

CHAPTER III

EXPERIMENTS

3.1. Reagents

Cetyltrimethylammonium bromide (CTAB, 98%), tetraethoxysilane (TEOS, 98%), 3-methyl-1-phenyl-2-pyrazolin-5-one (H₂PMP), stearylchloride were obtained from Fluka. Ethanol (EtOH), methanol (MeOH), hydrochloric acid and silica gel 60 (0.063-0.200 mm) were received from Merck. MnCl₂ · 4H₂O from J. T. Baker, Fe(NO₃)₃ · 9H₂O, Zn(NO₃)₂ · 6H₂O and Cu(NO₃)₂ · 3H₂O from Fluka were used to prepare metal ion solutions. Nitric acid and toluene were purchased from Merck. 1, 4-Dioxane, NaNO₃ and *n*-heptane were received from Carlo Erba Reagenti. Deionized water (>18 MΩ/cm³) from Millipore system (Milli Q, model Millipore ZMQSSV00Y) was used throughout. 1-Phenyl-3-methyl-4-stearylpyrazol-5-one (HPMSP) was synthesized through Jensen's method [41].

3.2. Equipments

A Perkin-Elmer model AAnalyst 100 atomic absorption spectrometer was used for the determination of metal ions. All instrumental settings were those recommended in the manufacturer's manual book. The absorbance spectra was registered with a HP8453 UV-Visible spectrophotometer. Temperature in the extraction was controlled by thermoregulated baths (JULABO model F10). A pH meter, Denver Instrument model 215 glass-electrode, was employed for measuring pH values in the aqueous phase. Surface area and pore size of materials were performed on Belsorp mini-II. X-ray diffraction was performed on Rigaku (DMAX 2200/ULTIMA) X-ray diffractometer (Cu-K_{α1} radiation, λ = 1.5406 Å). The FTIR spectra was recorded on a Nicolet (Impact 410) IR spectrometer using KBr pellet technique. The morphology of materials was observed using a JEOL JSM 5410LV scanning electron microscope. The CHN analysis performed on a CHN ANALYZER (Perkin Elmer PE2400 SeriesII) and the particle size performed on Malvern (model Mastersizer S) were measured by Scientific and Technological Research Equipment Centre at Chulalongkorn University.

3.3. Experimentals

As the aim of this work is to prepare the HPMSp doped mesoporous silica that can extract the maximum amount of metal ions; therefore, the type of silica precursors and the mole ratio of CTAB/silica precursor were investigated. The physical properties of the obtained materials were then examined. The extraction properties of the synthesized silica were studied in both batch and SPE column methods using Cu^{2+} as a demonstrated metal. Afterwards the optimum HPMSp doped mesoporous silica was served as a sorbent for further studies on the extraction of other metal ions. Finally, the application of the functionalized silica to the removal of metals from industrial wastewater was performed. The details of all experiments were described below.

3.3.1. Synthesis of HPMSp doped mesoporous silica

The synthesis method of HPMSp doped mesoporous silica in this research is similar to the procedure reported by Boos and co-workers [29]. TEOS, calcined mesoporous silica (its synthesis procedure shown in appendix II) and silica gel 60 were the type of silica precursors used for the synthesis. A cationic surfactant, cetyltrimethylammonium bromide (CTAB) was served as a template. The mole ratios of CTAB/silica precursor were 0, 0.09 and 0.18. The catalyst was 0.1 M NaOH. The general synthesis procedure was described below.

CTAB and an aqueous solution of 0.1 M NaOH were mixed and stirred at 60 °C for 4 hours. Methanol was then added. The extracting molecule (HPMSp) was next introduced into the mixture. Four hours later, the silica precursor was added. The final molar composition of each synthesis mixtures was 1 silica precursor : 140 H_2O : x CTAB : 13 MeOH : 0.06 HPMSp, where x was the mole ratio of CTAB/silica precursor. The mixture was stirred at 60 °C for 1 hour and later at ambient temperature for 23 hours. The silica was then filtered, washed copiously with water and dried at 110 °C overnight. The supernatant and washing solutions were collected and extracted with heptane to determined the amount of HPMSp that might be leaching out through the synthesis and washing process. The synthesis procedure of HPMSp doped mesoporous silica was summarized in Figure 3.1.

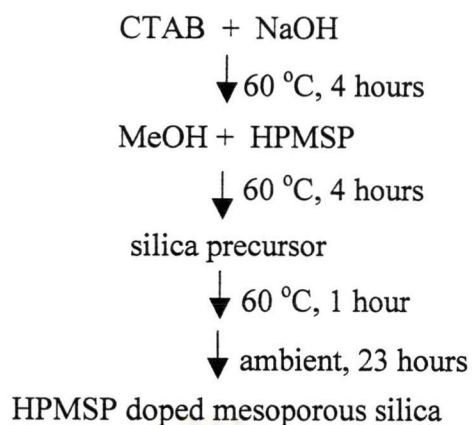


Figure 3.1 The synthesis procedure of HPMSP doped mesoporous silica.

3.3.2. Characterization of materials

The characterization of materials in this study was consisted of the determination of organic matter contents and CHN elemental analysis, the investigation of organic molecules in mesoporous silica using FTIR spectroscopy, the measurement of accessible HPMSP, XRD analysis, N₂-sorption analysis and particle size measurement. Each experimental procedure was given in detail below.

