CHAPTER 2

Experiment

2.1 Chemicals

All chemicals were of analytical reagent grade. Deionized water was used to prepare all solutions. Lists of chemicals used in this research are shown as follow:

1) Cadmium chloride ($CdCl_2 \cdot H_2O$), Himedia, India
2) Zinc chloride ($ZnCl_2$), Rankem, India
3) Hydrochloric acid 37% (HCl), RCI Labscan, Thailand
4) Nitric acid 65% (HNO_3), QRëC, New Zealand
5) Sodium hydroxide (NaOH), Merck, Germany
6) Cadmium standard solution (Cd 1000 mg/L), Fisher, UK
7) Zinc standard solution (Zn 1000 mg/L), Merck, Germany

2.2 Instrument and apparatus

1) Analytical balance, model PW 254, AE ADAM, USA
2) Atomic absorption spectrometer, model 3110, Perkin Elmer, USA
3) Digital precise shaking water bath, model WSB-45, Daihan scientific, Korea
4) Fourier transform infrared spectrometer, Tensor 27, Bruker, Germany
5) Oven, model UNE 400, Memmert, Germany
6) Particle size analyzer laser, Mastersizer S, Malvern, UK
7) pH meter, model pHTestr 20, Eutech, USA
8) PMC hot plate/stirrers, model 524C-2, Barnstead/Thermolyne, USA
9) Scanning electron microscope, model JSM-5910, Jeol, USA
10) Surface area analyzer, Autosorb 1 MP, Quantachrome, USA
11) X-ray diffractometer, D2 Phaser, Bruker, Germany
12) X-ray fluorescence spectrometer, model Magix pro, Phillips, Netherlands

2.3 Material

Leonardite was used as an adsorbent for studying the adsorption of Cd(II) and Zn(II) in aqueous solution. It was obtained from Mae Moh mine, Lampang province, Thailand. For the preparation of leonardite as adsorbent, raw leonardite was air dried to reduce the moisture content. Then, it was powdered in the ball mill and size adjusted by sieving through a 80 mesh screen. Finally, it was dried in the oven at 105 °C for 24 h and kept in the desiccators before being used.

2.4 Preparation of Solutions

2.4.1) Cd(II) standard solution (0.4 – 5 mg/L)

A 1000 mg/L cadmium standard solution (Cd(II) in 1 mol/L nitric acid, AAS standard) was used for preparation of Cd(II) working standard solutions. Working standard solutions of Cd(II) were freshly prepared by appropriate dilution of this standard solution with 1%v/v HNO_3.

2.4.2) Zn(II) standard solution (0.4 – 5 mg/L)

A 1000 mg/L zinc standard solution ($Zn(NO_3)_2$ in 0.5 mol/L nitric acid, AAS standard) was used for preparation of Zn(II) working standard solutions. Working standard solutions of Zn(II) were freshly prepared by appropriate dilution of this standard solution with 1%v/v HNO_3.

2.4.3) 500 mg/L of Cd(II) stock solutions

0.8954 g of $CdCl_2 \cdot H_2O$ was dissolved in deionized water and the volume was made up to 1000 mL in a volumetric flask.

2.4.4) 500 mg/L of Zn(II) stock solutions

1.0422 g of $ZnCl_2$ was dissolved in deionized water and the volume was made up to 1000 mL in a volumetric flask.

2.4.5) Cd(II) solutions at concentrations of 5 – 50 mg/L

The Cd(II) solutions at the concentrations of 5, 10, 15, 20, 25, 30, 40, and 50 mg/L were prepared by dilution of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 mL of the

500 mg/L Cd(II) stock solutions with deionized water. The final volume was made up to 100 mL in a volumetric flask.

2.4.6) Zn(II) solutions at concentrations of 5 – 50 mg/L

The Zn(II) solutions at the concentrations of 5, 10, 15, 20, 25, 30, 40, and 50 mg/L were prepared by dilution of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 mL of the 500 mg/L Zn(II) stock solutions with deionized water. The final volume was made up to 100 mL in a volumetric flask.

2.4.7) Binary solutions of Cd(II) and Zn(II)

The concentration used for both metal ions were 5, 10, 15, 20, 25, and 30 mg/L. This gives the series of 36 mixed solutions. The preparation of binary solutions of Cd(II) and Zn(II) are shown in Table 2.1. The final volume was made up to 100 mL in a volumetric flask.

2.4.8) 1 mol/L NaOH

The 1 mol/L NaOH solution was prepared by dissolving 4 g of NaOH in deionized water and the volume was made up to 100 mL.

2.4.9) 0.2 mol/L NaOH

The 0.2 mol/L NaOH solution was prepared by dissolving 0.8 g of NaOH in deionized water and the volume was made up to 100 mL.

