CHAPTER 3

EXPERIMENTAL

3.1 Materials, chemicals and instruments

3.1.1 Materials and chemicals

1) Leonardite, Mae Moh Mine, Lampang, Thailand
2) Copper(II) nitrate trihydrate($Cu(NO_3)_2{\cdot}3H_2O$), AR,CarloErba. Italy
3) Lead (II) nitrate ($Pb(NO_3)_2$), AR,CarloErba. Italy
4) Methylene Blue dihydrate ($C_{16}H_{18}N_3ClS{\cdot}2H_2O$), AR, UNILAB. Australia
5) Nitric acid (HNO_3), AR,CarloErba. Italy
6) Sodium hydroxide (NaOH), AR, BDH, England
7) Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), AR, Carlo Erba. Italy
8) Standard solution Cu (Cu 1000 mg/l), Merck, Germany
9) Standard solutionZn (Zn 1000 mg/l), Merck, Germany
10) Standard solutionPb (Pb 1000 mg/l), Merck, Germany

3.1.2 Apparatus and instruments

1) Analytical balance AB 204-S series, Mettler Toledo GmbH, Laboratory/Weighing Technologies, Switzerland
2) Atomicabsorptionspectrophotometer, series AA-275, Varian Company, Australia
3) Orbit shaker, model VRN 480, Gemmy Industrial Company, Taiwan
4) Oven, model UNE 400, Memmert Company, Germany

5) Particle size analyzer, Mastersizer, Melvern Instrument Ltd
6) pH meter, model FE 20-kit, Mettler-Toledo, Switzerland
7) Quantachrome autosorb automated gas sorption system, Mastersizer, MelvernInstrumentLtd
8) Universal Centrifuge, model PLC-012E, Gemmy Industrial Company, Taiwan
9) UV-Visspectrophotometer, Genesys^{TM}5, SpectronicInstrument,USA
10) X-raydiffractometer, BrukerD8AdvanceDiffractometer
11) X-ray fluorescence spectrometry, Phillips MagiX PRO PW 2400 Sequential

3.2 Preparation of raw materials and solution

3.2.1 Preparation of leonardite raw material

The sorbent, leonardite, was provided by Mae Moh lignite mine, Lampang province, Thailand, and was used without any additional pre-treatment except of grinding and a size classification by sieving. The material was prepared. They were dried sequentially at 110 ^{o}C for 12 hours, grinded by ball mill, and sieved through 80 mesh by sieving machine for a size classification.

3.2.2 Preparation of solutions

1) 1000 mg/L of copper(II), zinc(II) and lead(II) solutions

3.8017 g of $Cu(NO_3)_2{\cdot}3H_2O$, 4.5499 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 1.5977 g of $Pb(NO_3)_2$ were dissolved in 1 L of deionized water in volumetric flask.

2) 5.00 to 100.0 mg/L of copper(II), zinc(II) and lead(II)solutions

5.00 to 100.0 mg/L of the solutions were prepared by diluting 5.00 to 100.0 mL of the 1000-mgsolution, respectively, with deionized water to 1000 mL in a volumetric flask.

3) 1000 mg/L of methylene blue solution

1.1127 g of methylene blue ($C_{16}H_{18}N_3ClS{\cdot}2H_2O$) was dissolved in 1 L of deionized water in volumetric flask.

4) 60.00 to 200.0mg/L of methylene blue solutions

60.00 to 200.0mg/L of methylene blue solutions were prepared by diluting 60.00 to 200.0 mg/L of a 1000 mg/L of methylene blue solution, respectively, with deionized water to 1000 mL in a volumetric flask.

5) 0.5 M Nitric acid

0.5 M nitric acid was prepared by adding 1.731 mL of conc.HNO_3 to deionized water and diluted to 50 mL in a flask.

6) 0.5 M NaOH

1 g of NaOH was dissolved in 50 mL of deionized water.

7) 1% v/v HNO_3

1% HNO_3 was prepared by adding 11 mL of conc. HNO_3 to deionized water and diluted to 1000 mL in a flask.

3.3 Determination of the chemical and mineral composition of leonardite

3.3.1 Chemical composition determination

Leonardite was sieved through a 80 µm sieve and analyzed for their chemical composition. The chemical compositions were obtained by X-ray fluorescence spectrometry (XRF).Material compositions were analyzed on a Phillips MagiX PRO PW 2400 Sequential X-ray Spectrometer (wavelength dispersive spectrometer) using Rhodium (Rh) tube.

3.3.2 Mineral composition determination

The mineralogical compositions of leonardite were obtained by XRD patterns from randomly oriented powder mounts using CuK_{α} radiation. X-ray XRD was performed on powder samples using a BrukerD8 Advance diffractometer equipped with a copper anode at the School of Science, Mae Fah LuangUniversity. Diffraction patterns were recorded from 2 to 80^{o} 2θ with a step interval of 0.04^{o} 2θ and counting time of 1 s per step.

