentration

The effect of Cr(III) and Cr(VI) concentrations on amino sol-gel and silica amino were investigated at the initial concentration of 1.0, 10.0, 25.0 and 50.0 mg/L, while keeping the mixing time fixed at 30 minutes. Appropriate amount of amino sol-gel and silica amino (0.05 g) added into each solution (20.0 mL) and the mixtures were shaken as before. After filtration of the mixtures, the resultant solutions were analyzed by FAAS as stated before.

2.5.2.2.5. Desorption from the Amino Sol-Gel and Silica-amino

After collection of Cr(III) and Cr(VI) by sorbent, their release was investigated using eluent HCl range 0.1-2.0 M. For this purpose, 20.0 mL of 1.0 mg/L Cr(III) and Cr(VI) solutions were prepared and 0.05 g of sorbent was added to amino sol-gel, whereas 0.1 g of sorbent was added to silica amino. After shaking for 30 minutes, the mixture was filtered and the sorbent was taken into the eluent (20.0 mL). The new mixture was shaken once again for 15 minutes. At the end of this period, the solution was filtered and the filtrate was analyzed for their Cr(III) and Cr(VI) contents using FAAS.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterization of the Synthesized Sorbents

3.1.1. SEM/EDS Measurements

In order to check the success of modification (or mobilization) procedure, the surface of the synthesized sorbents was examined under SEM with surface mapping program. The distribution of the elements N and S was followed and was assumed to be representing the functional groups, namely amino and mercapto, respectively. To understand the morphology of the sorbent, EDS mapping microimages are investigated for silica amino, amino sol-gel, sol-gel mercapto, silica mercapto and silica 2-aminothiophenol; which are shown in Figure 3.1.-3.5.
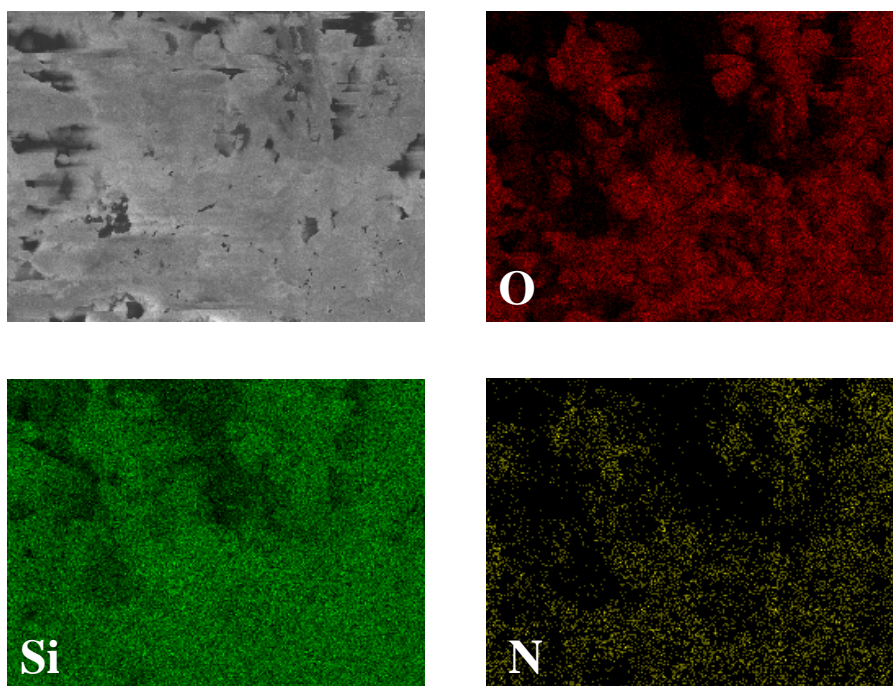
Figure 3.1. EDS mapping microimages of Silica amino (2500x).
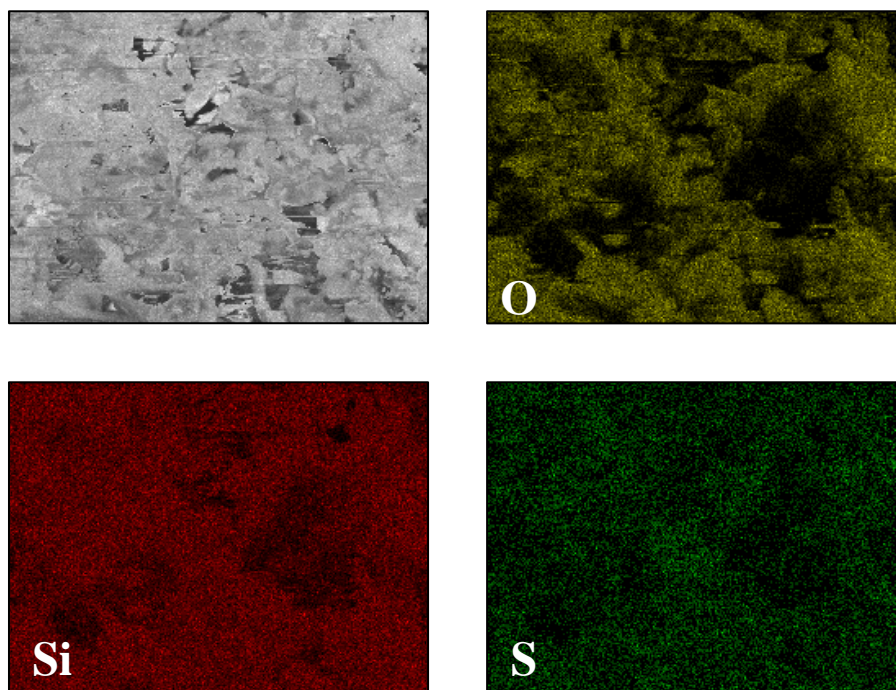
Figure 3.2. EDS mapping microimages of Silica Mercapto (8000x).

As can be seen from Figure 3.1, The O, Si and N atoms are dispersed homogeneously. The silica mercapto and sol-gel mercapto contains S atoms which are dispersed homogenously as shown in Figure 3.2. and 3.3. The N, O, and Si atoms in amino sol-gel are also dispersed homogenously.
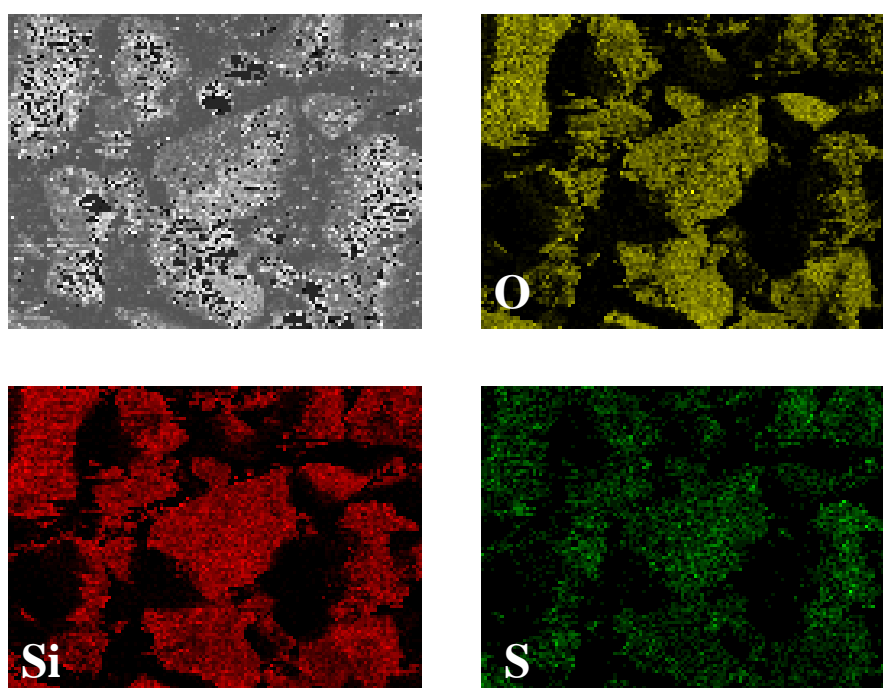
Figure 3.3. EDS mapping microimages of Sol-gel Mercapto (2500x).
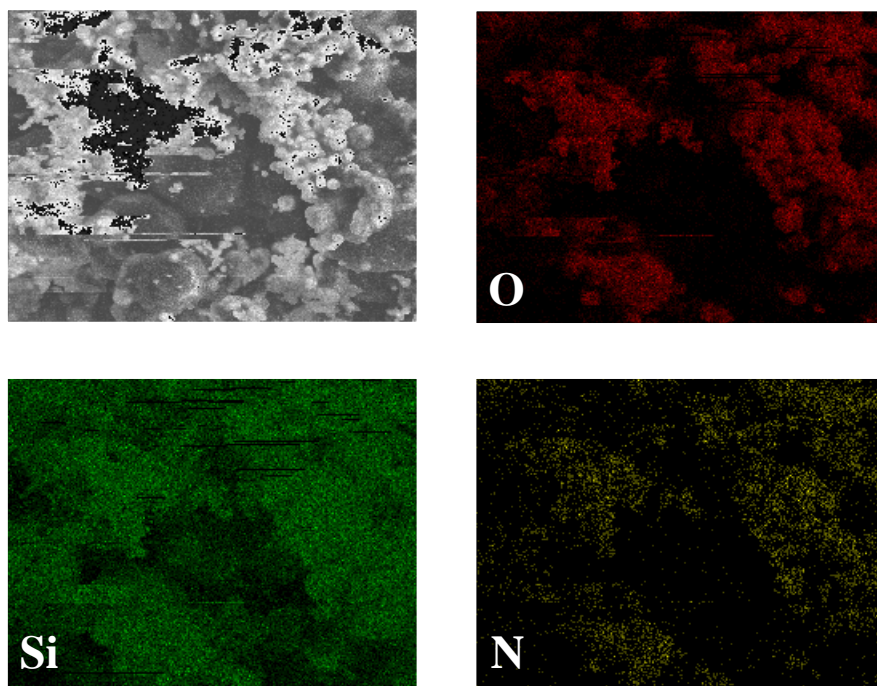
Figure 3.4. EDS mapping microimages of Amino sol-gel (8000x).
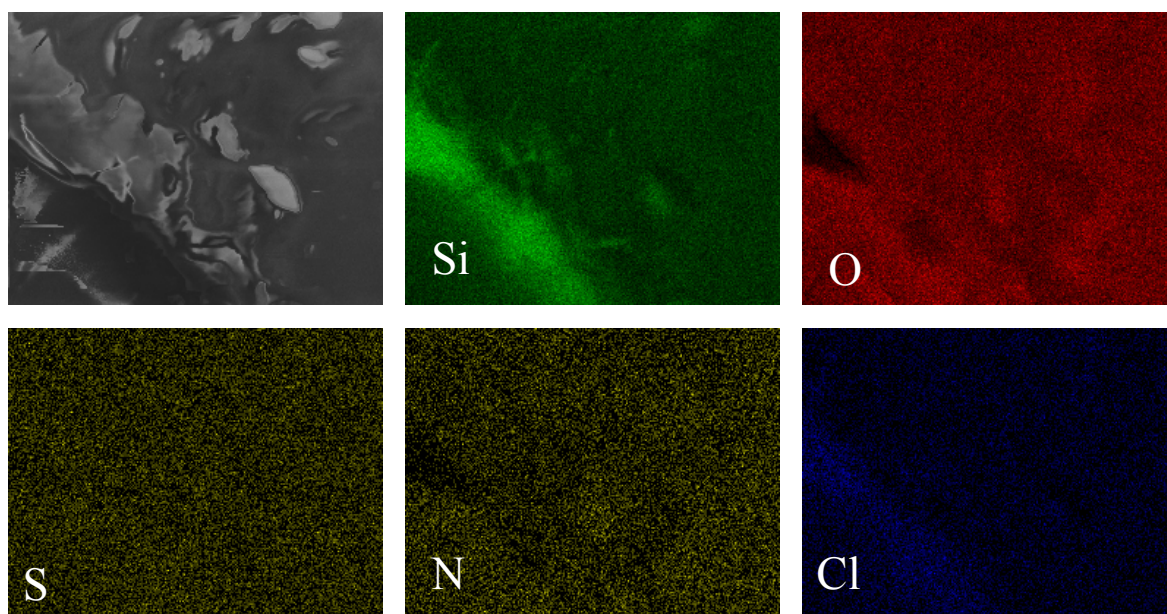
Figure 3.5. EDS mapping microimages of Silica 2-aminothiophenol (2500x).

