

CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

Instruments used in this thesis are listed in Table 3.1.

Table 3.1 List of instruments

| Instruments | Model, Manufacturer |
|--|--------------------------------|
| Inductively coupled plasma optical emission Spectrometer (ICP-OES) | iCAP 6500, Thermo Scientific |
| CHNS/O analyzer | PE2400 Series II, Perkin-Elmer |
| X-ray fluorescence | Philips model PW2400 |
| X-ray diffraction spectrometer | DMAX 2200 Ultima, Rigaku |
| Surface area analyzer (BET) | Autosorb-1, Quantachrome |
| pH meter | Ultrabasic, DENVER |
| Overhead shaker | Rotax 6.8, VELP scientifica |
| Stirrer | MS101, GEM |
| Oven | UM500, Memmert |
| Transferpipette | Brand |
| Analytical balance | SI-234, DENVER |
| Sonicator | CREST |
| Centrifuge | CENTAUR 2, Sanyo |
| Vacuum pump | Buchi, V-700 |
| Manifold | Supleco |

For ICP-OES, the operational parameters are listed in Table 3.2

Table 3.2 Operational parameters for ICP-OES

| Operation condition | Arsenic (As) |
|----------------------------|--------------|
| Wave length (nm) | 189.042 |
| Radio frequency power (W) | 1150 |
| Auxiliary gas flow (L/min) | 0.5 |
| Nebulizer gas flow (L/min) | 0.6 |
| Coolant gas flow (L/min) | 12 |
| Plasma view | Axial |
| Repeatability (times) | 3 |

3.2 Chemicals

All chemicals used in this thesis are listed in Table 3.3. They are analytical grade and used without purification.

Table 3.3 List of chemicals

| Chemical | Supplier |
|---|------------------------|
| The stock solution of 1000 mg As(V)/L | Sigma-Aldrich |
| The stock solution of 1000 mg As(III)/L | Sigma-Aldrich |
| Dimethylarsenic acid/Cacodylic acid | Sigma-Aldrich |
| Hydrochloric acid 37% | Merk |
| Nitric acid 65% | Merk |
| Sodium hydroxide | Merk |
| Na_2HPO_4 | Carlo Erba reagents |
| Na_2SO_4 | Carlo Erba reagents |
| KNO_3 | VWR International Ltd. |

3.3 Preparation of adsorbent

Sludge from tap water production (STWP) was obtained from Metropolitan Waterworks Authority (Bangkok, Thailand). The sludge was dried in an oven for 24 hours at 105 °C. After that, dried sludge was crushed and sieved (<500 µm). Finally, the sludge adsorbent was kept in a desiccator to prevent the moisture from the air.

3.4 Characterization of sludge

The sludge adsorbent was required to observe its properties including surface area, total pore volume, average pore diameter, elemental composition and chemical structure. In addition, the point of zero charge of sludge was also examined. The analytical techniques for characterization are listed in Table 3.4

Table 3.4 The techniques for characterization of sludge adsorbent

| Characteristic | Techniques |
|--|--|
| Surface area, total pore volume, average pore diameter | Surface area analyzer (BET) |
| Element composition | X-ray fluorescence spectrometry & inductively coupled plasma-optical emission spectrometer |
| C, H, N content | CHNS/O analysis |
| Chemical structure | X-ray diffraction spectrometry |
| pH of point of zero charge (pH _{pzc}) | Mass titration method |

3.4.1 Elemental content using ICP-OES

Aqua regia is a highly corrosive mixture of acids. It was used to digest dried sludge before analysis for elemental contents by ICP-OES. The sludge was weighed of 1 g then 30 mL of HCl and 10 mL of HNO₃ were added and the container was placed on a hotplate. After that, the mixture was stirred by a stirring rod until the reaction was complete and then it was diluted to 100 mL by deionized water. This

method should be done in fume hood since the nitrogen dioxide also occurred during experiment [56].

3.4.2 Measurement of point of zero charge

The pH_{pzc} or point of zero charge was studied by mass titration method. Different masses of sludge within the content range of 1-100 g/L were put into contact with a 0.03 M KNO_3 solution. And then, aqueous suspensions were agitated for 24 hours in an overhead shaker or until its equilibrium pH was reached. After that, the graph was established between pH value and adsorbent mass in KNO_3 (%w/v). The pH_{pzc} is the value at which a plateau is achieved when plotting equilibrium pH versus the sorbent mass [57].

3.5 Batch study

The batch study of arsenite (As(III)), arsenate (As(V)) and dimethylarsenic acid (DMA) adsorption was carried out. All experiments were performed in triplicate using batch method.

3.5.1 Effect of solution pH

The effect of pH was investigated by varying the pH values of arsenic solutions. The pH adjustment was done by 1% HCl and 1% NaOH solution in the pH range of 1-10. Next, 10 mL of 10 mg/L arsenic solution and 0.05 g of STWP was shaken by means of an overhead shaker at room temperature for 24 hours. Then, the solution was centrifuged at 3000 rpm for 10 minutes. Then, the pH of solution was measured. After that, the retained arsenic solution was filtered and analyzed by ICP-OES.