2.4.10) 1 mol/L HCl

The 1 mol/L HCl was prepared by diluting 8.3 mL of 37%v/v HCl with deionized water and the volume was made up to 100 mL.

2.4.11) 1%v/v HNO_3

The 1%v/v HNO_3 was prepared by dilution of 15.4 mL of 65%v/v HNO_3 with deionized water to 1000 mL.

Table 2.1 Preparation of binary solutions of Cd(II) and Zn(II)

Set	Conc. of Cd(II) (mg/L)	Conc. of Zn(II) (mg/L)	Volume of Cd(II) stock solution (mL)	Volume of Zn(II) stock solution (mL)	Set	Conc. of Cd(II) (mg/L)	Conc. of Zn(II) (mg/L)	Volume of Cd(II) stock solution (mL)	Volume of Zn(II) stock solution (mL)
1	5	5	1.0	1.0	4	5	20	1.0	4.0
	10	5	2.0	1.0		10	20	2.0	4.0
	15	5	3.0	1.0		15	20	3.0	4.0
	20	5	4.0	1.0		20	20	4.0	4.0
	25	5	5.0	1.0		25	20	5.0	4.0
	30	5	6.0	1.0		30	20	6.0	4.0
2	5	10	1.0	2.0	5	5	25	1.0	5.0
	10	10	2.0	2.0		10	25	2.0	5.0
	15	10	3.0	2.0		15	25	3.0	5.0
	20	10	4.0	2.0		20	25	4.0	5.0
	25	10	5.0	2.0		25	25	5.0	5.0
	30	10	6.0	2.0		30	25	6.0	5.0
3	5	15	1.0	3.0	6	5	30	1.0	6.0
	10	15	2.0	3.0		10	30	2.0	6.0
	15	15	3.0	3.0		15	30	3.0	6.0
	20	15	4.0	3.0		20	30	4.0	6.0
	25	15	5.0	3.0		25	30	5.0	6.0
	30	15	6.0	3.0		30	30	6.0	6.0

2.5 Characterization, chemical and physical properties of leonardite

2.5.1) Chemical compositions

X-ray fluorescence spectroscopy was used for determining the elemental composition of leonardite. The analysis was performed using X-ray fluorescence spectrometer.

2.5.2) Mineral compositions

The mineral composition of leonardite was determined by X-ray diffraction spectroscopy. Leonardite was ground and sieved through the 200 mesh screen. The prepared sample was analyzed using X-ray diffractometer.

2.5.3) Characterization of leonardite by FTIR analysis

Fourier Transform Infrared (FTIR) technique was applied to investigate the characteristics of leonardite. In order to determine the FTIR spectrum, sample was prepared using the KBr pellet method. First, a spatula full of KBr was added to the agate mortar and ground to the fine powder until no crystallites can be seen. Then, small amount of leonardite was added and the mixture was finely pulverized. After that, the mixture was put into the pellet-forming die and pressed under very high pressure to form the transparent thin disk.

To perform the measurement, a sample disk was placed on the IR sample holder and FTIR spectrum was recorded in the range of wavenumber 4000 - 400 cm^{-1} on the FTIR spectrometer.

2.5.4) Morphology

The morphology of leonardite was studied using scanning electron microscope (SEM). For sample preparation, leonardite was mounted on the stub using double-sided conductive tape. After that, it was coated with gold using sputter coater and then observed in the microscope.

2.5.5) Particle size

The particle size (μm) of leonardite was measured by a particle size analyzer laser using Mie theory of light scattering to calculate the particle size.

2.5.6) The BET surface area

The surface area (m^2/g) of leonardite was measured by nitrogen adsorption (BET) at 77 K using surface area analyzer.

2.5.7) Cation exchange capacity

Cation exchange capacity (cmol/kg) of leonardite was measured by ammonium acetate (pH 7) distillation method.

2.5.8) pH

Approximately 10 g of leonardite was thoroughly mixed with 10 mL distilled water. Let the mixture stood for 1 h. The pH value of the mixture was determined using a pH meter.

2.5.9) Density

The density of leonardite was determined by using pycnometer.

(1) The empty, dry pycnometer was weighed (W_0).

(2) About 1/3 of pycnometer volume was filled with leonardite and measured the weight (W_1).

(3) Distilled water was added such that pycnometer as well as capillary hole in the stopper is filled with water. Spare water that leaked through the capillary hole was dried with a filter paper and measured the weight (W_2).

(4) Empty pycnometer and filled it with distilled water only. Use the filter paper to dry the spare water again and measured the weight (W_3).

(5) The density was calculated according to

$$\text{Density} = \frac{(W_1 - W_0) \times \rho}{(W_3 - W_0) - (W_2 - W_1)}$$

where ρ is the density of water at the temperature of the test.

