

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

1. Acid Blue (Lab Scan)
2. Methylene Blue (Lab Scan)
3. Standard ICP Cadmium 1000 ppm in 2-3% HNO₃ (Merck)
4. Standard ICP Copper 1000 ppm in 2-3% HNO₃ (Merck)
5. Standard ICP Lead 1000 ppm in 2-3% HNO₃ (Merck)
6. Tetraethoxysilane 98% (ACROSS ORGANICS)
7. 3-aminopropyltriethoxysilane (Fluka)
8. 3-mercaptopropyltrimethoxysilane (Chisso)
9. Glycerol 85%
10. Methyl alcohol
11. Ammonium nitrate
12. Potassium persulfate
13. Potassium nitrate (Merck)
14. Sodium hydroxide (Lab Scan)
15. Sodium chloride
16. Hydrochloric acid 37%
17. Nitric acid 65%
18. Hydrogen peroxide
19. Potassium dihydrogenphosphate (Riedel-de-Haen)
20. Dipotassium hydrogenphosphate (Riedel-de-Haen)

3.2 Preparation of Adsorbents

3.2.1 SCP Synthesis (Kim et al. 2006; Liu et al. 2004; Ma et al., 2006)

Single coated Magnetic: Mix 0.86 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.36 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 40 ml of deaerated deionized water with vigorous mechanical stirring and heated to 80 °C. 5 ml of acetone and 0.1 ml of linolenic acid were added in the solution. Then 5 ml of ammonium hydroxide was added. Further additions of linoleic acid are made in five 0.2 ml volumes over 5 min. intervals. After 30 min. stirring, the particles can be separated by Nd-Fe-B permanent magnet. The obtained particles will be wash with deionized water six time.

Water-base Ferrofluid: Mix 1 g of single coated magnetite were added to 20 ml deionized water and heated to 60 °C under vigorous string. A solution of 10% ammonium salt of Linolenic acid (pH=10) is prepared separately by mixing 30 ml water, 3 ml of linolenic acid and 30-40 drops of solution of NH_4OH (30%w/w). This solution is added to the slurry dropwise under constant stirring at 60 °C until the slurry changes into a stable suspension.

Silica coated superparamagnetic particle: 30 mg of superparamagnetic Magnetite (water-based ferrofluid form) were dispersed in 80 ml of 2-propanol and 6 ml of deionized water by sonication for about 10 min. Then under continuous mechanical stirring 7 ml of ammonium hydroxide and 1 ml of TEOS were consecutively added to the reaction mixture. The reaction was allowed to proceed at room temperature for 6 hrs. under continuous stirring. The resultant with help of the permanent magnet and was thoroughly washed with deionized water six times (50 ml each time).

3.2.2 Grafting of Organic functional groups on SCP (Lui et al., 2004)

Mix 2 g of Silica coated superparamagnetic particle, 2.5 ml of water and 10 ml of 3-aminopropyltriethoxysilane (Fluka) or 3- mercaptopropyltrimethoxysilane were added into 250 ml of methanol. The mixture was treated by ultrasound for 30 min. mixed with 150 ml glycerol and then transferred to 100 ml three-necked flask equipped with mechanical stirrer the temperature was kept at 85-90°C with rapid stirring for 6 hrs. the resulting nanospheres were washed with deionization water and methanol for several times. These nanospheres were immersed in 5% (v/v) glutaraldehyde solution with 0.01 M phosphate buffer, pH 7.4 for 6 hrs. at the room temperature and then washed with deionized.

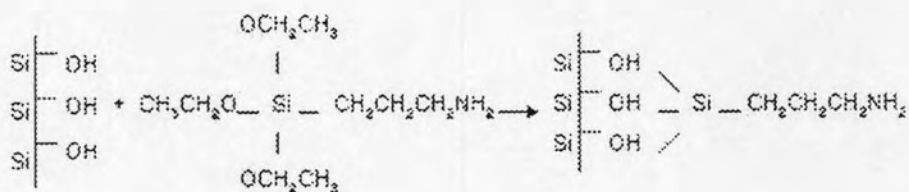


Figure 3.1: Silanization reaction of 3-aminopropyltriethoxysilane on SCP (AM-SCP).

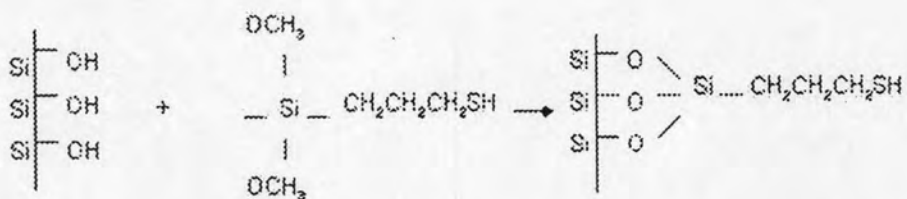


Figure 3.2: Silanization reaction of 3-mercaptopropyltrimethoxysilane on SCP (MP-SCP).

