CHAPTER III

EXPERIMENTAL SECTION

3.1 Apparatus

3.1.1 Flame atomic absorption spectrometer

Heavy metals (Gold, Silver, Cadmium, Chromium, Nickel, Lead and Zinc) concentrations were determined by a flame atomic absorption spectrometer (FAAS) model A Analyst 100 (Perkin Elmer). The instrumental conditions are listed in Table 3.1.

Table 3.1 FAAS conditions for determination of heavy metal concentration in solutions

Operating conditions	Au	Ag	Cd	Cr	Ni	Pb	Zn
Wavelength (nm)	242.8	328.1	228.8	357.9	232.0	283.3	213.9
Slit width (nm)	0.70	0.70	0.70	0.70	0.20	0.70	0.70
Lamp type	HCL*	HCL*	HCL*	HCL*	HCL*	HCL*	HCL*
Lamp current (mA)	15	15	4	25	25	10	15
C_2H_2 flow-rate (mL min^{-1})	3	3	3	3	3	3	3
Air flow-rate (mL min^{-1})	10	10	10	10	10	10	10

*Hallow cathode lamp.

3.1.2 pH meter

A pH meter model pH 211 (Hanna instruments) was used for pH measurements.

3.1.3 UV-Vis spectrophotometer

UV-Vis spectrophotometer model HP 8453 (Hewllet Packard) was used for the characterization of Humic acids.

3.1.4 Manifold

The solid phase extraction was performed using Visiprep^{TM} Vacuum Manifold (Supelco) connected to a vacuum pump. The hardware and accessories are shown in Figure 3.1.
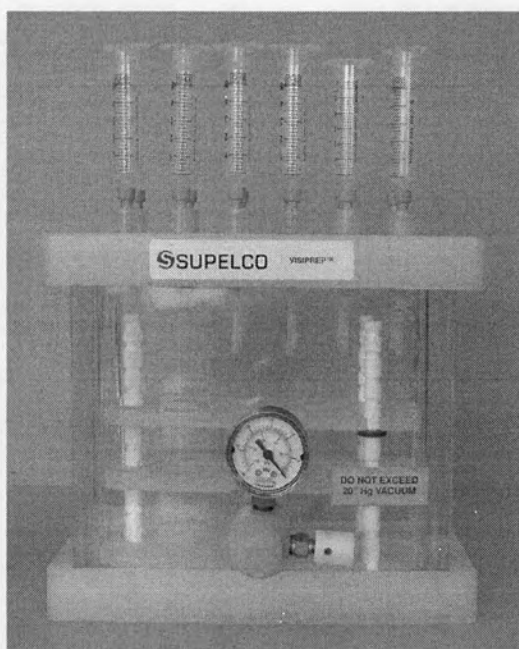

Figure 3.1 Visiprep ^{TM} SPE Vacuum Manifold.

3.1.5 Centrifuge

The centrifuge Centaur2 (Sanyo®) was used at 3500 rpm for 5 min to separate sorbents from metal ion solution in batch experiments.

3.2 Chemicals

All chemicals were standard analytical grade listed in Table 3.2. They were used without further purification unless otherwise noted.

Table 3.2 Chemicals list

Chemicals	Suppliers
3-aminopropyltriethoxysilane	MERCK
Calcium choride	CARLO ERBA
Calcium nitrate tetrahydrate	MERCK
Hydrochloric acid 37%	MERCK
Humic acid sodium salt (87.6%)	ALDRICH
Magnesium nitrate hexahydrate	MERCK
Nitric acid 65%	MERCK
Potassium nitrate	MERCK
Silica gel (70-230 mesh)	MERCK
Single standard solution of Au, Ag, Cd, Cr, Ni, Pb and Zn	BDH
Sodium chloride	CARLO ERBA
Sodium hydroxide	MERCK
Sodium nitrate	CARLO ERBA
Sodium sulfate	CARLO ERBA

3.3 Preparation of solution

Working standard solutions of metal ions were prepared by stepwise dilution of 1000 mg L^{-1} stock standard solutions to the required concentrations.

All working standard solutions were freshly prepared. The pH of solution was adjusted with 1-20 % HNO$_3$, HCl and KOH solutions. All solutions were prepared by using de-ionized water.

3.4 Preparation of sorbent

The sorbent, humic acid immobilized on aminopropyl silica, was synthesized and characterized. The synthesis of the sorbent consisted of two steps;

