CHAPTER III

EXPERIMENTS AND ANALYSIS TECHNIQUES

This chapter covers all of the experiments and analysis techniques in this study. The experiments and analysis techniques are divided into five sections. Firstly, the preparation method of adsorbents is mentioned. Secondly, this section covers adsorption experiments of mercury and arsenic. Thirdly, this section deals with characterization of liquid product. Fourthly, characterizations of adsorbents are summarized. Finally, properties of chemicals used in experiments and analysis are shown.

3.1 Experiments

Adsorbents Preparation

Adsorbents used in the experiments are Al_2O_3, Cu/Al_2O_3, Ni/Al_2O_3, $Cu-Ni/Al_2O_3$. The adsorbent comprised one or two metallic components on suitable support. These adsorbents were prepared by dry impregnation of neutral activated alumina (Aldrich) with solution of copper nitrate and nickel nitrate. Approximate 20 grams of neutral alumina were dehydrated in boiling flask that connected to vacuum pump under pressure at −750 mm Hg. The flask was heated at 120 ^{o}C under vacuum about 3 hours. After that, the flask was cooled to room temperature then the neutral alumina was impregnated by aqueous solution of nickel nitrate or copper nitrate under vacuum pressure. The amount of aqueous solution used was approximately 5.24 ml and the concentrations of the solution calculated from the metal loading on adsorbents. The impregnated neutral alumina was maintained at vacuum pressure for 30 minutes and then adjusted to atmospheric pressure. The impregnated neutral alumina was allowed

to rest at atmospheric pressure for 24 hours at room temperature before dried at 110 C for 12 hours and then calcined with air with a flow rate of 12 l/hr. The temperature was increased at the rate of 1°C/min to desiring temperature and maintained at this level for 3 hours. The calcination temperature was different for metal loading with heating rate was 1 C/min. The calcination procedure is listed below.

Alumina adsorbent:

Alumina support was calcined with air at 500 °C for 3 hours. The alumina adsorbent does not contain copper or nickel

Copper adsorbent:

Alumina support was impregnated with copper nitrate solution (2.5wt%), then dried at 110 C and calcined with air gas at 400 °C. The prepared adsorbent was referred as Cu.

Nickel adsorbent:

Alumina support was impregnated with nickel nitrate solution (2.5wt%), then dried at 110 C and calcined with air at 500 °C. The prepared adsorbent was referred as Ni.

Nickel-Copper adsorbent:

Alumina support was first impregnated with 2.5wt% nickel nitrate solution then dried at 110 C and calcined with air at 500 C. After that, 2.5wt% of copper nitrate solution was impregnated, dried and reduced at 400 C. The prepared adsorbent was referred as NiCu.

Adsorption Experiments

The study of mercury and arsenic compounds removal was carried out in 250-ml boiling flask. Liquid feed and adsorbent were placed in to the reactor. The temperature of system was measured by a thermometer which inserted in to the built in glass thermowell. The heating magnetic stirrer was used for heating and stirring the system.

After each experiment product were filtrated with filter papers Whatman No.1 to separate the spent adsorbent from liquid product.

3.2 Analysis Techniques

After each experiment liquid feed, product and adsorbents were analyzed for arsenic and mercury content. Fresh and spent adsorbents were analyzed for their characteristics.

Arsenic content

Arsenic in the liquid feed and product were determined by Graphite Furnace Atomic Absorption Spectroscopy that uses electrothermal tube made of graphite as atomizer. In the atomizer, sample was first evaporated at 120 ^{o}C and then ashed at about 1200^{o}C. After that, the temperature in the atomizer was raised to 2000^{o}C for atomization. However, toluene, as liquid feed, was organic material that trend to interfere the adsorption and because organic form of arsenic compounds shows poor sensitivity. So feed and product were digested to convert arsenic compounds to ionic form.

Arsenic digestion

Approximately 30 gram of sample was transferred to 250 ml flat round flask. After that 7 ml of nitric acid (concentrated), 3 ml of hydrochloric acid (concentrated), 3 ml of hydrogen peroxide (35%), and 10 ml of distillated water were added in to the flask. The flask was connected to a reflux condenser and subsequently heated at 100 ^{o}C for 3 hours. After that the flask was cooled to ambient temperature. The solution was transferred into 250 ml separating funnel and shaken vigorously. Then acid-phase was separated from toluene-phase. The remaining toluene-phase was extracted by water for transferring arsenic to water phase. The acid-phase and the extracted water were mixed and made the total volume to 100 ml.