The silica 2-aminopthihenol contains both S and N atoms which are dispersed homogenously as shown in Figure 3.5. According to EDS mapping, the sorbent contains Cl atoms in addition to the other atoms. This can be due to the intermediate reaction in silica 2-aminothiophenol synthesis where CPTS was used.

The energy-dispersive spectrometry (EDS) spectra of sol-gel, amino sol-gel and sol-gel mercapto are seen in Figure 3.6. EDS mapping analysis has detected the presence of S atoms which are homogenously distributed along with the matrix constituents, namely, Si and O. The presence of N, along with Si and O of the amino sol-gel are also detected by EDS elemental analysis.
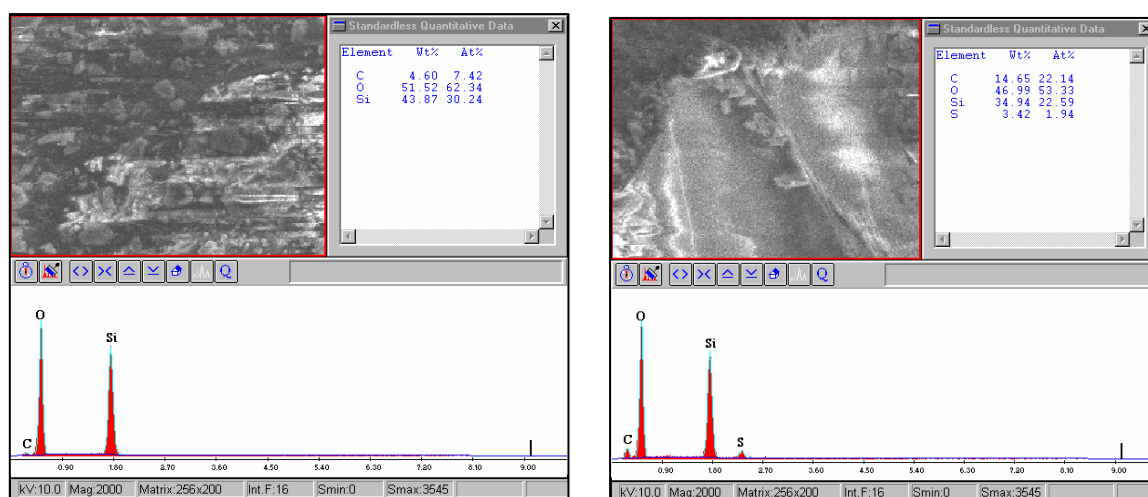
(a)   (b)
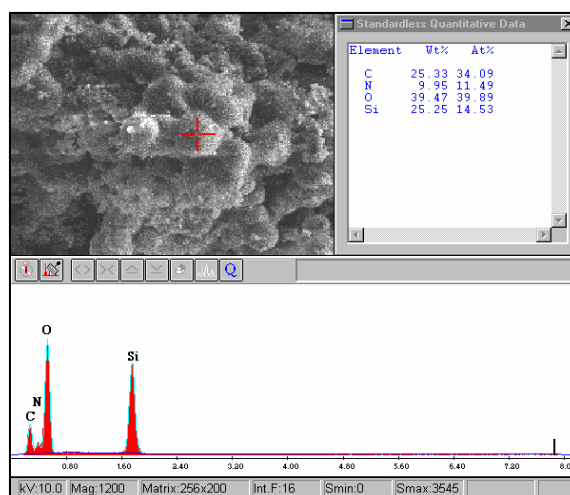
(c)

Figure 3.6. EDS spectra of a) sol-gel (2000x); b) sol-gel mercapto (2000x) and
c) amino sol-gel (1200x).

(a)   (b)

(c)
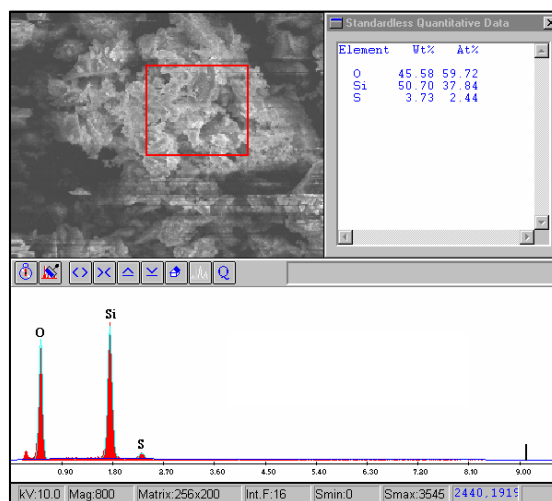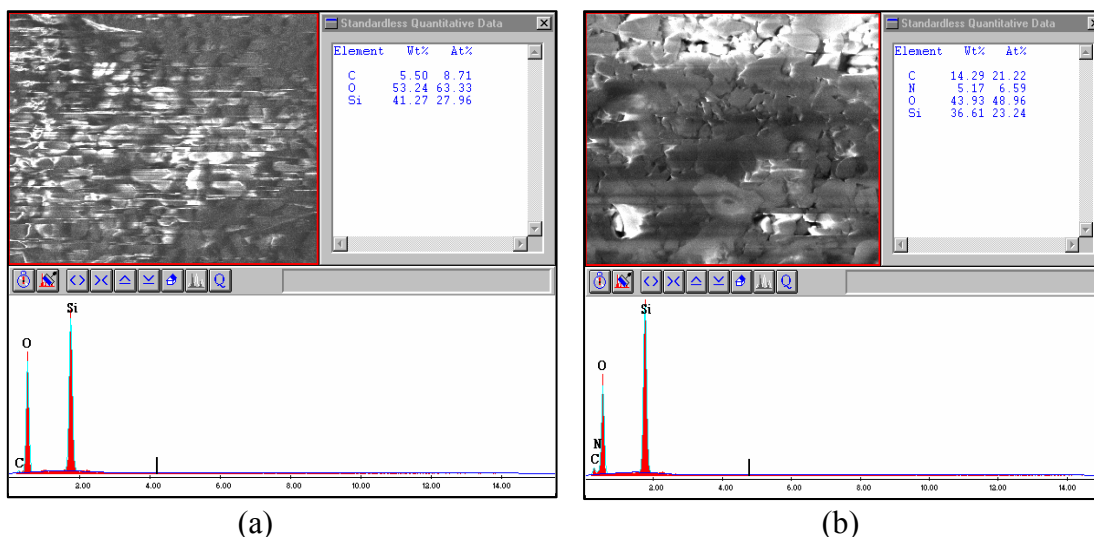
Figure 3.7. EDS spectra of a) silica-gel (1000x); b) silica amino (2500x) and c) silica mercapto (800x).

The EDS mapping analysis of silica mercapto (Figure 3.7) has shown the presence of S, along with Si and O of the silica mercapto. It can also be seen that S atoms are homogenously distributed as the matrix constituents.

Figure 3.8. shows the EDS spectra of silica amino acid, silica 2-amino-phenol, silica 2-aminothiophenol and silica 2-aminobenzothiazole. Similarly, N and S atoms appear to be homogenously distributed as the matrix constituents, Si and O of the silica. Presence of Cl atom must be due to the intermediate reaction in synthesis of sorbents.
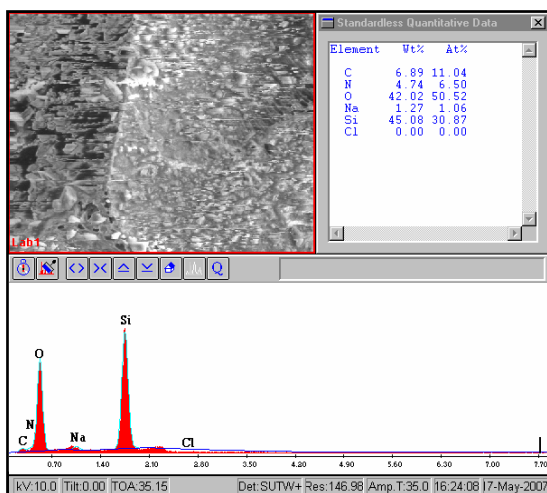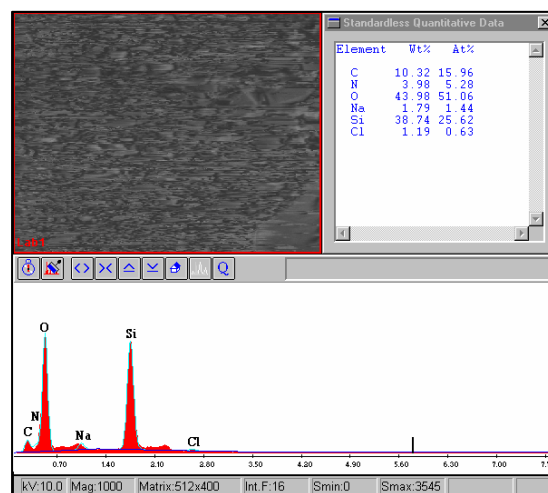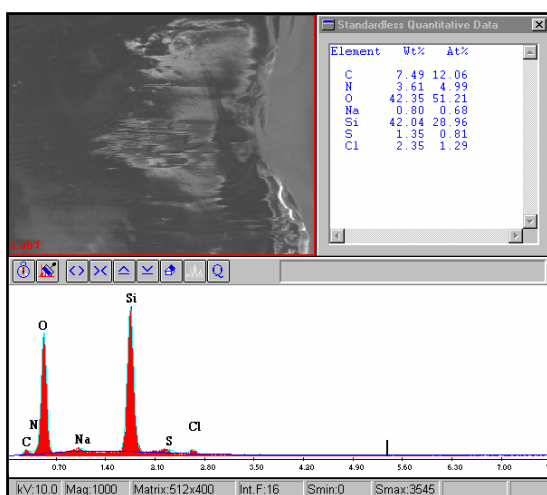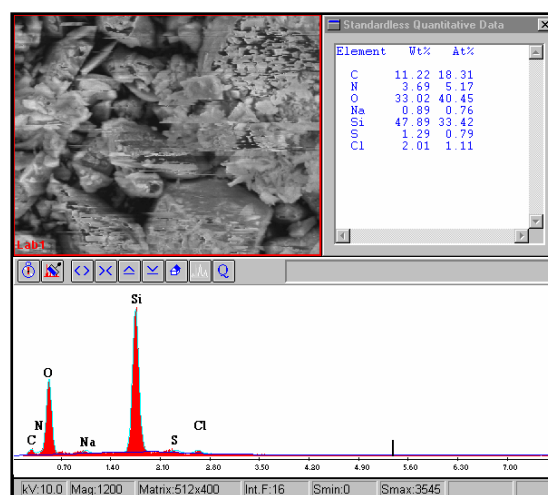
Figure 3.8. EDS spectra of a) silica amino acid (1200x); b) silica 2-amino- phenol (1000x); c) silica 2-aminothiophenol (1000x) and d) silica 2-amino benzothiazole (1200x).

