

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, we present the sorption capability of Si-Amidoxime and Si-Benzothiazole. The effect of several parameters is discussed. The spiked method is used to validate the proposed procedure for the preconcentration and speciation of chromium.

4.1 Adsorption study

The chromium adsorption efficiency is reported in term of sorption capacity which defined as the amount of sorbed chromium (mg) per the amount of sorbent according to equation 4.1:

$$\text{sorption capacity} = \frac{n_i - n_f}{m} \quad (4.1)$$

where n_i is the initial amount of chromium (mg), n_f is the amount of chromium species in supernatant (mg) and m is the amount of sorbent (g).

4.1.1 Effect of solution pH

The adsorption of chromium as a function of pH of aqueous solution onto Si-Amidoxime and Si-Benzothiazole was studied using batch system. The influence of solution pH strongly depends on the nature of the sorbent used. When the adsorption of chromium is based on chelation (either in the sample or on the solid sorbent), the sample pH is very important factor because most chelating ligands are conjugated bases of weak

acid groups and they have a very strong affinity for hydrogen ions. The acidity of solution has two effects on chromium adsorption. Firstly, nitrogen atoms of amine and imine groups on benzothiazolyl and amidoxime moieties acting as electron donor might be protonated resulting in positive charge of nitrogen on the surface. Secondly, several forms of Cr(III) and Cr(VI) in aqueous solution are found as described in section 2.1. Therefore, pH of solution was the first parameter to be optimized. The adsorptions of individual Cr(III) and Cr(VI) onto Si-Amidoxime and Si-Benzothiazole are shown in Figure 4.1 and Figure 4.2, respectively.

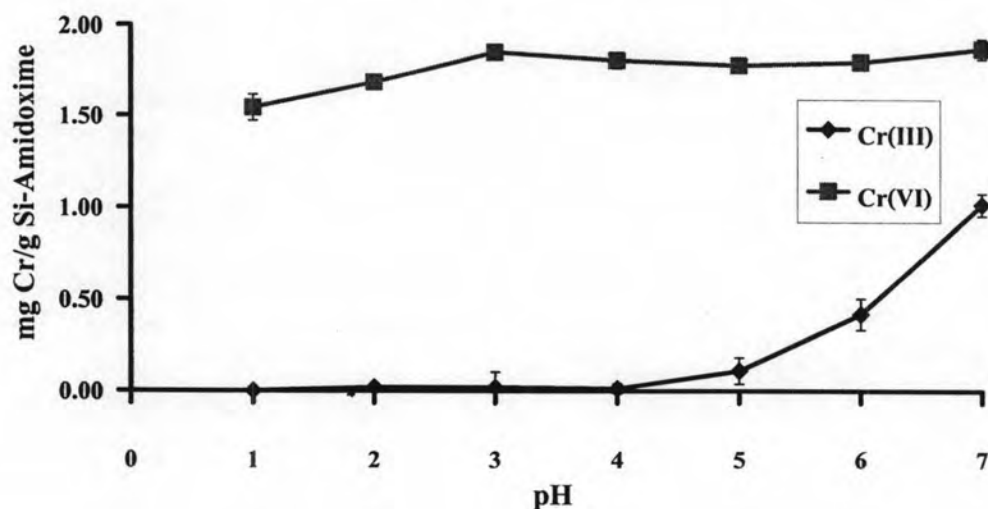


Figure 4.1 Effect of solution pH on Cr(III) and Cr(VI) adsorption onto Si-Amidoxime

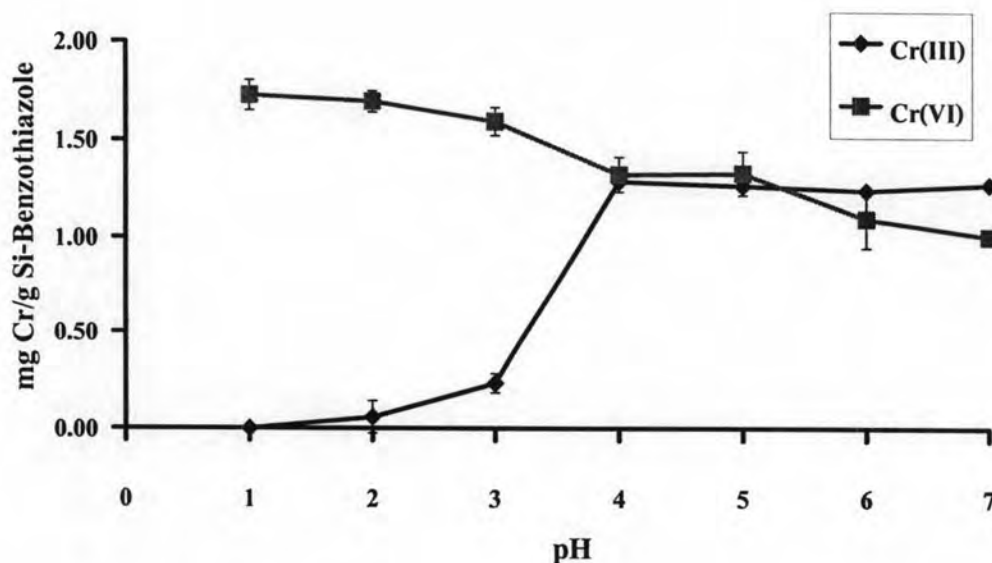


Figure 4.2 Effect of solution pH on Cr(III) and Cr(VI) adsorption onto Si-Benzothiazole

It was found that when pH values of solution increased, the Cr(III) adsorption efficiency increased. The maximum sorption capacity of Cr(III) onto Si-Benzothiazole was observed at pH ranging from 4.0-7.0 while the sorption capacity of Cr(III) by Si-Amidoxime was maximum at pH 7.0. However, it seems that the Cr(III) adsorption should increase while the pH values increase; nonetheless, the experiments were not performed because the precipitation of Cr(III) hydroxide occurred at pH higher than 7.

It can be explained that in strongly acidic solution, Si-Amidoxime and Si-Benzothiazole surface should be positively charged by protonation of amine and imine groups which cannot bind Cr(III). Therefore the Cr(III) adsorption efficiency was low. When pH values of solution increased, deprotonation of nitrogen donor atoms was occurred and they became electron donors for Cr(III), resulting in higher adsorption efficiency. We propose that Cr(III) would bind to the N, O moiety of benzothiazolyl on sorbent and would bind to the N, O moiety of amidoxime on sorbent. The assumption of the chelate complex by amidoxime group with metal ion proposed by Lutfor et al. [53] is shown in Figure 4.3.