Mercury content

Flow Injection Mercury Hydride System Analysis is a high sensitivity and suitable technique for measurement of mercury. The hydride technique involves the reaction of acidified aqueous samples with a reducing agent such as sodium borohydride. The sodium borohydride/acid reduction generates hydrides as shown in the following equations

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8H$$

$$E^{m+} + H(excess) \longrightarrow Ehn + H_2(excess)$$

where E = the analyze of interest and m may or may not equal n

This reaction generates a volatile hydrides which was transported to a quartz cell by argon carrier gas. In the quartz cell, the hydrides were converted to gaseous metal atoms. Although this technique is suitable for measuring of mercury in water-phase, it is applicable to the analysis of materials other than water-phase if and only if, an initial procedure for digesting and oxidizing the sample is carried out. Digestion and oxidization was performed to ensure that the mercury in the sample was converted to the mercuric ion, and dissolved in aqueous media. The digestion method used in this study is applied from ASTM D-3223 which is a standard method for determining of total mercury in water.

Mercury digestion

Approximately 30 g of sample was transfer to 250 ml flat round flask. After that 5 ml of concentrated sulfuric acid and nitric acid were added and mixed after each addition. Then, 15 ml of potassium permanganate solution was added to each flask. The mixture was stirred vigorously for at least 15 min. Then, 8 ml of potassium persulfate was added to the flask. The flask at the top was equipped with a reflux condenser and subsequently heated in heating mantle at 95 $^{\circ}C$ for approximately 2 hours. After that the flask cooled to ambient temperature, and added 6 ml of sodium chloride-hydroxylamine hydrochloride

solution. Then, shaken for a few seconds. The solution was transferred into 250 ml separating funnel and shaken vigorously. After that, acid-phase was separated from toluene-phase. The remaining toluene-phase was extracted by water for transferring mercury to water phase. The acid-phase and the extracted water were mixed and made the total volume to 100 ml.

Adsorbent characterization

In order to understand the behavior of an adsorbent it is essential to be adequately characterized. In this study the properties studied surface area, pore volume, and pore size distribution of adsorbents are aimed to analyze. A brief description of these measurements is given below.

Surface area, Pore volume and Pore size distribution

Surface area and pore characteristics of the samples were measured by the BET method, with nitrogen as the adsorbent using a micromeritics model ASAP 2000. The ASAP 2000 system consisted of two sample preparation ports and one sample analysis ports.

Approximate 100 mg of the adsorbent was weighted and transferred into the sample preparation tube. Most solid adsorbents adsorbed moisture and other contaminants when used. Thus the adsorbent must have been cleaned in sample preparation tube by thermal treating before analysis was performed. The sample preparation tube was attacked to the vacuum system and placed around by the heater. Sample preparation would then require more time to achieve the desiring condition before proceeding with and analysis. Once sample preparation was completed, the sample tube might be allowed to cool to ambient temperature. The sample tube would then remove from the sample preparation port and placed onto the analysis port.

Table 3.1 Properties of Toluene*

Formula	C_7H_8
Chemical Name	Toluene
Physical Properties	
Molecular Weight	92.13
Form	liquid
Color	colorless
Boiling Point (^{o}C)	110.8
Melting Point (^{o}C)	-95
Specific Gravity	0.866
Solubility	soluble in ether and alcohol
Purity	> 99%

* From Encyclopedia of Chemical Engineering

Table 3.2 Properties of Mercuric chloride*

Formula	$HgCl_2$
Chemical Name	Mercuric chloride
Physical Properties	
Molecular Weight	271.52
Form	solid
Color	white
Boiling Point (^{o}C)	302
Melting Point (^{o}C)	277
Specific Gravity	5.44
Solubility	soluble in water
Purity	> 99%

* From Merck Index

Table 3.3 Properties of Diphenylmercury*

Formula	$C_{12}H_{10}Hg$
Chemical Name	Diphenylmercury
Physical Properties	
Molecular Weight	354.8
Form	solid
Color	white
Melting Point (^{o}C)	121-124
Specific Gravity	2.32
Solubility	moderately soluble in toluene
Purity	> 99%

* From Merck Index

Table 3.4 Properties of Phenylarsine oxide*

Formula	C_6H_5AsO
Chemical Name	Phenylarsine oxide
Physical Properties	
Molecular Weight	168.03
Form	solid
Color	white
Melting Point (^{o}C)	150
Solubility	soluble in toluene
Purity	97%

