

## CHAPTER 3 RESEARCH METHODOLOGY



### 3.1 Materials

#### 3.1.1 Equipments

- Rotary Shaker, GFL, 3017
- pH-meter, HACH, SensIon 1 and SensIon 3
- Oven, WTB binder, FD115 (E2)
- Digital Balance (4 digits), Sartorius, BP2215
- Dessicator
- Water Purification System (For making DI water), ELGA, Ultraanalytic
- Filter paper No. 42, Whatman
- Filter paper GF/C, Toyo
- Vacuum Pump, KNF Neuberger, NO35AN. 18-IP20
- Refrigerator
- Inductively Couple Plasma (ICP) , Vista
- Fourier Transform Infrared Spectrometer (FT-IR), Perkin Elmer, Model 1760X
- Spectrophotometer, Spectronic® UV/VIS Helios Alpha spectrophotometer with Vision32 software –v1.25
- Laser Particle size Analyser, Malvern, Mastersizer-S long bed Ver 2.19
- Scanning Electron Microscopy (SEM), Jeol, JSM-5800LV
- Horizontal shaker
- Muffle furnace: type ESF 12/23 (0-1200 °C), Carbolite, England.
- Surface area analyzer: Micromeritics FlowSorb 2300
- Analytical Balance 2 digit (Sartorius, BP 3100S)
- X-ray Diffraction Spectroscopy(SIEMENS XRD D5000)
- Micropipette 5 ml
- Fraction collector, Amersham Biosciences FRAC-100,325

### 3.1.2 Glassware

- Erlenmeyer flasks
- Volumetric flasks
- Filtering Flasks
- Bushner Flasks
- Three ways junction
- Beakers
- Pipettes
- Cylinders
- Dropper
- Funnels
- Crucible 20 and 120 ml

### 3.1.3 Chemical reagents

- Deionized water (DI water)
- pH buffer solution  $4.00 \pm 0.02$ , Scharlau chemie
- pH buffer solution  $7.00 \pm 0.02$ , HACH
- Phosphoric acid, concentrated ( $H_3PO_4$ )
- Iodine ( $I_2$ )
- Potassium iodine (KI)
- Potassium iodate ( $KIO_3$ )
- Sodium thiosulfate ( $Na_2S_2O_3 \cdot 5H_2O$ )
- Sodium carbonate ( $Na_2CO_3$ )
- Starch, soluble potato
- Potassium phosphate ( $KH_2PO_4$ )
- Methylene blue
- Sodium phosphate ( $Na_2HPO_4$ )
- Citric acid ( $HOC(COOH)(CH_2COOH)_2 \cdot 2H_2O$ )
- Sodium hydroxide (NaOH)
- Copper Nitrate Solution ( $Cu(NO_3)_2$ )
- Lead Nitrate Solution ( $Pb(NO_3)_2$ )
- Nitric Acid ( $HNO_3$ )
- Sodium Hydroxide (NaOH)
- Sulfuric acid ( $H_2SO_4$ )

- Ammonium acetate ( $\text{CH}_3\text{COONH}_4$ )
- Acetic acid ( $\text{CH}_3\text{COOH}$ )

## 3.2 Preparation of activated carbon

### 3.2.1 Eucalyptus bark collection and preparation

1. Collect eucalyptus bark from Advance Agro Public Co., Ltd. in Prachinburi province, Thailand
2. Wash the eucalyptus bark with tap water
3. Dry the eucalyptus bark at  $105\text{ }^\circ\text{C}$  for 4 hours to remove excess water
4. Crush and sieve pass through out mesh number 10 (2.00 mm)
5. Store the eucalyptus bark in closed bottle

### 3.2.2 Preparation of activated carbon

#### 3.2.2.1 Determination of the optimal activation temperature

1. Weight 100 g of eucalyptus bark (from above) and impregnate into a 100 ml of phosphoric acid (85 wt.%) (weight by volume ratio of raw material and phosphoric acid to 1:1)
2. Stir thoroughly until well mixed at room temperature
3. Carbonize the eucalyptus bark in a muffle furnace at  $350\text{ }^\circ\text{C}$  for 1 hour
4. Wash the activated carbon several times by hot distilled water until the pH value of the leachates equals to 6
5. Dry at  $105\text{ }^\circ\text{C}$  for 4 hours
6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle
7. Repeat Steps 1-6 by changing activation temperatures to 400, 450, 500, 550 and  $600\text{ }^\circ\text{C}$

#### 3.2.2.2 Determination of the optimal weight by volume ratio of raw material and phosphoric acid (impregnation ratio)

1. Weight 100 g of eucalyptus bark (from above) and impregnate into a 100 ml of phosphoric acid (85 wt.%) (weight by volume ratio of raw material and phosphoric acid = 1:1)
2. Stir thoroughly until well mixed at room temperature

3. Carbonize the eucalyptus bark in a muffle furnace at suitable activation temperature (obtained from Section 3.2.2.1) for 1 hour
4. Wash the activated carbon several times with hot distilled water until the pH value of the leachates equals to 6
5. Dry at 105 °C for 4 hours
6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle
7. Repeat Steps 1-6 by changing impregnation ratios to 1:0.3, 1:0.5, 1:0.8, 1:2, and 1:3 as show in Table 3.1.