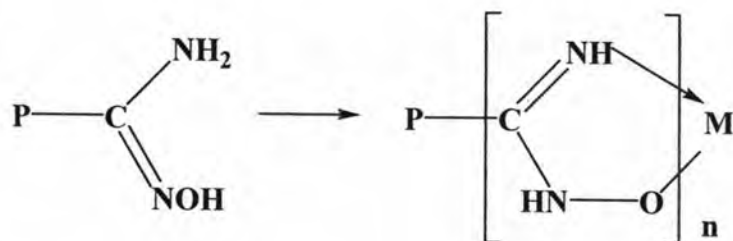


Figure 4.3 The chelate complex by amidoxime ligand with metal ion [53]

(P = backbone polymer, n = oxidation state of metal, M = metal)

Comparison with Cr(III), the higher sorption of Cr(VI) onto Si-Amidoxime was observed at pH range 1.0-7.0 while the higher sorption onto Si-Benzothiazole was observed in strongly acidic medium. The sorption capacities of Cr(VI) by Si-Amidoxime and Si-Benzothiazole showed little pH dependent effect.

As we described in section 2.1, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ become the dominant species of Cr(VI). So Cr(VI) exhibits a typical anionic sorption. The sorbent therefore acts as anion receptor which can be classified into two classes: the positively charged receptors and the neutral anion receptors. The latter is the way to avoid the problem of pH range. Si-Amidoxime and Si-Benzothiazole containing amine and imine functional groups which can be protonated, resulting in positive charge, can bind Cr(VI) anion species via electrostatic interaction at low pH. Moreover, amide linkage can also bind anion via hydrogen bonding at a wide range of pH. The similar explanation for extraction of Cr(VI) was described in several reports [61-63].

By comparing the two sorbents, the sorption capacities of Cr(III) and Cr(VI) at optimum pH are given in Table 4.1.

Table 4.1 Sorption capacities of Cr(III) and Cr(VI) at optimum pH onto Si-Amidoxime and Si-Benzothiazole

	Si-Amidoxime		Si-Benzothiazole	
	optimum pH	sorption capacity (mg g ⁻¹)	optimum pH	sorption capacity (mg g ⁻¹)
Cr(III)	7.0	1.02	4.0-7.0	1.29
Cr(VI)	3.0-7.0	1.87	1.0-2.0	1.73

The interesting feature of the experimental observation was that the highest sorption of Cr(VI) onto Si-Amidoxime at pH 4.0 was observed while the negligible sorption of Cr(III) was observed at this pH. Moreover, Cr(III) can be quantitatively sorbed onto Si-Benzothiazole at pH 4.0 (Figure 4.4). Therefore, we propose to use Si-Amidoxime for Cr(VI) adsorption and Si-Benzothiazole for Cr(III) adsorption for further studies.

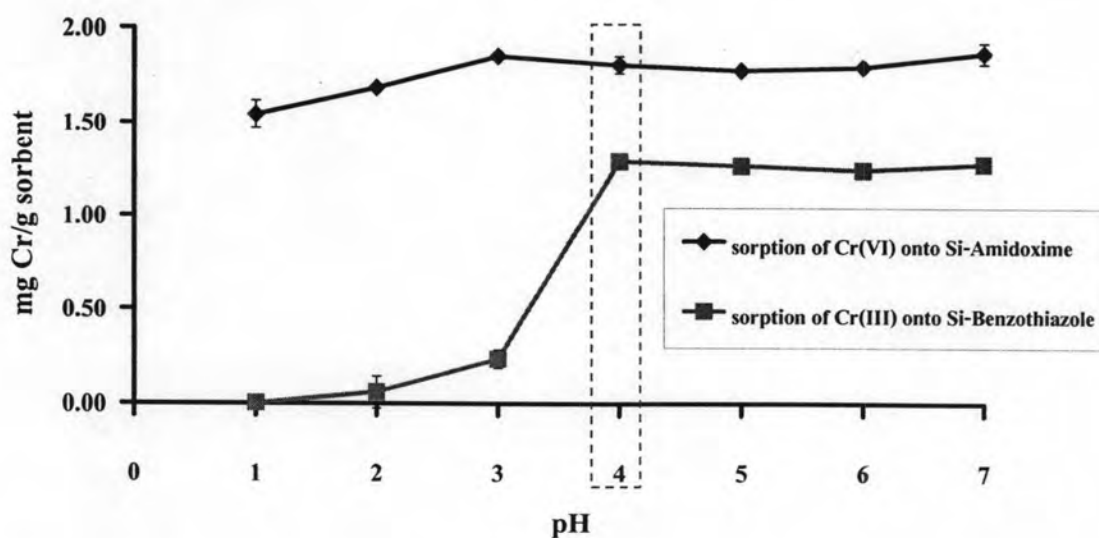


Figure 4.4 Comparison of Cr(VI) adsorption onto Si-Amidoxime and Cr(III) adsorption onto Si-Benzothiazole as a function of pH

A summary of the pH value for the retention of Cr(III) and Cr(VI) varied in the different sorbents is shown in Table 4.2.

Table 4.2 Values of pH for retention of different chromium species [64]

pH		sorbent	Ref.
Cr(III)	Cr(VI)		
3.8		Muromac A-1 resin	[65]
4.0-7.0		Si-Benzothiazole	Present work
4.5		Sephadex C-25	[25]
5.0-5.5		polyacrylamide modified with nitrilo triacetic acid	[66]
7.0		Si-Amidoxime	Present work
9.0		Ion exchange resin	[67]
	1.0-2.0	Si-Benzothiazole	Present work
	3.0-7.0	Si-Amidoxime	Present work
	6.0	sodium dodecyl sulphate coated alumina	[7]
2.0	2.0-3.0	Adogen 464 supported on silica gel	[47]
4.0	4.0	Si-Amidoxime and Si-Benzothiazole	Present work
7.0	1.5	C-18 bonded silicagel	[44]
2.0-2.5	3.5-4.5	anion- and cation-exchange columns	[38]

4.1.2 Effect of contact time

The rates of loading of chromium onto Si-Amidoxime and Si-Benzothiazole were determined by agitating the working standard solution with chemically modified silica gel at optimum pH with different contact times. The results are shown in Figure 4.5 and Figure 4.6 for Cr(III) and Cr(VI) adsorptions, respectively. The contact time required for reaching equilibrium was 60 and 5 min for adsorption of Cr(III) and Cr(VI), respectively. The rate of chromium adsorption is sufficiently rapid. Therefore, it is suitable for flow system.

