การบำบัดปรอทในน้ำเสียจากถังคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยการดูดซับด้วยถ่านกัมมันต์

นางสาวณิชยา โรจน์เพ็ญเพียร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ACTIVATED CARBON ADSORPTION

Miss Nichaya Lortpenpien

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
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Thesis Title	TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ACTIVATED CARBON ADSORPTION
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ณิชยา โรจน์เพ็ญเพียร : การบำบัดปรอทในน้ำเสียจากถังคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยกระบวนการดูดซับด้วยถ่านกัมมันต์. (Treatment of mercury in wastewater from condensate tank of petrochemical industry by activated carbon adsorption.)

อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. มนัสกร ราชากรกิจ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร. จินต์ อโณทัย, 91 หน้า.

งานวิจัยนี้ศึกษาวิธีการดูดซับปรอทในน้ำเสียจากถังคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยถ่านกัมมันต์ เพื่อหาวิธีการลดปริมาณปรอทที่ปนเปื้อนในน้ำทิ้งให้ได้ต่ำกว่า 5 μg/L ซึ่งเป็นค่ามาตรฐานของปรอทในน้ำทิ้งจากโรงงานอุตสาหกรรมของกรมควบคุมมลพิษ ในการศึกษานี้ได้เลือกถ่านกัมมันต์ 3 ชนิด ได้แก่ NORIT GAC 1240, CGC-12, และ MERSORB ®LW ซึ่งถ่านกัมมันต์ 2 ชนิดแรกนั้นเป็นถ่านกัมมันต์ธรรมดา ส่วน MERSORB ®LW นั้นเป็นถ่านกัมมันต์เจือกำมะถัน ซึ่งมีความจำเพาะกับปรอท โดยทำการศึกษาปัจจัยที่มีผลต่อการดูดซับ และค่าการออกแบบ เพื่อนำไปประยุกต์ใช้งานจริง การทดลองนั้นแบ่งเป็น 2 ส่วนในส่วนแรกเป็นการทดสอบแบบกะ ได้แก่ ค่าความเป็นกรดด่าง เวลาสมดุล และปริมาณของถ่านกัมมันต์ เพื่อหาไอโซเทอมการดูดซับ และคัดเลือกถ่านกัมมันต์และสภาวะที่เหมาะสม ในส่วนที่สองนั้นเป็นการทดสอบแบบคอลัมน์ โดยทำการศึกษาระยะเวลาสัมผัสในชั้นกรองว่าง เพื่อหาค่ากำหนดการออกแบบสำหรับนำไปใช้งานจริง ผลการทดสอบแบบกะพบว่าการดูดซับปรอทใช้เวลา 12 ชั่วโมงในการเข้าสู่สมดุล ประสิทธิภาพในการดูดซับปรอทของถ่านกัมมันต์ NORIT GAC 1240 เกิดได้ดีที่สุดพีเอช 2 โดยลักษณะการดูดซับเป็นไปในลักษณะที่ไม่ชอบ การอธิบายพฤติกรรมการดูดซับโดยอาศัยสมการของ Freundlich Isotherm นั้นทำได้ไม่ดีนัก เนื่องจากการรบกวนของสารมลพิษอื่นๆในน้ำเสียที่มีความเข้มข้นสูงกว่าปรอทมาก ส่วนผลการทดสอบแบบคอลัมน์ที่ระยะเวลาสัมผัสแบบชั้นกรองว่าง 2 ชั่วโมง ซึ่งเท่ากับระบบถังกรองถ่านกัมมันต์จริงในอุตสาหกรรมปิโตรเคมีพบว่า NORIT GAC 1240 มีความสามารถในการดูดซับปรอทสูงสุดเท่ากับ 111.3 ไมโครกรัมต่อกรัมถ่านกัมมันต์ซึ่งใกล้เคียงกับที่ทำนายจากสมการไอโซเทอมชี้ให้เห็นว่า NORIT 1240 มีความคัดเลือกเฉพาะกับปรอทค่อนข้างสูง สัดส่วนของน้ำเสียที่ผ่านการกรองต่อปริมาตรของถ่านกัมมันต์เมื่อเกิดการเบรคทรูมีค่าเท่ากับ 372.7 ซึ่งหากนำไปประยุกต์ใช้กับระบบจริงของอุตสาหกรรมปิโตรเคมี ซึ่งมีน้ำเสียจริงเข้าระบบที่อัตราไหล 8 ลูกบาศก์เมตรต่อวัน จะสามารถใช้งานได้ 30.7 วันโดยเสียค่าใช้จ่ายของถ่านกัมมันต์เท่ากับ 300 บาทต่อลูกบาศก์เมตรของน้ำเสีย

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ณิชยา โรจน์เพ็ญเพียร

ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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NICHAYA LORTPENPIEN: TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ACTIVATED CARBON ADSORPTION ADVISOR: ASST. PROF. MANASKORN RACHAKORNKIJ, Ph.D. CO-ADVISOR: ASSOC. PROF. JIN ANOTAI, Ph.D., 91 pp.

In this research the mercury adsorption from petrochemical industry by activated carbon was studied. The purpose of this study was to investigate mercury method to reduce the concentration of mercury in wastewater to 5 μg/L, according to the industrial effluent standard from Pollution Control Department, Thailand. Three activated carbons which were NORIT GAC 1240, CGC-12, and MERSORB ®LW were tested. NORIT GAC 1240 and CGC-12 were ordinary activated carbon, but MERSORB ®LW was an activated carbon impregnated with sulfur which was specific to mercury. Factors of mercury adsorption and design criteria were required for application in the real treatment unit. Adsorption tests were divided into two parts which were batch and column adsorption tests. The first part was batch test, pH, equilibrium time, and amount of activated carbon were studied so as to plot isotherm and select the suitable adsorbent and optimum conditions. In the continuous test, empty bed contact time was investigated to determine the design criteria for real application. Results from batch test showed that adsorption reached an equilibrium within 12 hours, NORIT GAC 1240 was the most appropriate adsorbent at pH 2, and it was unfavorable adsorption. Freundlich isotherm cannot be explained a mechanism of mercury adsorption directly, because other substances which were more concentrated than mercury can compete and interrupt the adsorption process. In continuous test, 2 hour empty bed contact time (EBCT) was set at the same as in the mercury treatment unit of the plant. Results indicated that NORIT GAC 1240 had a maximum adsorption capacity 111.3 μg/g which was closed to the calculation from adsorption isotherm. The outcomes specified that NORIT 1240 was highly selective to mercury. At breakthrough point, ratio of treated wastewater to amount of activated carbon was 372.7. When this design was applied in the real adsorption column which had inlet wastewater 8 m^3/day, the process can operate 30.7 days and cost of the treatment was 300 Baht/ m^3 wastewater.

Field of Study : Environmental Management Student's Signature Nichaya

Academic Year : 2010 Advisor's Signature

Co-advisor's Signature

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CHAPTER I

INTRODUCTION

1.1 General introduction

The advance of technology leads to the facilities and serious problems. Wastewater is one of the important and urgent troubles, especially the heavy metal contaminated wastewater. Mercury is the high toxic compound causing the adverse effect for organisms and environment. The issue of mercury contamination has received considerable critical attention. To meet the permitted limits 5 ppb from the Pollution Control Department, effective treatment techniques have been proposed for mercury removal in wastewater. Ideally, the best method should balance the economic, social, and environmental aspects. Previous research showed that several processes can remove mercury from wastewater such as chemical precipitation, ion exchange, coagulation, solvent extraction and membrane processes, and adsorption. Adsorption is one of the most common method, because it is an economically feasible alternative, simple, able to achieve a low limit of treatability, effective, widely applicable, efficient, and creates relatively little sludge. Activated carbon is a commonly use for adsorption processes. Although activated carbon can adsorb mercury in wastewater, the efficiency is not high enough; therefore, many researchers tried to apply the activated carbon with different techniques which are chemical, physical, and biological modification. They found that chemical modification by impregnation of foreign material on activated carbon has a higher mercury adsorption capacity. There are a number of chemicals can impregnate on activated carbon. Sulfur is one of the most suitable alternatives. Several researchers have reported sulfur impregnated activated carbon is high efficiency for mercury removal. However, research has consistently shown that that the available knowledge about the mechanism of mercury adsorption has not attained an adequate understanding (Wang, 2009),especially the aqueous mercury adsorption, because most studies in the field of mercury adsorption by sulfur activated carbon have only focused on removal of mercury vapor. This study aimed to address the following research question: the impregnated activated carbon is appropriate for removing aqueous mercury from condensate wastewater. The main purpose of this investigation is to study the favorable condition for adsorption process by using commercial activated carbon and sulfur impregnated activated carbon.

1.2 Objectives

To study the adsorption process of mercury contaminated wastewater from condensation process by using commercial activated carbon and sulfur impregnated activated carbon and to evaluate economic value of mercury adsorption by activated carbon adsorption.

1.3 Scopes

1. Use commercially available activated carbons which are ordinary activated carbon (CGC-12 and NORIT GAC 1240) and sulfur impregnated activated carbon (MERSORB^R LW mercury adsorbent).

2. Work with real wastewater from condensate tank of petrochemical industry.

3. Work at room temperature condition.

4. Target pollutant is mercury

5. Study in batch and column test

1.4 Hypotheses

Sulfur impregnated activated carbon can adsorb mercury contaminated wastewater from petrochemical industry better than ordinary activated carbon and may treat mercury to have the concentration less than 5 ppb.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Mercury

Mercury (Hg) is one of the most hazardous chemical in the list of pollutants contained in the Water Framework Directive. It naturally occurs in several forms (ATSDR, 1999), and can be founded in the rocks, soils, sediments and the atmosphere (Bhakta, 2009) including in petroleum. Mercury compounds are widespread distributed in the environment. For instance, inorganic mercury from industrial and mining process enters the air. Mercury compounds from natural deposits, wastes, and volcanic activity enter the water or soil. Bacteria can form methylmercury which is the most toxic form and this compound is found in water and soil causing the contamination in the fish tissues (ATSDR, 1999) and having a potential bioaccumulation in the food chains. The issues of mercury contamination in the environment are critical, because mercury compounds are persists in the environment for a long time and resulting in the trouble in long term (Bhakta, 2009). The famous case occurs in the late 1950s and 1960s when a large number of people in Minamata Bay, Japan are suffered from mercury poisoning as called Minamata disease (Zhang, Nriagu, and Itoh 2005)**.** Besides Minamata, mercury compounds are related to damage of sensitive organs such as brain, kidney, including developing fetus. These compounds lead to irritability, shyness, tremors, change in vision or hearing, and memory problems (ATSDR, 1999). Since each form of mercury has its unique characteristic, the studies of varied properties and the relationships between mercury compounds in liquid and gaseous phase.