2.6 Single-component adsorption study

Batch process was carried out to study the adsorption behavior of Cd(II) and Zn(II) on leonardite. The parameters that affect the adsorption process including pH, contact time, initial metal concentration and temperature were investigated.

2.6.1) Effect of pH

Effect of pH value on the adsorption of Cd(II) and Zn(II) was studied at different pH values between 2 – 6. The initial metal concentration of Cd(II) and Zn(II) was 30 mg/L. In the experiments, 0.100 g of leonardite was added to approximately 80 mL deionized water. The mixture was stirred for 5 min and pH of mixture was adjusted to the desired value. Next, 6.0 mL metal stock solution was added to the mixture. The final volume was made up to 100 mL together with the pH of mixture was re-adjusted. The mixture was then agitated continuously at speed of 120 rpm, 30 °C in thermostatic water-bath shaker for 5 h. After the agitation, metal solution was separated from leonardite by filtration using Whatman filter paper No. 6.

A blank was prepared as the same procedure but no metal stock solution was added. The metal concentration in solutions was determined using atomic absorption spectrometer. The amount of metal ion adsorbed at equilibrium, q_e (mg/g) was calculated as follow:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2.1}$$

where C_0 and C_e are the initial and equilibrium metal concentrations (mg/L), respectively. V is the volume of metal solution (L) and W is the weight of leonardite (g).

2.6.2) Effect of contact time

To study Cd(II) and Zn(II) adsorption as a function of contact time, the experiments were performed at optimum pH (as determined from 2.6.1) with a total time of 5 h. The initial metal concentration of Cd(II) and Zn(II) was 30 mg/L. 0.250 g of leonardite was added to approximately 220 mL deionized water. The mixture was stirred for 5 min and pH of mixture was adjusted to the optimum pH value. Next, 15.0 mL metal stock solution was added to the mixture. The final volume was made up to 250 mL

together with the pH of mixture was re-adjusted. The mixture was then agitated continuously at speed of 120 rpm, 30 °C in thermostatic water-bath shaker. Aliquots were taken at suitable time intervals (10, 20, 30, 40, 50, 60, 90, 120, 180, 240, and 300 min). Each aliquot was filtered using filter paper and determined the remaining metal concentration by AAS. A blank was prepared as the same procedure but no metal stock solution was added. The amount of metal ion adsorbed at equilibrium, q_e (mg/g) was calculated according to equation (2.1).

2.6.3) Adsorption isotherm

The equilibrium adsorption of Cd(II) and Zn(II) in single system was investigated at the initial metal concentration range of 5 − 50 mg/L. The adsorption process was performed under the condition of optimum pH (from 2.6.1) and contact time (from 2.6.2). The experiments were carried out by mixing 0.100 g of leonardite with approximately 80 mL deionized water. The mixture was stirred for 5 min and pH of mixture was adjusted to the optimum pH value. Next, desired volume of metal stock solution was added to the mixture. The final volume was made up to 100 mL together with the pH of mixture was re-adjusted. The mixture was then agitated continuously at speed of 120 rpm, 30 °C in thermostatic water-bath shaker until the equilibrium was reached. After the agitation, metal solution was separated from leonardite by filtration and the concentration of metal was measured by AAS. A blank was prepared as the same procedure but no metal stock solution was added. The amount of metal ion adsorbed at equilibrium, q_e (mg/g) was calculated according to equation (2.1).

2.6.4) Effect of temperature

The influence of temperature on the adsorption of Cd(II) and Zn(II) was studied at 10, 20, 30, and 40 °C. The experiments were conducted the same as 2.6.3 but the temperature of thermostatic water-bath shaker was set at 10, 20, 30, and 40 °C.

2.7 Binary-components adsorption study

Adsorption of Cd(II) and Zn(II) in binary system was studied at the initial metal concentration range of 5 – 30 mg/L. Various ratios of Cd(II) to Zn(II) were investigated. The adsorption process was performed under the conditions of optimum pH (from 2.6.1)

and contact time (from 2.6.2). In the experiment, binary solutions were prepared according to Table 2.1.

For example, the binary solution of Cd(II) and Zn(II) at the ratio of 5 mg/L to 5 mg/L was prepared by adding 0.100 g of leonardite to approximately 80 mL deionized water. The mixture was stirred for 5 min and pH of mixture was adjusted to the optimum pH value. Next, 1.0 mL of Cd(II) stock solution and 1 mL of Zn(II) stock solution were added to the mixture. The final volume was made up to 100 mL together with the pH of mixture was re-adjusted. The mixture was then agitated continuously at speed of 120 rpm, 30 °C in thermostatic water bath shaker until the equilibrium was reached. After agitation, the solution was separated from leonardite by filtration and the concentration of metal ion was measured by AAS. A blank was prepared as the same procedure but no metal stock solution was added. The amount of metal ion adsorbed at equilibrium, q_e (mg/g) was calculated according to equation (2.1).