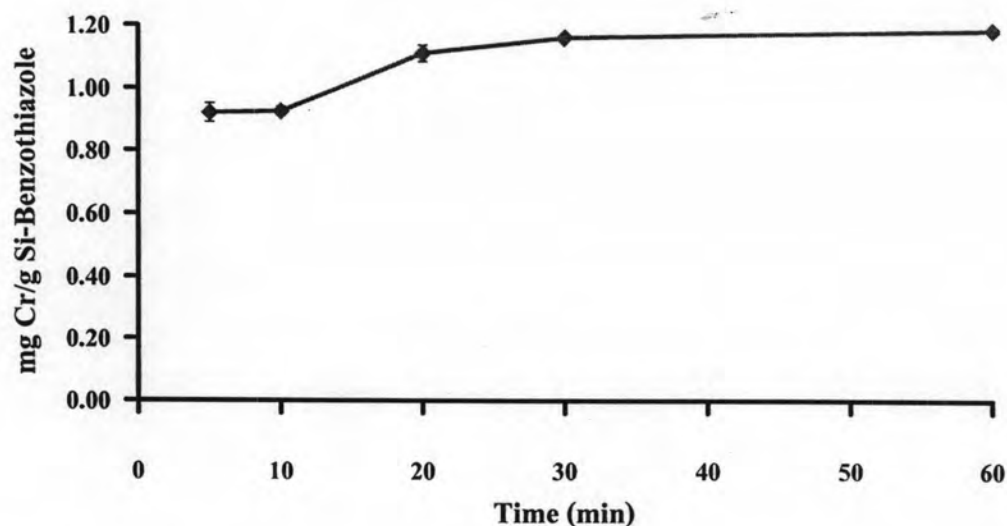


Figure 4.5 Effect of contact time of Cr(III) adsorption onto Si-Benzothiazole

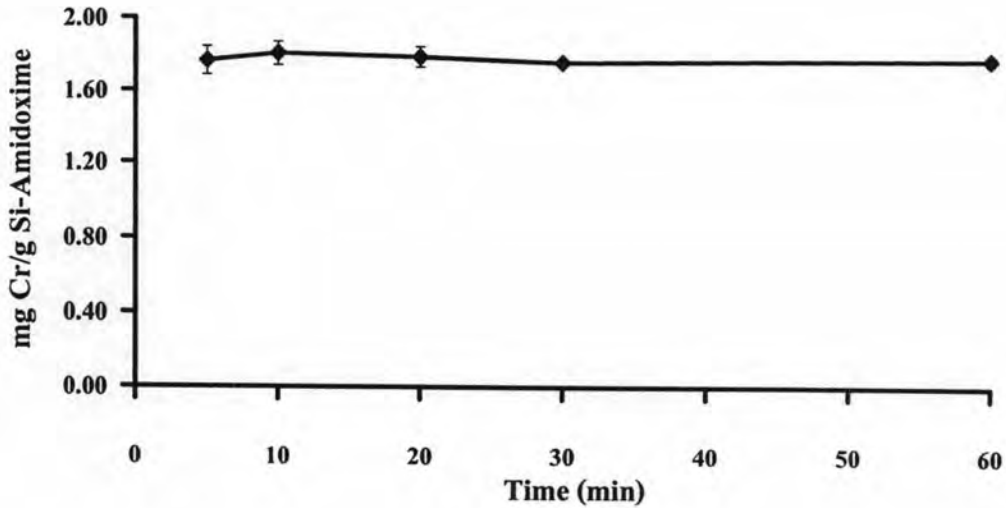


Figure 4.6 Effect of contact time of Cr(VI) adsorption onto Si-Amidoxime

4.1.3 Sorption capacity

The adsorption phenomena at the solid-liquid interface are commonly described by the adsorption isotherm model. The Langmuir treatment is based on the assumption that the maximum adsorption corresponds to saturated monolayer of adsorbed species on the silica surface and there is no other mechanism such as migration of the metal ions in the plane of the surface [68-73]. The data reveal that the adsorption process conforms to the Langmuir model [68-71], according to equation 4.2:

$$\frac{C}{N_f} = \frac{C}{N_f^s} + \frac{1}{bN_f^s} \quad (4.2)$$

where C = the concentration of metal ion solution at equilibrium (mol L^{-1})

N_f = the amount of metal ion per gram of sorbent (mol g^{-1})

b = the Langmuir constant related to energy of adsorption (L mol^{-1})

N_f^s = the maximum amount of metal adsorbed per gram of sorbent (mol g^{-1})

The results showed the linearity of the adsorption isotherm derived from the C/N_r as a function of C plot (illustrated in Figure 4.7 and Figure 4.8, respectively), indicating that the adsorption isotherm of Si-Benzothiazole for Cr(III) and Si-Amidoxime for Cr(VI) obeyed Langmuir type adsorption model