3.1.2. Elemental Analysis

It is possible to calculate the amount of attached molecules onto silica-gel and sol-gel surface from the percentage of nitrogen for synthesized sorbents containing N, the percentage of sulphur for synthesized sorbents containing S. Silica amino, amino sol-gel, sol-gel mercapto, silica mercapto, silica amino acid, silica 2-aminophenol, silica 2-aminothiophenol and silica 2-aminobenzothiazole were investigated in terms of

functionalization capacity. The molar content of the synthesized sorbents was calculated from N and S content of samples and is given in the Table 3.1-3.3.

Table 3.1. Elemental analysis results of synthesized sorbents with N functional group.

Sorbents	% C (w/w)	% N (w/w)	Calculated mmol of attached N / g sample
Silica-amino	10.07	3.20	2.29
Amino sol-gel	7.44	2.76	1.97
Silica amino acid	9.98	2.19	1.56
Silica 2-aminophenol	10.56	1.15	0.82

Table 3.2. Elemental analysis results of synthesized sorbents with S functional group.

Sorbents	% C (w/w)	% S (w/w)	Calculated mmol of attached S / g sample
Sol-gel mercapto	5.84	5.35	1.67
Silica mercapto	4.33	3.56	1.11

Table 3.3. Elemental analysis results of synthesized sorbents with both S and N functional groups.

Sorbents	% C (w/w)	% S (w/w)	% N (w/w)	Calculated mmol of attached S / g sample	Calculated mmol of attached N / g sample
Silica 2-aminobenzothizole	7.08	0.65	0.56	0.20	0.20
Silica 2-aminothiophenol	7.55	0.56	0.28	0.18	0.20

As can be seen from Table 3.1., the highest N content after functionalization was obtained for silica amino. Sol-gel mercapto contained the highest value of sulphur among the synthesized sorbents containing sulphur group. There is no significant difference, in terms of functionalization ratios of N, between silica 2-aminobenzothiazole and silica 2-aminothiophenol. The functionalization ratio for sulphur content is the smallest on silica 2-amino thiophenol and silica 2-aminobenzothiazole.

3.1.3. TGA Analysis

Thermal stability of the modified silica-gel has been established by thermogravimetric analysis. The TGA profiles indicate a comparable stability of the new materials, regardless of the synthetic method employed. The thermogravimetric curve of the silica-gel, sol-gel, amino sol-gel, silica amino, silica mercapto, sol-gel mercapto, silica amino acid, silica 2-aminothiophenol, silica 2-aminobenzothiazole and silica 2-aminophenol are shown in Figures 3.9-3.11. As can be seen from Figure 3.9, an initial 6.6% weight loss at 25-114 °C is attributed to physically adsorbed water on the surface. The following loss of mass of 2.4% reached at 529.23 °C is related to the condensation of free silanol groups on the surface to form siloxane groups. The thermogravimetric curve of silica-gel is similiar to that of sol-gel. For amino sol-gel, a second loss of mass of 9.5% reached at 654 °C, is probably due to decomposition of organic groups covalently bonded on the silica surface. A loss of mass at specified temperature range occured for silica mercapto, silica amino acid, silica 2-aminothiophenol, silica 2-aminophenol and silica 2-aminobenzothiazole. All these thermogravimetric results showed a direct relationship between the loss of mass to the amount of organic molecules anchored on silica gel surfaces.
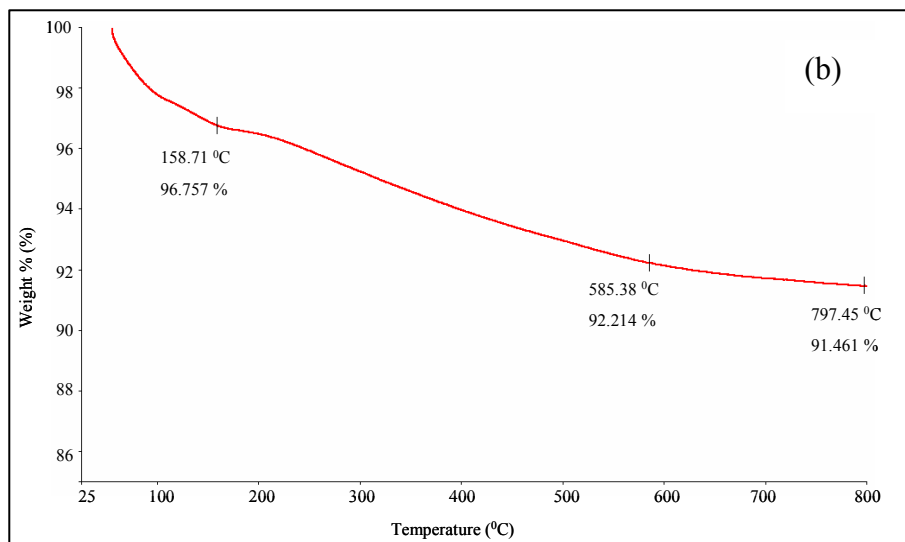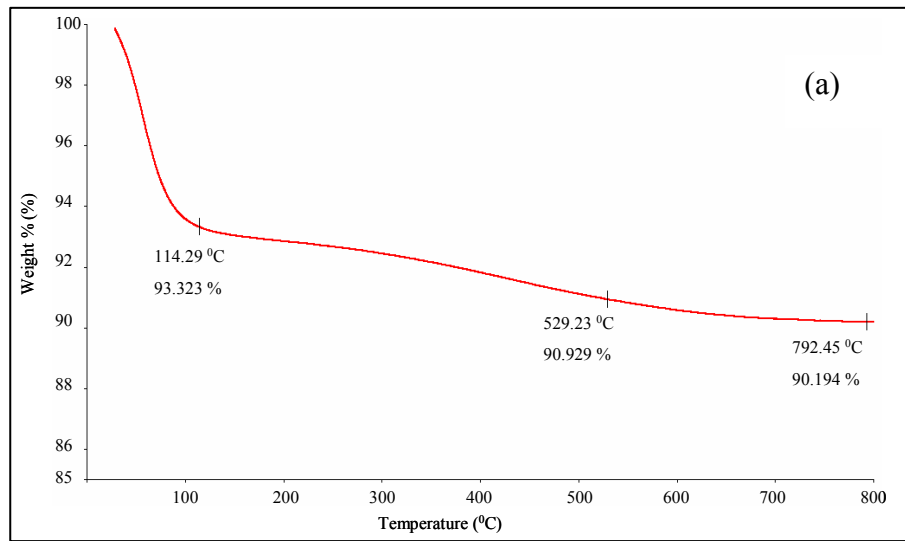
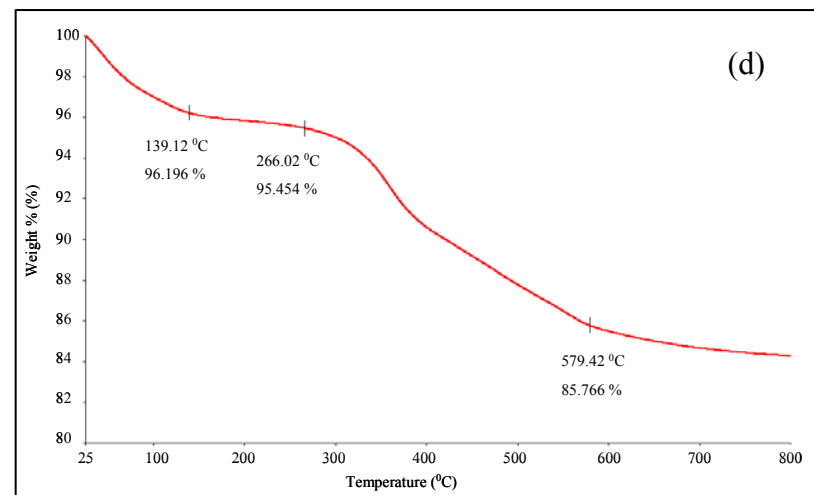**Figure 3.9.** Thermogravimetric data for a) silica-gel and b) sol-gel
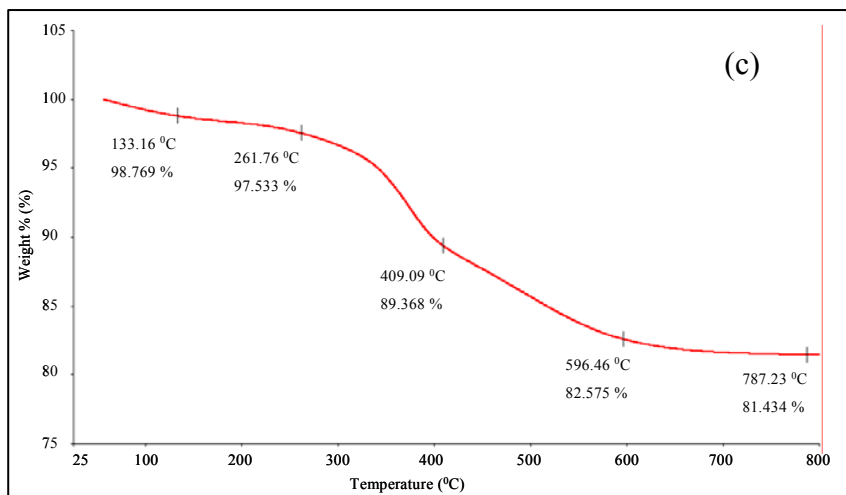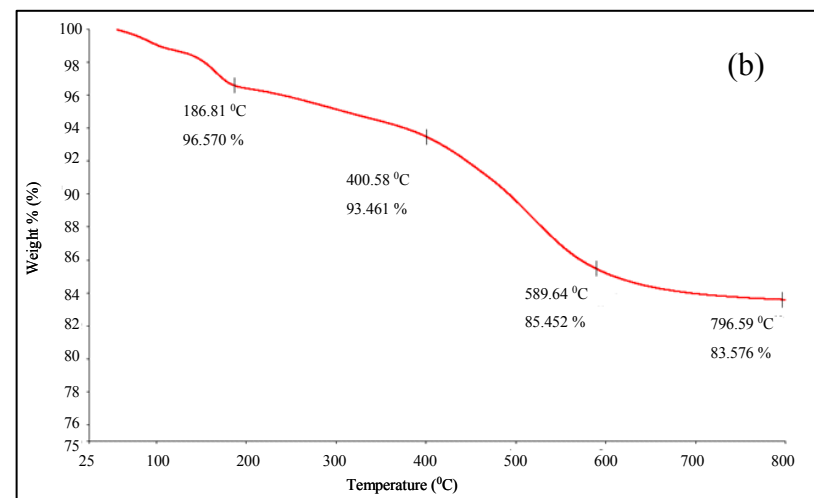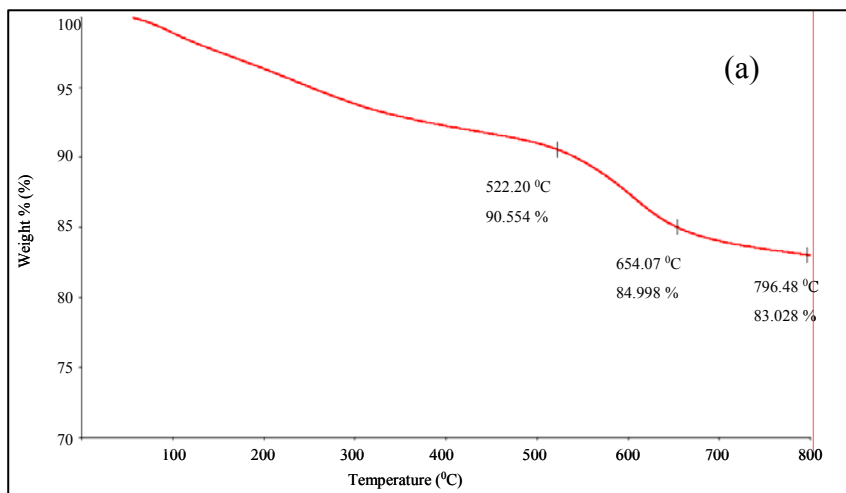
Figure 3.10. Thermogravimetric data for a) amino sol-gel; b) silica amino; c) sol-gel mercapto and d) silica mercapto.
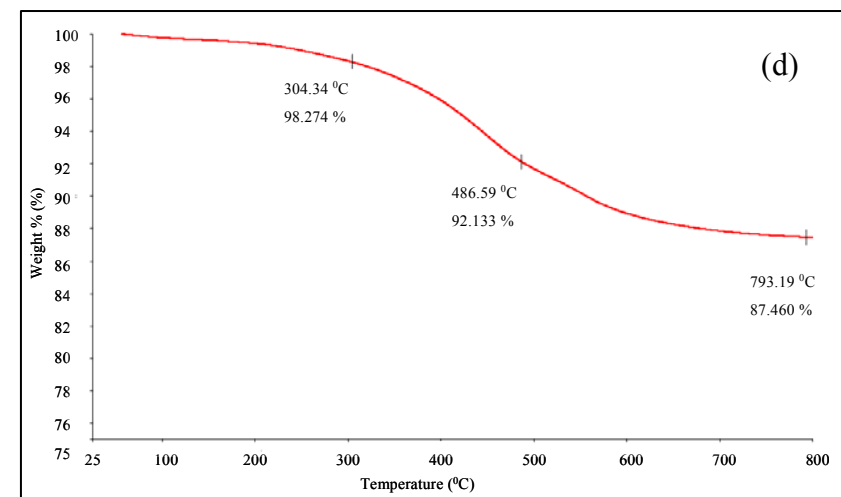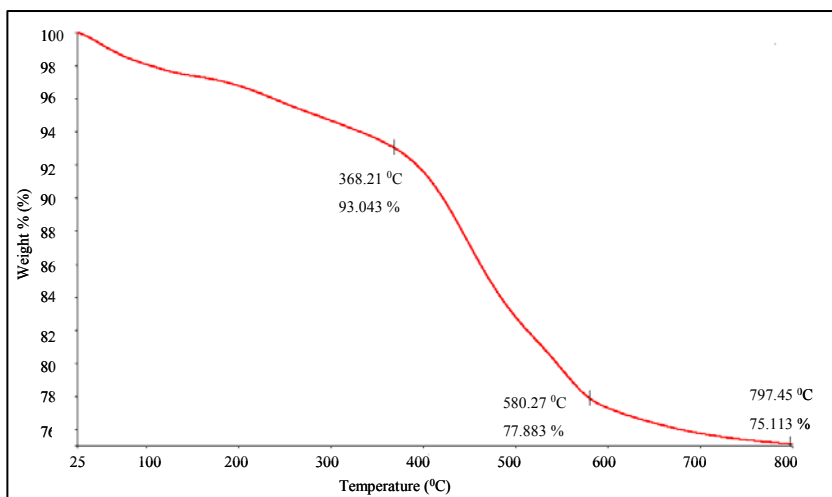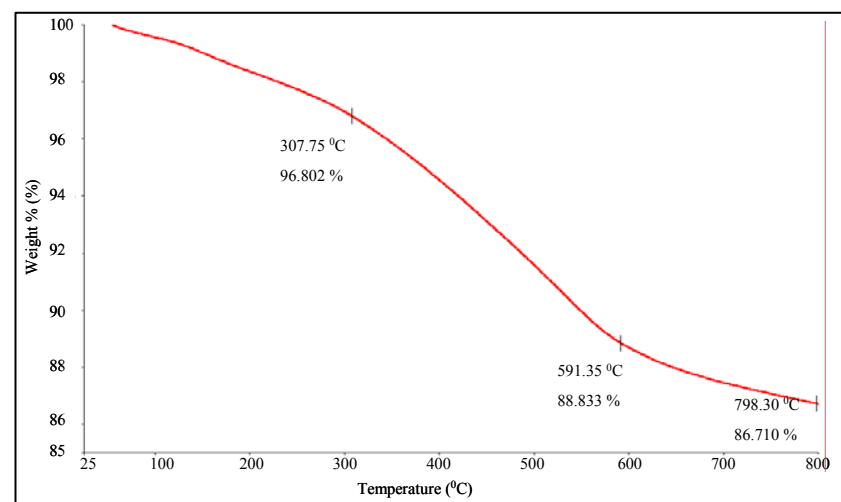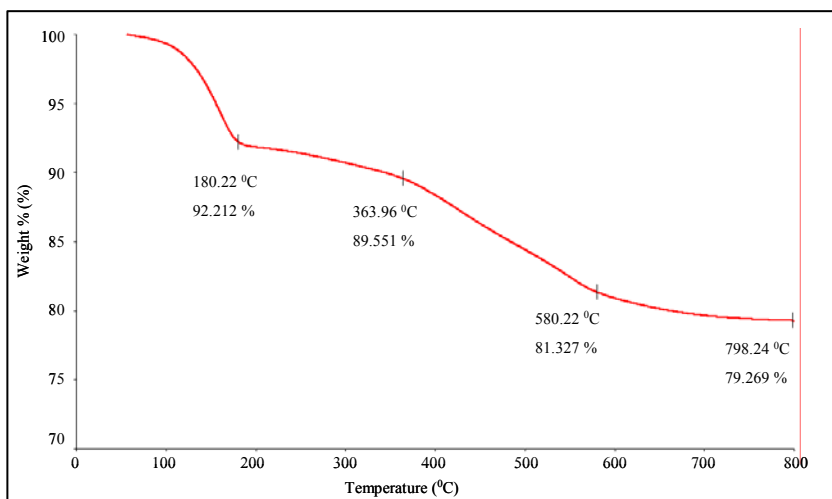
Figure 3.11. Thermogravimetric data for a) silica amino acid; b) silica 2-aminophenol; c) silica 2-aminobenzothiazole and

