MATERIALS AND METHODS

Materials

1. Reagents

Anhydrous potassium dihydrogen phosphate (KH_2PO_4) from BDH (England) used as a synthesis orthophosphate solution for the study of adsorption and desorption. Potassium chloride (KCl) was used as electrolyte and obtained from Merck (Germany).

In order to measure orthophosphate concentration, potassium antimonyl tartrate ($K(SbO)C_4H_4O_6.1/2H_2O$) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) were obtained from CARLO ERBA (Italy), ascorbic acid ($C_6H_8O_6$) was obtained from Ajex (Australia) and sulfuric acid (H_2SO_4) was purchased from Merck (Germany).

In addition, diversified materials as the adsorbents were used in this work. Activated granular natural zeolite was purchased from Kaset Center Company (Thailand). Perlite and diatomite were received from Department of Mineral Resource and ball clay and kaolin were received from Thailand Institute of Scientific and Technological Research (TISTR).

2. Apparatus

All adsorbents were calcined in a furnace (Lenton Thermal Desings). Nitrogen adsorption and adsorption measurement of adsorbent particles used a volumetric adsorption analyzer (Autosorb1) from TISTR. The specific surface area (S_{BET}) was calculated using the standard Brunauer-Emmett-Teller (BET)

method. The pore volume and pore width were calculated using the Barrett-Joyner-Halenda (BJH) method. For the characterization of adsorbent, the morphology was examined using scanning elecrtron microscope (SEM, JSM-6340F, JEOL, Japan), from TISTR. The chemical composition of an adsorbent was analyzed by energy dispersive X-ray spectroscopy (EDS). The chemical composition of adsorbents was in the oxide form of elements such as SiO_2, Al_2O_3. The X-ray diffraction (XRD, 6000RC, Japan) from TISTR was the equipment used to determine the structure of adsorbents. Fourier transform infrared spectrometer (FTIR, Perkin Elmer, System 2000, Germany) was used to identify the form of chemical compositions in natural zeolite structure and orthophosphate adsorption. Atomic Absorption Spectrophotometer (AAS, Perkin Elmer, 1100B, Germany) was used to determine amount of metal ions dissolved from the natural zeolite.

Orthophosphate adsorption measurements were done using a clifton shaking bath to shake the flasks and an ultracentrifuge (Hermle Z323, Germany) to centrifuge sample solutions. Orthophosphate concentration was determined by Ion chromatography (IC, Metrohm 761 Compact, Herisau, Switserland) and UV/Visible spectrophotometer (Model Genesys 5).

The zeta potential (ζ) of adsorbents was measured using a zeta sizer from TISTR.

Methods

1. Characterization

1.1 Analysis of surface area, pore volume, and pore size

The surface area was estimated by the Brunauer-Emmett-Teller (BET) method. The pore volume and pore size using the BJH method and nitrogen adsorption/desorption method. Each run was performed with 0.02-1.00 g of natural zeolite which was pretreated at 300 °C under vacuum.

1.2 Morphology of adsorbents

Scanning electron microscope (SEM) was used to investigate the natural zeolite morphology.

1.3 Analysis of the chemical composition of adsorbents

The surface chemical composition of adsorbents was analyzed using energy dispersive x-ray spectroscopy (EDS).

1.4 Analysis of the structure of adsorbents

The X-ray diffraction experiment (XRD) was performed on X-ray diffractometer operated at 30 kV and 30 mA using CuK_α radiation. Data were collected in the 2θ range of 2-80° and scan rate of 2°/minutes at room temperature.

1.5 Chemical bond analysis

The FT-IR spectra of natural zeolite and adsorbed orthophosphate on the natural zeolite surface were collected by taking 32 scans at 2 cm^{-1} resolution. The spectra were changed from 4000 to 400 cm^{-1} and for all samples were taken support in KBr.

2. Calcination of adsorbents

Prior to the study of orthophosphate adsorption, the natural zeolite was calcined in a tube furnace in order to study the effect of temperature on the adsorption. Calcination with the heating rate of 3.5°C/minute to the temperatures of 150, 300, 450, 600, 750, and 900°C, then left for 5 hours. After calcination, the natural zeolite was characterized and used to study orthophosphate adsorption. A schematic drawing of the procedure was shown in Figure 8.