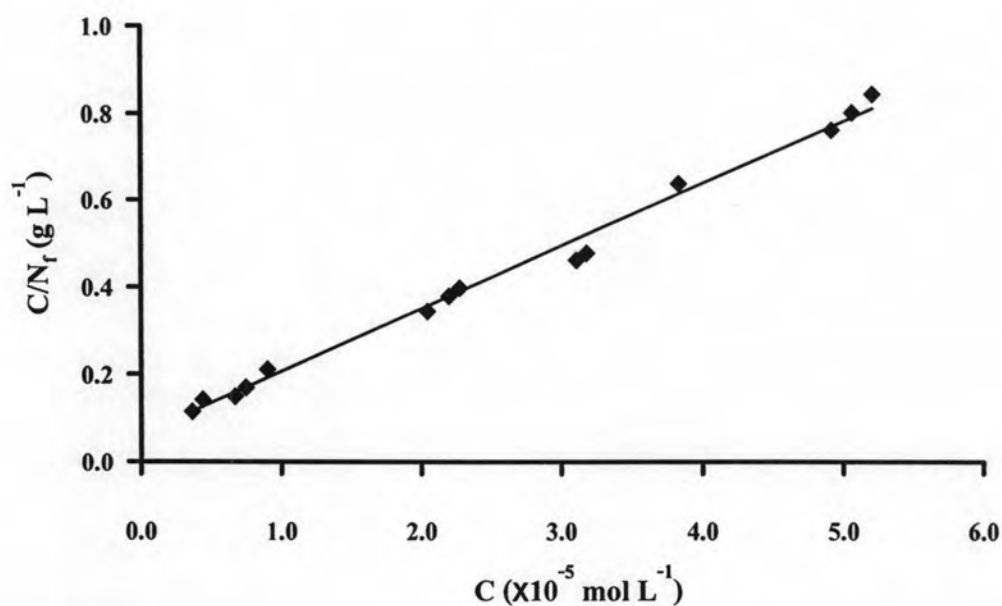


Figure 4.7 Langmuir adsorption model of Cr(III) onto Si-Benzothiazole at 298 K

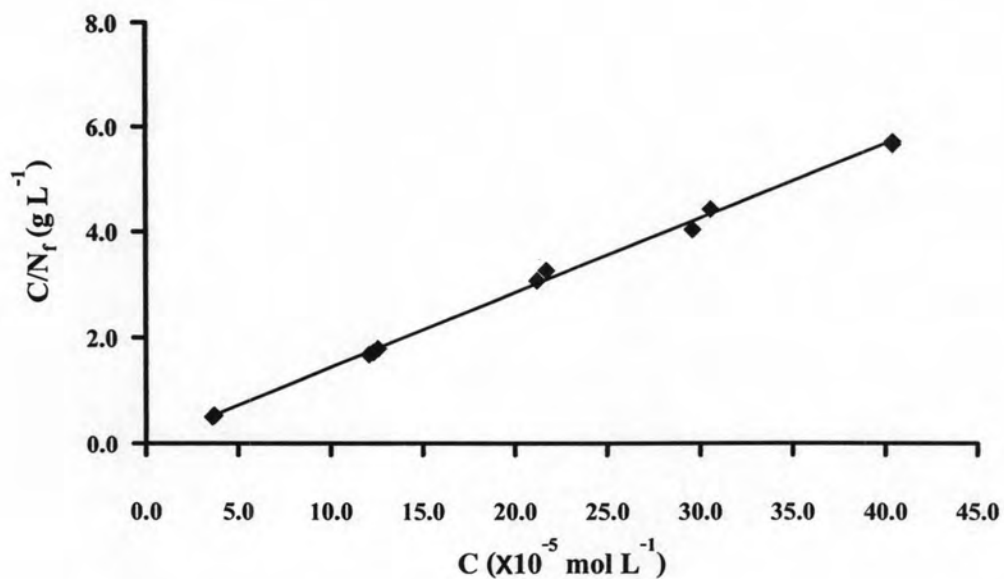


Figure 4.8 Langmuir adsorption model of Cr(VI) onto Si-Amidoxime at 298 K

The calculated parameters: maximum sorption capacity (N_f^s), b value and correlation coefficient (r) from the Langmuir plots, are reported in Table 4.3.

Table 4.3 Calculated Langmuir constants for Cr(III) and Cr(VI) adsorption at 298 K

	Equation	N_f^s (mol g ⁻¹) × 10 ⁻⁴	b (L mol ⁻¹) × 10 ⁴	r
Cr(III)-Si-Benzothiazole	$y = 14398x + 0.0623$	0.69	23.3	0.9961
Cr(VI)-Si-Amidoxime	$y = 14126x + 0.0268$	0.71	52.6	0.9993

The maximum sorption capacities were 0.69×10^{-4} and 0.71×10^{-4} mol g⁻¹ for Cr(III) and Cr(VI), respectively.

The b value were high corresponding to strong binding affinity of Cr(III) onto Si-Benzothiazole and Cr(VI) onto Si-Amidoxime.

The sorption capacities and the weight of sorbent used are compared with those of other modified silica gel, reported in the literature shown in Table 4.4.

Table 4.4 Comparison of sorbent weight, sorption capacity of Si-Amidoxime and Si-Benzothiazole with other modified silica gel

Modified silica	Sorbent weight (mg)	Species	Sorption capacity (mmol g ⁻¹)	pH	Ref.
Si-Amidoxime	20	Cr(VI)	0.071	4.0	Present work
Propylenediamine – butylcalix[4] arene	30	Cr(VI)	0.013	2.37	[74]
Si-Benzothiazole	50	Cr(III)	0.069	4.0	Present work
N-(3-propyl)-O-phenylene	40	Cr(III)	0.35-0.45	7.0-8.0	[75]
N-propylsalicylalimine	100	Cr(III)	0.36	9.0-9.5	[76]

4.2 Preconcentration study

4.2.1 Effect of sample flow rate

The sample flow rate through the sorbent should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. The results are illustrated in Figure 4.9 and Figure 4.10 for Cr(III) and Cr(VI), respectively.

