

CHAPTER III

EXPERIMENTALS

3.1 Instruments

In this thesis, the analytical instruments used for measurements are shown in Table 3.1.

Table 3.1 List of analytical instruments

Analytical instruments	Manufacture : Model
- Nuclear magnetic resonance spectrometer (NMR)	Varian : Mercury Plus 400
- X-ray diffractometer (XRD)	Rigaku : 1200+
- Fourier transforms infrared spectrometer (FT-IR)	Nicolet : Impact 410
- Thermo gravimetric analyzer	Netzsch : STA 409 C/CD
- Elemental analyzer	LECO : CHN 2000
- Surface area analyzer	Quantachrome : Autosorb-1
- Flame atomic absorption spectrometer (FAAS)	Perkin-Elmer : AAnalyst 100 (AAS condition see Table 3.3)
- Cold vapor atomic absorption spectrometer (CVAAS)	Perkin-Elmer : AAnalyst 300 coupled with FIAS400 system
- pH meter	Hanna instruments : pH 211
- Water bath	Bosstech Thailand : Thermal TMP/1

Table 3.1 List of analytical instruments (continued)

Analytical instruments	Manufacture : Model
- Transferpipette : 0.5-10, 10-100, 100-1000 μ L and 0.5-5 mL	Bran : -
- Centrifuge	Sanyo : Centaur 2
- Desiccator	Aris : DC56LA
- Digital balance	Mettler : AT 200
- Oven	Memmert : UM 500
- Stirrer	Gem : MS 101
- Stirrer/Hot plate	CORNING : PC-420 and PC-620
- Rotary evaporator	Eyela : N-1000
- Vacuum pump	Büchi : V-700
- Glassware	-

3.2 Chemicals

The chemicals used in this work were summarized in Table 3.2.

Table 3.2 List of chemicals

Chemicals	Suppliers / Grade
3-Aminopropyltriethoxysilane	Fluka / purum \geq 98% (GC)
Acetonitrile*	Merck / isocratic grade for LC
Cadmium (II) nitrate	CARLO ERBA / for analysis
Calcium hydride	Fluka / Assay \geq 95% (gas- volumetric)
Calcium nitrate tetrahydrate	Riedel-de Haën® / Assay 98% (GC)

Table 3.2 List of chemicals (continued)

Chemicals	Suppliers / Grade
Chloroform D1	Merck / 99.8% for NMR spectroscopy
Cobalt (II) nitrate	Fisher Chemicals / AR
Cysteamine hydrochloride	Fluka / purum $\geq 97\%$ (RT)
1,3-Dibromopropane	Merck / for synthesis
Dichloromethane	Fisher Chemicals / AR
Ethanol	Merck / for synthesis
Ethyl-2-bromopropionate	Aldrich / 99% (GC)
Hectorite	Volclay Siam Ltd.,
Hydrochloric acid 37%	Merck / for analysis
Hydroxylammonium choride	Merck / for analysis
Magnesium (II) nitrate hexahydrate	Merck / GR for analysis
Mercury (II) nitrate monohydrate	Merck / ACS
Nickel (II) nitrate hexahydrate	Merck / for analysis
Nitric acid 65%	Merck / for analysis
Potassium bromide	Merck / for IR spectroscopy
Potassium hydroxide	Merck / ACS
Potassium nitrate	BDH / AR
Potassium permanganate	Merck / for analysis
Potassium persulfate	Merck / for analysis
Silver (I) nitrate	BDH / AR
Single standard solution for $\text{Hg}(\text{NO}_3)_2$ and AgNO_3 (1000 mg L ⁻¹)	BDH / spectrosol
Sodium chloride	CARLO ERBA / for analysis
Sodium hydroxide	Merck / for synthesis
Sodium metal, lumps	RDH

Table 3.2 List of chemicals (continued)

Chemicals	Suppliers / Grade
Sodium nitrate	Fluka / purum p.a. > 99%
Sodium sulphate anhydrous	Fisher Chemicals / AR
Sulphuric acid 98%	Merck / for analysis
Tin (II) chloride dihydrate	Scharlau / ACS

* Acetonitrile was dried over calcium hydride under nitrogen atmosphere to remove moisture before use.

3.3 Methodology

3.3.1 Preparation of chemicals and reagents

De-ionized (DI) water was used for preparation of all reagents.