* From Encyclopedia of Chemical Engineering

Table 3.5 Properties of Arsenic oxide*

Formula	As_2O_3
Chemical Name	Arsenic trioxide
Physical Properties	
Molecular Weight	197.84
Form	solid
Color	white
Boiling Point (^{o}C)	465
Solubility	soluble in water
Purity	> 99%

* From Merck Index

Table 3.6 Properties of Aluminum oxide, activativated, neutral Brockmann*

Formula	Al_2O_3
Chemical Name	Neutral Alumina
Physical Properties	
Form	solid
Color	white
Standard grade	~150 mesh
Surface area	155 m2/g
pH of aqueous suspension	7.0+-0.5

* From Catalogue Handbook's Aldrich

Table 3.7 Properties of Nickel nitrate*

Formula	$Ni(NO_3)_2.6H_2O$
Chemical Name	Nickel nitrate hexahydrate
Physical Properties	
Molecular Weight	290.8
Form	solid
Color	green
Boiling Point (^{o}C)	136.7
Melting Point (^{o}C)	56.7
Specific Gravity	2.05
Solubility	soluble in water and ammoniumhydroxide
Purity	> 99%

* From Encyclopedia of Chemical Engineering

Table 3.8 Properties of Copper nitrate*

Formula	$Cu(NO_3)_2.3H_2O$
Chemical Name	Copper nitrate trihydrate
Physical Properties	
Molecular Weight	241.6
Form	solid
Color	blue
Boiling Point ($^{\circ}C$)	-
Melting Point ($^{\circ}C$)	114.5
Specific Gravity	2.32
Solubility	soluble in ether and alcohol
Purity	> 99%

* From Merck Index

Table 3.9 Properties of Nitric Acid*

Formula	HNO_3
Chemical Name	Nitric Acid
Physical Properties	
Molecular Weight	63.02
Form	liquid
Color	colorless
Boiling Point (^{o}C)	86
Melting Point (^{o}C)	-41.59
Specific Gravity	1.502
Solubility	soluble in water
Purity	69.0-70.5%

* From Merck Index

Table 3.10 Properties of Hydrochloric Acid*

Formula	HCl
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Form	liquid
Color	colorless
Melting Point (^{o}C)	-15.35
Specific Gravity	1.05
Solubility	soluble in water and alcohol
Purity	37%

* From Encyclopedia of Chemical Engineering

Table 3.11 Properties of Sulfuric Acid*

Formula	H_2SO_4
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	97.09
Form	liquid
Color	colorless
Boiling Point ($^{\circ}C$)	-
Melting Point ($^{\circ}C$)	205
Specific Gravity	2.03
Solubility	soluble in water
Purity	95.7%

* From Merck Index

Table 3.12 Properties of Hydrogen Peroxide*

Formula	H_2O_2
Chemical Name	Hydrogen Peroxide
Physical Properties	
Molecular Weight	34.02
Form	liquid
Color	colorless
Boiling Point (^{o}C)	151.4
Melting Point (^{o}C)	-0.89
Specific Gravity	1.13
Solubility	soluble in water, acid and ether
Purity	35-35.6%

* From Encyclopedia of Chemical Engineering

Table 3.13 Properties of Potassium Permanganate*

Formula	$KMnO_4$
Chemical Name	Potassium Permanganate
Physical Properties	
Molecular Weight	158.03
Form	solid
Color	dark purple
Specific Gravity	2.71
Solubility	soluble in water
Purity	> 99%

* From Merck Index

Table 3.14 Properties of Potassium Persulfate*

Formula	K_2SO_8
Chemical Name	Potassium Persulfate
Physical Properties	
Molecular Weight	270.32
Form	solid
Color	white
Specific Gravity	-
Solubility	soluble in water
Purity	> 99%

* From Merck Index

Table 3.15 Properties of Hydroxylamine-Hydrochloride*

Formula	$NH_2OH.HCl$
Chemical Name	Hydroxylamine-Hydrochloride
Physical Properties	
Molecular Weight	69.49
Form	solid
Color	white
Boiling Point (^{o}C)	58
Melting Point (^{o}C)	33
Specific Gravity	1.20
Solubility	soluble in water and ether
Purity	> 99%

* From Merck Index

Table 3.16 Properties of Sodium Chloride*

Formula	$NaCl_2$
Chemical Name	Sodium Chloride
Physical Properties	
Molecular Weight	58.54
Form	solid
Color	white
Boiling Point (^{o}C)	804
Melting Point (^{o}C)	-
Specific Gravity	2.17
Solubility	soluble in water
Purity	> 99%

* From Merck Index