d) silica 2-aminothiophenol.

3.2. Determination of Cr(III) and Cr(VI)

As explained in section 2.5., sorption behaviour of the sorbents towards Cr(III) and Cr(VI) species were evaluated using three atomic spectrometric methods, namely FAAS, ICP-MS and ICP-OES. The results were evaluated in terms of the reproducibility of the results, the agreement between the measurement techniques, and the change of the results in two consecutive days (Table 3.4 and 3.5). In ICP-OES measurements, two wavelengths (267.716 and 357.869 nm); and in ICP-MS measurements, two isotopes of Cr (m/z=53 and 54) were used. The sorption results were very close for the three techniques which demonstrated that any of them can be applied for Cr determination. In addition, the repeatability of the results were acceptable in almost all cases. Approximately 20 % sorption of Cr(VI) on silica gel at the pH values investigated could not be repeated in later experiments and therefore was assumed to be measurement error during the analysis. The results did not change from the first day of the measurement to the second which showed the stability of the solutions for at least one day. This was important especially for the situations where it was not possible to analyze the solutions immediately after preparation.

3.2.1. Calibration Curves for Cr(III) and Cr(VI)

Absorbance versus concentration plots were obtained for commercial Cr standard, Cr(III) standard prepared from $Cr(NO_3)_3$ and Cr(VI) standard prepared from $Cr(NO_3)_3.9H_2O$ as shown in Figure 3.12. All three calibration plots have very similar sensitivities and were linear at least up to 2.0 mg/L. The limit of detection (LOD) based on 3s (3 times the standard deviation above the blank value) for Cr(III) standard was 0.01 mg/L.

Table 3.4. Sorption of Cr(III) and Cr(VI) by various sorbents (ICP-OES, ICP-MS and FAAS were used in the measurements (Analysis was performed in the day of preparation)

pH	ICP-OES (λ=267.716 nm)		ICP-OES (λ=357.869 nm)		ICP-MS (m/z=53)		ICP-MS (m/z=54)		FAAS	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
silica-gel	% sorption									
3	32 (±4)	22	25	20	34 (±4)	0	21 (±5)	0	33 (±7)	0
4	86 (±2)	20 (±13)	84 (±3)	18 (±12)	87 (±1)	0	78	0	88 (±1)	0
5	98 (±1)	18 (±4)	97 (±1)	16 (±4)	99 (±1)	0	89 (±1)	0	98	0
9	88 (±1)	16 (±1)	86 (±1)	15 (±1)	88	0	78 (±1)	0	88	0
amino sol-gel	% sorption									
3	67 (±4)	96 (±1)	65 (±4)	95 (±1)	67 (±4)	96 (±1)	58 (±4)	88 (±1)	65 (±6)	97 (±1)
9	89 (±5)	18 (±1)	88 (±4)	18 (±1)	88 (±4)	0	79 (±5)	0	88 (±6)	0
aminobenzothiazole	% sorption									
5	76 (±2)	85 (±1)	74 (±1)	84 (±1)	78 (±2)	82 (±1)	70 (±1)	73 (±2)	77 (±2)	80(±2)
9	99	20 (±3)	98 (±1)	19 (±4)	100 (±1)	0	91	0	100	0
aminothiophenol	% sorption									
9	92 (±2)	17 (±1)	92 (±2)	17 (±3)	93 (±3)	0	82 (±1)	0	92 (±2)	0
aminophenol	% sorption									
4	85	97	84	95	87	97	79	88	86	100
9	94	9	93	10	94	9	85	0	94	0