#### 3.2.2.3 Determination of the optimal activation time

1. Weight eucalyptus bark and phosphoric acid at the most suitable impregnation ratio (as obtained from Section 3.2.2.2)
2. Stir thoroughly until well mixed at room temperature
3. Activation the eucalyptus bark in a muffle furnace at suitable activation temperature (obtained from Section 3.2.2.1) for 1 hour
4. Wash the activated carbon several times with hot distilled water until the pH value of the leachates equals to 6
5. Dry at 105°C for 4 hours
6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle
7. Repeat Steps 1-6 by changing activation times to 0.5, 1.5, 2, 2.5, and 3.0 hours.

### 3.2.2 Analysis of activated carbon properties

1. Chemical analysis of wood charcoal was examined according to the standard method ASTM D 1762-84: see detail in Appendix A.1.
2. Apparent (bulk) density of all samples was calculated as the ratio between weight and volume of packed dry material: see detail in Appendix A.2.
3. Moisture content of activated carbon was determined according to the standard method ASTM D 2867-95: see detail in Appendix A.3.
4. The ash content of the carbon was determined using a standard method ASTM D 2866-94 (ASTM, 1996). This method involves pre-drying the sample at 150°C, followed by burning in a muffle furnace at 650°C for 4 h in the

presence of air. The ash content is calculated from the combustion residue. This test is repeated until constant ash content is obtained: see detail in Appendix A.4.

5. Iodine number: 0.1 g of activated carbon is placed in 250 cm<sup>3</sup> dry Erlenmeyer flask and fully wetted with 10 cm<sup>3</sup> of diluted HCl (5% by weight). This is then mixed with 100 cm<sup>3</sup> of 0.1 molar iodine solution where the mixture is vigorously shaken for 30 s. After filtration with filter paper (Whatman No.42), 50 cm<sup>3</sup> is titrated with 0.01 mol l<sup>-1</sup> sodium thiosulfate: see full detail in Appendix A.5.

6. Methylene blue number: This is evaluated by adding a pre-weighed amount of carbon (0.05 g) to 25 ml of a solution of methylene blue (1,200 mg l<sup>-1</sup>). The mixture is stirred for 30 min at room temperature and the adsorbent is then removed by centrifuge at 10,000 rpm for 30 min. The dye concentration in the remaining solution is determined using light absorbance at 665 nm (UV-vis spectrophotometer): see full detail in Appendix A.6.

7. Surface areas are determined by nitrogen adsorption (- 196°C) on surface area analyzer (Thermo Finnigan, Sorptomatic 1990).

8. The surface morphology of activated carbon is visualized via scanning electron microscopy (SEM), and the corresponding SEM micrographs are obtained using a XL 30 ESEM FEG scanning electron microscope.

9. The yield of activated carbon is defined as the ratio of the weight of the resultant activated carbon to that of the original eucalyptus bark with both weights on a dry basis, i.e.

$$\text{Yield} = \frac{W_1}{W_0} \times 100 \quad (3.1)$$

where  $W_0$  is the original mass of the precursor on a dry basis and  $W_1$  the mass of the carbon after activation, washing, and drying.

10. The ultimate analysis of eucalyptus bark is performed in CHNS/O analyzer (Perkin Elmer PE2400 Series II), using gaseous products freed by pyrolysis in high-purity oxygen and are chromatographically detected with a thermal conductivity detector. The proximate analysis is developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84).

11. X-ray diffraction (XRD) patterns are obtained in a X-ray Diffraction Spectroscopy using Cu K $\alpha$  radiation ( $\lambda=0.154056$  nm), with a step size of 0.004° and a step time of 1.5 s.

12. The X-Ray Fluorescence spectrophotometer was used to determine the overall mineral composition of the product.

13. The point of zero charge (PZC) was the pH that surface charge of the sample equal to zero which was determined by measuring the surface charge of product in the DI water solution at various pH using Zeta Meter electrophoresis, Zeiss/3.0<sup>+</sup>. The pH of DI water was adjusted by nitric acid and sodium hydroxide to desired pH.