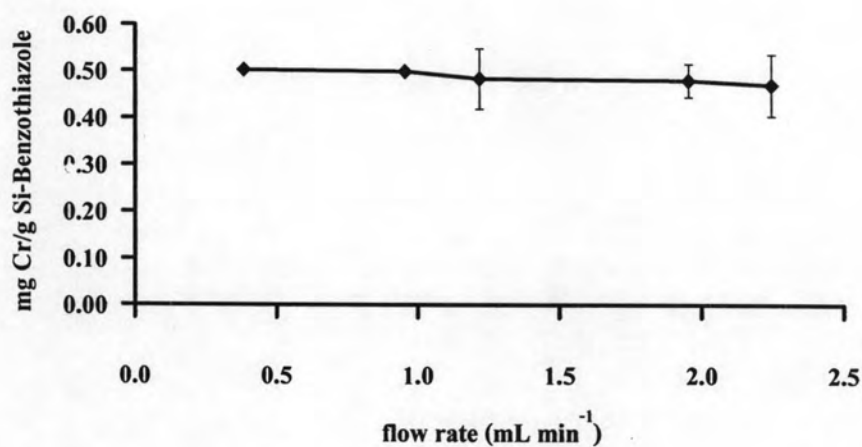


Figure 4.9 Effect of sample flow rate of Cr(III) sorption onto Si-Benzothiazole

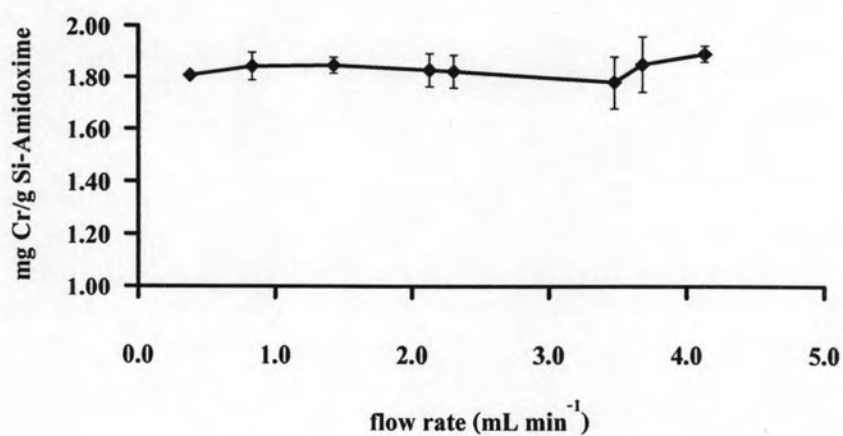


Figure 4.10 Effect of sample flow rate of Cr(VI) sorption onto Si-Amidoxime

The optimum flow rate for maximum sorption of Cr(III) onto Si-Benzothiazole was 0.5 mL min^{-1} . At high flow rate, sorption capacity was decreased due to the increasing in velocity of ions that reduced the contact time. The sorption capacity of Cr(VI) onto Si-Amidoxime showed no significant change in the flow rate of $0.5\text{-}4.0 \text{ mL min}^{-1}$. Thus, the flow rate of 0.5 mL min^{-1} was chosen for Cr(III) and the flow rate of 2.0 mL min^{-1} was found to be suitable for Cr(VI) to avoid a longer time of analysis.

4.2.2 Effect of eluent

Elution efficiency of Cr(III) and Cr(VI) from the sorbents was performed with various eluents in column method. The chromium desorption efficiency was determined by equation 4.3:

$$\text{elution (\%)} = \frac{n_e}{n_i - n_f} \times 100 \quad (4.3)$$

where n_e is the amount of chromium eluted from the sorbent (mg), n_i is the initial amount of chromium (mg) and n_f is the amount of chromium species in supernatant (mg).

The same kind of interactions usually occurs during the retention and the elution steps. The type of eluent must be correctly chosen to ensure stronger affinity of the eluent for metal ion. For example, if retention on the sorbent is due to chelation, the eluent should contain a chelating reagent that rapidly forms a stronger complex with metal ion. Elution may also be achieved using an acid that will disrupt the chelate and displace the free chromium.

As the results shown in section 4.1.1, the retention of Cr(III) onto Si-Benzothiazole is due to chelation under the optimum pH range of 4.0-7.0, the eluent could contain a stronger chelating reagent such as EDTA that forms a stronger complex with Cr(III) [77-78]. Desorption can be also induced by acidification that will disrupt the chelate and displace the free Cr(III), corresponding to non-sorption of Cr(III) onto Si-Benzothiazole at

low pH. Nitric acid was chosen for elution of sorbed Cr(III) because it is a suitable matrix for the determination step by FAAS. The acid concentration was an important factor because small amount of proton may be not enough to protonate the chelating site. The various concentrations of nitric acid solution and EDTA solution were therefore chosen to study the elution of Cr(III) from Si-Benzothiazole. The flow rate of 0.5 mL min^{-1} was chosen to ensure efficient elution. The results are summarized in Table 4.5.

Table 4.5 Effect of eluent on elution of Cr(III) from Si-Benzothiazole

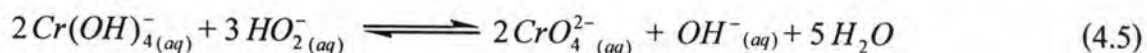
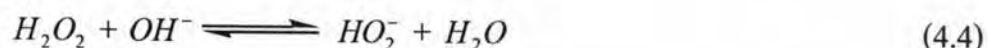
Type of eluents	Elution* (%)
% HNO₃ (v/v)	
1	39 (2)
5	40 (2)
10	44 (1)
EDTA solutions (0.0005 M)	
at pH <7	7 (2)
at pH >7	4 (1)
10 % (v/v) H₂O₂ in 0.1 M NaOH	100 (1)

*Mean value (SD), n = 3

It was found that 1-10 % HNO₃ was not able to quantitatively elute Cr(III) in range of 35-50 %. The similar results for the elution of Cr(III) from modified silica surface was reported by Csoban et al. [24, 26]. Some elution of Cr(III) from Si-Benzothiazole could be observed with 1-10 % elution for EDTA solutions. It seems that the binding constant of Cr(III) with ligand on Si-Benzothiazole is probably higher than that between Cr(III) and EDTA.

Due to the low elution efficiency, another eluent should be tried to elute Cr(III) from Si-Benzothiazole. The oxidation of Cr(III) to Cr(VI) before elution may be performed

in H_2O_2 in basic medium [79] and the Cr(VI) anion could be eluted by basic solution. The oxidation of Cr(III) to chromate by H_2O_2 in basic solution may be formulated as equation 4.4 and 4.5:



The results in Table 4.5 show that 10 % H_2O_2 in 0.1 M NaOH could quantitatively elute Cr(III) from Si-Benzothiazole. This indicated that the oxidation of Cr(III) into Cr(VI) was occurred. To confirm the oxidation of Cr(III), the solution after passing 10 % H_2O_2 in 0.1 M NaOH to the sorbed Cr(III) on Si-Benzothiazole was characterized by UV-vis spectrometry because the spectrophotometric method is a precise method to distinguish Cr(VI). It is based either on the yellow color of chromate ions present in alkaline solution, or on the orange color of dichromate color of dichromate ions, formed from acidification of the chromate ion solution. The maximum absorption peaks at 350 and 373 nm correspond to dichromate and chromate, respectively. Figure 4.11 shows the experimental result of absorption spectra of Cr(VI) in basic medium ($\lambda_{max} = 373$ nm) compared with the eluted Cr solution. The absorption spectrum of the eluted Cr solution was also observed at 373 nm. This result indicates that the oxidation of Cr(III) into Cr(VI) was occurred.

