

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Material

3.1.1.1 Koh-samed's sand

##### 3.1.2 Chemicals

3.1.2.1 Polyvinyl alcohol ( $M_w \sim 108,000 \text{ g/mol}$  and 99.7 mole% hydrolysis) was purchased from Polysciences.

3.1.2.2 Boric acid (Merck)

##### 3.1.3 Solvents

3.1.2.3 Distillation water

3.1.2.4 Acetone (Lab-Scan), 4 L

3.1.2.5 Ethanol (Merck), 2.5 L

#### 3.2 Equipments

##### 3.2.1 Centrifugal ball mill S100/ Ball Mill Machine

The collected Samed sand was grinded by ball mill machine, using 300 rpm for 45 minutes.

##### 3.2.2 Carbolite Furnace/ Furnace Equipment

A furnace was used to eliminate organic residue from Samed sand. The heating rate used to prepare calcium carbonate from Samed sand was set at 5 °C/min from 25° to 600 °C and held at 600 °C for 5 h.

##### 3.2.3 Thermo Nicolet, Nexus 670/ Fourier Transform Infrared (FTIR)

##### Spectrophotometer

FTIR spectra were obtained to determine the functional groups of chemical composition of calcium carbonate sand, PVA-CaCO<sub>3</sub> hybrid composite material, and the applied material which added dimethylglyoxime (DMA) to detect Nickel, using

an analysis range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The sample preparation was carried out by mixing fine powder of a sample with KBr powder.

#### 3.2.4 Perkin Elmer Thermogravimetric analyzer (TGA)

TGA thermograms were analyzed to investigate thermal stability, composition, and mechanism of degradation of calcium carbonate sand and PVA- $\text{CaCO}_3$  hybrid composite material. Approximately 5 mg of samples were analyzed, using a platinum pan and a temperature range from 30° to 700 °C in dynamic oxygen atmosphere with a flow rate of 80 ml/min and a heating rate of 10 °C.min<sup>-1</sup>.

#### 3.2.5 DMAX 2200 HV/X-Ray Diffractometer (XRD)

Koh Samed's sand was characterized by using XRD in 2 $\theta$  bragg angle to characterized of calcium carbonate. Peak positions were compared with the International Center for Diffraction Data Standard (JCPDS) patterns to identify crystalline phases.

#### 3.2.6 Hitachi FE-SEM S4800/Scanning Electron Microscope (SEM)

SEM was used to investigate morphology of PVA- $\text{CaCO}_3$  hybrid composite material.

#### 3.2.7 Quantachrome, Ultrapycnometer1000/ Pycnometer

The porosity of PVA- $\text{CaCO}_3$  hybrid composite material was characterized by a gas-pycnometer.

#### 3.2.8 Reflectance spectroscopy

The reflectance spectrum was measured with fiber-optic spectrophotometer (Ocean optic red tide USB 650), which was connected to a PC and used Avantes software. All the PVA- $\text{CaCO}_3$  hybrid composite material was tested for colorimetric response.