14. Fourier Transform Infrared Spectrophotometer (FT-IR) analysis.

For this, the activated carbon samples were brought to constant weight in a drying oven at 50°C for 24 h and kept in the desiccators. Then 1 mg of dried activated carbon was mixed with 100 mg of KBr, which was initially dried at 110°C, in the sample disk. FTIR spectra in the range of 450–4000 cm<sup>-1</sup> were obtained on a Perkin-Elmer, Model 1760X.

### 3.3 Sorption studies

#### 3.3.1 Preparation of synthetic wastewater

1. Pipette the desired volume of acetic acid and weight the desired weight of ammonium acetate and metal nitrate
2. Transfer into volumetric flask 2 l
3. Add deionized water until the level of solution reach the present mark
4. Stock in polyethylene bottles

#### 3.3.2 Effect of pH for adsorption

1. Weight 0.1 g of activated carbon
2. Place into a round centrifugal tube
3. Add 25 ml solution with initial copper nitrate concentration of 0.3 mM (pH 1)
4. Mix the solution with a rotary shaker with stirring rate of 200 rpm at room temperature
5. Collect activated carbon sample from the solution after 60 min
6. Triplicate the experiments

7. Analyze for the metal ions by Flame & Graphite Furnace Atomic Adsorption Spectrophotometer (AAS).

8. Repeat Steps 1-7 with lead nitrate solution and pH changed to 2, 3, 4, 5, and 6.

### **3.3.3 Determination of adsorption kinetics and adsorption isotherm of single component**

1. Weight 0.1 g of activated carbon
2. Place the carbon into a round centrifugal tube
3. Add 25 ml solution of 0.1 mM copper nitrate (pH= 5)
4. Mix the solution with a rotary shaker at 200 rpm, room temperature
5. Collect activated carbon sample at pre-determined intervals of time
6. Triplicate the experiments
7. Analyze for the metal ions by AAS
8. Repeat Steps 1-7 with 0.2, 0.3, 0.4, 0.5, 1, 2.5, 5, 10 mM of copper nitrate solution and 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2.5, 5, 10 mM of lead nitrate solution

### **3.3.4 Adsorption of single component in column experiments**

#### **3.3.4.1 Experimental setup**

The adsorption was carried out in a laboratory scale setup which consisted of a vessel that contained 2000 ml of metal nitrate solution and a pH controlling system. The column configurations are shown in Figure 3.1. The packed column was a simple plastic tube with an inner diameter (ID) of 1.5 cm, 12 cm in length. The glass wool and glass bead were introduced at the bottom of the column and at the top of the activated carbon sorbent. The packing density was constant at  $0.19 \text{ g cm}^{-3}$  for all column experiments. The experimental setup is schematically shown in Figure 3.2.

#### **3.3.4.2 Experimental procedure**

1. Add 2000 ml 0.3 mM of copper nitrate solution into vessel
2. Turn on the pH controller set and adjust to pH 5 using  $\text{HNO}_3$  (1% by volume) and NaOH solution (1% by volume)
3. Add 5.0 g of activated carbon into column (bed depths 1.5 cm)
4. Set the flow rate of peristaltic pump to  $2.5 \text{ ml min}^{-1}$
5. Collect activated carbon sample from the solution at pre-determined intervals of time

6. Repeat Steps 1-5 with lead nitrate solution and change flow rates to 5.0, 7.5 ml min<sup>-1</sup> and bed depth 3.0 and 4.5 cm (1.0 and 1.5 g of activated carbon).

### **3.3.5 Adsorption of binary components in column experiment**

#### **3.3.5.1 Experimental setup**

The adsorption was carried out in a laboratory scale setup which consisted of a vessel that contained 2000 ml of metal nitrate solution and a pH controlling system. The experimental setup is schematically shown in Figure 3.1.

#### **3.3.5.2 Experimental procedure**

1. Add 2000 ml metals solution (copper 0.15 mM-lead 0.15 mM) into the vessel
2. Turn on the pH controller set and adjust to pH 5 using HNO<sub>3</sub> (1% by volume) and NaOH solution (1% by volume)
3. Add 1.5 g of activated carbon into column (bed depths 4.5 cm)
4. Set the flow rate of peristaltic pump to 2.5 ml min<sup>-1</sup>
5. Collect activated carbon sample from the at pre-determined intervals of time

## **3.4 Desorption studies**

### **3.4.1 Type of solvent for desorption**

1. Add 100 ml of sulfuric acid solution (1N) into Erlenmeyer flasks
2. Add 1 g of activated carbon with adsorbed heavy metal
3. Mix the solution with a shaker water bath with stirring rate 200 rpm at 75°C for 24 h
4. Collect the activated carbon sample from the solution
5. Triplicate the experiments
6. Analyze for metal ions by AAS
7. Repeat Steps 1-7 with phosphoric and citric acids.