3.3 Physico-Chemical Characterization for Adsorbents

3.3.1 Surface Area

Nitrogen adsorption-desorption isotherms (BET) were measured at 77 K on a Surface area Analyzer Micromeritic model: ASAP 2020 version 1.04H. The BET specific surface areas were calculated by using adsorption data in the relative pressure from 0.06 to 0.14.

The BET equation can be represented in Equation 2.9 as below.

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \quad (2.9)$$

Where v = volume of N_2 adsorbed by the sample under pressure p , p_0 = Saturated vapor pressure at the same temperature, v_m = Volume of N_2 adsorbed when the surface is covered with a unimolecular layer, and c = Constant for a given adsorbate

The specific surface areas of samples are calculated from adsorption data by Equation 2.10:

$$S = \frac{N_0 v_m A}{22414m} \quad (2.10)$$

Where S = Specific surface area, N_0 = Avogadro number, m = Amount of solid adsorbent, A = Cross-section of the gas molecules (16.2 \AA^2 for N_2)

The Barrett-Joyner-Halenda(BJH) formula with the corrected Kelvin equation. The Kelvin equation describe as follows:

$$\ln \frac{p_0}{p} = \frac{2\gamma V_m}{rRT} \quad (2.11)$$

where p is the actual vapour pressure, p_0 is the saturated vapour pressure, γ is the surface tension, V_m is the molar volume, R is the universal gas constant, r is the radius of the droplet, and T is temperature.

3.3.2 Surface Functional group

Surface functional groups of prepared SCPs were investigated by Fourier Transform Infrared (FT-IR) Spectroscopy Nicolet Impact 410. KBr use as the background and sample mixer (KBr:Sample ratio = 10:1). Before measuring, sample was heated at 110°C for reducing the effect of H₂O at 3750 and 3457 cm⁻¹.

3.3.3 Elemental Analysis

3.3.3.1 Analysis of Nitrogen content

The amounts of nitrogen in synthesized SCPs will be measured by UV adsorption technique. Adsorbents will be digested by potassium persulfate (K₂S₂O₈) with base condition in autoclave. Chemical preparations were described as follows:

Mixture of sodium hydroxide (NaOH) and potassium persulfate was prepared by adding 3 g of potassium persulfate in solution of 4 g NaOH in 100 ml. This solution was newly prepared every time. Stock solution (0.1 mg N/ml) for total nitrogen standard curve was prepared by adding 0.722 g of dried potassium nitrate (KNO₃) in milli-Q water, and made volume to 1000 ml. HCl (1+500) was prepared by mixing of 1 HCl conc. in 500 ml of milli-Q water, and HCl (1+16) also was prepared by mixing 1 HCl conc. in 16 ml of milli-Q water.

Small amount of sample (50 mg) was added to autoclave glass bottle, and then 50 ml of milli-Q water was added. 10 ml of mixture of NaOH and $K_2S_2O_8$ were added into the mixture and autoclaved at 120°C for 30 min. Then sample was filtered and 25 ml of filtrate was taken. After that, 5 ml of HCl (1+16) were added to adjust pH to 2-3 and filled into 50 ml of colorimetric tube. Sample was diluted to 50 ml by milli-Q water. All samples were measured by UV spectrophotometer at 220 nm. Blank was prepared by adding 5 ml of HCl (1+500) into milli-Q water and diluted to 50 ml. Calibration curve was made by following procedure. 10 ml of prepared TN stock solution was taken and diluted ten times to 100 ml. Then 1-15 ml of obtained solution (0.01 mg N/ml) were added to each colorimetric tube and 5 ml of HCl (1+500) was added to each tube. All of tubes were made to 50 ml and measured by UV spectrophotometer with same condition. Amount of TN were plotted against UV-absorbance. TN (mg/g) was calculated by the following equation:

$$TN \text{ (mg/g)} = \{ [a \times (60 / 25)] / b \}$$

(2.12)

Where a is amount of TN obtained from calibration curve (mg) and b is amount of synthesized adsorbent (g).

3.3.3.2 Analysis of sulfur content

The synthesized SCPs will be digested with 7 ml of HNO_3 65% and 2 ml of HF 40% in Microwave equipment to analyze the amounts of sulfur. Microwave is temperature-programmed at 240°C in 10 minutes and held for 20 minutes. After microwave completion, samples were cooled by air until the solution reached room temperature. HF in solution was removed by adding 10 ml of H_3BO_3 5% before analysis. The amounts of sulfur will be analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3.3.4 Surface Charge

Acid/base titration method using 10 ml of adsorbents mixture (1 g/l) mixed with a predetermined amount of NaCl for adjustment of initial ionic strength at 1 mM when diluted to 25 mL. Different amounts of 0.025 M HCl or 0.025 M NaOH were added to a maximum of 3 samples to vary pH of each sample. Intrinsic pH was also measured for each samples without adding acid or base. Each sample was then dilute to a final volume of 25 mL with decarbonated Mili-Q water, and shaken overnight at ambient temperature ($25\pm 2^\circ\text{C}$). After equilibration, the supernatant pH of each sample was measured and the pH data of entire batch experiments were plotted against surface charge data that were calculated from the principle of electroneutrality shown in the following equation:

$$\text{Surface charge density (C/m}^2\text{)} = \{[\text{HCl}]_{\text{add}} - [\text{NaOH}]_{\text{add}} - [\text{H}^+] + [\text{OH}^-]\} \times F/S \quad (2.13)$$

Where F is the Faraday's constant (96,500 C/mol) and S (m^2/g) is BET surface area of adsorbents (Noh et al., 1988).