2.1.1 Properties of mercury

Mercury is found in crude oil, natural gas, soil, and water. Table 2.1 is shown typical properties of mercury.

Table 2.1 Properties of mercury (Wilhelm, 2001)

Properties	Expressions
Symbol	Hg
Synonyms	Quicksilver, hydrargyrum, and liquid silver
Standard atomic weight	$200.59 g\cdot mol^{-1}$
Element category	Transition metal
Physical state	Liquid
Odor	Odorless
Vapor pressure	0.002 mmHg at 25◦C
Vapor density	7.0
Boiling point	356.7 ◦C
Melting point	-38.87 ◦C
Specific density	13.59

Table 2.2 Properties of mercury compounds in crude oil (Wilhelm, 2001)

Mercury compounds	State	Volatility	Solubility (ppm) at 25°C		Amount in crude oil
			Water	Oil	
Elemental (Hg^0)	Liquid	Boiling point 357°C Vapor pressure $25 mg/m^3$(25°C)	0.05	2	>50%
Dimethylmercury ($(CH_3)_2Hg$)	Liquid	Boiling point 96°C	?	miscible	< 1 %, (10-50 %- not conclusive)

Mercury compounds	State	Volatility	Solubility (ppm) at 25°C		Amount in crude oil
			Water	Oil	
Mercuric chloride($HgCl_2$)	Solid	Boiling point 302°C	70,000	>10	10-50 %
Mercuric sulfide (HgS)	Solid	Sublimes under vacuum; decomposes 560°C	0.01	<0.01	Suspended
Mercuric oxide (HgO)	Solid	Decomposes 500°C	50	Low	Rarely detected
Methyl mercuric chloride (CH_3HgCl)	Solid	-	>10,000	1,000	< 1%- not conclusive

Table 2.3 Characteristic of mercury compounds in crude oil and gas condensate (Wilhelm, 2001)

Form of mercury	Characteristic
Dissolved elemental mercury (Hg^0)	It is soluble in crude oil and hydrocarbon liquids in atomic form to approximately 2 ppm. It is adsorptive on metallic components (pipes and vessels), suspended wax, sand and other suspended solid materials in liquids.
Dissolved organic mercury compounds (RHgR and RHgY, where R = CH_3, C_2H_5, etc., and Y = Cl-, etc.)	They are highly soluble in crude oil and gas condensate. They are similar to elemental mercury in adsorptive tendencies but differ in their boiling points and solubilities and thus they are partition to distillation fractions in a different fashion from Hg^0 . They include dialkylmercury (i.e., dimethylmercury, diethylmercury) and monomethylmercury halides (or other inorganic ions). Dialkylmercury compounds have been detected in condensates, but their natural abundance across classes of

	hydrocarbon liquids is unknown. Monoalkylmercury is seldom detected in oil and condensate, inferring that the dialkyls are likewise not abundant.
Inorganic (ionic) mercury salts ($Hg^{2+}X$ or $Hg^{2+}X_2$, where X is an inorganic ion)	They are soluble in oil and gas condensate but preferentially partition to the water phase in primary separations. Mercuric chlorides have a reasonably high solubility in organic liquids (about 10 times more than elemental mercury). Ionic salts also may be physically suspended in oil or may be attached (adsorbed) to suspended particles.
Complexed mercury (HgK or HgK_2)	They exist in hydrocarbons as a complex, where K is a ligand such as an organic acid, porphyrin or thiol The existence of such compounds in produced hydrocarbons is a matter of speculation at present depending in large part on the particular chemistry of the hydrocarbon fluid.
Suspended mercury compounds	The most common examples are mercuric sulfide (HgS) and selenide ($HgSe$), which are insoluble in water and oil but may be present as suspended solid particles of very small particle size. They typically contain suspended mercury compounds or mercury adsorbed on suspended solids or both
Suspended adsorbed mercury	This category includes elemental and organic mercury that is not dissolved but rather adsorbed on inert particles such as sand or wax. Suspended adsorbed mercury and suspended mercury compounds can be separated from liquid feeds to the plant by physical separation techniques such as filtration or centrifugation.

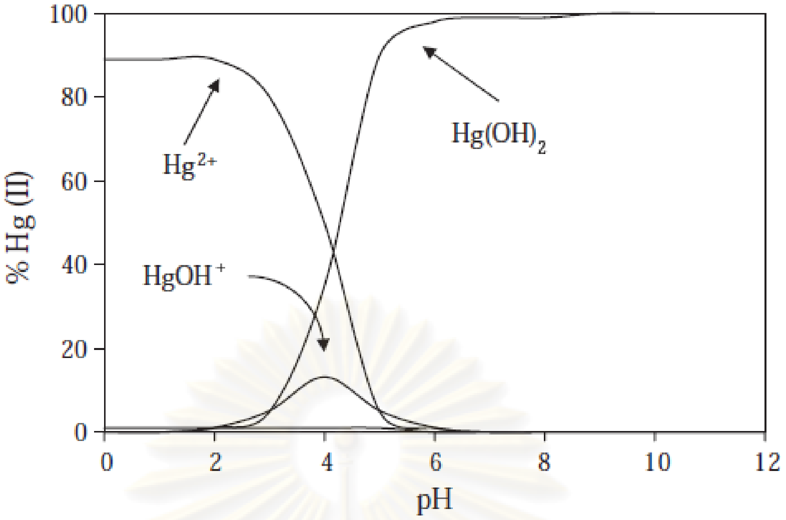

Figure 2.1 Distribution diagrams of mercury species established with PSEQUAD software for an initial concentration of Hg(II) = 80 mg/L. (Zhang, et al. 2005)

2.1.2 Fate and transport of mercury to environment

Mercury occurs naturally in the environment. The main steps of mercury cycle involve:

- Mercury emits from natural sources such as rocks, soils, surface water, volcanoes, and anthropogenic activities which are mining ore, combustion coal and waste, and manufacturing processes. The process causes elemental mercury (Hg^0) releasing to the atmosphere.
- Gaseous mercury moves to the atmosphere.
- Mercury can combine with water and then deposits in the land and surface water.
- Elemental mercury converts to insoluble mercury sulfide by photochemical oxidation.
- Mercury precipitates or converts into more soluble form; for example inorganic mercury converts into organic form by microorganisms. This step is significant, because methylmercury
- Mercury enters the atmosphere or bioaccumulation in the food chains. The possible pathways are the methylmercury –processing bacteria were consumed by the higher organisms and the bacteria release the methylmercury into the water, then methylmercury adsorb to plankton which are can be consumed by the next trophic levels such as small fish. Small fish were eaten by larger fish finally fish were eaten by human or animals.

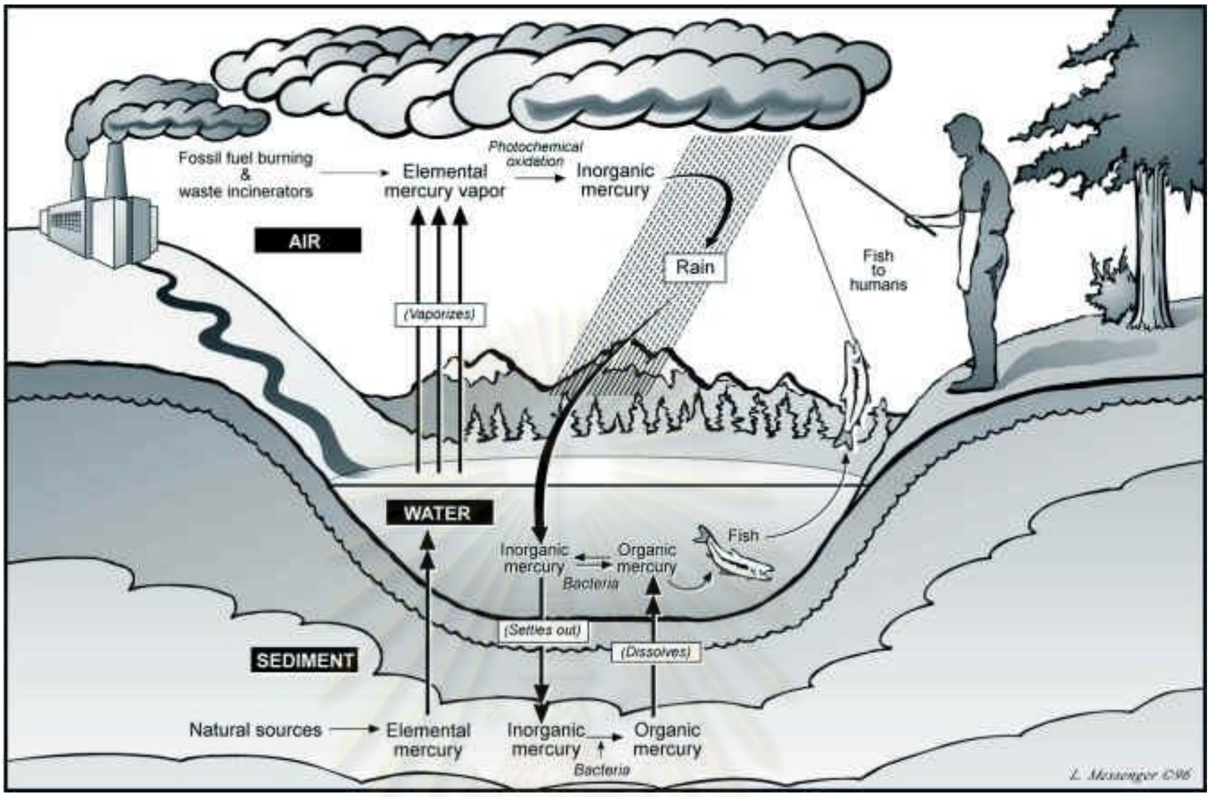

Figure 2.2 Mercury Cycle (http://www.mercury.utah.gov/atmospheric_transport.htm)

2.1.3 Hazard of mercury

Mercury is one of the most hazardous agent causing the bioaccumulation and biomagnification. Bioaccumulation occurs when the rate of intake contaminants more rapid than the rate of elimination, then they increases the toxic levels. Biomagnification occurs when chemicals becomes more concentrated when they pass through a food chain.

