

## Chapter 2

### METHOD OF STUDY

#### 2.1 Chemicals and materials

1. Zinc chloride,  $\text{ZnCl}_2$ ; A.R., Assay 98.8%, Baker Analysed.
2. Lead chloride,  $\text{PbCl}_2$ ; A.R., Assay 98%, Fluka.
3. Cadmium chloride -1- hydrate,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ; A.R., Assay 99%, Riedel-de Haen.
4. Sodium chloride,  $\text{NaCl}$ ; A.R., Assay 98%, Merck.
5. Sodium hydroxide,  $\text{NaOH}$ ; A.R., Assay 99%, Lab Scan.
6. Hydrochloric acid,  $\text{HCl}$ ; A.R., 37%, Merck.
7. Nitric acid,  $\text{HNO}_3$ ; A.R., 65%, Carlo Erba.
8. Potassium bromide,  $\text{KBr}$ ; IR grade, Fisher Chemical Scientific.
9. Filter papers No.1; Quantitative, Whatman.
10. Filter papers No.42; Quantitative, Whatman.
11. Filter papers; student grade, 125 cm diameter, Whatman.
12. Distilled water; Department of Chemistry, PSU.
13. Universal indicator; full range pH 1-14, Whatman.

#### 2.2 Instruments

##### 2.2.1 Department of Chemistry, PSU

1. Analytical balance; VA304-1YAZM13A-M, Oertling.

2. Agar mortar and pestle; Arthur H. Thomas.
3. Atomic absorption spectrophotometer, AAS; Aanalyst 300, Perkin Elmer.
4. Crucible
5. Hotplate and stirrer; MR 3001, Heidolph.
6. Fourier-transform infrared spectrophotometer and diffuse reflectance accessory, FT-IR and KBr techniques; Spectrum GX, Perkin Elmer.
7. KBr pellet presser; Graseby Specac.
8. Muffle furnace; Linn High Therm, VMK 39.
9. Micropipet; 0.01603A, 10-1000  $\mu\text{L}$ , Pipet Lite, Rainnin.
10. Oven; UM 500, Memmert.
11. pH meter; Model 15, Denver Instrument.
12. pH electrode; DI-620-285, SN6065262, Denver Instrument.
13. Pulveriser (laboratory jar mill); 02102-4038, Fritsch pulverisette.
14. Stainless steel boxes and covers.
15. Soxhlet extraction apparatus.
16. Test sieve and lid receiver; 70, 80 and 325 mesh U.S., Endecotts.
17. Thermometer.
18. Thermostat shaker water bath; Model WB/OB 7-45, WBU 45, Memmert.
19. Vacuum pump; B-169, Buchi.

### 2.2.2 Scientific Equipment Center, PSU

1. Scanning electron microscope, SEM; JSM-5800 LV.

2. Energy dispersive X-ray analyzer, EDA; EDA analyzer couple with scanning electron microscope (SEM), JSM-5800 LV.

### 2.2.3 Department of Chemical Engineering, PSU

1. Surface area and pore size analyzer; SA 3100, Coulter.

## 2.3 Methods

### 2.3.1 Preparation of activated carbons

Figure 1 shows the schematic representation of the activation procedure. The production process of activated carbons from bagasse and pericarp of rubber fruit, all consisted of carbonization and chemical activation with  $\text{ZnCl}_2$ . Activated carbons were prepared by the following steps:

1. Each dried raw material was cut into small pieces approximately  $1 \text{ cm}^2$  and placed into stainless steel box with cover. The carbonization was then conducted in a muffle furnace at  $300 \text{ }^\circ\text{C}$  and  $400 \text{ }^\circ\text{C}$  for bagasse and pericarp of rubber fruit, respectively. The heating period was 3 h for all materials.
2. After carbonization, the carbonized chars were then ground (laboratory jar mill) and sieved to 70 mesh and 325 mesh (Test sieve and lid receiver).
3. Prior to activation, the  $\text{ZnCl}_2$  powder was dissolved to a solution of 1 g/ distilled water 1 mL. The chemical activation was done in the next step by mixing the ground char for each size (both 70 and 325 mesh) with concentrated solution of  $\text{ZnCl}_2$  in crucible by using char