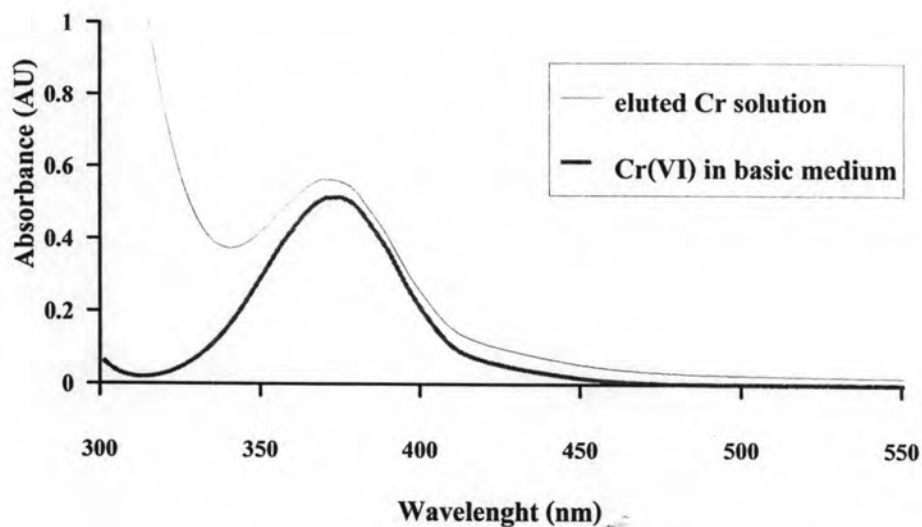
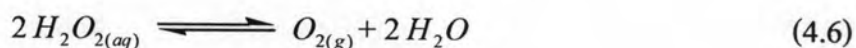


Figure 4.11 Absorption spectra of Cr(VI) in basic medium and eluted Cr solution

Although, the concentration of hydrogen peroxide was an important factor because of the decomposition of H_2O_2 in basic medium (shown in equation 4.6) as described by Andersen et al. [79], 10 % H_2O_2 in basic solution was enough to quantitatively elute chromium from Si-Benzothiazole.



In the case of the elution of Cr(VI) from Si-Amidoxime, as the retention of Cr(VI) on Si-Amidoxime is due to electrostatic attraction or H-bonding, the elution should be performed by basic solution such as NaOH [62]. The elution of Cr(VI) from Si-Amidoxime was performed with NaOH at different concentrations. The results are given in Table 4.6.

**Table 4.6** Effect of eluent on elution of Cr(VI) from Si-Amidoxime

Type of eluents	Elution* (%)
NaOH solution	
0.01 M	85 (1)
0.1 M	88 (2)
1.0 M	91 (1)
10 % (v/v) H₂O₂ in 0.1 M NaOH	101 (2)

*Mean value (SD), n = 3

It was noted that the color change of Si-Amidoxime from yellow to black, after contacting with Cr(VI) solution was observed. It was probably due to the redox property of amidoxime group, as reported by Lin et al. [54]. They studied the extraction of Au(III) by amidoxime reactive fiber and found the partially reduction of adsorbed Au(III) into spongy metallic gold and the oxidation of the amidoxime group into carboxyl group. This indicates that the oxidation-reduction between amidoxime moiety on Si-Amidoxime and some adsorbed Cr(VI), probably resulting in Cr(III), was occurred. The mechanism of retention of Cr(III) on Si-Amidoxime would be chelation, as mention in section 4.1.1. Therefore, 0.01-1 M NaOH could not be able to elute Cr(III) from Si-Amidoxime, resulting in less than 100 % elution.

To confirm the partially reduction of adsorbed Cr(VI) on Si-Amidoxime, the sequential elution using 5.0 mL of 0.1 M NaOH to elute Cr(VI) and 5.0 mL of 10% H₂O₂ in 0.1 M NaOH to elute Cr(III) resulting from amidoxime and Cr(VI) reaction was investigated. The results are shown in Table 4.7.

Table 4.7 Amounts of chromium in starting solution and effluents after sequential elution

Solution	Amount of Cr (mg)
Starting solution	0.041
Effluent 1 (0.1 M NaOH)	0.032
Effluent 2 (10% H ₂ O ₂ in 0.1 M NaOH)	0.007

It was observed that the sum of the amount of chromium from two effluents was not significantly different that of starting solution, indicating that the partially reduction of adsorbed Cr(VI) on Si-Amidoxime was occurred.

The elution of Cr(VI) from Si-Amidoxime was then performed with 10% H₂O₂ in 0.1 M NaOH, giving the quantitative elution as shown in Table 4.6. Therefore, this eluent was appropriated to elute Cr(VI) from Si-Amidoxime.

In order to evaluate the reuse of the solid sorbent, the effect of the solid sorbent regeneration on the sorption capacity was preliminary investigated using the following procedure:

For Cr(VI), 5.0 mL of 8.0 mg L⁻¹ Cr(VI) at pH 4.0 was passed through a mini-column packed with Si-Amidoxime with a flow rate of 2.0 mL min⁻¹. The retained chromium was eluted from the column by 5.0 mL of 10 % H₂O₂ in 0.1 M NaOH with a flow rate of 0.5 mL min⁻¹. This column was washed using 10.0 mL of milli-Q water before reuse.

The Si-Benzothiazole regeneration for Cr(III) was performed in the same manner using 5.0 mL of 5.0 mg L⁻¹ Cr(III) at pH 4.0.

The results are summarized in Table 4.8.

Table 4.8 Effect of Si-Amidoxime and Si-Benzothiazole regeneration on sorption capacity of Cr(VI) and Cr(III) at pH 4.0

Number of use	Sorption capacity (mg g ⁻¹)	
	Si-Amidoxime-Cr(VI)	Si-Benzothiazole-Cr(III)
1	1.89	1.25
2	0.21	1.23

The results showed no significant difference of sorption capacity for Cr(III) on Si-Benzothiazole. This indicates that the active site on Si-Benzothiazole was not destroyed by 10 % (v/v) H₂O₂ in 0.1 M NaOH. This result therefore suggests the possibility of the reuse of Si-Benzothiazole. On the other hand, Si-Amidoxime can use only once for the retention of Cr(VI) with high efficiency.