2.1.3.1 Route of entry:

Mercury absorbed through skin, dermal contact, inhalation, and ingestion and may cause damage to blood, kidneys, liver, brain, peripheral nervous system, central nervous system (CNS).

2.1.3.2 Acute effect

Mercury causes skin and eye irritation and tissue damage especially, mucous membranes of eye, mouth, and respiratory tract.

2.1.3.3 Chronic effect

Mercury is toxic to blood, kidneys, liver, brain, peripheral nervous system, central nervous system (CNS)

2.1.4 Application of mercury

Mercury compounds are widely used in various applications. Medicine, cosmetics, chlorine production, caustic soda, gold and silver mining, chlor-alkali, paint, pulp and paper, oil refining, electrical, rubber processing and fertilize, barometers, thermometer, electrical equipment, dental preparations, and fungicide and bactericide in agriculture.

2.2 Mercury removal

Mercury is one of the most toxic substances for organisms and environment. Previous research showed several processes can remove mercury from wastewater such as chemical precipitation, ion exchange, coagulation, solvent extraction and membrane processes, and adsorption.

Table 2.4 Summary of aqueous mercury treatments (EPA 625-R-97-004)

Treatment methods	Initial concentration (μg/L)	Achievable concentration (μg/L)	Percent removal (%)
Sulfide precipitation (+filtration)	300-50,000	10-100	95-99.9%
Co-precipitation	50-500	0.5-5.0	94-98%
Activated Carbon	10-10,000	0.5-20	80%
Starch and Xanthate	10-100	5-20	80%
Ion Exchange	200-70,000	0.5-5.0	95-99.9%
Reduction	1,800-5,000	10- >100	95-98%
Membrane separation	1,500-9,000	-	90%

2.2.1 Sulfide Precipitation

This method uses sulfide such as sodium sulfide, sodium hydrosulfide, and magnesium sulfide for converting the soluble mercury to the insoluble form:

$$Hg^{2+} + S^{2+} \longrightarrow HgS(s)$$

There contains several steps: pH adjustment, flocculation, and solid separation, respectively. In case of initial mercury concentration is more than 10 ppm, this technique can achieve 99.9 % removal. However, it is unsuitable for the pH of wastewater above 9.

Sulfide precipitation has many disadvantages which are the formation of insoluble mercury sulfide species when it has excessive dosage of sulfide, the difficulty of sulfide level monitoring, clarification, and sludge processing, the toxicity of residual sulfide, and the requirement for sulfide sludge disposal. Although the sulfide sludge was sent to landfill, mercury can resolubilize (Hansen and Stevens, 1992) then resulted in mercury contamination in groundwater.

2.2.2 Coagulation/co-precipitation

This method can be used for both inorganic and organic mercury. Coagulants are aluminum sulfate (alum), iron salts, and lime. The aluminum sulfate and iron usually use adsorptive co-precipitation for mercury removal mechanism (Patterson et al.,1992) The process is an ion adsorbed into the bulk solid; therefore, the optimization of the bulk solid formation and pH control can help to increase the treatment performance. The reason why the pH manipulation acts as an important step is because it optimizes bulk solid surface change and soluble mercury speciation.

2.2.3 Xanthate Treatment

Xanthates are a family of compounds prepared by mixing organic matter in alkaline condition with carbon disulfide. Similar to the reaction between sodium sulfide and heavy metals, the xanthates reacted with metals to form metal-xanthate complexes, coagulation, and subsequent flocculation of metal xanthate complex by the polymer. Due to the low solubility product of metal-xanthate complexes, the xanthate treatment had been reported to have high removal efficiency for heavy metals in wastewater (Rao,1971;Wing et. al.,1974; Bricka, 1988).

2.2.4 Ion Exchange Treatment

Ion exchange is one of the useful aqueous mercury treatments, especially at the concentration 10 to 100 ppb. This method replaces the ion of contaminants such as mercuric chloride in the aqueous solution by other ions. Resin has the functional groups that can interact with both cation and anion depending on the types of resin. Because this process is a reversible chemical reaction, it can be reversed when the binding force between the functional group and the attached ion is loose.

2.2.5 Chemical Reduction

This process can remove the ionic mercury in the solution. Aluminum, zinc, iron, hydrazine, stannous chloride, and sodium borohydride are the reducing agents for mercury reduction. In case of stannous chloride, the reaction is

$$HgCl_2^0 + Sn^{+2} = Hg^0 + 2Cl^- + Sn^{+4}$$

This reaction shown that if there is an adequate stannous chloride for reducing the dissolved mercury (II) in the solution, mercury will become elemental mercury.

2.2.6 Membrane Separation

The principle of the method can be applied for the mercury treatment. A membrane or semi-permeable barrier is used for separating the selected contaminants from the water. This membrane has the specific properties that allow only some compounds to pass, but it blocks the others. This process includes the ultrafiltration, charged filtration, crossflow microfiltration, magnetic filtration, and reverse osmosis.

2.2.7 Biological treatment

Biological treatment refers to the capability of mercury-resistant microorganisms or plants to assimilate or accumulate mercury compounds, or convert from form of mercury to others (Stepan *et al*. 1993). Generally, this process is not expensive, but it is a long term of remediation. Several bacteria can detoxify mercury compounds by converting soluble ionic mercury compound into elemental mercury by using mercuric reductase. Some bacteria may change ionic mercury compound into methylmercury which can be converted into demethymercury or elemental mercury and methane.

2.2.8 Adsorption

Adsorption is a powerful process for removing mercury from wastewater (Zhang, Nriagu, and Itoh, 2005;Inbaraj and Sulochana, 2006) because it is inexpensive, widely applicable, efficient, and creates relatively little sludge (Kannan and Rengasamy, 2005; Anoop Krishnan and Anirudhan, 2002).

Adsorption is a natural process which accumulates a dissolved substance at or near an interface relative to its concentration in the bulk solution and it occurs when the attractive forces at the surface of adsorbent are higher than liquid. This process plays an important role in the transport, bioavailability, and fate of contaminants and naturally occurring trace compounds in both natural and engineered aquatic systems (Eddy, 2003). The process can occur at solid-solid, gas-solid, gas-liquid, liquid-liquid, or liquid-solid interfaces. Adsorption is divided into two methods that are physisorption and chemisorptions. Both methods occur when the molecules in the liquid phase attached to the solid surface resulting from the attractive forces at the solid surface of adsorbent. This force overcomes the kinetic energy of the liquid of adsorbate.

Physisorption or physical adsorption resulting from energy differences or electrical attractive forces like weak van der Waals forces. When this interaction takes place, the adsorbate molecules are physically fastened to the adsorbent molecules. This force is multilayered causing each molecular layer can form on top of the previous layer. The number of layers helps to indicate the contaminant concentration. The more molecular layers occur, the higher concentrated contaminants adsorbed.

Chemisorption or chemical adsorption happens when the reaction between the adsorbate and the adsorbent. This process is one molecule thick and irreversible, because it has to require energy for both perposes that are the formation of a new chemical at the surface area of adsorbent and the reverse the process. On the other hand, physisorption is the reversible process depends upon the strength of attractive forces between adsorbate and adsorbent. The desorption occurs when the attractive forces are weak (Cheremisinoff, 1993)

Mercury adsorption consists of the three steps: macro transport, micro transport, and sorption. Macrotransport or bulk diffusion occurs when adsorbate from the solution diffuse to the film around the activated carbon, then it diffuses through the film and internal pore respectively. Finally, adsorbate is adsorbed at adsorption site.

Table 2.5 Comparison between physical and chemical adsorption

Physical adsorption	**Chemical adsorption**
Low heat of adsorption (<2 or 3 times latent heat of evaporation)	High heat of adsorption (>2 or 3 times latent heat of evaporation)
Non specific	Highly specific
Monolayer or multilayer adsorption	Only monolayer adsorption
No dissociation of adsorbed species	May involve dissociation
Relatively low temperatures	Possible over a wide range of temperature
Rapid, non-activated, and reversible	Activated, may be slow, and irreversible
No electron transfer although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface (strong chemical bonds)
Molecules are adsorbed without change in their chemical bonds	Adsorbed molecules will change in chemical bonds