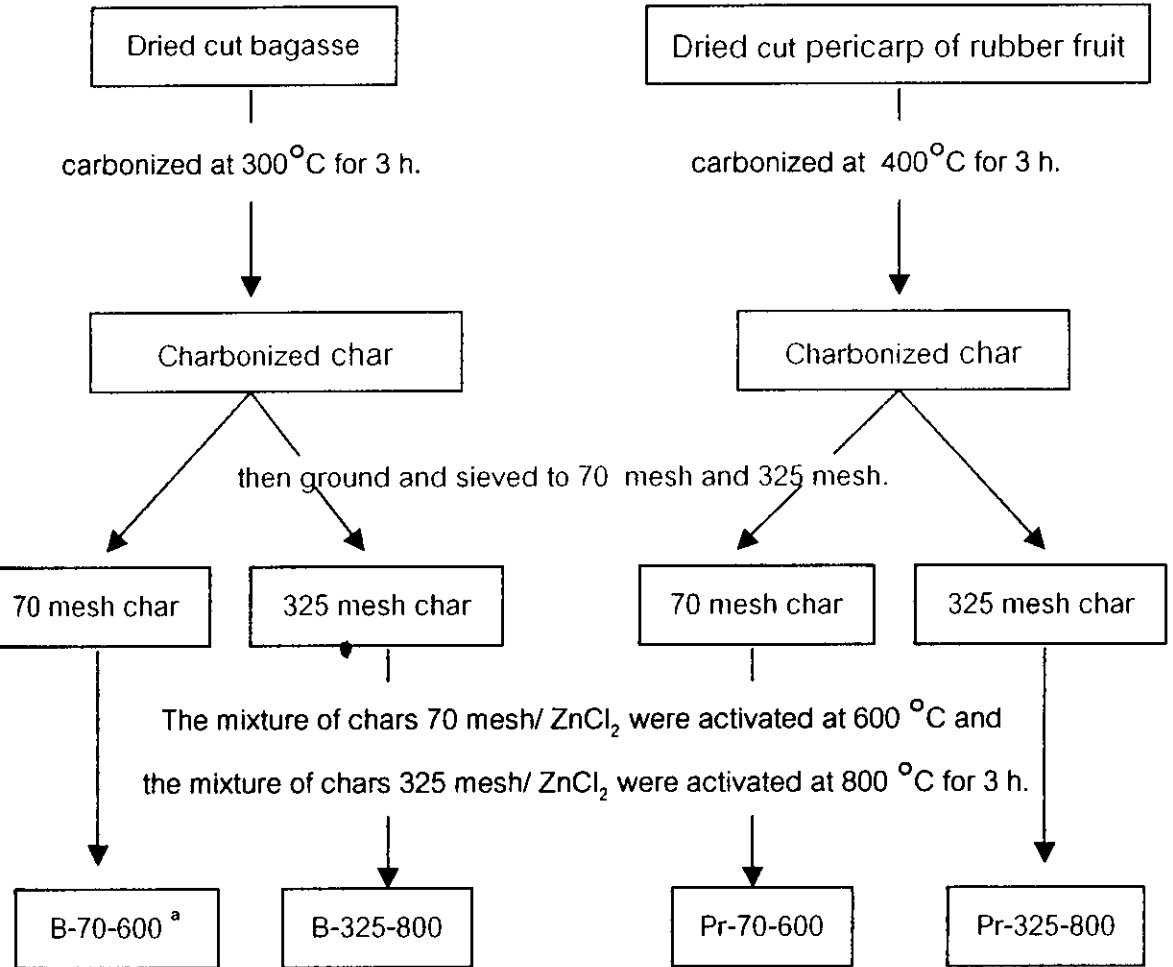
to  $\text{ZnCl}_2$  powder ratio 1:2 by weight. Activation had been carried out by varying activation temperatures. Each char with difference of mesh sizes was activated by using two different temperatures. The mixture of chars of 70 mesh/  $\text{ZnCl}_2$  were activated at  $600^\circ\text{C}$  and the mixture of chars of 325 mesh/  $\text{ZnCl}_2$  were activated at  $800^\circ\text{C}$  for 3 h in a muffle furnace. Therefore, we got four kinds of activated carbons the sample codes were designed as shown in Table 1.