4.2.3 Effect of sample volume

An important parameter to control in SPE and to deal with real samples containing very low concentration of trace chromium is the maximum applicable sample volume that percolate through a given mass of sorbent after which analytes start to elute from the sorbent resulting in non-quantitative recoveries. Therefore, the effect of sample volume on the recoveries was investigated. It was studied by a procedure using an increasing volume of chromium solution, and keeping the total amount of loaded chromium constant: 15 µg for Cr(III) and 25 µg for Cr(VI). The recovery (%) was calculated by the following equation 4.7:

$$\text{recovery (\%)} = \frac{n_e}{n_i} \times 100 \quad (4.7)$$

where n_e is the amount of chromium eluted from the sorbent (mg) and n_i is the initial amount of chromium (mg).

The recoveries obtained will be compared with the acceptable range of estimated recovery and RSD summarized in Table 4.9.

Table 4.9 Analyte recovery and precision at different concentration [80]

Analyte, %	Analyte ratio	Unit	Mean recovery, %	RSD, %
100	1	100%	98-102	1.3
10	10^{-1}	10%	98-102	2.8
1	10^{-2}	1%	97-103	2.7
0.1	10^{-3}	0.1%	95-105	3.7
0.01	10^{-4}	100 ppm	90-107	5.3
0.001	10^{-5}	10 ppm	80-110	7.3
0.0001	10^{-6}	1 ppm	80-110	11
0.00001	10^{-7}	100 ppb	80-110	15
0.000001	10^{-8}	10 ppb	60-115	21
0.0000001	10^{-9}	1 ppb	40-120	30

The results are shown in Table 4.10.

Table 4.10 Effect of sample volume on the recovery

Sample volume (mL)	Recovery (%)*	
	Cr(III)-Si-Benzothiazole	Cr(VI)-Si-Amidoxime
5	89 (3)	**
10	95 (3)	**
25	98 (1)	98 (1)
50	86 (3)	98 (4)
100	92 (0)	98 (1)
250	**	95 (1)
500	**	96 (1)

*Mean value (SD), n = 3

** not performed

It was found that the recovery of Cr(III) onto 50 mg of Si-Benzothiazole was not effected by the sample volume in range of 5-100 mL with the percent recovery of 86-98. The sample volume higher than 100 mL was not performed because the adsorption kinetic of Cr(III) onto Si-Benzothiazole was too slow resulting in time consuming, probably not suitable for preconcentration of Cr(III). In the case of Cr(VI), the results showed good recoveries of Cr(VI) onto 20 mg of Si-Amidoxime in all sample volumes in range of 25-500 mL. No breakthrough volume was occurred in these sample volume ranges.

In order to apply the preconcentration procedure to speciation analysis of Cr(III)/Cr(VI), the suitable sample volume of 100 mL was chosen for further experiments.

4.2.4 Effect of interfering ions

The presence of ions other than the considered species in the sample may cause problems during the preconcentration. In particular, due to their usually high levels, they may hinder the preconcentration step by overloading the sorbent or cause interferences during determination step. Therefore, their influence should be studied. The cations and anions used in this study were chosen from their major abundance in nature, i.e. Na^+ , K^+ , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} . The salts used for interfering cation and anion studies were chloride salt and sodium salt, respectively. The experiments were performed in 3 levels of the interfering ion concentration under the optimum conditions of Cr(III) and Cr(VI). The interference was apparent if the recovery of chromium decreases in the presence of interfering ions. The results obtained are given in Table 4.11.

Table 4.11 Effect of interfering ions on the recovery of Cr(III) and Cr(VI)

Interfering ions	Recovery* (%)			
	no interfering ion	10 mg L ⁻¹	100 mg L ⁻¹	1000 mg L ⁻¹
Cr(III)	92 (0)	-	-	-
<i>Na</i> ⁺		90 (7)	92 (7)	95 (3)
<i>K</i> ⁺		84 (1)	91 (2)	90 (1)
<i>Ca</i> ²⁺		90 (3)	93 (3)	92 (4)
Cr(VI)	98 (1)	-	-	-
<i>Cl</i> ⁻		93 (3)	87 (2)	31 (7)
<i>NO</i> ₃ ⁻		103 (9)	91 (5)	17 (2)
<i>SO</i> ₄ ²⁻		16 (1)	6 (1)	2 (1)

* Mean value (SD), n = 3

It was found that the recoveries of Cr(III) at all 3 levels of interfering ion concentration were not different from those in the absence of Na^+ , K^+ , Ca^{2+} . These results indicated that all interfering ions did not interfere Cr(III) adsorption and Si-Benzothiazole has a potential to apply to real sample.

On the other hand, the interfering anions affected Cr(VI) adsorption onto Si-Amidoxime. However, Cl^- and NO_3^- anions at 10 and 100 mg L^{-1} slightly decreased Cr(VI) adsorption, but they significantly affected at high level concentration. In the case of sulfate ion, it significantly quenched Cr(VI) adsorption at all 3 concentrations. This indicated that these three anions act as competitive anion to Cr(VI) onto Si-Amidoxime.

Two factors that are probably involved in anion adsorption onto Si-Amidoxime are geometry and size of anions, given in Table 4.12, which account for the selective anion receptors because of the complementary binding sites in a proper three-dimension arrangement [81].

Table 4.12 The size and geometry of various anions [21, 82]

Anions	Radius (pm)	Geometry
Cl^-	181	spherical
NO_3^-	179	trigonal planar
SO_4^{2-}	230	tetrahedral
CrO_4^{2-}	240	tetrahedral

4.3 Speciation analysis

Speciation of chromium in synthetic sample by FAAS with dual mini-column containing Si-Amidoxime and Si-Benzothiazole was investigated. In this system, Cr(VI) was collected on the first column (packed with 20 mg of Si-Amidoxime). The effluent containing Cr(III) from the first column was collected on the second column (packed with 50 mg of Si-Benzothiazole). This procedure was performed under the optimum conditions given in Table 4.13.

Table 4.13 The optimized conditions of preconcentration and speciation of chromium

Parameters	Optimized conditions
Sorbent	50 mg Si-Benzothiazole and 20 mg Si-Amidoxime
Starting concentration	150 $\mu\text{g L}^{-1}$ Cr(III) and 250 $\mu\text{g L}^{-1}$ Cr(VI)
Sample volume	100 mL
Sample flow rate	0.5 mL min ⁻¹
Eluent	5.0 mL of 10% H ₂ O ₂ in 0.1 M NaOH
Eluent flow rate	0.5 mL min ⁻¹
Preconcentration factor	20

The results are shown in Table 4.14.