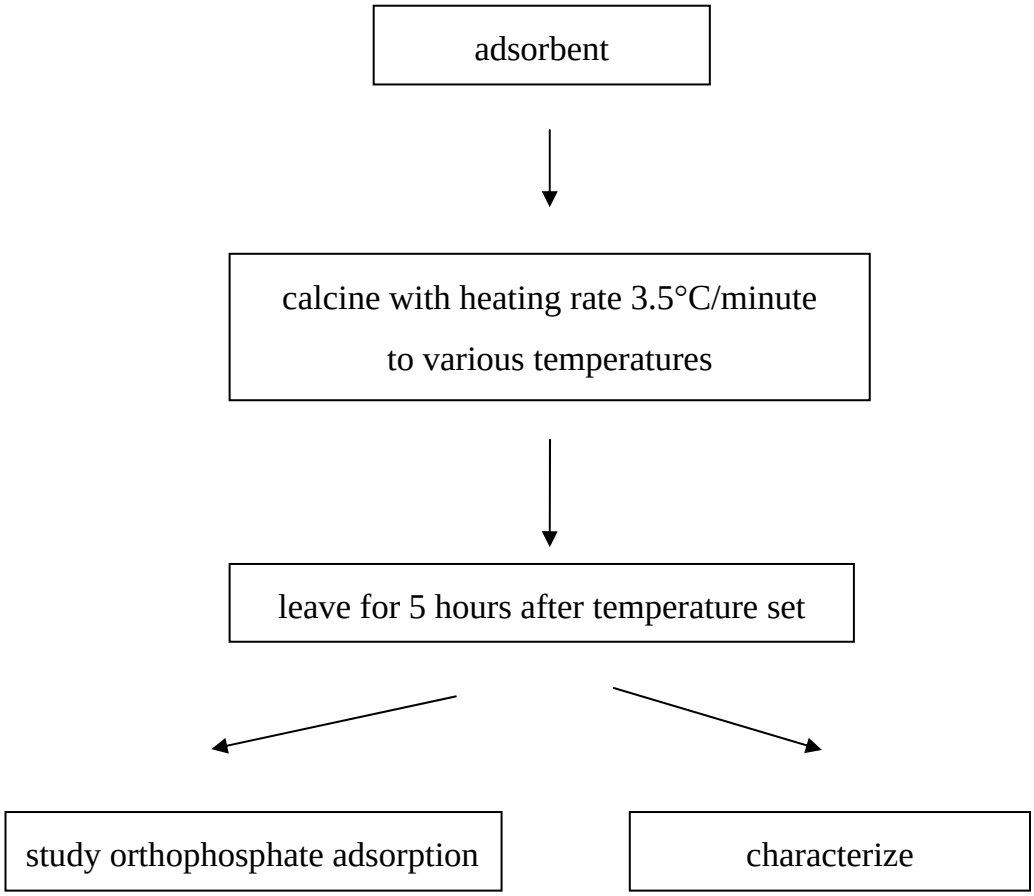

Figure 8 The scheme of natural zeolite calcination

3. Preparation of orthophosphate solution

The stock orthophosphate solution was prepared by dissolving 0.4393 g of anhydrous potassium dihydrogen phosphate (KH_2PO_4) with deionized water into 1,000 ml volumetric flask and adjusting to 1,000 ml. The stock solution has the concentration of 100 mg-P/L. Then, the stock solution was diluted to 5, 10, 20, and 30 mg-P/L.

4. Measurement of orthophosphate concentration

Because the phosphate in this study was in the orthophosphate form, the ascorbic acid method, one of colorimetric methods, was used for orthophosphate determination (Eaton, 1995). The reagents preparation of ascorbic acid method as shown in Appendix A.

4.1 The procedure of ascorbic acid method

Fifty ml of solution after orthophosphate adsorption by adsorbents were pipetted into a clean dry 125 ml erlenmeyer flask. Then, 1drop of phenolphthalein indicator was added. If a red color is developed, 5N H_2SO_4 solution was added drop wise to just discharge the color. Then, 8 ml of combined reagent was added and mixed thoroughly. The color absorbance of each sample was measured using UV/VIS spectrophotometer at wavelength (λ) 880 nm, using the reagent blank as the reference solution, at least 10 minutes after mixing but no longer than 30 minutes.

4.2 Calibration curve of orthophosphate determination

The stock solution was diluted to 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mg-P/L. After preparation, orthophosphate concentration was measured following the measurement procedure of samples. Absorbance and orthophosphate concentration were plotted on y-axis and x-axis, respectively and gave a straight line passing through the origin.