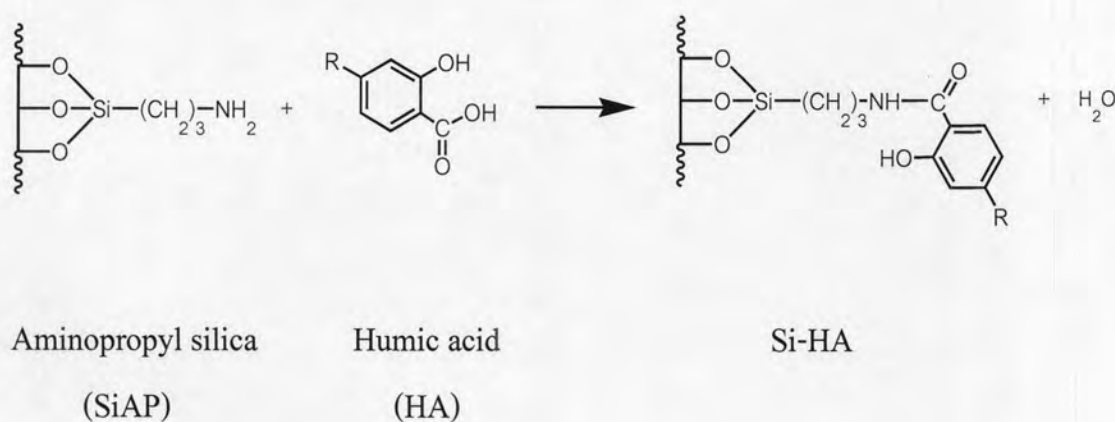### Step I : Synthesis of aminopropyl silica

Silica gel (50 g) was mixed with dried toluene (200 mL). The mixture was then refluxed under nitrogen atmosphere for 2 hours and then aminopropyltriethoxysilane (20 mL) was added by a dropper, the mixture was refluxed again for 24 hours. The solid was filtered, cleaned with ethanol and dried. The reaction is depicted in Scheme 3.1.
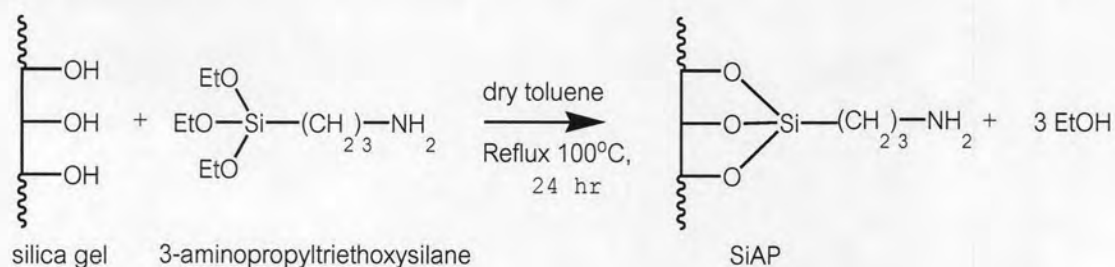
Scheme 3.1: Synthesis pathway of aminopropyl silica (SiAP).

Step II : Immobilization of Humic acids on aminopropyl silica

The immobilization procedure of Humic acids on aminopropyl silica was based on the method proposed by Koopal and coworkers [27], 30 mL aqueous solution of 300 mg Humic acids was prepared by slowly adding freshly prepared 0.1 M NaOH solution to Humic acids dispersed in water. The obtained solution was added to a vessel containing 1.00 g of aminopropyl silica and the volume of the mixture was adjusted to 50 mL with de-ionized water and the pH to 7.5-8.0. The mixture was stirred for 20 hours at room temperature. The solid was separated by centrifugation. Before drying, the sample was rinsed several times, first using 0.2 M NaCl (pH 7.5) and then with water of the same pH. The dried product was cured at 120 °C for 5 hours. After curing, the product was rinsed several times with 1 M NaCl (pH 10) to remove loosely bound Humic acids. The reaction is illustrated in Scheme 3.2. The product was named Si-HA.

Aminopropyl silica   Humic acid   Si-HA

(SiAP)   (HA)

Scheme 3.2 Synthesis pathway of humic acids immobilized on aminopropyl silica.

3.5 Extraction study

This work was divided into two parts: batch system and column system.

3.5.1 Batch system

The effect of various parameters such as the pH of solution and the contact time on extraction efficiency was investigated using batch system, and all experiments were performed in triplicate.

3.5.1.1 Effect of pH on metal extraction

The pH of a solution containing 10.0 mg L^{-1} of single metal ion was adjusted to a value ranging from 1.0 to 7.0 by using KOH, HCl or HNO_3 solution. After adjusting the pH, the solution (10.0 mL) was pipetted into a test tube. Then, 10 mg of Si-HA was added to the test tube and the mixture was stirred for 60 minutes at room temperature. The sorbent was separated by centrifugation at 3500 rpm for 5 minutes. The residual metal concentration in the supernatant was determined by FAAS.

3.5.1.2 Effect of contact time

A suspension of 10 mg of Si-HA in 10.0 mL of 10.0 mg L^{-1} metal ion solution (after adjusting its pH to 4-5) was stirred at different contact time ranging from 10 minutes to 60 minutes at room temperature. The sorbent was separated by centrifugation at 3500 rpm for 5 minutes. The residual metal concentration in the supernatant was determined by FAAS.