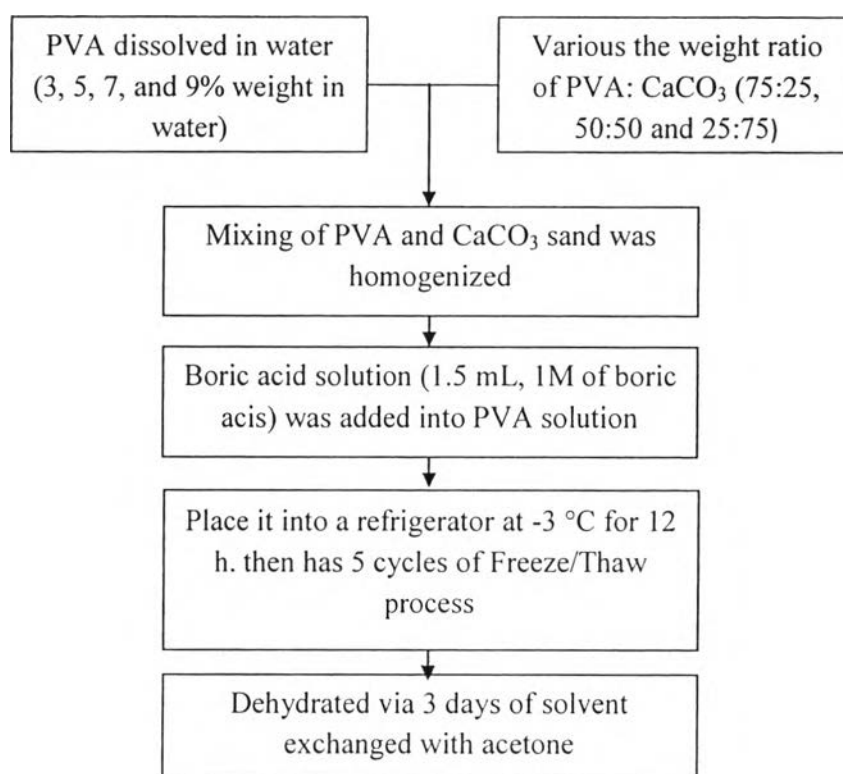
### **3.3 Methodology**

#### **3.3.1 Synthesis of calcium carbonate (CaCO<sub>3</sub>) from Samed sand**

Samed sand was finely ground by a ball mill. The obtained samed sand powder was separated by a sieving machine to collect particles less than 150 micron, followed by calcination in a furnace from room temperature to 700 °C with a heating rate of 5 °C/min and held at 600 °C for 5 h. White powder of CaCO<sub>3</sub> sand was kept in a dessicator.

#### **3.3.2 Synthesis of PVA-CaCO<sub>3</sub> hybrid composite material**

Polyvinyl alcohol was dissolved in water at 85 °C for 4 h. with magnetic stirrer (400 rpm), followed by adding calcium carbonate sand. Various amounts of polyvinyl alcohol in water (3, 5, 7, and 9% weight in water) by fixing the optimum content of boric acid which was a crosslinking agent at 1.5 mL of 1M boric acid. Different the weight ratios of poly vinyl alcohol and calcium carbonate sand (75:25, 50:50 and 25:75) were varied. Then the mixture of poly vinyl alcohol and calcium carbonate sand was homogenized for 1 h with magnetic stirrer (400 rpm). Boric acid solution (1.5 mL, 1M of boric acid) was added into polyvinyl alcohol solution at 85 °C and stirred until homogeneous. After mixing, the obtained highly viscous solution and was added into a plastic mold before placing into a refrigerator at -3 °C for 12 h. This freeze/Thaw process was repeated for 5 cycles, followed by immersing in acetone for solvent exchange for 3 days.



**Figure 3.3.1** Flow diagram showing synthesis of PVA-CaCO<sub>3</sub> hybrid composite material via sol-gel process.

**Table 3.3.2** The preparation of material with different ratio components

% PVA in water (wt)	Content of PVA (g)	Content of boric acid solution (mL)
3%	25 : 75	1.0
		1.5
		2.0
	50 : 50	1.0
		1.5
		2.0
	75 : 25	1.0
		1.5
		2.0

5%	25 : 75	1.0
		1.5
		2.0
	50 : 50	1.0
		1.5
		2.0
	75 : 25	1.0
		1.5
		2.0
7%	25 : 75	1.0
		1.5
		2.0
	50 : 50	1.0
		1.5
		2.0
	75 : 25	1.0
		1.5
		2.0

### 3.3.3 Testing of PVA-CaCO<sub>3</sub> hybrid composite material as nickel sensor

In this study, Dimethylglyoxime (DMG) was added to the material as a supplement to form complex with nickel. Finally, its properties will be used as heavy metal (Nickel) detector.