Mercury solutions

Mercury standard solution (1000 mg L^{-1}) was used to prepare the mercury solutions of required concentrations by dilution with DI water. In the experiments of real water sample, the mercury stock solution was prepared daily by dissolving the appropriate amount of $\text{Hg}(\text{NO}_3)_2$ in DI water.

Silver solutions

The silver stock solution (1000 mg L^{-1}) was prepared daily by dissolving the appropriate amount of AgNO_3 in DI water. This stock solution was used to prepare the silver solutions of desired concentrations by dilution.

Nitric acid solutions

Nitric acid solutions (1 and 5 %v/v) were prepared daily by direct dilution of the concentrated solution (65 %) for pH adjustment and dilution of metal solution before the analysis by AAS.

Potassium hydroxide solutions

Potassium hydroxide solutions (1, 5 and 10 %w/v) were prepared daily by dissolving the appropriate amount of KOH in DI water.

Sodium nitrate solutions

Sodium nitrate solutions (1 and 3 M) were prepared daily by dissolving the appropriate amount of NaNO_3 in DI water.

Acid carrier

Hydrochloric acid solutions (3 %v/v) were prepared daily by direct dilution of the concentrated solution.

Tin (II) chloride solutions

100 g of SnCl_2 were dissolved in 200 mL of HCl 37% (v/v). Then, the volume was adjusted to 1000 mL with DI water and was filtered by using a membrane filter.

Interfering ions solutions

Solutions containing cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) at 0.1, 0.5, 1.0 and 2.0 M and heavy metal ions (Ni^{2+} , Cd^{2+} and Co^{2+}) at 0.25, 0.65, 2.5 and 6.5 mM were prepared by dissolving the appropriate amount of NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DI water.

Solutions containing anion (NO_3^- , SO_4^{2-} and Cl^-) at 0.1, 0.5, 1.0 and 2.0 M were prepared by dissolving the appropriate amount of NaNO_3 , Na_2SO_4 and NaCl in water.

Potassium permanganate solutions

Potassium permanganate solutions (50 g L^{-1}) were prepared daily by dissolving the appropriate amount of KMnO_4 in DI water.

Potassium persulfate solutions

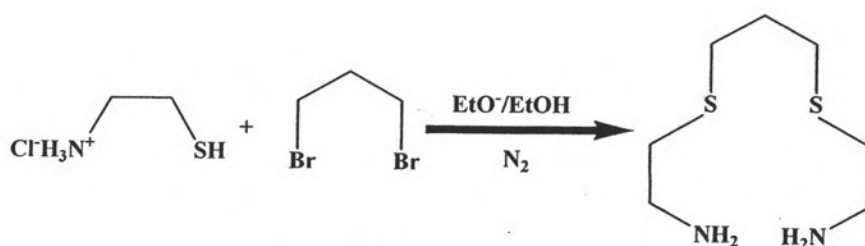
Potassium persulfate solutions (50 g L^{-1}) were prepared daily by dissolving the appropriate amount of $\text{K}_2\text{S}_2\text{O}_8$ in DI water.

Sodium chloride - hydroxylammonium chloride

Sodium chloride - hydroxylammonium chloride (120 g L^{-1}) were prepared daily by dissolving the appropriate amount of NaCl and $(\text{NH}_2\text{OH})\text{HCl}$ in DI water.

3.3.2 Synthesis of chelating ligand AEPE

The chelating ligand 2-(3-(2-aminoethylthio)propylthio)ethanamine (AEPE), was synthesized for the modification of hectorite. The steps of this synthesis [41] is shown in Scheme 3.1.

