



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Clay Minerals

Bentonite (BTN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43.5 mmol/100g of clay.

#### 3.1.2 Surfactants

Cetyltrimethylammonium [ $C_{16}H_{33}N^+(CH_3)_3$ ] bromide was supplied by Fluka.

#### 3.1.3 Co-surfactant

Dodecylamine,  $C_{12}H_{27}N$ , (98% purified) was supplied by Aldrich.

#### 3.1.4 Silica Sources

Tetraethyl orthosilicate (TEOS),  $Si(OC_2H_5)_4$  and Methyltriethyl orthosilicate (MTS),  $CH_3Si(OC_2H_5)_3$ , was supplied by Fluka.

#### 3.1.5 Solvents

Methanol ( $CH_3OH$ ) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

#### 3.1.6 Chemicals

*N,N*-Dimethyldecylamine (DMDA),  $CH_3(CH_2)_8CH_2N(CH_3)_2$  was supplied by Aldrich.

#### 3.1.7 Metal Standard Solution

ICP Multi Element Standard Solution (1000 ppm) was supplied by Merck.

### 3.1.8 Organic Pollutant Solution

2,6-Dinitrophenol,  $C_6H_4N_2O_5$ , (95% purified) was supplied by Aldrich and 4-Chloro-2-methoxyphenol or 4-chloroguaiacol,  $C_7H_7ClO_2$ , (99% purified) was supplied by Acros Organics.

## 3.2 **Equipment**

### 3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay, PCH, MP-PCH and DM-PCH and to investigate the crystal structure of nanocomposites. X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered  $Cu K_{\alpha}$  radiation operated at 40 kV and 30 mA. The powder samples were observed on the  $2\theta$  range of 1.2-20 degree with scan speed 2 degree/min and scan step 0.01 degree.

### 3.2.2 Surface Area Analyzer (SAA)

$N_2$  adsorption-desorption isotherms were obtained at  $-196^{\circ}C$  on a Sorptomatic. Samples were degassed at  $150^{\circ}C$  during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

### 3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of organoclays, PCH, MP-PCH and DM-PCH were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of  $4000-400\text{ cm}^{-1}$  with 32 scans at a resolution of  $2\text{ cm}^{-1}$ . KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network is investigated by using FTIR.

#### 3.2.4 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL JSM-5410 lv Model to observe surface morphology of PCH. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

#### 3.2.5 Transmission Electron Microscope (TEM)

Transmission electron microscopy was performed on JEOL JEM-2100 electron microscope with an accelerating voltage of 160 kV was used to observe the structure of pores. TEM samples were prepared by embedding the powder in resin and sectioning on an ultramicrotome. The thin sections were supported on 300 mesh copper grids.

#### 3.2.6 X-ray Fluorescence spectrometer (XRF)

X-ray Fluorescence spectrometer was used to identify the presence of an element in the BTN, PCH, MP-PCH and DM-PCH and to confirm the functionalization of PCH. X-ray Fluorescence was measured on a PHILIPS Model PW-2400 of wavelength dispersive type (WDS) with Rh target X-ray tube excited source operated at 3 kw power. The powder samples were observed with the tube current 438  $\mu$ A for the acquisition livetime 30.0s.

#### 3.2.7 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP- OES)

Inductively Coupled Plasma-Optical Emission Spectrometry was performed on PerkinElmer Optima 4300 DV to measure concentration of heavy metal in sample. The pre-optical system was purged with Argon gas for 4h, operated with an axial view of 5 KVA. The concentration of metal was detect by using UV-Vis detector at appropriate wavelength of each element. The sample was prepared by dissolution with 1 M HNO<sub>3</sub> to obtain the required concentration before analyze.

### 3.2.8 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) was performed on Perkin Elmer 200LC to determine quantitatively of organic pollutant solution. The concentration of pollutants was measured by HPLC using UV-Vis detector and C18 column (Alltech). The mobile phase was 85:15 v/v methanol/water for 4-Chloro-2-methoxyphenol and 59:40:1 methanol/water/acetic acid for 2,6-dinitrophenol. The detector was set at 254 and 270 nm for 2,6-dinitrophenol and 4-Chloro-2-methoxyphenol, respectively.

## 3.3 Methodology

### 3.3.1 Purification of Bentonite

Bentonite was pulverized and sieve through 325 mesh. The passing part were purified by centrifugation and then washed with distilled water. The samples were air-dried overnight and pulverized in a mortar.

### 3.3.2 Synthesis of Porous Clay Heterostructure (PCH)

The purified bentonite was stirred with cetyltrimethylammoniumbromide at 50 °C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50 °C following which TEOS was added at molar ratio of organoclay:dodecylamine:TEOS was 1:20:150. The mixture was allowed to stir for further 4 h at room temperature. The modified clay was separated from the solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH has been added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactanted-extracted PCH was filtrated and washed with a mixture of methanol and water and air-dried at room temperature overnight.

### 3.3.3 Synthesis of Functionalized PCH for Utilizing as Heavy Metal

#### Adsorbent

The purified bentonite was stirred with cetyltrimethylammonium bromide at 50 °C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50 °C. Then a mixture of TEOS and MPTMS in a mole fraction of 1:1 or 4:1 was added under N<sub>2</sub> atmosphere for further 24 h at room temperature. The modified clay was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH was added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactant-extracted PCH was filtrated and washed with a mixture of methanol and water and air-dried at room temperature overnight. The mercaptopropyl- functionalized PCH was denoted MP-PCH; MP-PCH(1) for MP-PCH which prepared at mol ratio of MPTMS:TEOS was 1:4 and MP-PCH(2) which prepared at mol ratio of MPTMS:TEOS was 1:1.

### 3.3.4 Synthesis of Functionalized PCH for Utilizing as Organic Pollutant

#### Adsorbent

The purified bentonite was stirred with cetyltrimethylammonium bromide at 50 °C for 24 h. After the reaction time, the intercalated clay was filtered out, washed with a mixture of methanol and water and then air-dried. The 2 g of obtained organoclay was stirred in dodecylamine for 30 min at 50 °C. Then a mixture of TEOS and DMDA in a mole fraction of 1:1 or 4:1 was added under N<sub>2</sub> atmosphere for further 24 h at room temperature. The modified clay was separated from solution by filtration and air-dried overnight at room temperature to form the as-synthesized PCH. The surfactant was removed from the as-synthesized PCH by solvent extraction using a mixture of methanol and HCl. Typically, 1 g of the as-synthesized PCH was added to 45 mL of methanol and 5 mL of HCl and refluxed for 2 h. The surfactant-extracted PCH was filtrated and washed with a mixture of

methanol and water and air-dried at room temperature overnight. The DMDA-functionalized PCH was denoted DM-PCH.

### 3.3.5 Adsorption properties of functionalized-PCH

The 0.05 g of MP-PCH or DM-PCH was stirred in 100 mL of heavy metal standard or organic pollutant standard solution at certain concentration and pH value. The stirring continued for 24 h before the slurries were filtered, and obtained solution was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) for heavy metal standard solution and High Performance Liquid Chromatography (HPLC) for organic pollutant standard solution.