Table 4.14 Speciation of chromium in 100 mL synthetic sample

Cr species	Recovery*, %	RSD, %
Cr(III)	83	4
Cr(VI)	99	2

*Mean value, n = 3

It was observed that the recovery of Cr(III) from Si-Benzothiazole decreased in comparison with the recovery of individual Cr(III). It is probably due to the slightly adsorption of Cr(III) onto Si-Amidoxime.

4.3.1 Method development

Method development is the process of obtaining data on preconcentration and speciation of chromium in order to determine its characteristic performance and to establish confidence in the use of this method to obtain reliable results.

The accuracy and precision of the proposed method are presented as % recovery and %RSD, respectively. The detection limit, or LOD (limit of detection), is the lowest quantity of a substance that can be distinguished from the absence of that substance (a *blank value*) within a stated confidence limit (generally 1%). LOD is calculated by equation 4.8:

$$LOD_{(mgL^{-1})} = 3 \times SD_{(mgL^{-1})} \quad (4.8)$$

where $SD_{(mgL^{-1})}$ is standard deviation of the concentration of blank solution.

Limit of quantitation (LOQ) is regarded as the lowest limit for precise quantitative measurements. LOQ is calculated by equation 4.9:

$$LOQ_{(mgL^{-1})} = 10 \times SD_{(mgL^{-1})} \quad (4.9)$$

Method detection limit (MDL) is the ability of a measurement method to determine an analyte in a sample matrix, estimated by equation 4.10:

$$MDL = \frac{LOD}{P.F. \times (\%R \pm \text{uncertainty})} \quad (4.10)$$

where P.F. is the preconcentration factor which is the ratio of the starting sample volume and final volume, %R is the percent recovery included uncertainty.

Table 4.15 shows the recovery, precision, LOD, LOQ and MDL of spiked synthetic solution. The recoveries obtained for preconcentration and speciation of Cr(III) and Cr(VI) are more than 80% with less than 10 % RSD, indicating the performance, the accuracy and the precision of this method.

Table 4.15 Recovery, precision, LOD, LOQ and MDL of proposed chromium speciation method using spiked synthetic solution

Cr species	P.F.	Recovery ^a , %	RSD ^a , %	LOD ^b ($\mu\text{g L}^{-1}$)	LOQ ^b ($\mu\text{g L}^{-1}$)	MDL ^b ($\mu\text{g L}^{-1}$)
Cr(III)	20	84±9	6	39.8	132.8	2.4 ± 0.3
Cr(VI)	20	95±5	4	39.8	132.8	2.1 ± 0.1

^a Mean value $\pm \frac{t_{0.05} S}{\sqrt{n}}$, n = 6

^b n = 10

The spiked real sample was also performed using drinking water and tap water, as matrix components (such as other ions) may change the chromium retention on the sorbent, thereby decreasing recoveries of the considered species. Water sample was used without other pretreatment. The results are shown in Table 4.16 and Table 4.17 for drinking water and tap water, respectively.

Table 4.16 Cr(III) and Cr(VI) speciation in drinking water by dual mini-column preconcentration

Cr species	Added, μg	Found ^a , μg	Recovery ^a , %	RSD, %
<i>Individual Cr</i>				
Cr(III)	0	nd	-	-
	15	13 \pm 1	83 \pm 5	3
Cr(VI)	0	nd	-	-
	25	23 \pm 1	97 \pm 4	2
<i>Mix Cr</i>				
Cr(III)	0	nd	-	-
	15	14 \pm 1	86 \pm 7	3
Cr(VI)	0	nd	-	-
	25	24 \pm 1	95 \pm 4	2

^a Mean value $\pm \frac{t_{0.05} S}{\sqrt{n}}$, n = 6

nd = not detectable

The recoveries of individual chromium in drinking water were 83% and 97% for Cr(III) and Cr(VI), respectively. In the case of mix chromium (speciation analysis), the recoveries of Cr(III) and Cr(VI) in drinking water were 86 % and 95 %, respectively. All the recoveries were in the acceptable range. These results indicated good accuracy of the method. In the precision point of view, the %RSD of 6 replicates was less than 10%.

These results showed that the proposed method gave a high precision and could be used with high repeatability.

Table 4.17 Cr(III) and Cr(VI) speciation in tap water by dual mini-column preconcentration

Cr species	Added, μg	Found ^a , μg	Recovery ^a , %	RSD, %
<i>Individual Cr</i>				
Cr(III)	0	nd	-	-
	15	3 ± 1	20 ± 3	7
Cr(VI)	0	nd	-	-
	25	3 ± 1	13 ± 2	8
<i>Mix Cr</i>				
Cr(III)	0	nd	-	-
	15	13 ± 1	88 ± 4	2
Cr(VI)	0	nd	-	-
	25	10 ± 1	39 ± 2	2

^a Mean value $\pm \frac{t_{0.05} S}{\sqrt{n}}$, n = 6

nd = not detectable

It was found that the reduction in the retention of individual Cr(III) on Si-Benzothiazole and individual Cr(VI) on Si-Amidoxime occurred, probably due to the presence of organic species in tap water. Cr(III) may form complex with organic species and they may not dissociate. Therefore, Cr(III)-complex cannot retain on Si-Benzothiazole. In addition, the presence of other cations such as Fe(III) and Zn(II) in tap water might also retain on the solid sorbent resulting in overloading Si-Benzothiazole.

As the results described in section 4.2.4, the interfering anions affected the retention of Cr(VI) on Si-Amidoxime, the presence of anions other than Cr(VI) species in tap water may hinder the preconcentration step by overloading Si-Amidoxime.

The preconcentration of tap water containing Cr(III) and Cr(VI) species was not achieved because of interference effect. However, % recovery of Cr(III) in mix chromium increased to 88% in comparison with that of individual Cr(III). The results suggest the retention of Cr(VI) also occur on Si-Benzothiazole. Normally, Cr(VI) should be collected on the first mini-column containing Si-Amidoxime but because of the interference effect, there was little retention of Cr(VI) on first column. The effluent containing Cr(III) and Cr(VI) from the first mini-column was collected on the second mini-column containing Si-Benzothiazole resulting in high % recovery.