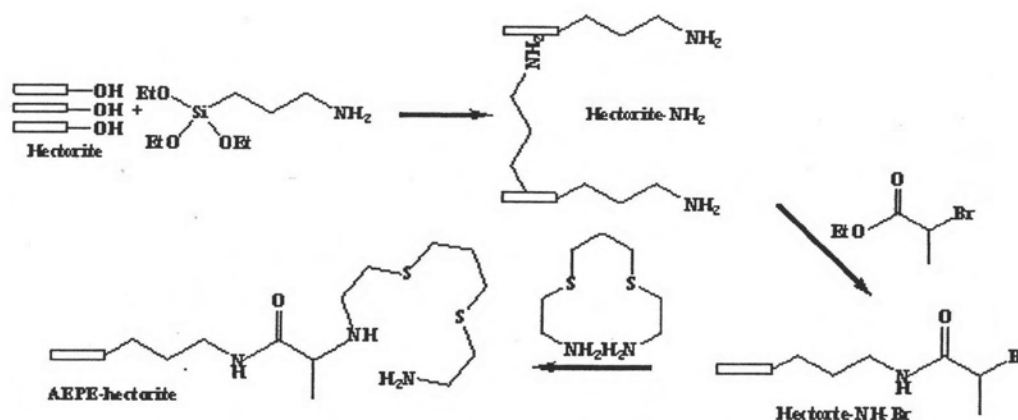


Scheme 3.1 Synthesis of AEPE.

Dissolve 1 g of sodium metal in 20 mL of ethanol. This solution was added into the two-necked round bottom flask that contained cysteamine hydrochloride (2.3 g, 20 mmol) and stirred for 15 min at 15°C . Then 1,3-dibromopropane (1.0 mL, 9.8 mmol) was added and the mixture was stirred for 4 hr at 40°C under nitrogen atmosphere. Thereafter, ethanol was evaporated (at 50°C) by rotary evaporator. Sodium hydroxide solution (5 g NaOH in 15 mL of DI water) was added and the mixture was put in a refrigerator overnight for the isolation of AEPE and aqueous solution. Dichloromethane (10 mL) was used to extract AEPE. The dichloromethane phase was washed with DI water (2 x 20 mL) and the moisture was removed by sodium sulphate anhydrous. The dichloromethane phase was filtered and the solvent was removed by rotary evaporator at 40°C . The obtained AEPE was yellow oil product. The ligand was characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

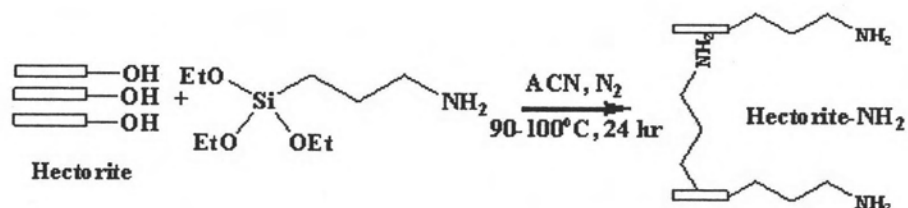
3.3.3 Modification of hectorite

The modification of hectorite with AEPE was carried out in three steps as shown in Scheme 3.2.



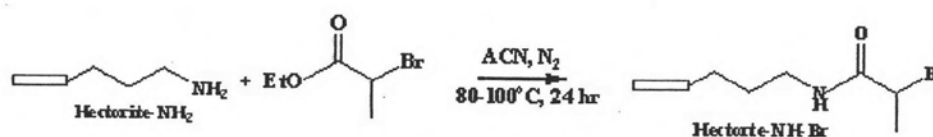
Scheme 3.2 Modification of hectorite with AEPE.

In the first step (Scheme 3.3), 10 g of hectorite was dispersed into 250 mL of dried acetonitrile in the two-necked round bottom flask (500 mL) for 24 hr under nitrogen atmosphere and then 20 mL of 3-aminopropyltriethoxysilane was added. The mixture was stirred for 24 hr at 90-100°C under reflux condition.



Scheme 3.3 Synthesis of hectorite modified with 3-aminopropyltriethoxysilane.

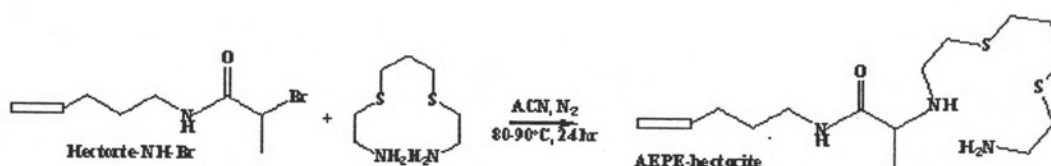
In the second step, ethyl-2-bromopropionate was used to functionalize hectorite-NH₂ as shown in Scheme 3.4.



Scheme 3.4 Functionalization of hectorite-NH₂ with ethyl-2-bromopropionate.

The product of step I (hectorite-NH₂) was dispersed into 250 mL of dried acetonitrile for 24 hr at room temperature and 12 mL of ethyl-2-bromopropionate was further added. This mixture was stirred for 24 hr at 80-100°C in nitrogen atmosphere under reflux condition.