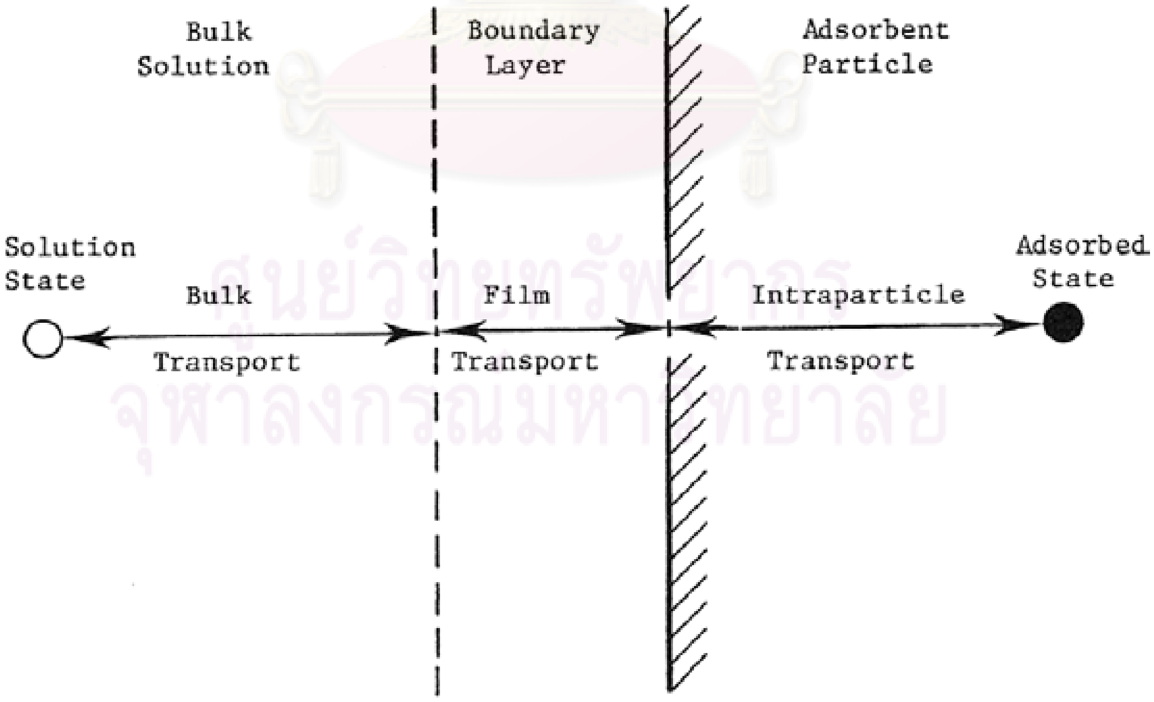

Figure 2.3 Mass transfer

2.2.8.1 Factors of adsorption process

There are several factors considering important for the adsorption capacity which are pH (Dias, 2007; Zabihi, 2010), total Hg(II) (Blankenship, 1984), specific surface area (Ruthven, 1984;Dias et al., 2007), the type of precursor, the temperature during the activation stage, the frequency of regeneration (Ruthven, 1984), the chemistry of the metal ion (speciation) or metal ion complex, the surface composition (oxygen), the size of adsorbing species (hydrated ions about 1.0–1.8 nm), and heteroatoms in activated carbon (Dias et al., 2007). The function of pH plays a significant role in the adsorption capacity, because it influences the forms of metal ions and the surface charge of activated carbon. The surface charge can be a positive charge when the pH of solution is lower than the pH of point of zero charge (pHpzc) and can be a negative charge when the pH is higher than pHpzc; therefore, a pH increase resulting in an improvement in metal ion adsorption (Le Cloirec et al., 2008). In 1984, Blankenship et al. studied the removal capacity of 11 different types of commercial activated carbon for treating mercury(II) from synthetic waste. They found that Nuchar SA and Nuchar SN showed the potential to remove mercury (>99.9) in pH 2.5 to 11. Some activated carbons have optimal pH about 4 to 5. On the other hand, the capacity of mercury removal drastically decreases in the pH condition greater and less than 4 to 5. Specific surface area is related to the availability of adsorption site, on the other hand the pore size and the distribution of micropores are associated with the composition of the activated carbon. In 2004 Moreno-Castilla pointed to the molecular size, solubility, pKa, and nature of the substituents (only aromatic adsorbates) mainly influence the adsorption process of activated carbon, because the molecular size can determine the accessibility of the adsorbate to the pore of the activated carbon, the solubility determines the degree of hydrophobic interactions between the adsorbate and the carbon surface and pKa mainipulates the dissociation of the adsorbate (only an electrolyte). In case of aromatic, the substituents have the capability to release electrons, which affects the non-electrostatic interactions between the adsorbate and the surface of activated carbon (Dias et al., 2007). Dias et al. (2007) reviewed the literature from the period and found that the heteroatoms in the activated carbon such as oxygen, hydrogen, nitrogen, and sulfur are influential in the chemistry of the activated carbon surface, because they are relevant to the charge and hydrophobicity, electronic density of the surface, and both electrostatic and non-electrostatic interactions.

2.2.8.2 Adsorption Isotherm Models

Adsorption isotherm is a principal instrument using for evaluating the feasibility of activated carbon usage. The adsorption isotherm relates to the amount of adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in solution. The constants for the adsorption isotherm determine the adsorption capacities of each activated carbon for different chemicals. There are several factors affecting the isotherm, which are carbon preparation and dosage, pH solution, temperature, and contact time. Carbon dosage should be enough for adsorption and the maximum adsorption capacity. Solution of pH is the essential factor, because adsorption process is pH dependent. Generally, high temperature provides a faster rate of diffusion of contaminants into the pores of adsorbent. The last factor is contact time, a sufficient contact time must be provided to reach adsorption equilibrium. Adsorption isotherm provides the useful information of the adsorbability of chemical to activated carbon, the weight of chemical adsorbed per unit weight of activated carbon, the degree of removal, and the pH effect.

2.2.8.2.1 The Freundlich Model

The Freundlich expression is an empirical model using for nonideal adsorption that involves adsorption on a heterogeneous surface. The Freundlich model is commonly presented as

$$q_e = K_F C_e^{1/n}$$

The equation can be linearized by taking loarithms

$$\log q_e = \log K_F + \frac{}{n}\log C_e$$

The constant K_F (mol g) and 1/n which related to the adsorption capacity and adsorption intensity of the adsorbent can then be evaluated from the intercept and slope of $\log q_e$ against $\log C_e$ plot.

2.2.8.2.2 The Langmuir Model

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, once an adsorbate occupied a site, no further adsorption can take place at this site. The Langmuir model is expressed as

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e}$$

where, q_{max} is the maximum amount of metallic mercury adsorbed (mol g)

K_A is the affinity coefficient of activated carbon for metal ions, coefficient in the Langmuir equation (mol)

q_e is the amount of metallic mercury adsorbed at equilibrium (mol g)

C_e is the equilibrium concentration (mol).

The constants q_{max} and K_A can be evaluated from the linear form represented by the equation

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + (\frac{1}{K_A q_m})\frac{1}{C_e}$$

A plot of $1/q_e$ versus $1/C_e$ results in a straight line with a slope of $1/\ K_A q_{max}$ and an intercept of $1/q_{max}$.

2.2.8.2.3 The Brunauer-Emmett-Teller (BET) model

The Brunauer-Emmett-Teller (BET) model extends the Langmuir model, which is a monolayer adsorption, to include multilayer adsorption phenomena.

The BET isotherm model is:

$$q_e = \frac{C_e\ q_{max}}{C_s\text{-}C_e \qquad - \quad C_e\ C_s}$$

The BET equation can be linearized as

$$\frac{C_e}{C_s\text{-}C_e\ q_e} = \frac{}{q_{max}} + (\frac{-}{q_{max}})(\frac{C_e}{C_s})$$

where, q_e is the amount adsorbed per unit weight of adsorbent ()

C_e is the concentration of solute remaining in solution at equilibrium

C_s is the saturation concentration of the solute

q_{max} is the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface

 is the constant expressive of the energy of the interaction with the surface.

A plot of C_e / C_s versus C_e /[(C_s – C_e) q_e] results in a straight line with a slope of [(-)/ q_{max}] and intercept of 1/K_B qmax.

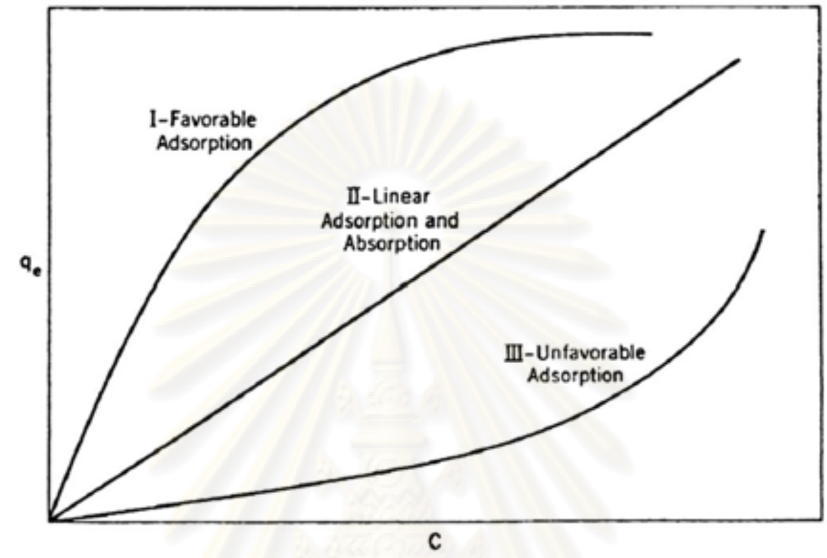

Figure 2.4 Adsorption isotherms

2.2.8.3 Adsorption column

Adsorption by granular activated carbon can be used in batch, column, and fluidized-bed operations. A continuous process utilizes adsorption capacity of activated carbon higher than a batch mode and results in more efficient and economical process. In addition, there are three main parameters influences on the granular adsorption design which are contact time, rate of carbon usage, and pretreatment. The contact time involves the amount of activated carbon used for adsorbing chemicals in the wastewater, equipment size, and the capital cost. The rate of carbon usage indicates how often the activated carbon must be replaced. The pretreatments which rely on the pH solution, suspended solid, and oil of the wastewater are required to reach the optimum adsorption process. This information cannot be provided by batch test; therefore, the column adsorption test performs. Column may accomplished by upflow or downflow. In case of downflow operation, the granular activated than a batch mode, because it operates more efficiently and economically. Column may accomplished by upflow or downflow. In case of downflow operation, the granular activated carbon acts as the adsorption and filtration, but it requires eliminating pretreatment filters and frequent backwashing. On the other hand, upflow operation takes the advantages of minimization of head loss, channeling, and fouling of granular activated carbon. The operating data for column adsorption test are carbon characteristics, column diameter, flow rate of wastewater, weight of carbon, inlet, outlet, and target concentration of contaminants. In this experiment, the purpose of column tests is to obtain breakthrough curves showing how the concentration of the effluent vanes varies with the volume of liquid treated. Breakthrough curve will increase when higher bed depth of column, lower flow rate and concentration of adsorbate, and smaller size of adsorbent to increase surface area for adsorption.