5. Orthophosphate adsorption

By modifying the experimental procedure of Sakadevan and Bavor (1998), the experiments were performed in order to study the effect of orthophosphate concentrations and periods of shaking on the adsorption. A gram of natural zeolite was added to a 50 ml erlenmeyer flask. Then, KH_2PO_4 30ml at 5, 10, 20, and 30 mg-P/L concentration and three drops of 0.01M KCl was added into the flasks. The flasks were shaken in a shaking bath at the speed of 100 rpm at room temperature with the periods of shaking set at 20, 40, 60, 120, 180, and 240 minutes. At the end of the equilibration period, the samples were centrifuged at 10,000 rpm for 5 minutes. Centrifugates were measured for leftover orthophosphate concentration by colorimetric method (Andrew, 1995). A schematic drawing of the experimental procedure was shown in Figure 9.

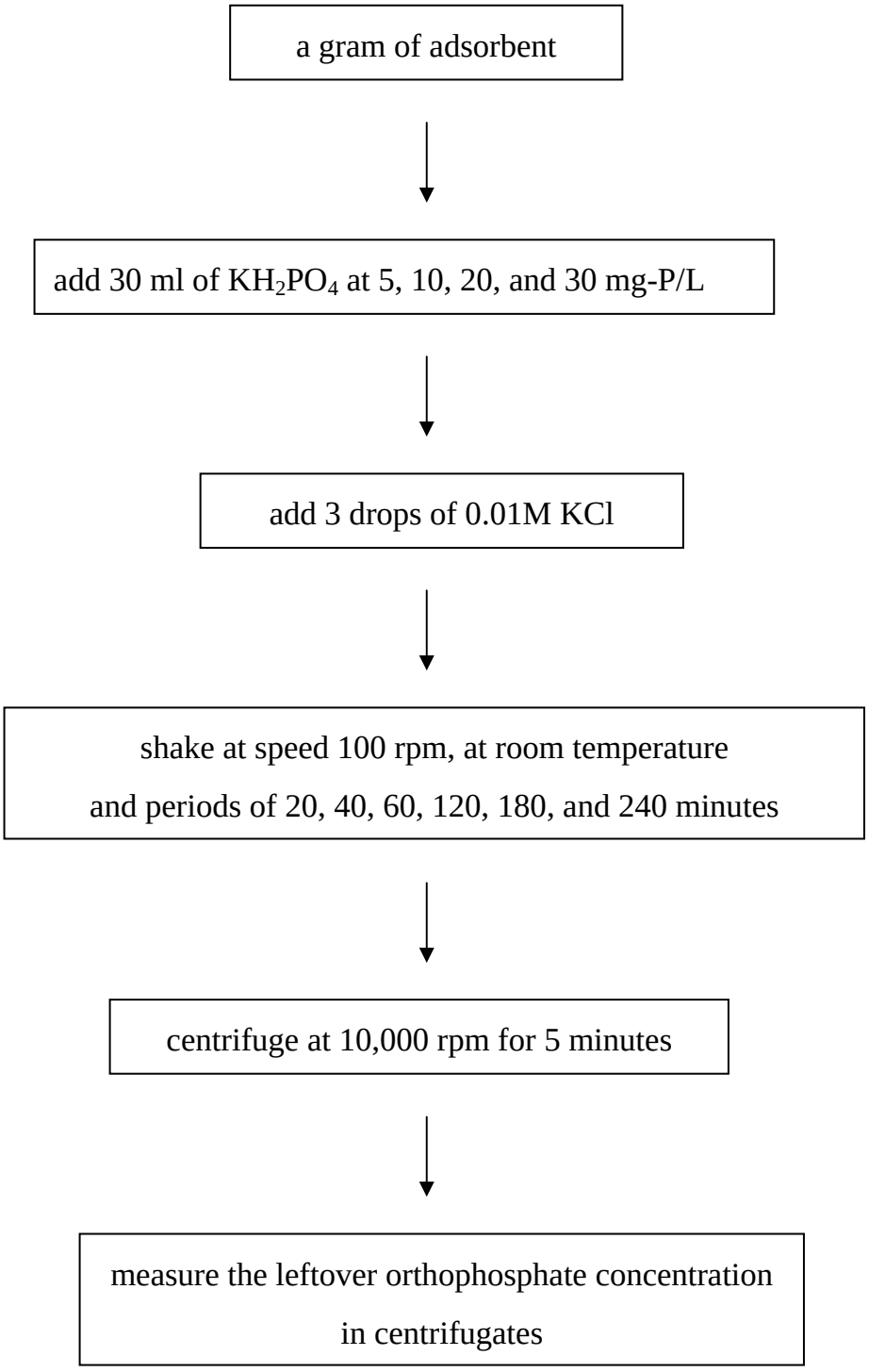

Figure 9 The scheme of orthophosphate adsorption procedure

6. Desorption of adsorbed orthophosphate

Desorption of orthophosphate was studied after obtaining the optimum adsorption condition and equilibrium periods for each initial orthophosphate concentrations. After the equilibrium adsorption on natural zeolite, the experiment was performed by having natural zeolite in 30 ml of deionized water and three drops of 0.01M KCl was added into the flasks. The flasks were shaken in a shaking bath at the speed of 100 rpm at room temperature with various periods of shaking. The measurement of orthophosphate concentration was the same method for adsorption experiment.

7. Metal dissolution from natural zeolite

7.1 Metals dissolution in 0.05M EDTA

0.05M EDTA was prepared by dissolving 9.306 g of EDTA salt (MW 372.24 g/mol) by deionized water into 500 ml volumetric flask and adjusting to 500 ml with deionized water.

The amount of 0.05M EDTA 30 ml was added into the flask with 1 g of natural zeolite before shaking the flasks in shaking bath at the speed of 100 rpm at room temperature for 4 hours. After that the suspension was centrifuged at 10,000 rpm for 5 minutes, and the centrifugate was collected. Natural zeolite was rewashed with 30 ml of deionized water. The suspension was recentrifuged for 2 hours before separating certrifugate from natural zeolite. Both certrifugates were combined and amount of Fe^{2+} determined by AAS. Natural zeolite was dried in the oven at 105ºC to use in the further orthophosphate adsorption and desorption study.

7.2 Metals dissolution in 0.5M HCl