Table 3.5. Sorption of Cr(III) and Cr(VI) by various sorbents (ICP-OES, ICP-MS and FAAS were used in the measurements (Analysis was performed one day after the preparation)

pH	ICP-OES (λ=267.716 nm)		ICP-OES (λ=357.869 nm)		ICP-MS (m/z=53)		ICP-MS (m/z=54)		FAAS	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Silica-gel	% sorption									
3	36 (±6)	7 (±1)	34 (±5)	3 (±1)	32 (±5)	0	23 (±4)	0	31 (±2)	0
4	88 (±1)	1 (±1)	87 (±1)	0	86 (±2)	0	77 (±2)	0	86 (±1)	2 (±2)
5	98	1 (±1)	98 (±1)	0	99	0	88 (±1)	0	96	20 (±6)
9	89 (±1)	0	88 (±1)	0	88 (±1)	0	77 (±2)	0	87 (±1)	22 (±4)
amino sol-gel	% sorption									
3	70 (±4)	96 (±1)	70 (±4)	96	62 (±6)	96	52 (±6)	85	67 (±4)	77 (±2)
9	89 (±4)	5 (±4)	89 (±9)	1	88 (±5)	0	73 (±7)	0	89 (±4)	4 (±1)
aminobenzothiazole	% sorption									
5	80 (±1)	85 (±1)	79 (±2)	83 (±1)	75 (±3)	79 (±2)	64 (±1)	67 (±2)	80 (±2)	77
9	99 (±1)	6 (±1)	99	1	100	0	88	0	98 (±1)	0
aminothiophenol	% sorption									
9	93 (±2)	6 (±1)	92 (±1)	0	92 (±3)	0	77	0	92 (±1)	0
aminophenol	% sorption									
4	88	97	87	97	85	96	74	84	86	100
9	94	16	95	8	95	0	81	0	94	0
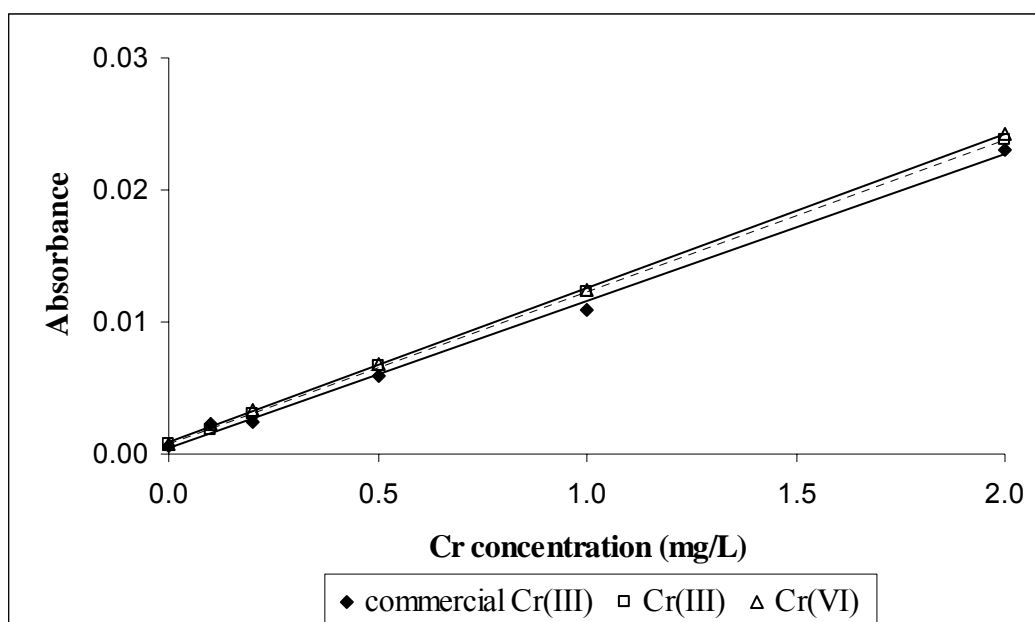
Figure 3.12. Calibration curves for Cr obtained with ($\blacklozenge$) commercial Cr(III) standard (y = 0.0111x + 0.0005, R^2 = 0,997), ( ) Cr(III) standard prepared from Cr(NO$_3$)$_3$.9H$_2$O (y = 0.0115x + 0.0008, R^2 = 0,9999), (Δ) Cr(VI) standard prepared from K$_2$Cr$_2$O$_7$ (y = 0.0116x + 0.0009, R^2 = 0.9998). All standard solutions contained 1% (v/v) HNO$_3$.

3.2.2. Speciation and Preconcentration Studies

3.2.2.1. Sorption Studies of Cr(III) and Cr(VI)

3.2.2.1.1. Types of Sorbents

As explained in section 2.5.2.1.1., various sorbents were investigated for Cr(III) and Cr(VI) sorption using batch process. The percent sorption graphs for Cr(III) and Cr(VI) are given in Figures 3.13. and 3.14., respectively. Nearly all of the sorbents offer significant results for the sorption of Cr(III) at pH's greater than 3. Except for Duolite A-7 resin, the materials investigated has shown low sorption affinity for Cr(VI) under the studied conditions. Both Cr(III) and Cr(VI) species on Duolite A-7 resin shows high percentage sorption between pH 3 and 7, whereas only Cr(III) is sorbed at pH 9. In

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further studies, -SH and/or –NH functionalization of silica-gel and sol-gel was tested for sorption of Cr(III) and Cr(VI). After synthesis and characterization of the novel sorbents, the subsequent experiments were realized with these sorbents.
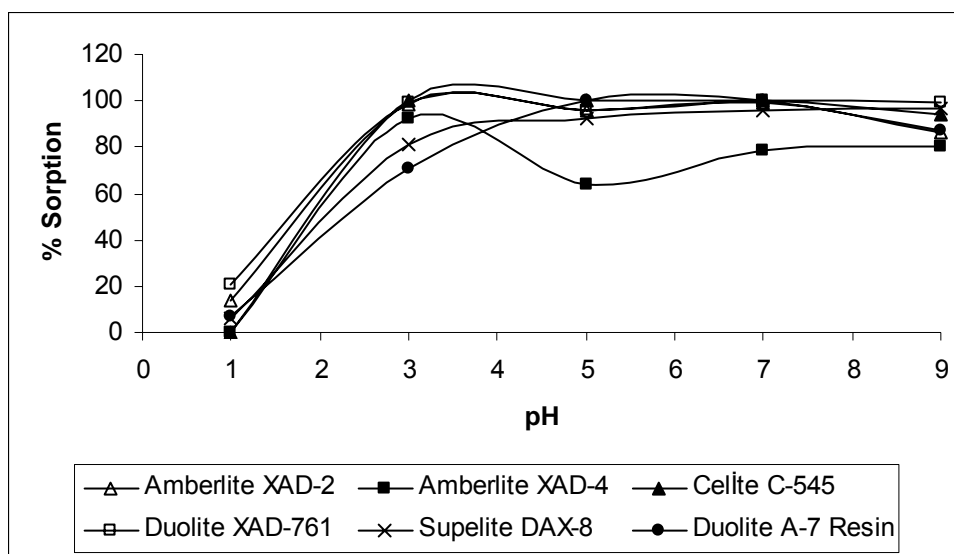
Figure 3.13. Cr(III) sorption as a function of pH on different sorbents
(20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
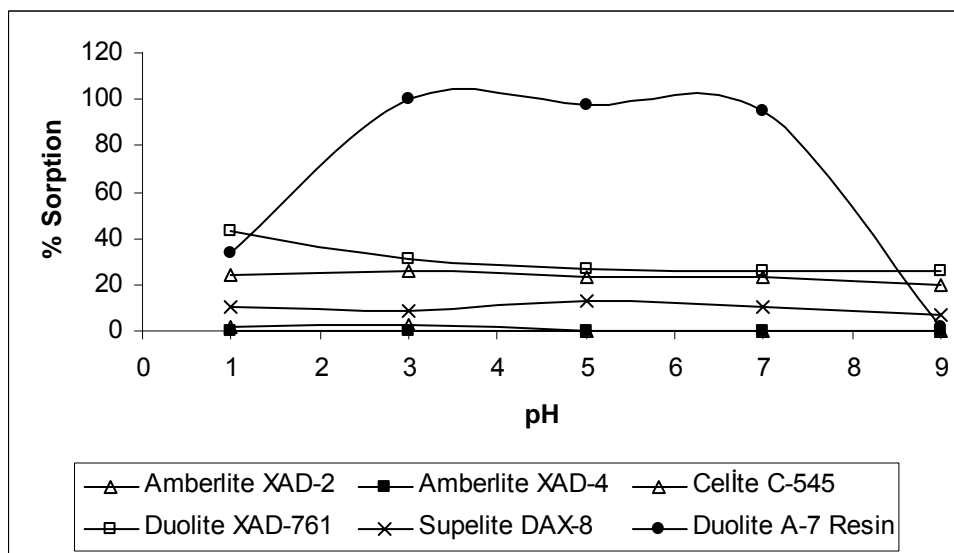
Figure 3.14. Cr(VI) sorption as a function of pH on different sorbents
(20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).

3.2.2.2. Studies with Synthesized Sorbents

3.2.2.2.1. Effect of Solution pH

Cr(III) and Cr(VI) sorption studies with the novel sorbents (silica-gel, sol-gel, amino-sol-gel, silica-amino, silica-mercapto, sol-gel mercapto, silica amino acid, silica 2-aminobenzothiazole, silica 2-aminothiophenol and silica 2-aminophenol) were performed using the same procedure as described in section 2.5.2.1.1. The percent sorption graphs for Cr(III) and Cr(VI) species at different pH values are shown in Figures 3.15-3.22, respectively.