2.2.8.3.1 Adsorption column model

There are many methods for designing the column adsorption test such as scale-up approach and Bohart Adams model. The purpose of column tests is to obtain breakthrough curves showing how the concentration of the effluent vanes varies with the volume of liquid treated.

2.2.8.3.1.1 Scale-up approach

In 1966 Fornwalt and Hutchins developed the scale-up approach so as to design the column of carbon adsorption. This method relies on the data of a breakthrough curve from a column test. This column test can be laboratory or pilot scale which operates at the same flow rate and contact time as the design column. The contact time can be estimated from the breakthrough volume, the solute concentration, the maximum solid-phase concentration, and other relevant data. The major advantages of the design procedure are to simplicity and little experimental information required.

T_c = contact time and equal to $\varepsilon\ Q_b$

ε = the pore fraction

The bed volume of the design column is determined by

$$\text{Bed volume (BV)} = \frac{Q}{Q_b}$$

Q = flow rate of design column in terms of bed volumes per unit time

Q_b = flow rate of test column in terms of bed volumes per unit time (usually 0.2-3.0 bed volumes per hour). This value results from the assumption that the same contact time (T_c)

of test and design column given the same volume of liquid treated per unit mass of adsorbent ($\hat{V}_B$) of test and design column

$T_c = \varepsilon \ Q_b$

ε = the pore fraction

The mass or weight of the adsorbent is given by

$$M = \ V \quad \rho_s)$$

ρ_s = the adsorbent bulk density

The volume of liquid treated per unit mass of adsorbent ($\hat{V}_B$) is computed from

$$\hat{V}_B = \frac{V}{M}$$

V_B = the breakthrough volume from the breakthrough curve of the test column. This value is determined for the allowable effluent solute concentration (C_a).

M = the mass of the adsorbent in the test column.

The mass of adsorbent exhausted per hour (M_t) of the design column is determined by

$$M_T = \frac{Q}{\hat{V}B}$$

Q = the design liquid flow rate

The breakthrough time (T) is given by

$$T = \frac{M}{M}$$

M = the mass of adsorbent in the design column.

The breakthrough volume from the breakthrough curve of the test column for the allowable breakthrough concentration (V_B) is computed from

$$V_B = QT$$

when activated carbon particles are placed in a solution containing an organic solute and the slurry is agitated or mixed to give adequate contact, the adsorption of the solute occurs. The solute concentration will decrease from an initial concentration, C_0, to an equilibrium value, C_e, if the contact time is sufficient during the slurry test. Usually, equilibrium occurs within about 1 to 4 hr. By employing a series of slurry tests, it is usually possible to obtain a relationship between the equilibrium concentration (C_e) and the amount of organic substance adsorbed (x) per unit mass of activated carbon (m).

2.2.8.3.1.2 Bohart Adams model

Bohart Adams model is used for describing the breakthrough curve

$$\frac{C_t}{C_0} = \frac{}{\exp\left(\frac{{}_0kH}{v}\right) kC_0t}$$

C_0 = the feed mercury concentration (

C_t = the effluent mercury concentration (mg/l)

N_0 = the adsorption capacity of the bed (mg/l)

k = the rate constant (l/mg h)

H = the bed height (cm)

v = the linear flow rate (cm/h) obtained by dividing the flow rate by the column section area.

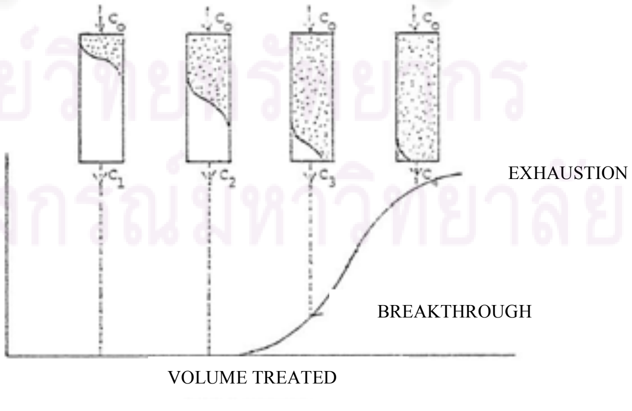

Figure 2.5 Mass transfer steps in adsorption by activated carbon

2.3 Activated carbon

Numerous studies have attempted to investigate mercury adsorption by activated carbon (Anoop Krishnan and Anirudhan, 2002; Khalkhali, 2005; Kannan and Rengasamy, 2005). Presently, activated carbon is the most widely used adsorbent. It is categorized as a physical and nonpolar adsorbent. It can be produced from a wide variety of carbonaceous materials such as bones, coals, wood dust, peat, nutshells, and wood charcoal can produce to be activated carbon. It has an extremely high internal surface area. A total surface area range of 450-1,800 m^2/gram has been studied. Typically, a commercial activated carbon has a surface area about 1,000 m^2 per gram. It means that it can accumulate a large number of contaminants. Chun et al. (2007) demonstrated that activated carbon (AC) is an efficient adsorbent for the removal of various contaminants in aqueous and gaseous phase, due to its high efficiency and easy application (Mohan, 2001), high surface areas, well-developed internal microporosity structure, and several surface functional groups (Chingombe, 2005; Zabihi et at., 2010), resistant structure to acidic and basic condition, stable structure at high temperature including above 1000K, several physical forms such as granules, pellets, and fibers, modifying hydrophilicity, simple recover the active phase by burning the carbon support (Marsh et al., 2006) . In his major study, Świątkowsk 999 identifies a typical activated carbon has an extensive internal surface area implied by high specific surface areas (commonly in the range of 1000-1500 m^2/g), a highly developed porosity, a high degree of surface reactivity and a large capacity for adsorbing chemicals from liquids or gases. From its utilities, the demand of activated carbon has expanded greatly in an attempt to solve the hazardous problems rising due to the contamination of water supplies and flue gases Świątkowski, 999 . The characteristics of various activated carbons are considered for the application. Zabihi (2010) identifies that the characteristics of activated carbon depend on the physical and chemical properties of the raw materials and the activation method. According to the particle shapes and size of activated carbon, it is divided into five group; powdered, granulated, spherical, pelletized or fibrous activated carbons Świątkowski, 999 . Granular activated carbon is an effective and common adsorbent system for industrial wastewater treatment(Capsule Report: Aqueous Mercury Treatment, 1997) due to its high surface area to volume ratio; therefore, it can accumulate abundant contaminates (Granular activated carbon, 1992). In 1999, Świątkowsk reported that granular activated carbon is an option that can remove mercury from water. Moreover, commercial activated carbons such as powder and granular have been applied to remove mercury (Blankenship, 1984).

In the adsorption process, the interactions between the surface of carbon and the adsorbate occur. These interactions can be electrostatic or non-eletrostatic forces. In case of the adsorbate is an electrolyte, the electrostatic interaction happen when adsorbate dissociates in aqueous solution. There are three main factors that cause this force can be attractive or repulsive: charge density of carbon surface, chemical characteristics of the adsorbate, and the ionic strength of the solution. Other interactions are non-electrostatic forces that can be van der Waals or hydrophobic including the hydrogen bonding. These interactions are attractive forces (Dias et al., 2007).

The issue of adsorption mechanism has received considerable critical attention. Dias et al. (2007) highlight three mechanisms that explain how the ionic species can attach to the surface of activated carbon in order to remove these ions from the solution. First mechanism is based on the electrostatic interaction between the adsorbate and the adsorbent. This process relies on the function of the surface areas of activated carbon, especially oxygen surfaces complexes (ion-exchange). Second mechanism states that raised adsorption potentials-like the narrowest microporosity- may cause adsorb and hold ions. Third mechanism indicates that the hard and soft acids and bases concept resulting in the amphoteric nature of carbon surfaces (Dias et al., 2007). Not only electrostatic, van der Waals, and hydrophobic interactive, but also the chemical interaction which is the relationship between the chemical groups at the surface of carbon and the solute (Gaspard, 2006). United States Environmental Protection Agency (1997) reported that chemisorption help to enhance the mercury removal. Although the activated carbon has a variety of application, it has some limitations, for example, it is not proper to adsorb toxic gas with low molecular weight, low boiling point, and polarity, because of its low capacity and limited retentivity of adsorbate (Marsh et al., 2006). There are several studies that are attempted to overcome the limitation and add the additional capacities to the activated carbon. Yin, Aroua, and Daud (2007) carried out a number of investigations into the modification of activated carbon. The purpose of modification is to develop affinity of activated carbon for contaminants from various industrial wastewater. The modification of activated carbon is divided into three major groups that are physical, chemical, and biological characteristics.

In the chemical characteristic, it refers to acidic, basic, and impregnation of foreign material. Heat treatment and bioadsorption are related to the physical and biological modification respectively. Each modification technique has the advantages and disadvantages as follows in the Table 2.6.