3.3.2.1. *Determination of organic matter contents*

The organic matter content in mesoporous silica was determined using a calcination method described below.

Mesoporous silica with a constant weight was placed in a muffle furnace. The sample was heated from room temperature to 100 °C at a rate of 1 °C/min. The temperature was held at this degree for 60 minutes. Finally, the sample was heated to 540 °C at a rate of 1 °C/min and held at this temperature for 10 hours. After the calcination process, the sample weight loss was calculated to determine the amount of organic matter in mesoporous silica. The thermal profile for calcination is shown in Figure 3.2.

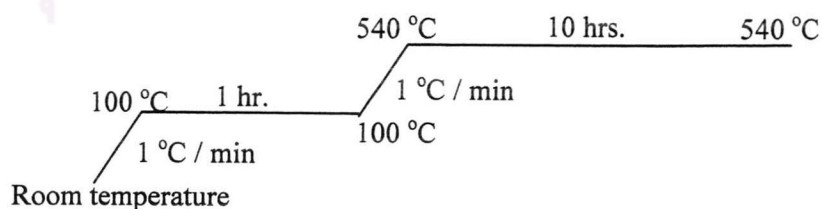


Figure 3.2 Thermal profile for calcination process.

3.3.2.2. CHN elemental analysis

5 mg of sample was placed in capillary tube and put into a CHN analyzer. Gaseous products were freed by pyrolysis in high-purity oxygen (900 °C) and chromatographically separated by frontal analysis with quantitatively detected by thermal conductivity detector.

3.3.2.3. Investigation of organic molecules in mesoporous silica using FTIR spectroscopy

The spectrometer used for the FTIR analysis was a Nicolet (Impact 410) IR spectrometer. Samples were analysed by transmission on a potassium bromide (KBr) thin plate. A recording between 4000 and 400 cm^{-1} was made with KBr thin plate alone (reference acquisition) and then with the sample. Spectra were recorded with 32 scans.

3.3.2.4. Determination of accessible HPMSF

The amount of accessible HPMSF may indicate the amount of reactive HPMSF molecules in the HPMSF doped mesoporous silica. The procedure for the determination of accessible HPMSF is as follow.

10 mL of 1 : 1 (v/v) heptane/EtOH were added to 0.1 g of HPMSF doped mesoporous silica. The mixture was stirred for 3 hours. The liquid phase was then separated from the solid by centrifugation at 200 rpm and measured by UV-visible spectrophotometer.

3.3.2.5. XRD analysis

100 mg of each powder sample was evenly dispersed onto a glass slide. The XRD patterns were collected using a Rigaku diffractometer with a diffractometer beam monochromator and $\text{Cu-K}_{\alpha 1}$ radiation source. Scattering patterns were collected from 1 to 10° (2θ) with a scan time of 2° (2θ) per minute.

3.3.2.6. N_2 -sorption analysis

N_2 -sorption analysis were examined using an Autosorb-1. Prior to this measurement, the non-doped and HPMSF doped mesoporous silica were calcined according to the thermal profile described previously (section 3.3.2.1). 20 mg of each sample was outgassed to less than 5 mTorr at 200 °C for 3 hours. The sorption of nitrogen was recorded using equilibration time of approximately 10 min per point. Surface area and pore size calculations were made using the Brunauer, Emmett, and Teller (BET) equation fitted to the first 10 points of each isotherm. Pore volume and pore size distributions were calculated using BJH (Barrett-Joyner-Halenda) formula.

3.3.2.7. Particle size measurement

The particle size of materials was measured by the Malvern laser diffraction technique. The sample was dispersed in water, passed through the laser beam. The diffraction angle of the laser beam inverted proportional to particle size was measured.

3.3.3. Extraction properties of materials

The extraction properties of non-doped and HPMSp doped mesoporous silica were studied in both batch and SPE column method. Various parameters such as type of metal, pH of sample solution and the recyclability of materials were studied. The general experimental details were described below unless specified otherwise.

3.3.3.1. Batch method

25 mL of 200 ppm of metal solution were added to 0.2 g of mesoporous silica. The mixture was stirred for 24 hours at 25 °C in thermoregulated bath. The resulting adsorbent was recovered by filtration. The concentration of metal in aqueous solution was analyzed using flame atomic absorption spectrometer. The amount of metal ions on the adsorbent and the distribution ratio was calculated according to the equations 2.6 and 2.7 shown in chapter II.

3.3.3.2. SPE column method

A frit was placed on the bottom of a 15 mL of syringe, which was later filled with 0.2 g of HPMSp doped mesoporous silica and covered with the cotton wool. Then the syringe was connected to a vacuum manifold. Before the extraction process, the sorbent was manually conditioned with 25 mL of deionized water followed by 25 mL of 0.01 M HNO₃. For the sorption experiment, 25 mL of 200 ppm of metal solution were drawn through the syringe. The sorbent was then washed once with 10 mL of deionized water to remove other sources of interferences. The analytes were eluted with 10 mL of 1 M HNO₃ and 2x2 mL of deionized water. The concentration of the metal after passing syringe and in the eluate were determined by flame atomic absorption spectrometer. The amounts of metal ions on the adsorbents were calculated according to equation 2.6.