3.5.2 Adsorption kinetics

The effect of adsorption time of As(III), As(V) and DMA was studied by varied contact times in the range of 0.5-24 hours. The solution containing 10 mg/L of arsenic solution was prepared with the optimal pH value and adjusted its pH by HCl or NaOH. Then, 10 mL of arsenic solution was added in a test tube containing 0.05 g

of STWP and the mixture was shaken at room temperature. The experiments were performed for arsenic solution using different contact times. At the end of mixing, the adsorbent was separated from solution using centrifugation at 3000 rpm for 10 minutes. Then, the pH of solution was measured. The remaining arsenic in solutions was filtrated and determined by ICP-OES.

3.5.3 Adsorption isotherms

The adsorption isotherms were studied at room temperature by varying the initial arsenic concentration of 1 to 100 mg/L. The results were treated with Langmuir or Frundlich adsorption models to determine the maximum adsorption capacity for arsenic on the sludge and the phenomenon of adsorption on the surface of sludge.

An amount of 0.05 g of STWP was shaken with 10 mL of various initial concentrations of arsenic solution in the range of 1 to 100 mg/L using optimal conditions from previous experiments at room temperature. The adsorbent was separated by centrifugation at 3000 rpm for 10 minutes. After that, the pH of solution was measured. The residual arsenic in solution was determined by ICP-OES after filtration.

3.5.4 Effect of competing ions

Not only arsenic but other anions such as phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) can be commonly found in wastewater. Therefore, the influence of phosphate and sulphate was evaluated in various mole ratios of such competing anions to arsenic of 1:1, 5:1, 10:1 and 20:1. Then, 0.05 g of STWP was shaken with 10 mL of binary mixture solutions (10 mg As/L and PO_4^{3-} or SO_4^{2-}) using optimal pH and time from previous experiments at room temperature. After that, the adsorbent was separated by centrifugation at 3000 rpm for 10 min. After that, the pH of solution was measured. The residual arsenic solution was filtrated and analyzed by ICP-OES.

3.6 Column study

This technique is commonly applied to extract the contaminant compounds from wastewater. Wastewater is fed continuously through a column packed with appropriate adsorbent. Hence, this experiment is interesting to use a homemade cylinder column (Figure 3.1) for studying the efficiency of arsenic removal in solution under continuous flow condition.

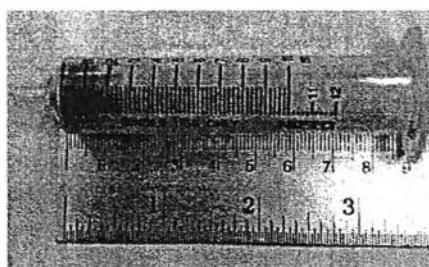


Figure 3.1 Photograph of the homemade cylinder column.

3.6.1 Effect of flow rate

A homemade cylinder column (10 mL of disposable syringe, NIPRO) was used to study in column system. Cotton ball was firstly placed at the end of the column to prevent the loss of adsorbent. The column was packed with the sludge at the height 1 cm. The effect of flow rate of arsenic solution was elucidated at 0.5, 1, 2, 3 and 4 mL/min that was pre-calibrated with deionize water. Then, 25 mL of 10 mg/L arsenic solution was passed through the column. The solution was passed through the syringe by means of a manifold connected to a vacuum pump. After that, the filtrate was kept and subject to the determination of arsenic amount by ICP-OES.

3.6.2 Effect of adsorbent layer height

Firstly, cotton ball was placed at the end of the column to prevent the loss of adsorbent. The column was packed with the adsorbent layer height 0.5, 1, 1.5 and 2 cm. The optimal flow rate of arsenic solution was 1 mL/min from studying the effect of column height. Then, 25 mL of 10 mg/L arsenic solution was passed through

the column. The filtrate was collected and the retained arsenic in solution was measured by ICP-OES.

3.6.3 Breakthrough curve

To estimate the sorption capacity of this method, the proper column height and flow rate were chosen from the previous experiment. Twenty-five milliliters of 10 mg/L arsenic solution was passed through this column. Then, each 25 mL of arsenic solution was added onto the column until the column was completely exhausted. Each volume of 25 mL was collected and measured the residual As concentration in solution using ICP-OES. Finally, the graph was plotted between C_t/C_0 and the volume for the determination of the breakthrough curve.

3.7 Application in real contaminated water samples

Real wastewater samples were obtained from a petroleum industry (Thailand) for total arsenic removal in the batch and column system. Firstly, the wastewater was filtered and analyzed for total arsenic concentration by ICP-OES.

For the batch system, 0.05 g of sludge was shaken with 10 mL of wastewater which was previously adjusted to the suitable pH value before adsorption. Then, the solution was mixed thoroughly by an overhead shaker for 12 hours. Finally, the retained arsenic concentration in solution was determined by ICP-OES after filtration.

For the column system, the adsorbent layer height at 2 cm was used. Then, the solution of 25 mL of water sample was passed through the column at a flow rate of 1 mL/min. After that, the amount of residual arsenic after adsorption was determined by ICP-OES.

Furthermore, a surface water sample was collected from the Chulalongkorn University pond. The water sample was spiked with arsenate (As(V)) in a level of 10 mg/L. The removal of As(V) using the sludge sorbent in both batch and column methods was performed in the same manner of real wastewater samples.