3.4 Adsorption Experiments

3.4.1 Adsorption Kinetic

Heavy metals (Lead, Copper, and Cadmium)

The equilibrium contact time for heavy metal adsorption was performed by varying contact time from 0 to 24 hrs under batch conditions at heavy metal concentration of 5 mg/l and amount of adsorbent of 2.5 g/l. The pH of solution was fixed at pH 3 and 5 by phosphate buffer and sulfuric acid (ionic strength = 0.01 M). Samples were shaken in water bath at 25°C , 150 rpm. After that the adsorbent was separated adsorbent by filtration and the rest of heavy metal concentration then was analyzed by ICP-AES.

Ionic dyes (Acid Blue 45 and Methylene Blue)

The equilibrium contact time for ionic dye adsorption was performed by varying contact time from 0 to 24 h under batch conditions at ionic dyes concentration of 30 mg/l and amount of adsorbent of 2.5 g/l. The pH of solution was fixed at pH 5, 7 and 9 by phosphate buffer (ionic strength = 0.01 M). Samples were shaken in shaking water bath at 25°C, 150 rpm. After that they were separated adsorbent by filtration and the rest of ionic dye concentration then were analyzed by using UV-VIS spectroscopy.

3.4.2 Adsorption Isotherm

i) Single Solute

Heavy metals (Lead, Copper, and Cadmium)

The single solute adsorption isotherm for each heavy metal adsorption were performed by varying heavy metal concentration of 0-10 mg/l under batch condition and amount of adsorbent of 0.33 g/l. The pH of solution was fixed at pH 3 and 5 and ionic strength 0.01 M by phosphate buffer. Samples were shaken in shaking water bath at 25°C, 150 rpm. After that they were filtered by filter paper no.42 and the rest of heavy metal concentration then were analyzed by using ICP-AES.

Ionic dyes (Acid Blue 45 and Methylene Blue)

The single solute adsorption isotherm for ionic dye adsorption were performed by varying ionic dye concentration of 0-100 mg/l under batch condition and amount of adsorbent of 0.33 g/l. The pH of solution were fixed at pH 5 and ionic strength 0.01 M by phosphate buffer. Samples will be shaken in shaking water bath at 25°C, 150 rpm. After that they will be filtered by filter paper no.42 and the rest of ionic dye concentration then will be analyzed by using UV-Visible spectroscopy.

ii) Binary solute

The equilibrium contact time for mixing two solutes of selected heavy metal and ionic dye adsorption was performed by varying contact time from 0 to 24 h under batch condition at selected heavy metal concentration of 5 mg/l, and ionic dye concentration of 50 mg/l and amount of adsorbent of 0.33 g/l as same as single solute. The rest of selected heavy metal, and ionic dye concentration then were analyzed by using ICP-AES and UV- VIS spectroscopy, respectively.

3.4.3 Effect of pH

The effect of pH for all of single-solute pollutants adsorption will be performed by varying pH from 5 to 9 for ionic dyes and 3 to 5 for heavy metals by phosphate buffer and sulfuric acid with ionic strength at 0.01M. The amount of adsorbent was 0.33 g/l. Samples will be shaken in shaking water bath at 25°C, 150 rpm until equilibrium. After that, they will be filtered through the filter paper and the rest of heavy metal and ionic dye concentration then will be analyzed by using ICP-AES and UV-Visible spectroscopy, respectively.

3.5 Separation by magnet

Separation for SCP and functionalized SCPs were performed by varying amount of adsorbent, pH and the presence of studied pollutants. The mixture was agitated at 300 rpm for 5 min. After the agitation stopped, the turbidity meter will be recorded as turbidity at 0 min. Then the residual turbidity of the supernatant was measured up 0 to 60 min or when there was no further sedimentation observed. The magnetic field strength was controlled by changing the number of permanent magnets below the flask (Ching-Ju et al., 2005).

3.6 Analytical Method

The concentration of heavy metal and ionic dye were determined using ICP-AES and UV-Visible spectroscopy.

i.) Single solute

- Heavy metal use ICP-AES

- Ionic dye use UV-Visible spectroscopy

Acid Blue 45 (AB) at wavelength of 670 nm.

Methylene blue (MB) at wavelength of 595 nm.

ii.) Binary solute

- Heavy metal use ICP-AES

- Ionic dye use UV-Visible spectroscopy

Acid Blue 45 (AB) at wavelength of 670 nm.

Methylene blue (MB) at wavelength of 595 nm.