CHAPTER III
METHODOLOGY

3.1 Materials and Equipments

3.1.1 Equipments

Fourier transform infrared spectrophotometer (FT-IR) was used to characterize the functional group of the adsorbent. Scanning electron microscope (SEM) was used to obtained surface morphology of the adsorbent. Surface area analyzer (AS 1-MP) was used to obtained surface area. Ultraviolet–visible spectrophotometer (UV-VIS) was used to measure the amount of PEI loaded in polyHIPEs.

3.1.2 Chemicals

An oil phase consists of divinylbenzene (80% DVB), supplied by Merck Schuchardt, and vinyl benzyl chloride (90% VBC), supplied by Aldrich, as monomers. Mixed surfactants include sorbitan monooleate (Span 80, supplied by Fluka), cetyl trimethylammonium bromide (CTAB, 96%, supplied by Fluka) and dodecylbenzenesulfonic acid sodium salt (DDBSS, supplied by Aldrich). Toluene (99.5%, supplied by RCI Lab scan) was used as a porogen. In aqueous phase consists of potassium persulphate ($K_2S_2O_8$, 99%, supplied by Merck Schuchardt) as an initiator. Calcium chloride dihydrate ($CaCl_2\,2H_2O$, supplied by J.T. Baker Chemicals) is an electrolyte. Polyethyleneimine (PEI, 50 wt% in water, M_n 1200, M_w 1300) was supplied by Aldrich. Distilled water is used as an internal phase. Ethanol (99.9%, supplied by RCI Lab scan) was used for washing polyHIPEs via soxhlet extraction.

3.2 Preparation of PolyHIPEs

Preparation of polyHIPEs (polymerized high internal phase emulsions) was divided into two phases: oil phase and aqueous phase. In the oil phase, mixture of surfactants (0.36 g. of SPAN80, 0.0224 g. of CTAB and 0.0171 g. of DDBSS)

porogen (1 mL. toluene) and monomers (DVB+VBC, total volume 1 mL) were added into flask and then the solution was stirred (700 rpm) at room temperature for 30 minutes. The aqueous phase contained initiator (0.04 g. $K_2S_2O_8$), electrolyte (0.2 g. $CaCl_2.2H_2O$) and 18 mL water. Then, the aqueous phase was slightly added into the oil phase and stirred (700 rpm) at room temperature for an hour until the system became emulsion. Finally, the emulsion was poured into a mold and immersed in a water bath at 70 °C for 24 hours to obtain polyHIPE. Finally, the solid polyHIPE was removed from the mold, left outside until dry and washed with ethanol for 6 hours in a soxhlet apparatus. Solid foams were then dried under vacuum at 100 °C overnight and then kept in a desiccator. The methodology flow diagram is shown in Figure 3.1.