3.5.1.3 Adsorption isotherm

A suspension of 5 mg of Si-HA in each single metal ion solution whose concentration was varied between 1.0-50.0 mg L^{-1} was stirred for 45 minutes. The pH of the solution was adjusted to an optimum value before adding the sorbent. The volume of metal ion solution and its concentration range are list in Table 3.3. The temperature was controlled at 298±1 K. The solid sorbent was separated by centrifugation at 3500 rpm for 5 minutes. The residual metal concentration of the supernatant was determined by FAAS.

Table 3.3 The volume of metal ion solution and the range of concentration used in sorption capacity study

Metal ions	Concentration Range (mg L^{-1})	Volume (mL) of solution pipetted
Ag(I)	1 – 7	10
Cd(II)	2 - 8	5
Cr(III)	2 - 8	5
Ni(II)	2 - 8	5
Pb(II)	6 - 24	10
Zn(II)	10 - 50	5
Au(III)	4 - 10	10

3.5.2 Column system

The column system was used to investigated the extraction of metal ions. The effect of flow rate both for extraction and elution, amount of sorbent and interfering ions were studied. The obtained optimum conditions for metal retention and elution were used for metal extraction from real water sample.

3.5.2.1 Effect of sample flow rate

3.5.2.1.1 Effect of loading flow rate

An aliquot of 20.0 mL of 10.0 mg L^{-1} mixed metal ion solution (Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II)) at pH 4-5 was passed through a column packed with 1.0 g Si-HA at different flow rates ranging from 0.5 – 5.0 mL min^{-1}. The filtrate was collected and analysed for residual metal concentration using FAAS.

The extraction of Au(III) was studied separately. The extraction procedure was the same as mentioned above.

3.5.2.1.2 Effect of elution flow rate

In this method, 10% (v/v) nitric acid was chosen to elute metal ions from the column due to its strong acidity. The experiment was focused on the flow rate of the elution.

After extraction, 20.0 mL of 10% (v/v) nitric acid was passed through the column at a flow rate of 0.5 – 5.0 mL min^{-1}. The amount of metal ions in the stripped solution was determined by FAAS.

For the elution of Au(III) ion from column, 10% (v/v) hydrochloric acid was chosen. The elution procedure of Au(III) ion was the same as mention above.

3.5.2.2 Effect of sorbent amount

An aliquot of 20.0 mL of mixed metal ion solution (Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II)) adjusted pH to 4 - 5 was passed through a column packed with 0.1, 0.3 and 0.6 g of Si-HA at a flow rate of 3.5 mL min^{-1}. The sorbed mixed metal ions were eluted by 20.0 mL of 10 % (v/v) nitric acid at a flow rate of 3.5 mL min^{-1}. The amount of metal ions in the effluent was determined by FAAS.

The extraction of Au(III) was studied separately. The extraction procedure was the same as mentioned above.

3.5.2.3 Effect of interfering ions

A mixed metal ion solution of (Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II)) containing Na$^+$ ion at 10, 100 and 1000 mg L^{-1} was prepared by dissolving the amount of NaNO$_3$ 0.9, 9.2 and 92.4 mg in 25 mL of de-ionized water (adjusted pH to 4–5). For mixed metal ion solutions containing other cations such as K$^+$, Ca^{2+} and Mg^{2+} and anions such as Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ at 10, 100 and 1000 mg L^{-1} were prepared by the same procedure but different chemicals. The amount of chemicals to dissolved in 25 mL of de-ionized water are shown in Table 3.4.

Table 3.4 Preparation of mixed metal ion solutions with interfering ions

Types of interfering ion	Types of Chemical	Chemical weight to dissolve in 25 mL of de-ionized water (mg)		
		10 mg L^{-1}	100 mg L^{-1}	1000 mg L^{-1}
K^+	KNO_3	0.6	6.5	64.7
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	1.5	14.7	147.3
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	2.6	26.4	263.8
Cl^-	$NaCl$	0.4	4.1	41.2
NO_3^-	$NaNO_3$	0.3	3.4	34.3
SO_4^{2-}	Na_2SO_4	0.4	3.7	37.0

An aliquot of 20.0 mL of mixed metal ion solution (Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II)) was passed through a column packed with 1.0 g of Si-HA at a flow rate of 3.5 mL min^{-1}. The sorbed metal ions were eluted by 20.0 mL of 10 % (v/v) nitric acid at a flow rate of 3.5 mL min^{-1}. The amount of metal ions in the effluent was determined by FAAS.

The extraction of Au(III) was studied separately. The extraction procedure was the same as mentioned above.

3.6 Application for real sample

Wastewater (from factory in Eastern Seaboard Estate 20.0 mL), which collected and filtered was adjusted the pH to 4-5. The amount of metal ions in the sample was determined by FAAS.

A spike method was used to evaluate the efficiency of the proposed extraction procedure. The filtered wastewater (20.0 mL) spiked with 100 μg of each metal ion (Ag(I), Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) was passed through a column with a flow rate of 2.0 mL min^{-1}. The retained metal ions in the column were eluted by 20.0 mL of 10 % (v/v) nitric acid at a flow rate of 2.0 mL min^{-1}. The amount of each metal ion in the effluent was determined by FAAS.

This experiment was performed in triplicate.