#### 3.5.1 Material

- PVA-CaCO<sub>3</sub> hybrid composite material
- Syringe

#### 3.5.2 Chemicals

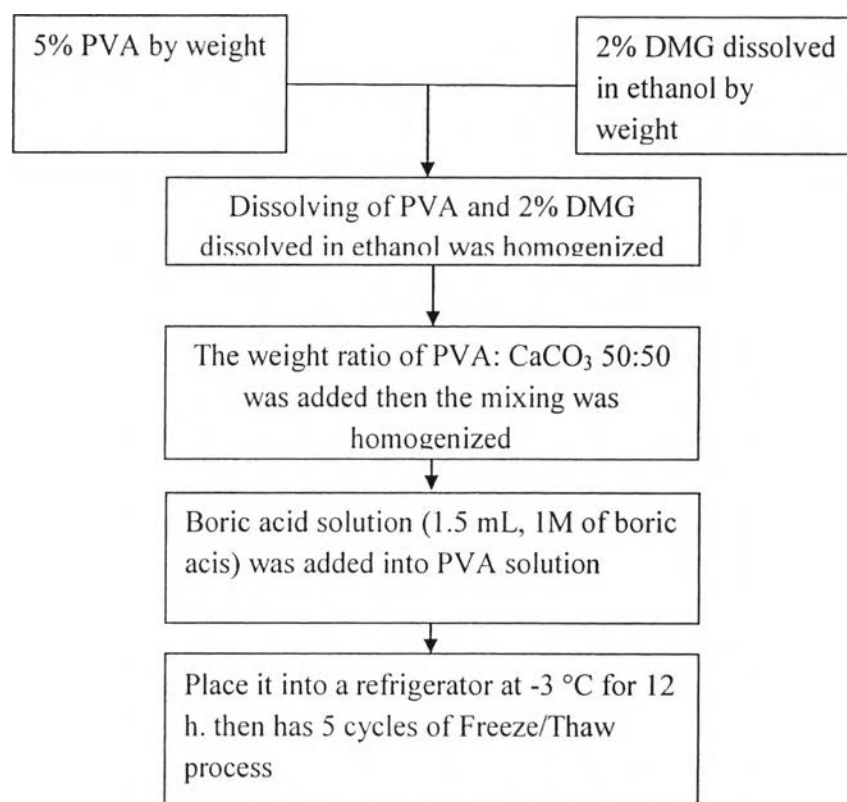
- Dimethylglyoxime (Univar), 100 g
- Nickel-Standard solution (Merck), 1000 mg/L Ni

### 3.5.3 Solvents

- Distillation water
- Ethanol (Merck), 4 L

### 3.3.4 Synthesis of PVA-CaCO<sub>3</sub> hybrid composite as a nickel sensor

The synthesis produces were similarly to preparation of PVA-CaCO<sub>3</sub> hybrid composite material as mentioned earlier, but the first step, 2 wt% DMG dissolved in ethanol was mixed together with 5 wt% of PVA in water. The volume ratios of water and 2 wt% of DMG in ethanol were varied as follows: (9:1, 8:2, 7:3, 6:4 and 5:5) with 1.5 mL of 1M boric acid solution.



**Figure 3.3.3** Flow diagram showing synthesis of PVA-CaCO<sub>3</sub> hybrid composite material as nickel sensor via sol-gel process.

The optical response of the sensor is based on the well known reaction between nickel and DMG leading to the formation of a red complex of  $\text{Ni}(\text{DMG})_2$  with an absorbance peak at 547 nm. 2% DMG in ethanol by weight was directly mixed with PVA- $\text{CaCO}_3$  in a water and then crosslinked with boric acid solution.

The content of PVA was fixed at 5% wt in solvent which was water and 2% wt DMG in ethanol in different ratio that shown in table 3.3.4. The mixture was heated at 85 C to dissolve PVA with 200 rpm stirring.

**Table 3.3.4** The mixture of the PVA- $\text{CaCO}_3$  composite sensor to synthesized

condition	Content of PVA (g)	Content of water (g)	Content of 2% wt DMG in ethanol (g)
1	5	9	1
2	5	8	2
3	5	7	3
4	5	6	4
5	5	5	5

### 3.3.5 Sensor performance testing

The Ni (II) solutions (0.1, 0.5, 1, 2, 3, 4, 5, 8 and 10 ppm) were prepared by diluting 1000 ppm stock solution with distilled water and adjusting the pH to 9 with 10% ammonium solution. The samples were cut into a disc-shape with the diameter of 2.4 cm and placed in Ni (II) solutions for 2 hrs. After drying in air, the color change of the samples was then observed by UV-spectrophotometer at 547 nm.