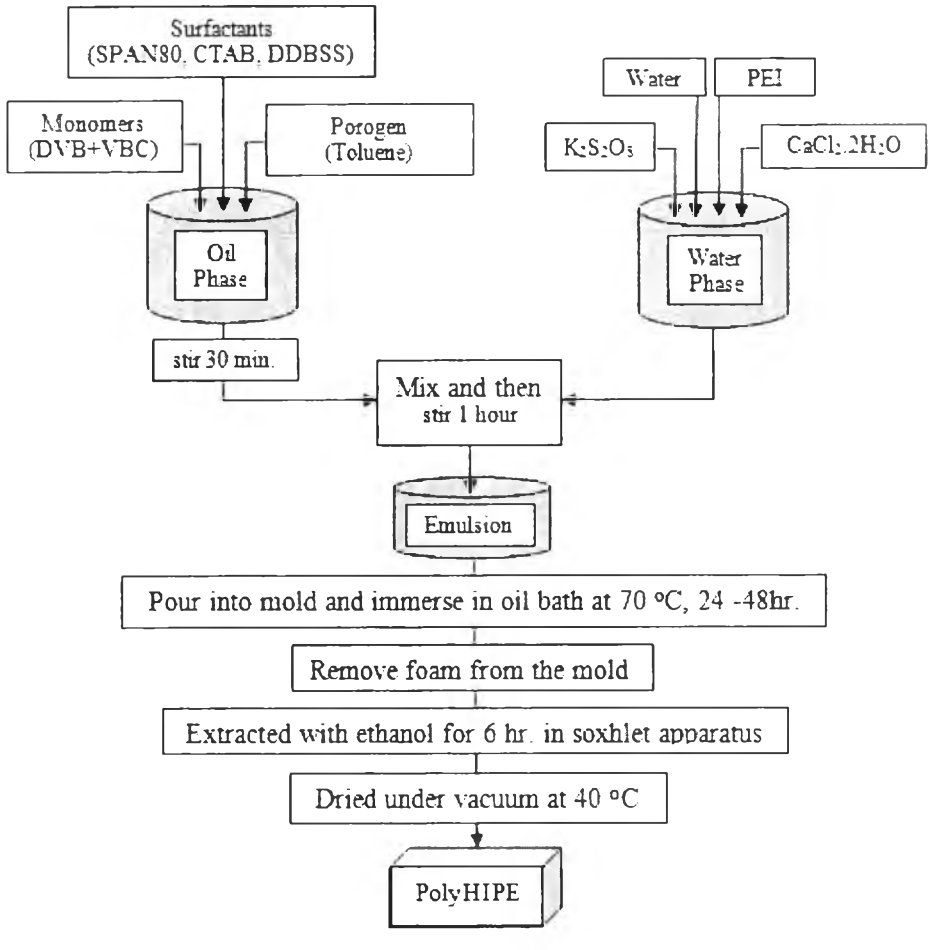

Figure 3.1 Methodology flow diagram.

3.2.1 Effect of Monomer Ratio on PolyHIPEs

To obtain the most suitable monomer ratio, the ratios of DVB/VBC were varied from 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 with a total volume of 1 mL and the polyHIPEs was prepared the same way as described previously.

3.2.2 Effect of PEI Loading on PolyHIPEs

When the most suitable monomer ratio was obtained, the amount of PEI loaded on polyHIPEs was studied by varying the amount of PEI added into the polyHIPEs, from 0, 1, 5, 10, 15, 25 and 30 wt% related to weight of monomer. The first step was the preparation of stock solution of 30 wt% PEI by dissolving 7.6170 g of 50 wt% PEI solution in distilled water, and making the volume of solution to 250 mL. For lower wt% PEI, the 30 wt% PEI stock solution was diluted to desired concentration by using **Eq. 3.1** to calculate the volume of 30 wt% PEI solution needed. The second step was a preparation of aqueous phase by weighing $K_2S_2O_8$ and $CaCl_2.2H_2O$ followed the preparation of polyHIPE.

$$C_1V_1 = C_2V_2 \qquad \textbf{Eq. 3.1}$$

Where C_1 and C_2 are initial and final concentrations of PEI and V_1 and V_2 are initial and final volumes, respective.

3.3 Characterization

3.3.1 Surface Morphology of PolyHIPEs

Scanning electron microscope (SEM), Hitachi/S - 4800 Model (Ontario, Canada), was used to analyze the morphology and porous features of polyHIPEs. The condition of the analyzer was: voltages of 15 kV, current of 10 mA and 1k, 3k and 10k magnification. Samples were coated with platinum under vacuum before observation to make them electrically conductive.

3.3.2 Measurement of Surface Area of PolyHIPEs

Before the solid foams were characterized, they must be dried in vacuum oven because the polyHIPEs is hydrophilic, which adsorbs moisture. Specific surface area and pore size distribution were characterized by BET nitrogen adsorption/desorption measurements with a surface area analyzer (Quantachrome/ Autosorb 1-MP Model, Florida, USA). The samples were out gas at temperature 100 - 110 ^{o}C for 8 – 10 hours until the outgas pressure rise limit was lower than 10 micron/min. For the characterization method, a full isotherm of macropore was used.