**Table 1** Sample codes of obtained activated carbons.

Sample codes	Raw materials	Size of chars (mesh)	Activation temperatures ( $^\circ\text{C}$ )
B-70-600	Bagasse	70	600
B-325-800	Bagasse	325	800
Pr-70-600	Pericarp of rubber fruit	70	600
Pr-325-800	Pericarp of rubber fruit	325	800

- The obtained activated carbon was then washed with 5% HCl solution and followed by hot distilled water to remove chloride including zinc compounds until the washing water was free from chloride ions and then dried at  $120^\circ\text{C}$  for 3 h. The obtained activated carbons were kept in a dessicator. Prior to using activated

carbons with any purposes or at anytime, the samples will be dried at  $120^{\circ}\text{C}$  for at least 3 h.



**Figure 1** Schematic representation of the activation procedure.

<sup>a</sup> The notation of activated carbons refer to material, size mesh and temperature of activation, respectively. For example, B-70-600 means that raw material is bagasse was ground to 70 mesh and activated with ZnCl<sub>2</sub> for 3 h at  $600^{\circ}\text{C}$  (Pr is pericarp of rubber fruit).

## 2.3.2 Characterization of activated carbons surfaces

### 2.3.2.1 Surface area and pore size analysis (physical or porous texture characterization)

Specific surface areas (BET surface areas) and micropore volumes of activated carbons were determined by nitrogen adsorption isotherms at 77 K carried out with Coulter model SA3100 apparatus by using Brunauer-Emmett-Teller (BET) and t-plot equations, respectively. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model (program for calculation these parameters is already in this apparatus). Prior to the nitrogen adsorption experiments, all samples were degassed for 1 hour at 120 °C for maintaining the integrity of the chemical surface properties (The measurement was conducted at Department of Chemical Engineering, PSU).

### 2.3.2.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to analyze the porosity of activated carbon samples (textural images) by using a scanning electron microscope JSM-5800 LV (at Scientific Equipment Center, PSU).

### 2.3.2.3 Fourier-transform infrared spectrophotometry (FT-IR)

Activated carbon samples with and without adsorbed metal ions were studied spectroscopically with Fourier-transform infrared spectrophotometer, FT-IR. The transmission IR spectra of the carbon samples were obtained using KBr technique. The KBr disks were prepared by activated carbon-KBr mixtures in a ratio about of 1:300 were finely ground by pestle in an agate mortar and then dried at 120 °C in oven and finally pressed in a hydraulic press (KBr pellet presser). Before the spectrum of a sample was recorded, the

background line was obtained arbitrarily and subtracted. The spectra were recorded from 4000 to 400  $\text{cm}^{-1}$  at a scan rate of 0.2  $\text{cm s}^{-1}$ , and the numbers of interferogram at a nominal resolution of 4  $\text{cm}^{-1}$  was scanned more than 10 times for the best resolution.

In the case of raw materials and carbonized chars, IR spectra of these samples were carried out with the same method.

#### 2.3.2.4 Point of Zero Charge Measurements ( $\text{pH}_{\text{pzc}}$ )

The pH at the potential zero charge ( $\text{pH}_{\text{pzc}}$ ) of various activated carbons was measured using the pH drift method. The pH of a solution of 0.1 M NaCl (prepared in preboiled water to eliminate  $\text{CO}_2$ ) was adjusted between 2 and 12 by adding either diluted HCl or NaOH. Activated carbon sample (0.0500 g) was added to 50 mL of the NaCl solution in 125 mL flask. The flasks were sealed to eliminate any contact with air and then left at ambient temperature. After the pH had stabilized (typically after 24 h), the final pH was recorded. The graphs of final versus initial pH were used to determine the points at which initial pH and final pH values were equal. This was taken as the  $\text{pH}_{\text{pzc}}$  of the activated carbon.

