

CHAPTER III

MATERIALS AND METHODS

3.1 Analyzing Instruments

- ◆ Atomic Absorption Spectrophotometer (AAS.)
Varian, Spectr AA-300 model
- ◆ Fourier Transform Infrared Spectrometer (FT-IR)
Perkin Elmer, 1760x model
- ◆ Scanning Electron Microscope (SEM)
Jeol, JSM-35CF model
- ◆ Flask Shaker
Janke & Kunkel, HS 500 model

3.2 Chemical substances

- ◆ Heavy metal ions standard
 - Copper (II) sulphate ; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 - Nickel (II) sulphate ; $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
 - Zinc (II) sulphate ; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

All of heavy metal ions standard were analytical grade and were purchased from Faimitalia Carlo erbra S.P.A. Milano.

- ◆ Inorganic acids
 - Hydrochloric acid ; HCl (37 %)
 - Sulfuric acid ; H_2SO_4 (95-97 %)
 - Nitric acid ; HNO_3 (69-71 %)

◆ Indicators.

- Eriochrom Black T ; $C_{29}H_{12}N_3NaO_7S$
- Phenolphthalein ; $C_{20}H_{14}O_4$

◆ Others chemical substances.

- 37 % v/v Formaldehyde ; CH_2O
- Potassium hydrogen phthalate ; $KOOC.C_6H_4COOH$ (KHP)
- Ammonia Solution ; NH_4OH
- Ammonium chloride ; NH_4Cl
- Ethylene diamine tetraacetic acid di-sodium salt (di-sodium EDTA);
[$CH_2.N(CH_2.COOH).CH_2COONa$]

HCl, H_2SO_4 , phenolphthalein, Eriochrom Black T, 37 % CH_2O , KHP, di-sodium EDTA and NH_4Cl were analytical grade and were purchased from E. Merck, Darmstadt, Germany while HNO_3 and NH_4OH were obtained from J.T. Baker Inc, Phillipsburg, NJ 08865, USA.

3.3 Water hyacinth substrate.

Water hyacinth was collected from Thapra region located in Bangkok province, ranging in weight from 100 to 150 grams/plant because the medium plant could be collected some of heavy metals in its tissue higher than the small and large plant about 2 to 6 % approximately. (Khowtip and Pimol, 1990). Most parts of water hyacinth were selectively used, excepted for the root part.

3.4 Preparation of substrate

The selected water hyacinth substrate was cleaned with water and exposed directly to the sunlight for 2 to 3 days until apparently dried. Then the untreated water hyacinth (UWH) was dried again at $60\text{ }^\circ\text{C}$ for 24 hours, ground and sieved to obtain the desired particle sizes, ranging from 60 to 80 mesh. The dried weight of UWH was 5 % of all weight.

3.5 Testing contamination of original substrate

From the preparation mentioned above, 5.00 grams of the sieved substrate was continuously agitated with 0.4 N. H_2SO_4 at 100 r.p.m. for 30 min. Then the filtrate and leaching solution were digested separately by mixture of conc. HNO_3 and conc. H_2SO_4 (1:2 v/v) until obtaining the clear solution. Both samples were analyzed by AAS.

3.6 Pretreatment of substrate

The sieved substrate was agitated with the same procedure as above. The substrate mixture was filtered, and washed thoroughly with de-ionized water until the pH of the filtrate was 4-5. The pretreated water hyacinth (PWH) was oven dried at 60 °C for 24 hours.

3.7 Batch experiments

Effect of contact time

One hundred ppm of synthetic solutions of Cu^{2+} , Ni^{2+} and Zn^{2+} were freshly prepared to study the effect of contact time on the water hyacinth. The experiment was conducted by adding 0.5 g of PWH to 100 ml of each synthetic solutions at pH 5. Continuous mixing of all samples was performed by a flask shaker at a speed of 120 hub/min. Each of synthetic solutions was withdrawn after 1, 2, 5, 10, 20, 40, 60 and 80 min intervals and analyzed quantitatively by complexometric method.