3.3.3 Analysis of Functional Groups of PolyHIPEs

Fourier transform infrared spectrophotometer or FT-IR (Nicolet/Nexus 670 Model, Massachusetts, USA) was used to determine N-H stretching at 3400-3380 cm^{-1} and 3345-3325 cm^{-1}, N-H bending vibration at 1650-1550 cm^{-1} and C-Cl vibration at 1260 cm^{-1}. Firstly, 0.0030 g of polyHIPE was ground and mixed with 0.0100 g potassium bromide, and then the mixture was transferred into a mold and compressed into pellet. The obtained pellet was placed in an IR sample holder and in the sample compartment. The measurement was carried out in a transmission mode with 16 resolutions, 64 numbers of scans in a range of wave number from 400 to 4000 cm^{-1} by using air as a background. For PEI solution sample, the solution was dropped onto IR sample stand. The measurement was carried out in the same mode as pellets.

3.3.4 Analysis of PEI Loading

The amount of PEI present in polyHIPE was determined by ultra violet-visible spectrophotometer or UV-VIS (Shimadzu, UV-VIS Spectrometer 2550 Model, Tokyo, Japan). The polyHIPE samples were ground, accurately weighed 0.0300 g and then immersed in 100 mL of 0.02*M* solution of salicylaldehyde in a methanol/1% acetic acid aqueous solution (80/20, v/v). After 24 h, the mixture was filtered with filter paper ; 1 mL of the filtrate was diluted for 400 times with a solution of methanol/1% acetic acid aqueous solution (80/20, v/v). The UV absorbance at 255 nm was measured and converted to the residual concentration of salicylaldehyde by using calibration curve as shown in Figure 3.2 (Qu *et. al.*, 1999).

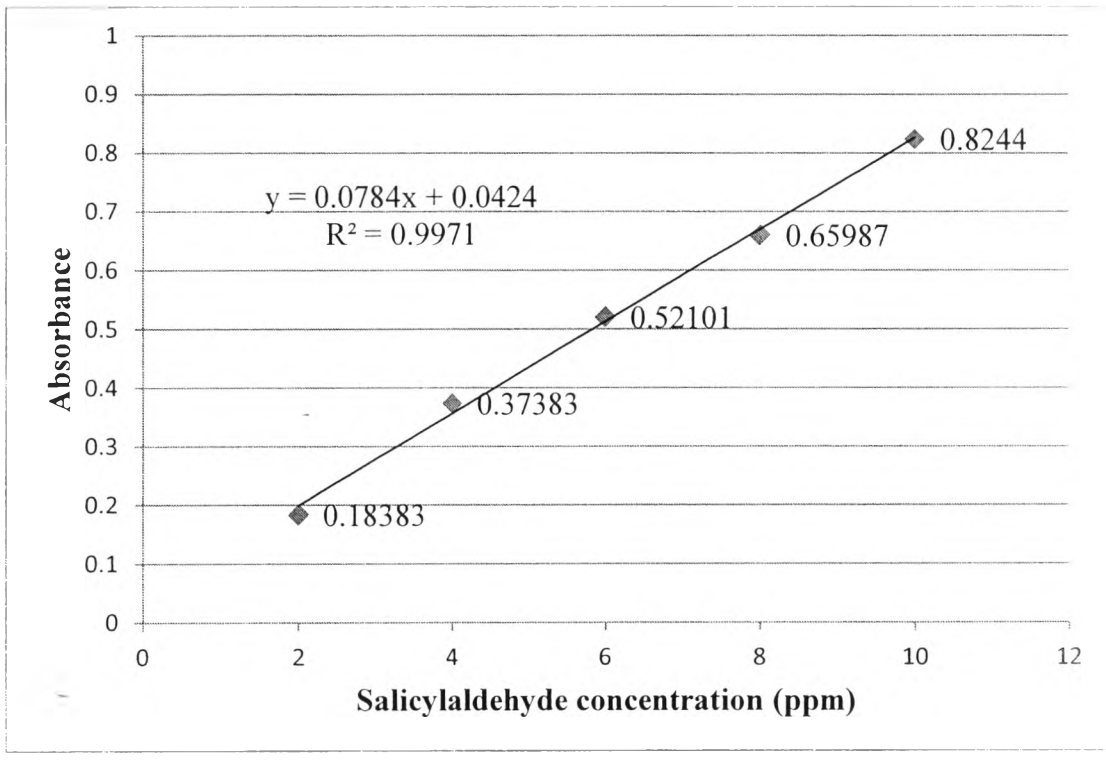

Figure 3.2 UV-VIS calibration curve.