Figure 3.15. Cr(III) and Cr(VI) sorption on silica-gel and silica amino as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
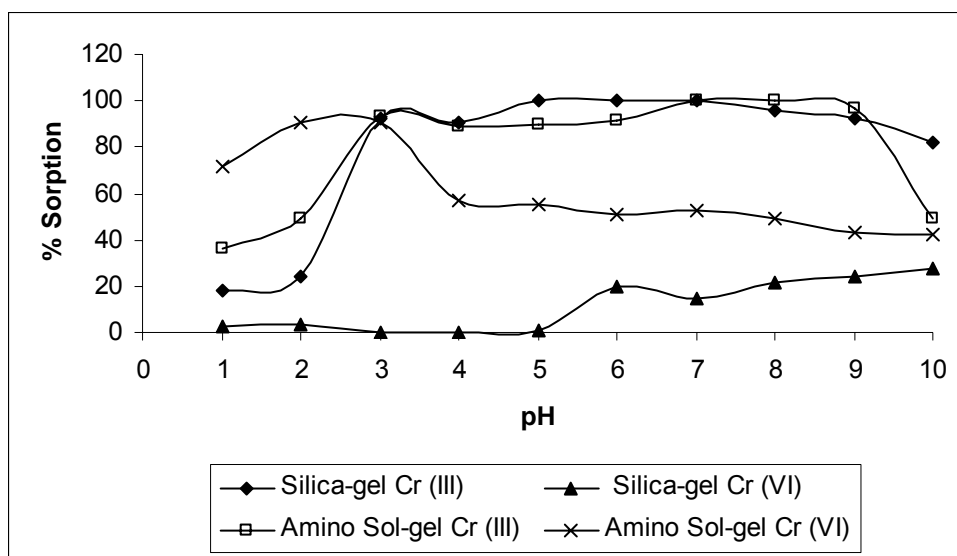
Figure 3.16. Cr(III) and Cr(VI) sorption on silica-gel and amino sol-gel as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
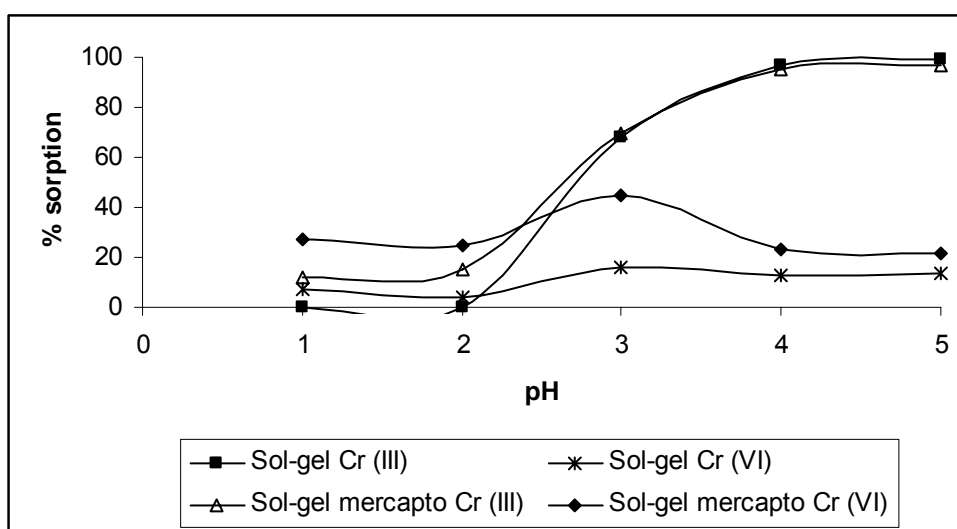
Figure 3.17. Cr(III) and Cr(VI) sorption on sol-gel and sol-gel mercapto as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
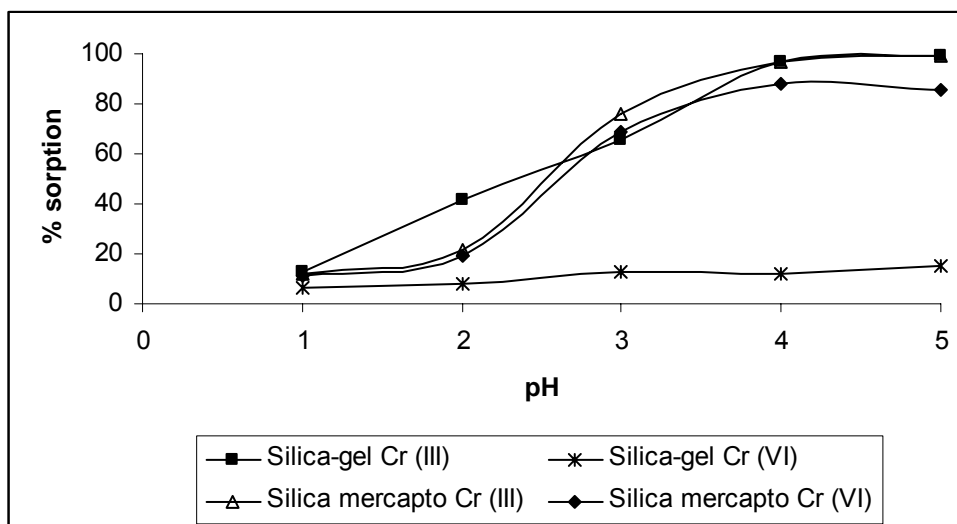
Figure 3.18. Cr(III) and Cr(VI) sorption on silica-gel and silica mercapto as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
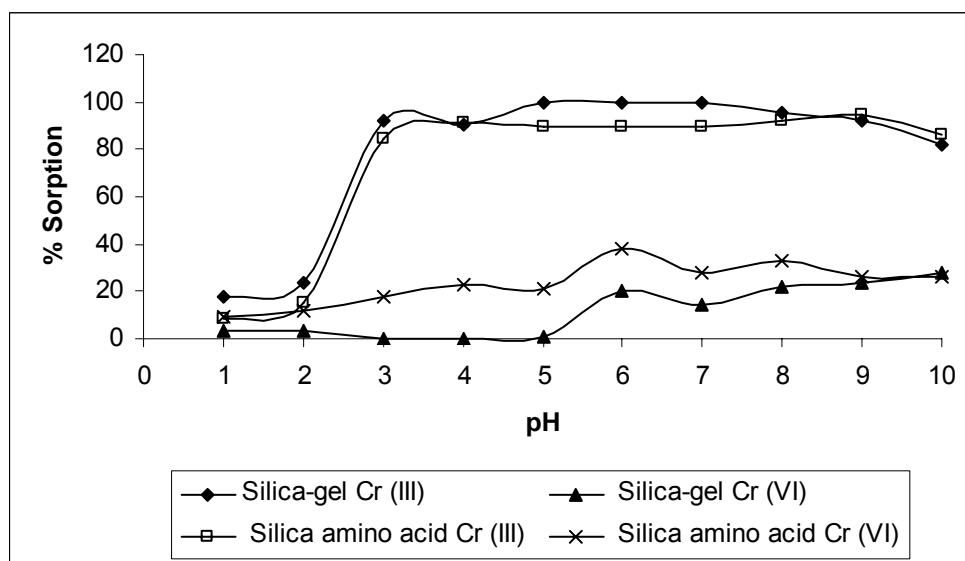
Figure 3.19. Cr(III) and Cr(VI) sorption on silca-gel and silica-amino acid as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
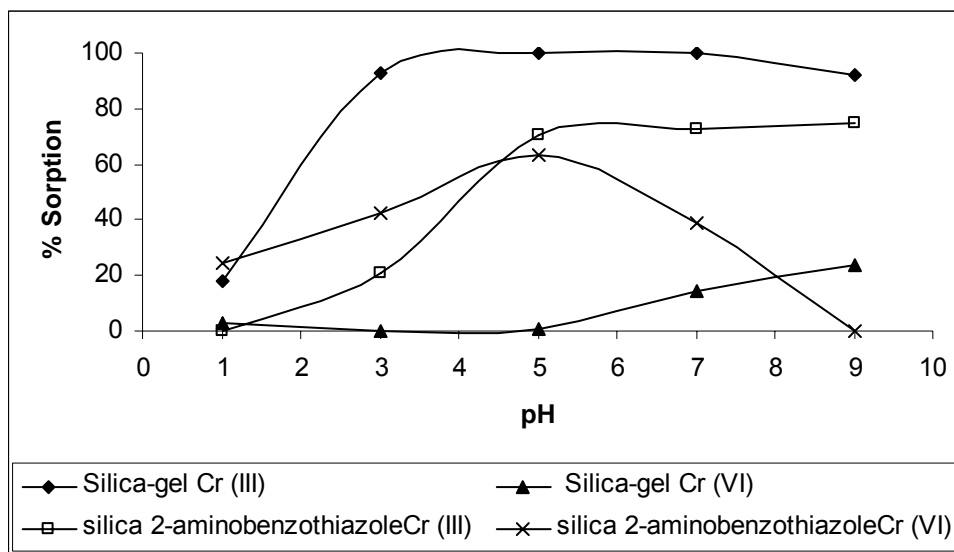
Figure 3.20. Cr(III) and Cr(VI) sorption on silica-gel and silica 2-aminobenzothiazole as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
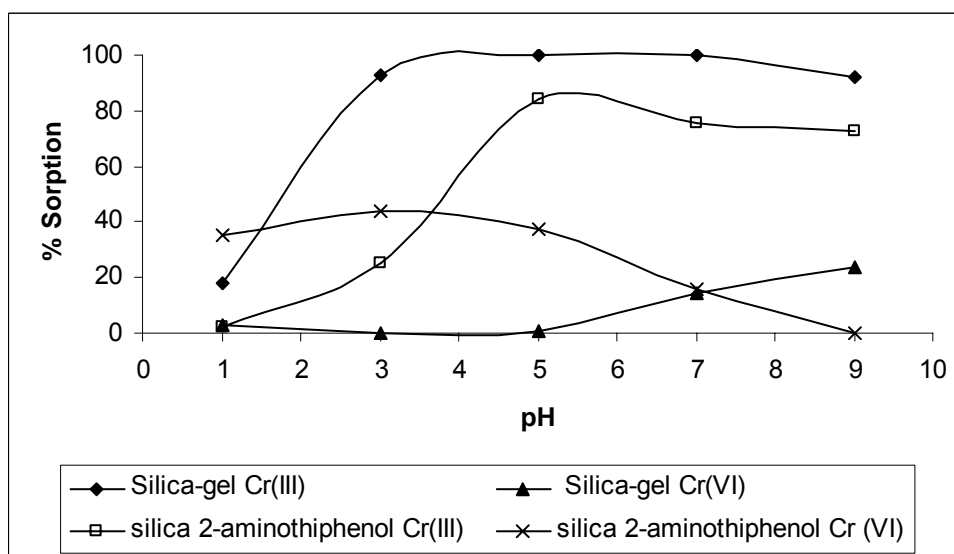
Figure 3.21. Cr(III) and Cr(VI) sorption on silica-gel and silica 2-aminothiophenol as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).
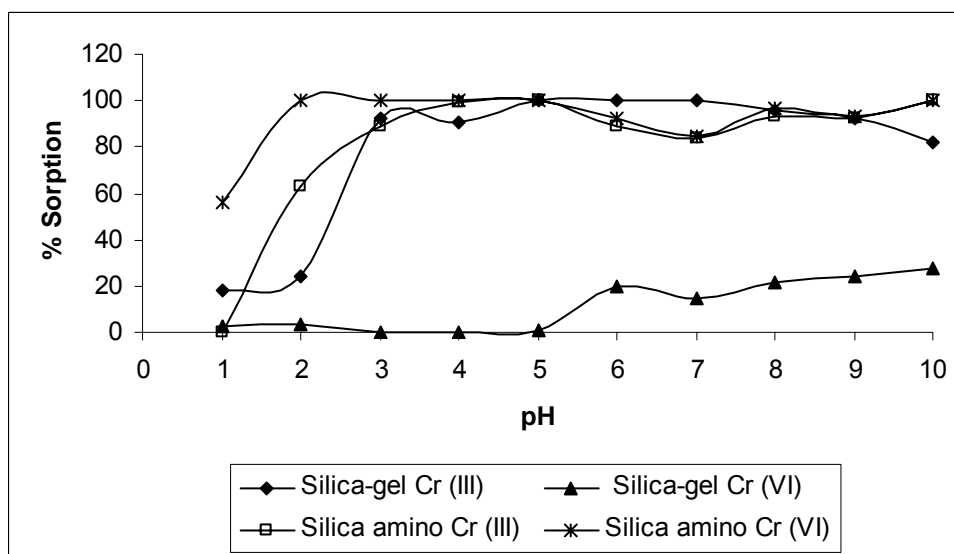
49
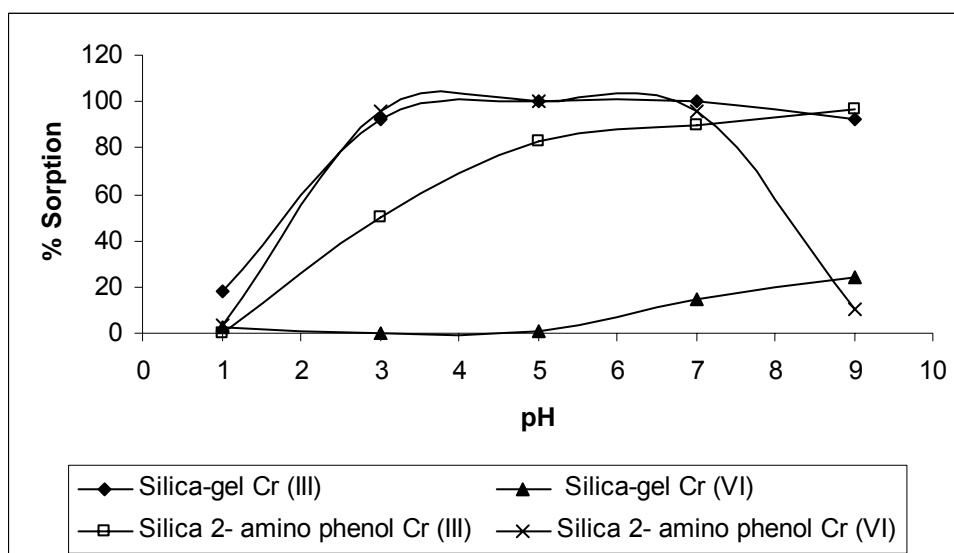
Figure 3.22. Cr(III) and Cr(VI) sorption on silica-gel and silica 2-aminophenol as a function of pH (20.0 mL of 1.0 mg/L solution, sorbent amount: 0.05 g).