Effect of formaldehyde treatment

The sieved substrate was treated with 2, 5, 10, 20, 30 and 37 % (v/v) of CH_2O and 0.4 N. H_2SO_4 in a ratio of 1:12:40 (modified from Randal et al., 1978). The mixture was agitated for 2 hours at 50 °C. The formaldehyde treated water hyacinth (FTWH) mixture was filtered, and washed thoroughly with de-ionized water until the pH of the filtrate was 4-5. The experiments were conducted by adding 0.5 g of various % CH_2O treatment to 100 ml of 25, 50, 75 and 100 ppm Cu^{2+} , Ni^{2+} and Zn^{2+} at pH 5. Continuous mixing of all samples were made in polypropylene bottles; minimizing

with various heavy metal ions adsorption, were performed by a flask shaker at speed 140 hub/min for 20 mins that was optimum time interval obtained from the effect of contact time experiment. Each of separated sample was filtered and the filtrate was determined for heavy metal ions by classical complexometric method. The optimum condition for formaldehyde treatment was achieved by using analysis of variance (ANOVA; calculated by computer program SPSS), considering with cost-benefit relation and waste discharge content.

3.8 Physical properties and characterization

Almost of solid substrates were determined their physical properties including percent of dry moisture, degree of swelling and SEM analyzing. Methods of degree of swelling determination were carried out by placing the dried sample in a graduated cylinder and reading the initial volume. An excess of selected solvent, including water and 10 % NaCl, was added, and the volume was read periodically until the sample had ceased to swell. Percentage of swelling at a predetermined contact time was calculated as (Okay et al., 1985).

$$\frac{\text{final volume} - \text{initial volume}}{\text{Initial volume}} \times 100$$

For characterization, all solid samples in KBr discs were identified quantitatively for functional groups using an Fourier Transform Infrared Spectrophotometer (FT-IR).

3.9 Column experiments

Determination of the total capacity

The synthetic solution of each heavy metal ions (0.5 N ~250 ml) were percolated a 1.0 cm diameter column at a flow rate about 2 ml/min, then filled with accurate amount of both substrates (~0.5 g). The distilled water was percolated for

washing the non-retaining of heavy metal ions. Then, the retained heavy metal ions were eluted with 100 ml of 1 N HCl at a flow rate about 2 ml/min. The eluting solutions were quantitatively analyzed by Atomic Absorption Spectrophotometer (AAS.) for both of substrates (modified from Jeffery et al., 1989).

Determination of the ion exchange capacity

A small column, 15 cm x 1 cm was filled with distilled water that contained about 0.5 g of the air-dried substrate and added amount of distilled water to cover the substrate. The air bubbles that stick to the resin beads by applying intermittent pressure via the rubber tubing. The level of distilled water was adjusted by a value at the column to about 1 cm above the resin after percolating about 30 minutes for equilibrium. Then, a 250 ml of ca 0.50 M Sodium chloride solution in separatory funnel was filled on the top of this column. Allow this solution to drip in a 500 ml conical flask at a flow rate of 2 ml/min. When all the solution has passed through the column, titrate the effluent with standard 0.1 M sodium hydroxide using phenolphthalein as an indicator. Both of substrates; Purolite and 5% FTWH, were analyzed by the same procedure (modified from Jeffery et al., 1989).

Note : Both of ion exchange and total capacity is expressed as meq/g of dry weight substrate.

Effect of acid regeneration

This experiment was similar to the determination of the total capacity section, but it was conducted for 5 times repeatedly.

Heavy metal ion removal

The removing of heavy metal ions was conducted in glass column of 2 cm internal diameter filled with a precise amount of 5% FTWH ; the packed bed was approximately 20 cm in height. Initial concentrations of synthetic solution of heavy metal ions were 5,10,20 and 50 ppm, respectively. Synthetic solutions were percolated through the packed bed at flow rate of 3 ml/min, controlled by a valve at bottom of the

packed bed column. Fractions of 30 ml were collected and the concentration of heavy metal ions were analyzed by AAS (Maranon and Sastre, 1991).

Regeneration

After exhaustion of 5% FTWH substrate, the adsorbed metal ions were recovered by eluting with 0.5 N HCl at a flow rate of 10 ml/min, followed by washing with water to eliminate the excess of mineral acid. The packed bed column was ready to re-use (Maranon and Satre, 1992).

Note : 5% FTWH was used in this regeneration experiment because it was considered the most suitable substrate concentration in this study based on ANOVA analyses, cost-benefit relation, removal capacity and waste discharge content.



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