3.4 Study of physical and chemical properties of leonardite

3.4.1 Determination of chemical compositions by digestion method and AAS

Leonardite samples (0.200 g each) were heated at 70-80°C in a solution of conc. HNO_3 and 30% H_2O_2 until almost dry, and kept cool to room temperature. The samples were then dissolved in 1% (v/v) HNO_3, filtered using filter paper No. 40, washed several times with 1% (v/v) HNO_3, and then adjusted volume by 1% HNO_3 to

50 mL. Finally the samples were analyzed by AAS for some chemical composition determination.

3.4.2 Surface areadetermination

After passing through a 80μm sieve and dried at 110 ^{o}C for 12 hours, leonardite was used for analysis of surface area. The specific surface area (m^2/g) was measured by a Quantachrome Autosorb automate with nitrogen gas (version 2.46).

3.4.3 Cation exchange capacity determination

The Cation exchange capacity (CEC) was measured to evaluate the adsorption capacity by the ammonium acetate method.

3.4.4 Particle size analysis

Leonardite was sieved through a 80μm sieve and dried at 110 ^{o}C for 12 hours. Afterwards, the particle size of leonardite was analyzed by particle size analyzer, Mastersizer Instrument at the Department of Industrial Chemistry, Faculty of Science, Chiang Mai University.

3.4.5 Topology determination

After grinding in motar, leonardite was put on a copper plate. SEM was used to determine the topology of the materials.

3.5 Adsorption study of copper(II), zinc(II) and lead(II) on leonardite

3.5.1 Effect of pH

50.00 mL of the 5.00 or 20.00 mg/L of Cu^{2+}, Zn^{2+} and Pb^{2+}solutions containing in 50 mL conical flasks and each concentration, were adjusted to initial pH of 2, 3, 4, 5 and 6 with 0.5 M $HNO_3$and/or 0.5 M NaOH solutions. The leonardite (0.400 g) was added into each solution, and the pH was re-adjusted. Each flask was then closed with parafilm and maintained under continuous agitation at 130 rpm for 24 h at room temperature. After agitation, the mixture was centrifuged and filtered.A fewdrops of conc. HNO_3 were added to the mixture, and the remaining metal ion concentrations were determined by AAS.

A blank was prepared by adding 0.400g of leonardite to 50.00 mL of DI water to verify whether the leonardite transferred metal ions to the water. The control test solutions (10 mL) were filtered and analyzedto ensure that no precipitates formed prior to contact with the sorbent.

3.5.2 Effect of the contact time

200.0 mL of the 5.00 or 20.00 mg/L of Cu^{2+}, Zn^{2+} and Pb^{2+}solutions containing in 250 mL conical flasks were adjusted to the optimum pH (from 3.5.1) with 0.5 M $HNO_3$and/or 0.5 M NaOH solutions. The leonardite (1.600 g) was added into each solution, and the pH was re-adjusted. The mixture was then shaken at 130 rpm at room temperature and 10.00 mL of the mixture was collected one after another at 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360 min.Each mixture was centrifuged, filtered, added a few drops of conc. HNO_3, and the remaining metal ion concentrations were determined by AAS.

A blank was prepared by adding 1.600g of leonardite to 200.0 mL of DI water, and the experimental conditions used were the same as those mentioned above.

3.5.3 Effect of leonardite quantity

Various amounts of leonardite in the range of 0.400 to 3.000 g were added into flasks, each containing 50.00 mL of 5.00or20.00 mg/L of the Cu^{2+}, Zn^{2+} and Pb^{2+} solutions at optimum pH (from 3.5.1), and the pH was then re-adjusted. Each flask was shaken until equilibrium was reached (from 3.5.2) at 130 rpm at room temperature. Each mixture was centrifuged, filtered, added a few drops ofconc. HNO_3, and the remaining metal ion concentrations were determined by AAS.

A blank was prepared by adding various amounts of leonardite in the range of 0.400 to 3.00 g to 50.00 mL of DI water, and the experimental conditions used were the same as those mentioned above.

3.5.4 Adsorption Isotherm

0.400 g of leonardite were added into flasks containing 50.00 mL of different concentrations (5.00-100.0 mg/L) of the Cu^{2+}, Zn^{2+} and Pb^{2+}solutions at optimum pH (from 3.5.1), and the pH was re-adjusted. Each flask was shaken until equilibrium was reached (from 3.5.2) at 130 rpm and room temperature. Finally, the mixture was centrifuged, filtered, added a few dropsof conc. HNO_3, and the remaining metal ion concentrations were determined by AAS.

A blank was prepared by adding 0.400g of leonardite to 50.00 mL of DI water, and the experimental conditions used were the same as those mentioned above.