Several functional groups as amino/mercapto were tried to be immobilized onto silica surface. Therefore silica was assumed to be blank in these pH graphs. Among the sorbents tried, amino sol-gel gave the most promising results for the speciation of Cr. When Cr(III) species on amino sol-gel shows high percentage sorption at any pH except pH 3, Cr(VI) species on amino sol-gel shows nearly no sorption. At pH 3, both Cr(III) and Cr(VI) species show quantitative sorption. As can be seen from Figure 3.15, any pH values greater than 4 can be used for an efficient sorption. The efficieny of sorption on silica amino acid and sol-gel mercapto is similar to that of silica-gel. The percentage sorption of Cr(III) and Cr(VI) on Silica 2-aminobenzothiazole and silica 2-amino-thiophenol is nearly similiar to each other. However, amino sol-gel and silica amino were quite suitable in the study.

3.2.2.2.2. Effect of Shaking Time

Effect of shaking time on the sorption of Cr(III) and Cr(VI) by silica-gel, amino sol-gel and silica-amino was examined as explained in 2.5.2.2.2. The sorption rate for Cr(VI) species was rapid (Figure 3.23); an interaction period of 15 minutes supplied 89% sorption whereas the equilibrium was reached after 60 minutes. For Cr(III) species, an interaction period of 120 minutes led to a limited sorption level (21 %).
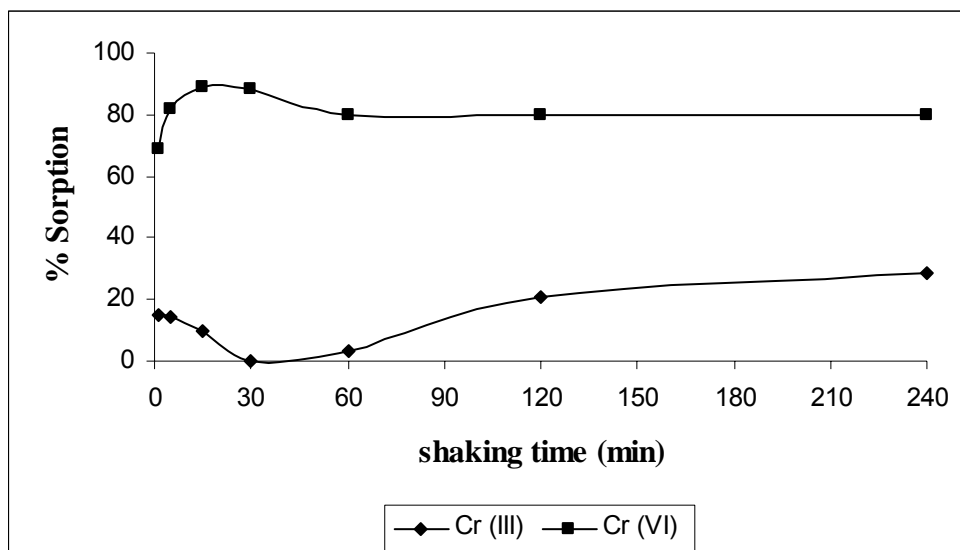
Figure 3.23. Cr(III) and Cr(VI) sorption on silica-amino as a function of shaking time (20.0 mL of 50.0 mg/L solution, sorbent amount: 0.05 g, pH=4).
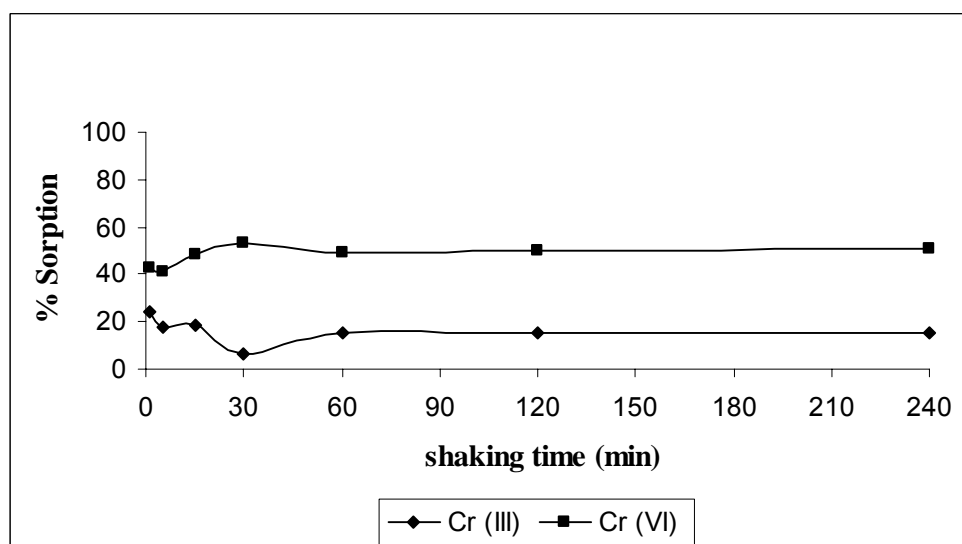
Figure 3.24. Cr(III) and Cr(VI) sorption on amino sol-gel as a function of shaking time (20.0 mL of 50.0 mg/L solution, sorbent amount: 0.05 g, pH=3).

3.2.2.2.3. Effect of Sorbent Amount

As explained in section 2.5.2.2.3, the optimum amount of the sorbent for maximum sorption was determined by increasing the amount of silica-gel, silica amino and amino sol-gel added into 20.0 mL of 50.0 mg/L Cr(III) and Cr(VI) solutions. As can be seen from Figure 3.27., an efficient sorption of Cr(VI) was obtained with 100.0

mg. of sorbent. However, in Figure 3.26., an efficient sorption of Cr(III) was obtained with 50.0 mg. of amino sol-gel (the V/m ratio was kept at 50.0 in all experiments) and 50.0 mg. of this sorbent was used in the following experiments. The sorption capacity of Cr(III) on silica-gel was obtained as 1.84 mg Cr(III)/g sorbent. The sorption capacity of Cr(III) and Cr(VI) on silica-amino were obtained as 4 mg Cr(III)/sorbent and 4.8 mg Cr(VI)/g sorbent. For amino sol-gel, the sorption capacity of Cr(III) and Cr(VI) were 6.8 mg Cr(III)/g sorbent and 8.4 mg Cr(III)/g sorbent.
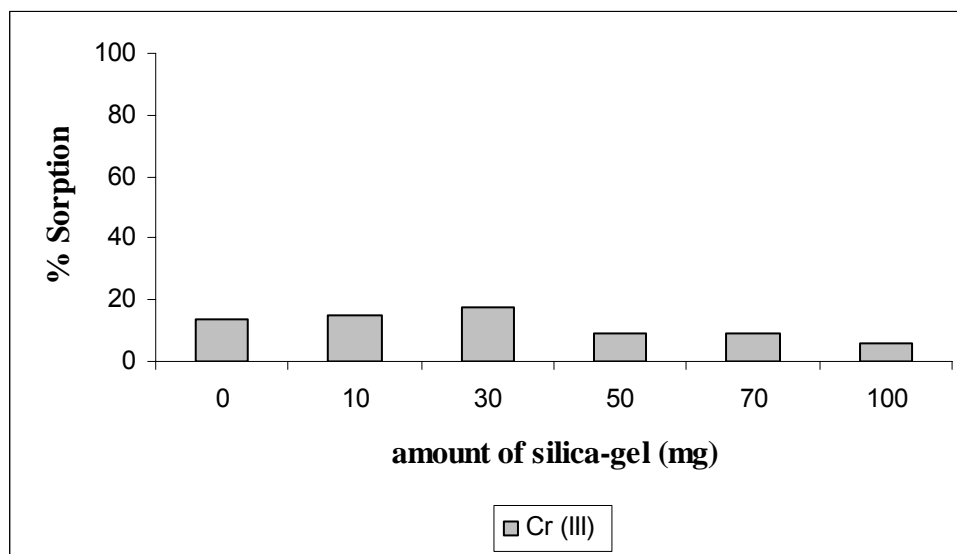
Figure 3.25. Percent sorption versus the amount of silica-gel (pH=3; Cr(III)
concentration = 50.0 mg/L, solution volume = 20.0 mL and
shaking time = 30 min.)
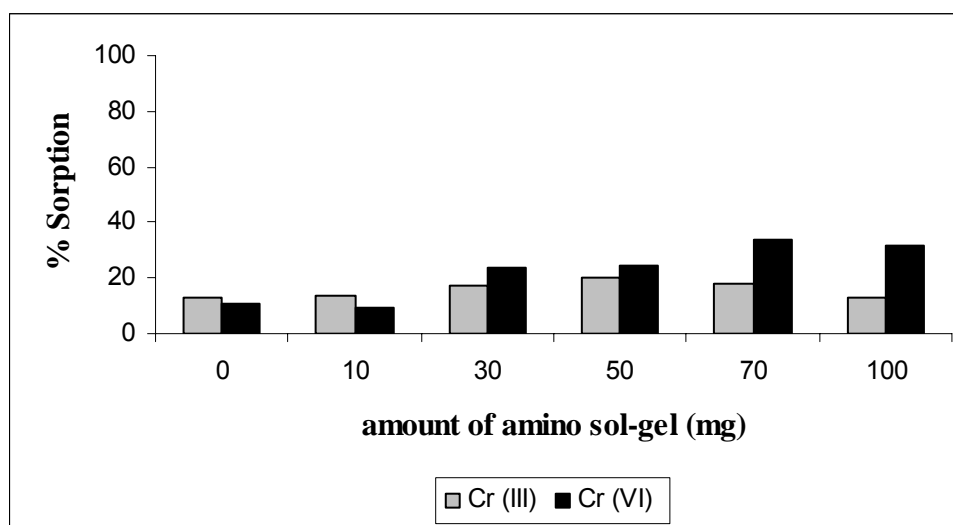
Figure 3.26. Percent sorption versus the amount of amino sol-gel (pH=3; Cr(III) and
Cr(VI) concentration = 50.0 mg/L, solution volume = 20.0 mL and
shaking time = 30 min.).