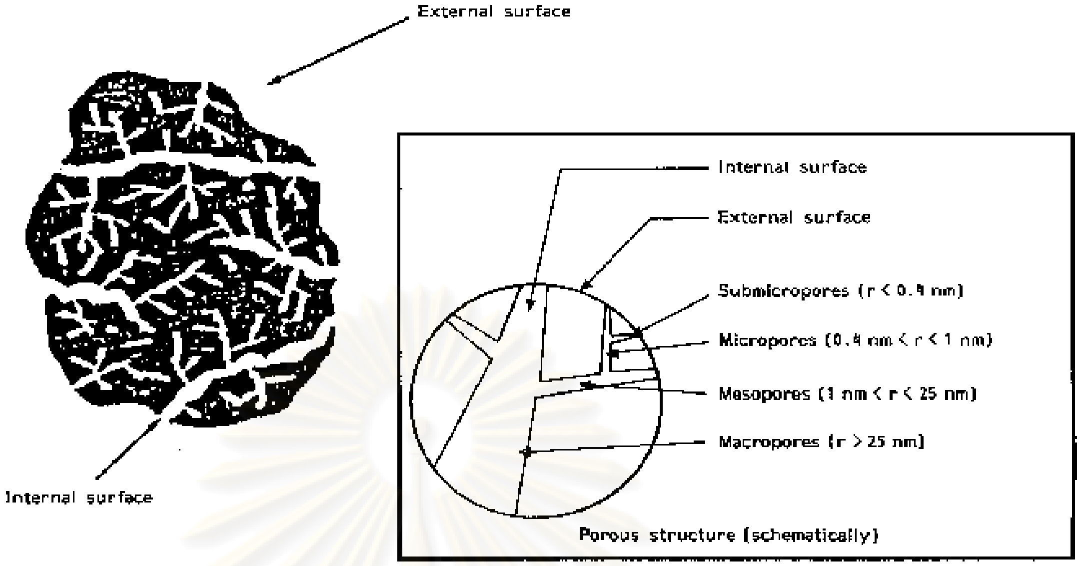

Figure 2.6 The structure of activated carbon (http://www.activated-carbon.com/enviro.html)

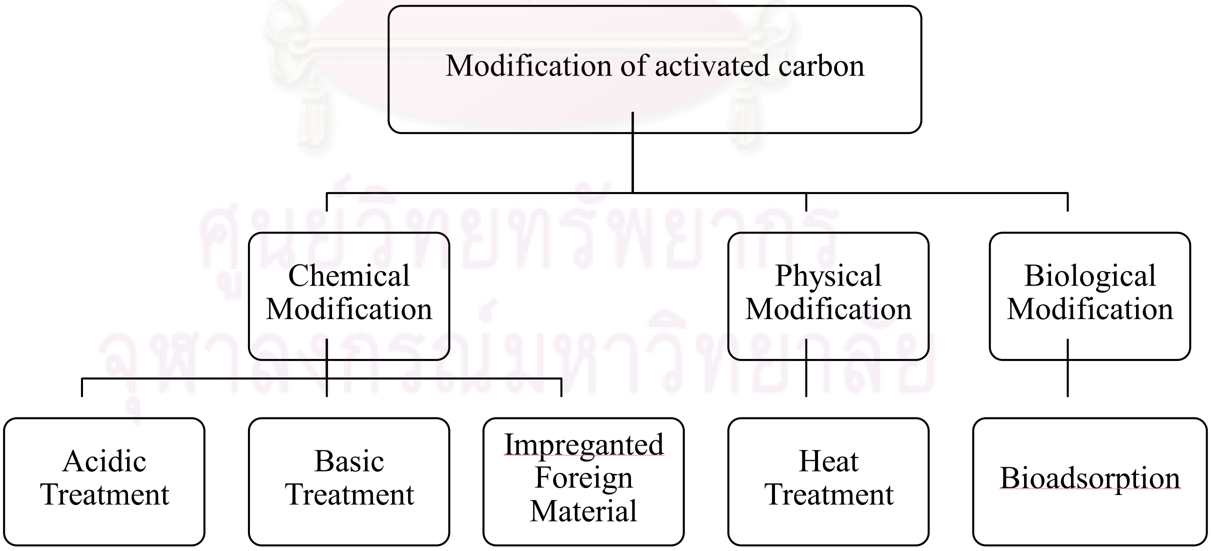

Figure 2.7 Chart of categories of activated carbon modification techniques

Table 2.6 Lists of advantages and disadvantages of the modification techniques (Yin et al., 2007)

Modification	Treatment	Advantages	Disadvantages
Chemical characteristics	Acidic	Increases acidic functional groups on activated carbon surface and chelation ability with metal species	May decrease BET surface area and pore volume Has adverse effect on uptake of organics May give SO_2 (from the treatment with H_2SO_4) or NO_2 (from the treatment with HNO_3)
	Basic	Enhances uptake of organics	May decrease the uptake of metal ions
	Impregnation of foreign material	Increases in-built catalytic oxidation capability	May decrease BET surface area and pore volume
Physical characteristics	Heat	Enhances BET surface area and pore volume	Decreases oxygen surface functional groups
Biological characteristics	Bioadsorption	Bacteria can help to prolong activated carbon by rapid oxidation of organics.	Impede diffusion of adsorbate by biofilm encapsulating activated carbon

From Table 2.6, it is showed that impregnation of foreign material techique can be a suitable method to enhance the adsorption capacity of the activated carbon. The definition of impregnation is a fine distribution of chemicals on the internal surface of activated carbon (Schäfer). Schäfer highlights the principal three reasons that impregnation proposes the additional capacities which are   optimization of existing properties of activated carbon, synergism between activated carbon and impregnating agent, and use of activated carbon as an inert porous carrier material. In case of oxidation, the impregnation help to boost the oxidation capacity of activated carbon, for example, potassium iodide impregnated activated carbon support the oxidation of hydrogen sulfide to sulfur Sulfur on the surface of impregnated activated carbon can help the reaction between mercury and sulfur occurs at room temperature. In addition, the impregnant on the surface of activated carbon provides the availability of a large internal surface area for reactants, for example, phosphoric acid impregnated activated carbon can be used for the removal of ammonia vapors.

$$H_3P0_4 + 3\ NH_3 = (NH_4)_3P0_4$$

According to the a number of research such as sulfur, halide, and thiols impregnated activated carbon, they support that the impregnated activated carbon has a superior properties to activated carbon (Chung et al., 2009; Yin et al., 2009). Schäfer reviewed different types of commercial impregnated acitivated as in the Table 2.7.

Table 2.7 Commercial impregnated activated carbon (www.activated-carbon.com/enviro.html)

Chemicals	Quantity (wt %)	Activated carbon	Examples for application
Sulfuric acid	2-25	pelletized	Ammonia, amine, mercury
Sulfur	10-20	pelletized and granulated	Mercury

Therefore, the studies of impregnated activated carbon for mercury removal occur. Several research found that the impregnated activated carbon help to develop the capacity of mercury removal (Gomez-Serrano et al., 1998; Li et al., 2003; Bylina et al., 2009). There are different chemicals such as sulfur, chlorine, bromine and iodine that have been found to be potential impregnants for capture of elemental mercury (Padak, 2006).

From Table 2.9, it shows the information that should consider when use these impregnants in the mercury removal system.

Table 2.8 Group of components supported on activated carbon (Nishino et al., 1985)

Group	Component
I	Sulfur
II	Sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	Oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodine of K, Na or NH_4

Table 2.9 Impregnated activated carbon qualities for mercury removal

Impregnation agent	Purification efficiency	Adsorption capacity	Corrosion problems
None	Poor	Poor	None
Potassium iodide	Good	Good	None
Sulfuric acid	Good	Very good	Possible
Sulfur	Very good	Very good	None

Chemicals of sulfur impregnated activated carbon (SIAC) can be disulfide, elemental sulfur, and thiophene which were suggested to increase the capacity of mercury adsorption (Cai and Jia, 2010; Mohan et al., 2001). Feng, Borguet, and Vidic (2006) demonstrated that sulfur is the most efficient for mercury adsorption. The cause of SIAC is more efficient than activated carbon, because the impregnation agents on the surface of activated carbon provide sites where the chemisorption occurs (Vidic and Siler, 2001). United States Environmental Protection Agency (1997) reported that chemisorption help to enhance the mercury removal. This issue is supported by the studies that found the mercury is adsorbed on the activated carbon surface, especially at the high concentration areas (Karatza, 2000; Vidic and Siler, 2001).

The process of adsorption can shift from physical adsorption which is exothermic to chemical adsorption (endothermic) resulting from the increasing temperature. Particularly at low temperatures, physical adsorption refers to the mercury adsorption on activated carbon that has higher surface area and lower sulfur content. At high temperature, chemisorptions refer to the activated carbon that has low specific area and high sulfur content (Bylina et al., 2009). To have the effective mercury adsorption should be concerned about the impregnation temperature and sulfur carbon ratio (SCR). In 1998, Liu, Vidic, and Brown published a paper in which they found the temperature of impregnation is more important for the adsorption capacity than SCR, because temperature has a large impact on the physicochemical properties of SIAC such as surface area, sulfur forms, and the contents (Hsi et al., 2001) In the impregnation method, the proper chemicals, organic and inorganic process of impregnation such as soaking and spraying are concerned (Marsh et al., 2006). Although SIAC is prove to be the potential alternative for mercury adsorption both gas and liquid phase (Ho et al.,2005), few research are dealing with mercury contaminated wastewater comparing to the mercury vapor adsorption(Wang et al., 2009). There are still lacking the studies of aqueous mercury removal by SIAC, because the information such as the effect of water chemistry and mechanism is not enough to clarify. It is important to understand the characteristic of mercury adsorption and associated mechanisms before SIAC can use for removing mercury from complex solution (Wang et al., 2009). Since mercury contaminated wastewater treating in this research coming from condensation process, the dominant mercury species in hydrocarbon are considered, because the properties of each form are different.

As dissimilar properties result in varying method for mercury removal, Table 2.10 performs the appropriate options for mercury removal in hydrocarbon and water.

As shown in Table 2.10, the activated carbon adsorption is a suitable mercury removal method for both hydrocarbon and water.

Table 2.10 Comparison of the mercury removal systems for hydrocarbons and water (adapted Wilhelm, 1999)

Mercury in	Method	
Hydrocarbons	Reactant	Substrate
	Sulfur	Carbon
	Metal Sulfide	$A l_2O_3$ Carbon
	Iodide	Carbon
	Pd + H_2; Metal Sulfide	Al_2O_3
	Ag	Zeolite
	Metal Oxide	Sulfided metal oxide
Water	Sulfide Precipitation	
	Other Precipitant	
	Ion Exchange	
	Iron Cementation	
	Activated Carbon	

CHAPTER III

METHODOLOGY

3.1 Experimental framework

This section described the details of the mercury adsorption by activated carbon. As can be seen from the Figure 3.1, the overview of all experiments and expecting outcomes were presented. The purpose of this study is to investigate the mercury adsorption capacity of several activated carbons. This work began from the wastewater characterization, which was one of the most important steps, because it can guide the characteristics of wastewater and indicate the problems of existing mercury treatment unit of petrochemical industry; therefore, a suitable method was performed. The second step was about a preparation of adsorbents. Before using adsorbents in the process, it was necessary to prepare activated carbons in order to achieve the maximum capacity. Batch adsorption test was provided in the next step. The results from this part will indicate the optimum conditions for applying in the test and design column. Column adsorption part will inform the desired conditions and parameters requiring for design criteria for the column in the petrochemical industry. To be the practical treatment, efficiency of the mercury treatment and cost analysis were carefully considered; thereby, the cost of the treatment per unit was analyzed in the finally step.