For the final step, schematically shown in Scheme 3.5, the modified hectorite from step II (hectorite-NH-Br) was dispersed in 250 mL of dried acetonitrile and stirred for 24 hr under nitrogen atmosphere. Then, AEPE (5.1 g) was added and the mixture was stirred for 24 hr at 80-90°C under reflux condition.



Scheme 3.5 Reaction of hectorite-NH-Br with AEPE.

The product of each step was filtered, washed with ethanol (3 x 300 mL) and dichloromethane (4 x 300 mL) and dried in vacuum at room temperature before using in another modification step. The products were kept in a desiccator. Thereafter, the modified hectorite obtained from each step was characterized by XRD, FT-IR, TGA, EA and nitrogen adsorption.

3.4 Characterization

The characterization is required to confirm the success of both the synthesis of the ligand AEPE and the modification of hectorite. Certain techniques were used to characterize the product of each step such as NMR, XRD, FT-IR, TGA, EA and nitrogen adsorption.

3.4.1 Characterization of chelating ligand AEPE

The ligand AEPE was dissolved in deuterated chloroform D1 (CDCl_3) and characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

3.4.2 Characterization of modified hectorite

The unmodified and modified hectorite were characterized by XRD, FT-IR, TGA, EA and nitrogen adsorption. The details of each techniques are given as following.

X-ray diffraction spectroscopy (XRD)

X-ray diffractometer was used to record the XRD patterns and the basal spacing of the unmodified and modified hectorite were determined. XRD was equipped with a monochromator and operated at $0-30^\circ 2\theta$ using a $\text{CuK}\alpha$ radiation (40 kV, 30 mA).

Fourier transforms infrared spectrometry (FT-IR)

The organic functional groups modified onto the surface of hectorite were characterized by FT-IR using the KBr pellet technique. Infrared spectra were recorded from 400-4000 cm^{-1} in the transmittance mode.

Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis was performed to confirm the difference of the chemical composition of the unmodified and modified hectorite by using Simultaneous Thermal Analyzer (STA) under nitrogen atmosphere from 30 to 800°C at heating rate of 10°C min^{-1} .

Elemental analysis (EA)

The percentages of C (carbon), H (hydrogen) and N (nitrogen) in the unmodified and modified hectorites were determined by CHN elemental analyzer.

Surface area analysis

The unmodified hectorite and AEPE-hectorite were analyzed for the specific surface area by nitrogen adsorption method using BET model.

3.5 Adsorption study using batch method

The adsorption of Hg(II) and Ag(I) ions in aqueous solutions by AEPE- Hectorite was studied using batch method. 0.01 g of adsorbent were added to 5 mL of solution containing Hg(II) or Ag(I) ions. The ionic strength of the solutions was controlled by using 0.01 M NaNO₃ and the initial pH of Hg(II) and Ag(I) ion solutions were 4.0 ± 0.2 and 5.0 ± 0.2, respectively. The extraction time used was 60 min. Thereafter, adsorbents were separated from metal ion solutions by centrifugation at 3000 rpm for 10 min. The pH at equilibrium was also measured. Atomic absorption spectrometer was used to determine the concentration of metal ions in solutions after separation. Conditions for measurement of metal ion concentration in aqueous solutions are shown in Table 3.3.

Table 3.3 AAS conditions for measurement of metal concentration in aqueous solutions

<i>Operating conditions</i>	Hg^a	Ag^a
Wavelength (nm)	253.7	328.1
Slit width	0.70	0.70
Lamp type	HCL ^b	HCL ^b
Lamp current (mA)	8	15
C₂H₂ flow-rate (min⁻¹)	-	3
Air flow-rate (min⁻¹)	100 ^c	10
Working range (mg L⁻¹)	0.05-0.3	0.5-3.0

^aThe concentrations of mercury and silver were determined by CVAAS and FAAS, respectively.

^b Hallow Cathode Lamp

^c Argon flow rate

Moreover, the effect of pH of metal ions solution, extraction time, adsorbent dose, ionic strength, interfering ions and initial concentration (adsorption isotherms) were investigated in this thesis. All adsorption experiments were performed in triplicate.