3.5.5 Determination of copper(II), zinc(II) and lead(II) by AAS

3.5.5.1 Preparation of standardsolution

For copper and zinc ions, standard solutions concentration 1.00, 2.00, 3.00, 4.00 and 5.00 mg/L were prepared by diluting 0.0500, 0.100, 0.150, 0.200 and 0.250mL of a 1000-mg/L standard stock solution of copper and zinc for AAS, respectively, with 1% HNO_3 to 50.00 mL in a volumetric flask.

For lead ion, standard solutions concentration 5.00, 10.00, 20.00, 30.00 and 40.00 mg/L was prepared by diluting 0.250, 0.500, 1.00, 1.50 and 2.00mL of a 1000-mg/L standard stock solution of lead for AAS, respectively, in 1% HNO_3 to 50.00 mL in a volumetric flask.

3.5.5.2 Measurement of copper, zinc and lead concentration

The concentrations of Cu^{2+}, Zn^{2+} and Pb^{2+} ions in the solutions were measured by AAS and a blank reagent was run through the entire procedure.

3.6 Adsorption study of methylene blue on leonardite

3.6.1 Effect of the contact time

In this experiment, washed leonardite with water and dried at 100 °C overnight (type I)and unwashed leonardite (type II) were used and compared.

1.600 g of leonardite (both types) was added into flasks containing 200 mL of 60.00or 110.0 mg/L of the methylene blue solutions. The pH of the mixture was measured, and the mixture was shaken at 130 rpm at room temperature.10.00 mL of the mixture was collected one after another at 10, 20, 30, 40, 50, 60, 120, 180, 240 and 300 min.Each mixture was centrifuged, filtered by using a 0.2 μm nylon filtered, and the remaining metal ion concentrations were determined by UV-Vis spectrophotometer.

A blank was prepared by adding 0.400 g of leonardite to 50.00 mL of DI water, and the experimental conditions used were the same as those mentioned above.

3.6.2 Effect of pH

50.00 mL of 60.00 or 110.0 mg/L of the methylene blue solutions containing in 50 mL conical flasks were adjusted to initial pH of 2, 3, 4, 5, 6 and 7 with 0.5 M $HNO_3$and/or0.5 M NaOHsolutions.0.400 g of leonardite (selected type from 3.6.1) was added into each solution, and the pH was re-adjusted. Each flask was maintained under continuous agitation until the equilibrium time (from 3.6.1), at room temperature and 130 rpm. The mixture was then centrifuged, filtered by using a 0.2μm nylon filtered and the remaining concentrations were determined UV-Vis spectrophotometer.

A blank was prepared by adding 0.400 g of leonardite (selected type from 3.6.1) to 50.00 mL of DI water to confirm that no any color leached by leonardite. The control tests were run without any adsorbent to determine the impact of pH change on the methylene blue solutions, by adjusting pH at 2-7.

3.6.3 Effect of leonardite quantity

Various amounts of leonardite (selected type from 3.6.1) in the range of 0.200 to 3.00 g were added into flasks containing 50.00 mL of 60.00or 110.0 mg/L of the methylene blue solutions at optimum pH (from 3.6.2), and the pH was re-adjusted. Each flask was shaken until equilibriumwas reached (from 3.6.1) at 130 rpm and room temperature. The mixture was then centrifuged, filtered by using a 0.2 μm nylon filtered and the remaining concentrations were determined by UV-Vis spectrophotometer.

A blank was prepared by adding various amounts of leonardite (selected type from 3.6.1) in the range of 0.200 to 3.00 g to 50.00 mL of DIwater, and the experimental conditions used were the same as those mentioned above.

3.6.4 Adsorption Isotherm

0.400g of leonardite (selected type from 3.6.1) was put into flasks containing 50.00 mL of 60-200 mg/L of the methylene blue, and the pH was adjusted to optimum pH (from 3.6.2). Each flask was shaken until equilibriumwas reached (from 3.6.1) at 130 rpm and room temperature.Finally, the mixture was centrifuged, filtered by using a 0.2 μm nylon filtered,and the remaining concentrations were determined by UV-Vis spectrophotometer.

A blank was prepared by adding 0.400g of leonardite to 50.00 mL of DIwater, and the experimental conditions used were the same as those mentioned above.

3.6.5 Determination of methylene blue by UV-Vis spectrophotometer.

3.6.5.1 Preparation of standardsolution

Standard solutions of methylene blue at concentrations of 1.00, 2.00, 3.00, 4.00 and 5.00 mg/L was prepared by diluting 50.0, 100.0, 150.0, 200.0 and 250.0μL of a 1000-mg/L standard stock solution of methylene blue 1000 mg/L, respectively, in deionize water to 50 mL in a volumetric flask.

3.6.5.2 Measurement of methylene blue concentration

The methylene blue concentrations in the solutions were measured byUV-Vis spectrophotometer (at λ_{max} 664 nm) and ablank solutionwas run through the entire procedure.