These tasks were categorized into five sections followed experimental framework (Figure 3.1). It referred to wastewater characterization, selected adsorbent preparation, batch adsorption test, column adsorption test, and design criteria, and cost analysis.

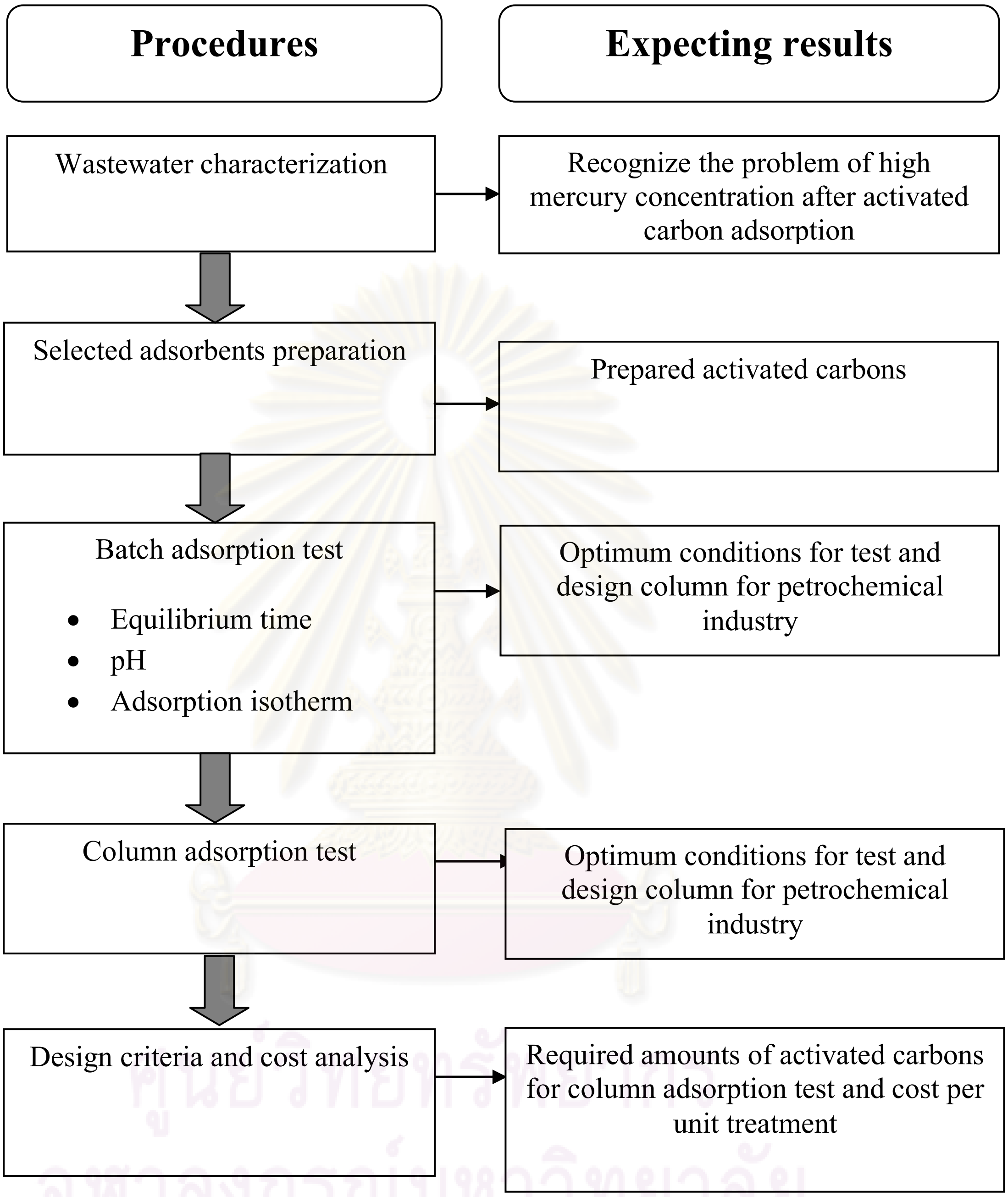

Figure 3.1 Experimental framework

3.2 Chemicals and materials

Chemicals and materials using in this experiments were shown in Table 3.1, 3.2, 3.3, and 3.4.

Table 3.1 Chemical and materials

Chemicals and materials	Company
CGC-12	C. Gigantic Carbon Co.,Ltd.
Filter paper	Whatman®Schleicher&Schuell
Hydroxylamine hydrochloride	Carlo Erba
Mercury(II)nitrate	Ajax Finechem
MERSORB ®LW	NUCON International, Inc.
Nitric acid 65%	Carlo Erba
NORIT GAC-1240	NORIT Americas Inc.
Potassium permanganate	Ajax Finechem
Potassium persulphate	Ajax Finechem
Sulfuric acid 96%	Carlo Erba

Table 3.2 Properties of CGC-12 (application for solvent recovery)

Properties	Value
Total surface area m^2/gm	1,100-1,150
Pore volume (within particle) c.c/gm	0.75
Void in dense packed column	50%
Apparent density (bulk density densepacking)	0.46-0.51
Particle density (Hg displacement) gm/c.c.	0.85

Properties	Value
Real density (He displacement) gm/c.c.	2.2
Ignition temperature (°C) minimum	450
Iodine number (mg/g) minimum	1150
Carbon tetrachloride adsorption (%weight) minimum	65
%Ash maximum	5
Moisture (% as packed) maximum	5
Hardness number (ball pan) minimum	98
pH	9-11
Surface Area, base carbon, N_2 BET (m^2/g)	1,000
CCl_4 activity (ASTM D 3467) weight %	60
Hardness (ASTM D 3802) %	97
Apparent Density (ASTM D 2854) lbs/ft^3 (550 kg/m^3)	34
Moisture Content (ASTM D 2867) weight %, max., as packed	3
Sulfur Content weight %	13
pH (ASTM D 3838)	6-8
Hg Capacity, max. weight %	75

Table 3.3 Properties of MERSORB ®LW (Sulfur impregnated activated carbon)

Physical properties	Value
Total surface area m^2/gm	1000
Apparent density (bulk density dense packing)	35 lb/ft^3 (560 Kg/m^3)
Carbon tetrachloride adsorption (%weight) minimum	60
Moisture (% as packed) maximum	3
Hardness number (ball pan) minimum	97
pH	3-5
Sulfur content	13 wt.%

Table 3.4 Properties of NORIT GAC 1240 (Activated carbon used in the petrochemical industry)

Physical properties	Value
Apparent density (bulk density dense packing)	31 lb/ft^3
Moisture (% as packed) maximum	2
Mesh size	2
Iodine number	1020
Molasses number	230

3.3 Wastewater characterization

Physical and chemical analyses of mercury contaminated wastewater of petrochemical industry were performed to evaluate the performance of the existing treatment units for mercury in this petrochemical plant. There were four times for collecting wastewater from condensate tank. The first time of sampling, raw wastewater, and the wastewater passing each treatment process was collected so as to study the efficiency of existing treatment unit of this plant. Other collections were only provided for adsorption tests. Table 3.2 presented various parameters were analyzed for wastewater followed by Standard Methods for the Examination of Water and Wastewater of APHA, AWWA, and WEF in 1992.

Point 1: Before cartridge filter (representing raw wastewater before treatment)

This point will examine pH, soluble solids, TOC, total and soluble mercury, FOG, COD and chloride.

Point 2: After cartridge filter (representing a filtered wastewater before mercury removal and sample at this point will be used in this study)

This point will examine pH, soluble solids, total and soluble mercury.

Point 3: After wastewater passing through the adsorption tower #1 (representing the treated effluent)

This point will examine pH, TOC, and soluble mercury.

Point 4: After wastewater passing through the adsorption tower #2 (representing the treated effluent)

This point will examine pH, TOC, and soluble mercury.

Point 5: After wastewater passing through the adsorption tower #3 (representing the final effluent from existing mercury treatment system)

This point will examine pH, TOC, soluble mercury, and COD.

Table 3.5 Parameters detecting in each point of wastewater sampling

Parameters	**Sampling point**				
	Raw wastewater(1)	**Cartride filter (2)**	**AC#1 (3)**	**AC#2 (4)**	**Effluent (5)**
pH	✓	✓	✓	✓	✓
TSS (mg/l)	✓	✓	×	×	×
TDS (mg/l)	✓	×	×	×	×
FOG (mg/l)	✓	×	×	×	×
COD (mg/l)	✓	×	×	×	✓
TOC (mg/l)	✓	×	✓	✓	✓
Hg (μg/l)	✓	✓	✓	✓	✓
As (mg/l)	✓	✓	✓	✓	✓

Table 3.6 Method using for wastewater characterization

Parameter	Method
pH	Electrometric method (4500-H-B)
COD	Closed reflux, Titrimetric method (5220-C)
TOC	High-temperature combustion method (5310-B)
FOG	Partition-gravimetric method (5520-B)
TSS	Total suspended solids (In-house method SPS T02)
TDS	Total dissolved solid dried at 104 ± 2 °C (In-house method SPS T03)
Hg (mg/l)	Cold vapour atomic absorption spectrometric method (3112-B)
As (mg/l)	Hydride generation/atomic absorption spectrometric method (3114-C)

3.4 Selected adsorbents preparation

In order to pursue the maximum capacity of adsorbent, the pretreatment of activated carbons were provided. The activated carbon will then be rinsed with 15 mΩ DI water to clean the dirt and will be dried at room temperature and 103 °C for a day, respectively, and kept in a desiccator until used.

3.5 Batch adsorption test

The purpose of this section was to determine the optimum conditions of mercury adsorption process for designing the continuous test. This section had three major parts which were equilibrium time, effect of pH, and adsorption isotherm.