3.5.1 Effect of pH of metal ions solutions

The effect of pH on adsorption efficiency was studied in a pH range of 1.0-8.0. The initial concentrations of Hg(II) and Ag(I) ion in solutions were 50 and 40 mg L⁻¹, respectively. The extraction experiments were carried out using 0.01 g of adsorbent in 5 mL of Hg(II) solutions or 10 mL of Ag(I) solutions. The pH of solutions were adjusted to a desired value with KOH (1, 5 and 10 %w/v) and HNO₃ (1 and 5 %v/v) solutions.

3.5.2 Effect of extraction time

The effect of extraction time was investigated by varying the extraction time in the range of 1-120 min. The initial concentration of Hg(II) and Ag(I) ions in solutions were 50 and 200 mg L⁻¹, respectively.

3.5.3 Effect of adsorbent dose

In this experiment, the amount of adsorbent was varied in a range of 0.01-0.1 and 0.005-0.05 g of AEPE-hectorite for 5 mL of Hg(II) and Ag(I) ion solutions, respectively. The contact time was also varied from 1 to 120 min. The adsorption efficiencies were determined for each adsorbent dose as a function of contact time. The initial concentration of Hg(II) and Ag(I) ions in solutions were 100 and 200 mg L⁻¹, respectively.

3.5.4 Effect of ionic strength

The effect of ionic strength on the adsorption of Hg(II) and Ag(I) ions by AEPE-hectorite were studied using NaNO_3 in a concentration range of 0.01-2.0 M.

3.5.5 Effect of interfering ions

The effects of cations, anions and heavy metal ions other than Hg(II) and Ag(I) ions on adsorption were studied using the concentration of cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) and anions (NO_3^- , SO_4^{2-} and Cl^-) of 0.5 and 2.0 M and heavy metal ions (Ni^{2+} , Cd^{2+} and Co^{2+}) of 0.25 and 2.5 mM for the extraction of Hg(II) ions in solution (50 mg L^{-1}).

The extraction of Ag(I) ions in solution (70 mg L^{-1}) was performed using the same procedure but the concentrations of cations and anions were 0.1 and 1.0 M and the concentrations of heavy metal ions were 0.65 and 6.5 mM.

3.5.6 Effect of initial concentration (Adsorption isotherms)

The initial concentration of Hg(II) and Ag(I) ions in solutions used in the extraction experiments were varied in the range of 30-400 and 40-500 mg L^{-1} , respectively. The initial pH was 3.0 ± 0.2 and the temperature was controlled at $25.0 \pm 0.5^\circ\text{C}$.

3.6 Application to real water sample

The real water samples employed in this study were sea water from Rayong province and wastewater from the laboratory of Gem and Jewelry Institute of Thailand.

The removal efficiency of Hg(II) and Ag(I) ions by AEPE-hectorite was determined.

Sea water from Rayong province

Before the application for extraction experiments, the sea water sample was filtered and the pH of sample solution was measured. Then, the sea water was digested, using ASTM D 3223 method [42], and analyzed for the concentration of mercury by CVAAS.

The mercury stock solution of 3000 mg L^{-1} (1.67 mL) was spiked into the sea water and the final volume of sample was 100 mL. This sample solution (5 mL), having the initial pH and the initial concentration of Hg(II) ions about 8.0 and 50 mg L^{-1} , was extracted by using 0.01, 0.02 or 0.04 g of AEPE-hectorite with a contact time of 60 min. Thereafter, AEPE-hectorites were separated by centrifugation at 3000 rpm for 10 min. The pH and residual concentration of Hg(II) ions in the sample solutions were determined. This adsorption experiments were performed in triplicate.

Wastewater from the laboratory of Gem and Jewelry Institute of Thailand

Before the application for extraction experiments, the wastewater provided from the laboratory of Gem and Jewelry Institute of Thailand was analyzed for concentration of Ag(I) ions by FAAS. The pH was also measured.

The sample solution of the experiments was prepared by dilution 1 mL of the wastewater to 100 mL with DI water. This sample solution had the pH and the concentration of Ag(I) ions about 1.5 and 60 mg L^{-1} , respectively. The sample solution of 5 mL was extracted by using 0.01, 0.02 or 0.03 g of AEPE-hectorite with a contact time of 60 min. Thereafter, AEPE-hectorites were separated by centrifugation at 3000 rpm for 10 min. The pH and residual concentration of silver were determined. This adsorption experiments were performed in triplicate.