### **3.4.2 Effect of solvent concentration**

1. Add 100 ml of suitable solution (1N) from Section 3.4.1 into Erlenmeyer flasks
2. Add 1 g of activated carbon with adsorbed heavy metal
3. Mix the solution with a shaker water bath with stirring rate 200 rpm at 75°C for 24 h



4. Collect the activated carbon sample from the solution
5. Triplicate the experiments
6. Analyze for metal ions by AAS
7. Repeat Steps 1-7 with 0.5, 2, 2.5, and 3 N of suitable solution from

Section 3.4.1.

#### **3.4.3 Effect of contact time**

1. Add 100 ml of suitable solution from Section 3.4.1 (N is suitable N from section 3.4.2) into Erlenmeyer flasks
2. Add 1 g of activated carbon with adsorbed heavy metal
3. Mix the solution with a shaker water bath with stirring rate at 200 rpm at 75°C
4. Collect activated carbon sample at pre-determined intervals of time
5. Triplicate the experiments
6. Analyze for the metal ions by AAS

#### **3.4.4 Effect of temperature**

1. Add 100 ml of suitable solution from Section 3.4.1 (N is suitable N from section 3.4.2) into Erlenmeyer flasks
2. Add 1 g of activated carbon with adsorbed heavy metal
3. Mix the solution with a shaker water bath with stirring rate 200 rpm at 75°C for suitable contact time from Section 3.4.3
4. Separate activated carbon from solution
5. Triplicate the experiments
6. Analyze for the metal ions by AAS
7. Repeat Steps 1-7 at 25 and 50 °C

Table 3.1 Determination of impregnation ratio of activated carbon.

Eucalyptus bark (g)	Phosphoric acid (85 wt%) (ml)	Impregnation ratio
100	30	1:0.3
100	50	1:0.5
100	80	1:0.8
100	100	1:1
100	200	1:2
100	300	1:3

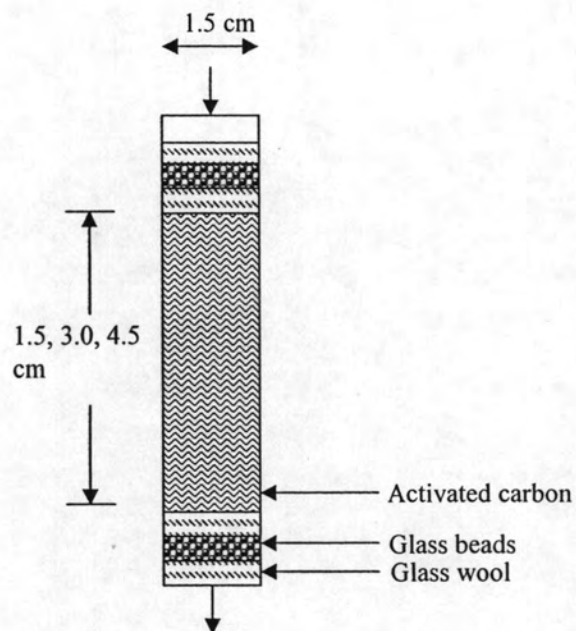


Figure 3.1 Column configurations

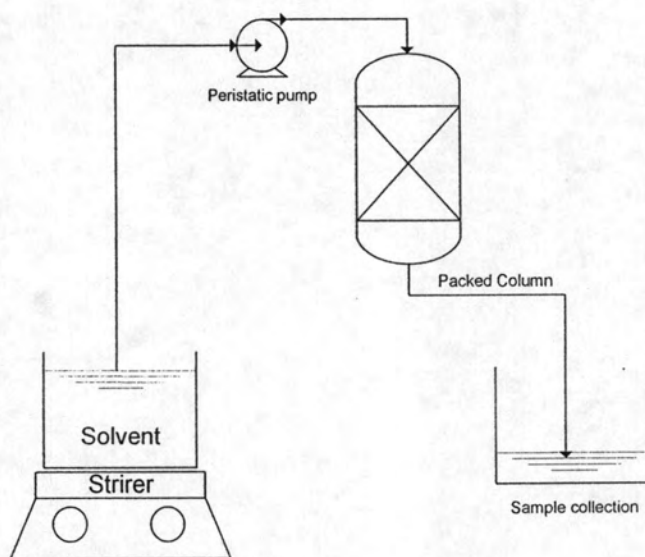


Figure 3.2 Experimental setup for adsorption