#### 2.3.2.5 Energy dispersive X-ray analysis (EDA)

EDA studies of activated carbons with and without adsorbed metal ion species were carried out using a JSM-5800 LV scanning electron microscope (SEM) couple with a EDA analyzer. Mapping for distribution of various elements was also conducted. Prior to analyzing with EDA (Scientific Equipment Center, PSU), activated carbons after metal ions adsorption were

washed by Soxhlet extraction using water as solvent to eliminate reversible adsorbed metal ions (physisorbed metal ions).

### 2.3.3 Adsorption studies

#### 2.3.3.1 Adsorbate (metal ions solution)

Two metal ions were studied ( $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ). Their atomic weight are  $112.4 \text{ g mol}^{-1}$  for Cd(II) and  $207.2 \text{ g mol}^{-1}$  for Pb(II). Adsorbate stock solutions,  $1000 \text{ mg L}^{-1}$  were prepared by dissolving commercially available metal salts in HCl solution ( $\text{pH} = 5$ ) to prevent hydrolysis formation. Salts of metal ions used were  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  for  $\text{Cd}^{2+}$  and  $\text{PbCl}_2$  for  $\text{Pb}^{2+}$  with a high degree of purity, respectively higher than 98% and equal to 98% (as shown in section 2.1), The stock solutions were diluted with distilled water to obtain standard solutions with concentration ranging from  $10\text{-}200 \text{ mg L}^{-1}$ .

#### 2.3.3.2 Adsorption isotherm studies of cadmium and lead ions on activated carbons

Adsorption equilibrium study of both metal ions was carried out in a 125 mL stoppered conical flask by adding 0.0500 g of activated carbon to 50 mL of metal solution. The concentrations of both metal ions solutions were varied in the range of 10 to 200 mg/L. Adsorption experiment of all activated carbon samples was done at desired initial pHs as adjusted by HCl or NaOH (5 for Pb (II) ion and 5 and 6 for Cd (II) ion) and temperatures ( $40^\circ\text{C}$ ,  $60^\circ\text{C}$  and  $80^\circ\text{C}$  for both ions). After gentle shaking for more than 6 h (for ensuring to reach equilibrium) in a thermostat shaker water bath, the contents were filtered through filter paper No.1 by neglecting the first 10 mL of the filtrate in order to saturate the filter paper with metal solution. Metal ions concentrations of both



before and after adsorption were then determined by Perkin-Elmer AAnalyst 300 model atomic absorption spectrophotometer. The amounts of metal ions adsorbed were calculated based on the difference between the metal ions concentration in aqueous solution before and after adsorption.

The amount adsorbed was calculated from the formula (Salame and Bandosz, 2003)

$$Q = \frac{V \times (C_0 - C_e)}{W}$$

where  $Q$  is the amounts of metal ions adsorbed,  $V$  is the volume of the liquid phase,  $C_0$  is the concentration of solute in the bulk phase before it comes in contact with the adsorbent,  $C_e$  is the concentration of the solute in the bulk phase at equilibrium, and  $W$  is the amount of the adsorbent. In this method, it is assumed that the change in volume of the bulk liquid phase is negligible because the solute concentration is very small and the volume occupied by the adsorbent is also very small. The amount of metal ions adsorbed on the sample was calculated based on the previously determined calibration curve.

#### 2.3.3.3 pH effect on adsorption of cadmium and lead ions on activated carbons

The pH of cadmium ions solution of 80 mg /L was adjusted between 1 and 6 and pH of lead ions solution of 80 mg /L was also adjusted between 1 and 5 by adding either diluted HCl or NaOH. Activated carbon sample (0.05 g) was added to 50 mL of each metal solution in 125 mL flask. The flasks were then shaken at 40°C in thermostat shaker water bath. After the equilibrium

obtained (more than 6 h), the filtrate was obtained by filtering. Metal ions concentrations and calculation of metal ions adsorbed were carried out with the same method as shown in adsorption isotherm study.