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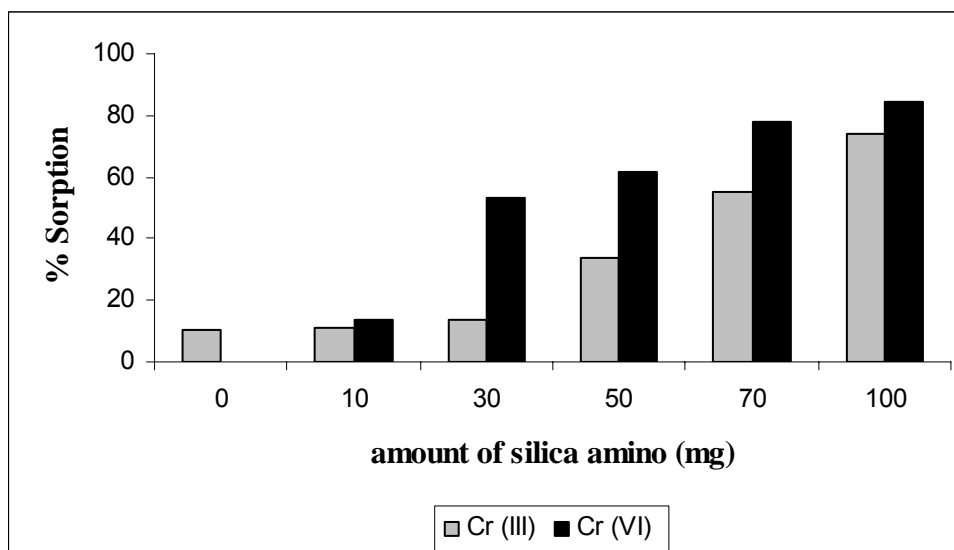
Figure 3.27. Percent sorption versus the amount of silica amino (pH=4; Cr(III) and Cr(VI) concentration = 50.0 mg/L, solution volume = 20.0 mL and shaking time = 30 min.).

3.2.2.2.4. Effect of Initial Cr(III) or Cr(VI) Concentration

As explained in the experimental part, sorption studies with silica amino and amino sol-gel were performed for Cr(III) and Cr(VI) species. Appropriate amount of amino sol-gel and silica amino (0.05 g) added into each solution (20.0 mL). The range of concentration of Cr(III) and Cr(VI) species were varied from 1.0 to 50.0 mg/L. As can be seen from Figure 3.28., the percentage sorption of silica-gel decreases with increasing the concentration of Cr(III). The same result is obtained for the concentration of Cr(III) and Cr(VI) species on silica-amino and amino sol-gel. Here, a prominent finding is that, silica amino and amino sol-gel can be used for the sorption of higher concentrations of Cr(III) and Cr(VI) whereas the silica (blank) works only for lower concentrations of Cr(III).
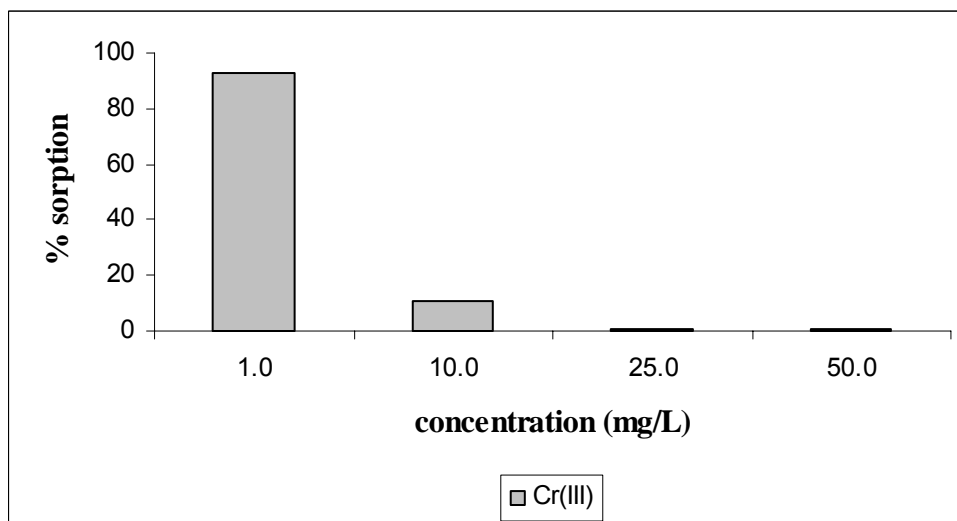
Figure 3.28. Percent sorption with silica-gel versus the initial concentration of Cr(III) (pH =3, solution volume = 20.0 mL, sorbent amount = 50.0 mg and shaking time = 30 min.)
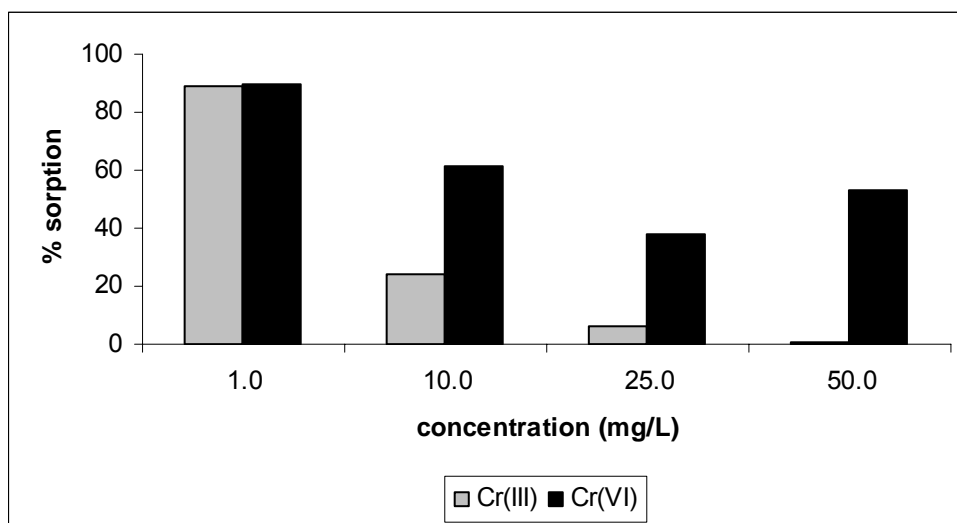
Figure 3.29. Percent sorption with amino sol-gel versus the initial concentration of Cr(III) and Cr(VI) (pH = 3 for Cr(VI) and pH = 4 for Cr(III); solution volume = 20.0 mL, sorbent amount = 50.0 mg and shaking time = 30 min.)
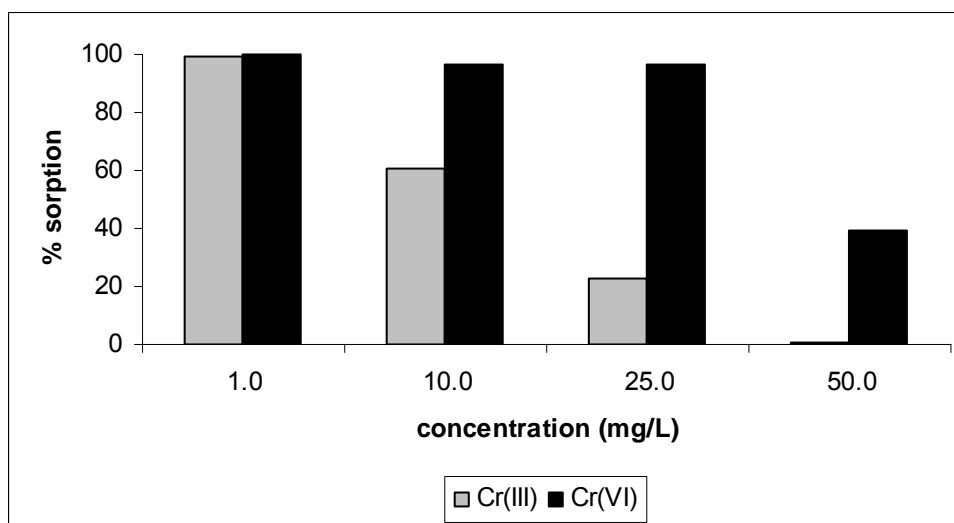
Figure 3.30. Percent sorption with silica amino versus the initial concentration of Cr(III) and Cr(VI) (pH = 4; solution volume = 20.0 mL and sorbent amount = 50.0 mg and shaking time = 30 min.)

3.2.2.2.5. Desorption from the Amino Sol-Gel and Silica-amino

In order to study the desorption behaviour of Cr(III) and Cr(VI) species from the amino sol-gel and silica-amino, HCl was used as eluent and examined at different acid concentrations (0.1-2.0 M). Recovery studies were first performed using batch process. After the usual sorption process (mixing and shaking 20.0 mL of 1.0 mg/L Cr(III) and Cr(VI) species with 0.05 g of amino sol-gel and with 0.1 g of silica amino), the mixture was filtered through filter paper and the resin was taken into the eluent. The mixture was shaken for another 15 minutes and at the end of this period, the contents were filtered and the filtrate was analyzed by FAAS. The eluent concentrations and the corresponding recoveries are given in Table 3.6. These values of Cr(VI) on both sorbents were between 60-80% with 2.0 M HCl giving a maximum recovery of 80%. Therefore, 2.0 M HCl was chosen as the desorption solution (eluent).

Table 3.6. Desorption of sorbed Cr(III) and Cr(VI) from sorbents (n=2).

| Eluent | % Recovery | | | |
| | amino sol-gel | | silica amino | |
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0,1 M HCl	51 (±2)	39 (±1)	4 (±1)	20 (±4)
0,5 M HCl	51 (±1)	51 (±2)	6 (±1)	39 (±2)
1 M HCl	55	56 (±2)	8 (±2)	74 (±2)
2 M HCl	**55 (±2)**	**60 (±3)**	**15 (±6)**	**79 (±4)**

CHAPTER 4

CONCLUSION

The purpose of this study was to develop a speciation and/or preconcentration method for Cr(III) and Cr(VI) in waters. For this purpose, the initial part of the study has focused on the search of an appropriate commercial sorbent. The relevant experiments employed Amberlite XAD-2, Amberlite XAD-4, Duolite XAD-761, Supolite DAX-8, Celite C-545 AW), anion exchanger (Duolite A-7) and chelating resins (Duolite C-467). These materials exhibited high sorption capacity for Cr(III), but not for Cr(VI).

In addition to the investigated commercial sorbents, a resin having immobilized mercapto or amino functional groups was prepared by modifying silica gel with 3-mercaptopropyltrimethoxy silane, 3-aminopropyltrimethoxy silane, L-glutamic acid dimethyl ester, aminophenol, aminothiophenol and aminobenzothiazole for the preconcentration of Cr(III) and Cr(VI) species in waters prior to their determination by FAAS. The characterizations of new sorbents were performed with SEM/EDS, TGA and elemental analysis.

After synthesis and characterization of the new sorbents, optimum application conditions for separation and/or preconcentration of Cr(III) and Cr(VI) species were investigated by batch method. The choice of the adsorbent will be based on the working pH. After pH 4, silica amino could quantitatively sorb both Cr(III) and Cr(VI) whereas amino sol-gel sorbed only Cr(III). Effect of the amount of silica amino and amino sol-gel was examined at the optimum pH. Silica amino has a better sorption performance for small amounts (<100 mg). The optimum amount of silica amino for quantitative sorption was found as 0.1 g for 20.0 mL 1.0 mg/L Cr(III) and Cr(VI) solutions whereas that of amino sol-gel was 0.05 g for 20.0 mL 1.0 mg/mL. The effect of Cr(III) and Cr(VI) concentrations on amino sol-gel and silica amino were investigated at the initial concentrations of 1.0, 10.0, 25.0 and 50.0 mg/L. The percentage sorption of silica amino and amino sol-gel decreased with increasing the concentration of Cr(III) and Cr(VI) species. Elution was realized with 2.0 M HCl, and the percent recovery values (after sorption and elution steps) changed between 60 and 80 %.

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