The amount of 0.5M HCl 30 ml was added into the flask with 1 g of natural zeolite before shaking the flasks in shaking bath at the speed of 100 rpm at room temperature for 1 hour. After that the suspension was centrifuged at 10,000 rpm for 5 minutes and the centrifugate was collected. Natural zeolite was rewashed with 30 ml of deionized water. The suspension was recentrifuged for 1 hour before separating certrifugate from natural zeolite. Both certrifugates were combined and amount of Fe^{2+} determined by AAS. Natural zeolite was dry in the oven at 105ºC to use in the further orthophosphate adsorption and desorption study.

The metals dissolution in 0.5M HCl experiment was repeated with the shaking period of 5 hours before centrifugation. The centrifugate was collected to determine the amount of Fe^{2+} and Ca^{2+} by AAS.

7.3 Metals dissolution in deionized water

The amount of deionized water 30 ml was added into the flask with 1 g of natural zeolite before shaking the flasks in shaking bath at the speed of 100 rpm at room temperature for 5 hours. After that the suspension was centrifuged at 10,000 rpm for 5 minutes and the centrifugate was collected. The centrifugate was determined the amounts of Fe^{2+} and Ca^{2+} by AAS.

7.4 Metals dissolution in NaOH

The amount of NaOH 30 ml was added into the flask with 1 g of natural zeolite before shaking the flasks in shaking bath at the speed of 100

rpm at room temperature for 5 hours. After that the suspension was centrifuged at 10,000 rpm for 5 minutes and the centrifugate was collected. The certrifugate was determined the amount of Fe^{2+} and Ca^{2+} by AAS.

8. Zeta potential

The surface potential of natural zeolite was measured by zeta potential measurement. After the adsorbent preparation, 1 g of natural zeolite at different calcination temperature in deionized water was ground, then diluted 200 times. The zeta potential was measured at pH of solution and then added 1M NaOH to adjust its pH to 12. After that, 1M HCl was gradually added into the solution to decrease the pH to 2. The zeta potential was measured at every pH of the solution. After orthophosphate was adsorbed to equilibrium on 1 g of calcined natural zeolite at different temperature and the uncalcined one, the adsorbed natural zeolite particles in orthophosphate solution were then ground. The zeta potential measurement was followed the procedure of the natural zeolite indicated previously.

9. Orthophosphate adsorption on other adsorbents

In the preliminary study, the orthophosphate adsorption on other adsorbents, including perlite, diatomite, ball clay, and kaolin, was also investigated in this work. The adsorbent preparation of all other adsorbents had been followed the calcination procedure of natural zeolite as shown in Figure 8. The orthophosphate adsorption procedure was also as same as the method for natural zeolite as shown in Figure 9.