3.5.1 Equilibrium time

This part will be carried out by agitating 100 ml of real wastewater with 100 mg of activated carbons in a 250-ml erlenmeyer flask on a mechanical shaker at room temperature. At predetermined time of 0, 1, 2, 6, 12, 24, and 48 hr, 15 ml aliquot will be sampled by a syringe and filter through 6 μm filter paper. The pH of each sample will be measured by a pH meter. Filtered samples will be analyzed for the total mercury concentration.

3.5.2 Effect of pH

Mercury treatment by activated carbon involved adsorption of soluble mercury onto the carbon. As a result, pH was an important factor for precipitation of metals and organic compounds, including formation of complex compounds. Study of solubility of mercury in various pH levels, which were 2 to 9, was required.

In this part, 100 ml of real wastewater with 100 mg of activated carbons will be added into each 250-ml erlenmeyer flask and adjust pH to 2, 5, and 7 by either HNO_3 or NaOH. The flasks will then be mixed by a mechanical shaker controlled at 30°C until reaching the equilibrium (obtained from previous part). Fifty ml of sample will be taken by a syringe and filter through 6 μm filter paper and then digest wastewater followed EPA 7470A Mercury in Liquid Waste (Hydride Generation Technique), and finally, analyzed for mercury content by Atomic Absorption Spectrophotometer. The pH of each sample will be measured by a pH meter.

3.5.3 Adsorption isotherm

Different amounts of activated carbons will be added to 250-ml erlenmeyer flask containing 100 ml of real wastewater at optimum pH obtained from Section 2. All testing procedure will follow those described in Section 2. Obtained data will be used to determine the adsorption isotherm which best explains the observation.

3.6 Column test

Information obtained in the batch test was used to setup experimental scenarios for the column test. In this part, bed depth and filtration flow rate were investigated for desired empty bed contact time (EBCT). The column test continued until reach the breakthrough point at the concentration of mercury exceeded 5 μg/L (industrial effluent standard for mercury in Thailand). Sometimes it operated until the inlet concentration of mercury equals to the outlet concentration of mercury to calculate the maximum adsorption capacity of activated carbon under column operating condition. The outcome of this section will be applied in the design criteria for real treatment unit of petrochemical industry and evaluate cost analysis for economic approach.

Table 3.7 Parameters of existing and tested column

Parameters	Existing column	Tested column
Size of column	57 cm (Ø) x 258 cm (h)	5 cm (Ø) x 22.5 cm (h)
Adsorbent volume	658 L	0.44 L
Flow rate	8 m^3/day (5.56 L/min)	3.67 mL/min
V_{flow}	2.18 cm/min	0.19 cm/min
EBCT	2 h	2 h

3.7 Design criteria and cost analysis

Obtained outcomes from batch and column adsorption tests were applied for design the real treatment unit for mercury contaminated wastewater from condensate tank. Calculate the expenses of a treatment per unit for cost analysis.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Wastewater characteristics

Wastewater from mercury treatment system of petrochemical industry were collected at five sampling points and analyzed as shown in Table 4.1. The characteristics of raw wastewater collected on 7th June 2010, indicated that it was acidic, low suspended solid, even though it contained high dissolved solid which might compete with mercury for adsorption sites of activated carbon. The level of FOG (fat, oil, and grease) is not a barrier for adsorption process. Due to high levels of TOC and COD, mercury adsorption by activated carbon might be interfered by organic carbon. The average mercury concentration was about 459 μg/L , but it reduced to 125 μg/L after filtration through 6 micron filter paper. It showed that mercury was most adsorbed on suspended solids which are easily separated by filtration. The filter papers accumulated high levels of mercury; therefore, the appropriate methods for elimination were carefully considered. Another hazardous contaminant is arsenic. The concentration of arsenic was 167 mg/L which is higher than industrial effluent standards of 0.25 mg/L from Pollution Control Department (PCD). Most forms of arsenic are arsenate (AsO_3^-) and arsenite (AsO_2^-) which are negative charges. These ions hardly affect to adsorption process of mercury that is positive charge at neutral and acidic conditions. High concentrations of chloride were concern, because it can form complex with mercury causing less adsorption at the surface of activated carbon.

Sampled wastewater from point 2 had lower pH, because wastewater was adjusted to be acidic. Suspended solids lowered after filtration with 5 micron filter papers. Concentrations of mercury and arsenic in wastewater from point 2 were closed to concentrations of raw wastewater, which were contrast to the results showing that the major parts of mercury were separated after filtration.

After the first activated carbon column, the mercury concentration was found to decrease slightly, but TOC was considerably three times higher than that in the raw wastewater. Wastewater passing through the second column was slightly different from that passing through column 1. However, the characteristics of wastewater passing the third column was not similar to the former, it had high pH, TOC although mercury concentration decreased significantly. The variations of wastewater characteristics from each point of treatment unit were different from the theoretical profiles resulting from the varied qualities of raw wastewater and holding wastewater in the condensate tank. These causes were the reasons why mercury concentration and organic carbon did not decrease respectively. The results indicated that activated carbons in the columns were exhausted and the rates of wastewater input were too fast to be adsorbed by activated carbons. Nevertheless, filtration with 5 micron filter paper used as a pretreatment process which can trap grease and suspended solids so as to make wastewater suitable for the adsorption process. The deterioration of activated carbon from fat coating and suspended solids occurred gradually, because the raw wastewater was contained little of them.

In addition to first sampling on 7th June 2010, wastewater was collected two more times on 30th September 2010, and 24th December 2010 during the project. The results showed that each sampling produced wastewater with different characteristics. In the second collection, the concentration of total mercury and filtrate mercury (after filtrate with 6 micron filter paper) were 85 and 18 μg/L respectively. For the last sampling, it was found that the concentration of total mercury and filtrate mercury were 22.5 and 4.8 μg/L respectively. The summary of wastewater characteristics from three time collections were performed in Table 4.1.

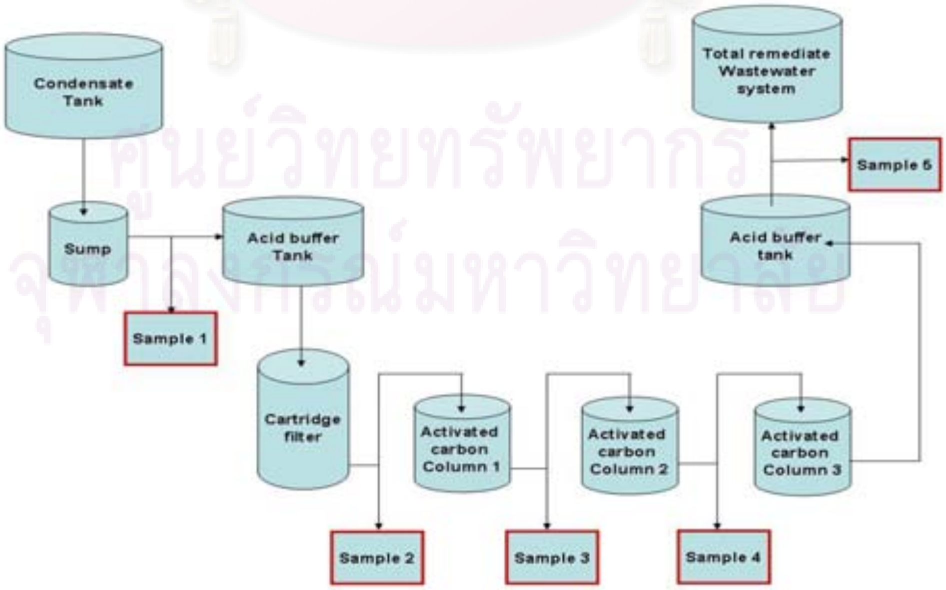

Figure 4.1 Sampling points from the mercury treatment system

Table 4.1 Wastewater characteristics

Parameter	7 Jun 2010					30 Sep 2010	24 Dec 2010	3 Mar 2011
	Raw wastewater (1)	Cartridge filter (2)	AC column 1 (3)	AC column 2 (4)	AC column 3 (5)	Raw wastewater	Raw wastewater	Raw wastewater
pH	5.01	2.43	2.39	2.46	6.01	4.4	4.36	4.34
TSS (mg/l)	43	22	-	-	-	-	-	-
TDS (mg/l)	5,769	-	-	-	-	1,364	1,788	-
FOG (mg/l)	6	-	-	-	-	-	-	-
COD (mg/l)	6,749	-	-	-	9,537	2,498	5,976	3,316
TOC (mg/l)	1,394	-	5,116	5,218	1,692	923	2,097	1,002
BOD (mg/l)		-	-	-	-	298	300	308
Hg (µg/l):- Total	508	572	372	411	130	85	73	22.5
- 6µm Filtrate	125	-	-	-	-	18	1.3	4.8
As (mg/l)	167	174	161	168	99	-	-	52.05
Chloride (mg/l)	926	-	-	-	-	-	-	-

This analysis showed that wastewater from condensate tank contained a variety of elements affecting the adsorption of mercury by activated carbon.

Table 4.2 Chemical analysis of wastewater sampled on 3 Mar 2011

Element	Concentration (mg/L)
Ag	0.007
Al	0.392
B	ND
Ba	0.041
Bi	ND
Ca	23.798
Cd	0.014
Co	0.022
Cr	0.141
Cu	ND
Fe	88.046
Ga	0.012
In	0.043
K	12.213
Li	0.116
Mg	13.016
Mn	1.745
Na	265.187
Ni	50.910
Pb	ND
Sr	0.217
Tl	ND
Zn	0.937

4.2 Effect of pH in mercury solubility in water

Mercury treatment by activated carbon adsorption concentrated on soluble mercury. As a result, pH is the important factor for precipitation of metal and organic compounds including formation of complexes. Consequently, study of mercury solubility at various pH values was required.

Previous research described the favorable condition for activated carbon adsorption at neutral pH. In this study, the wide range of pH values, from pH 2 to 9 were investigated as shown in Figure 4.2. The graph showed that the concentration of filtrate mercury increased slightly when the pH rose. The advantage of this study was the results were more accurate when mercury concentrations were compared at different pHs.

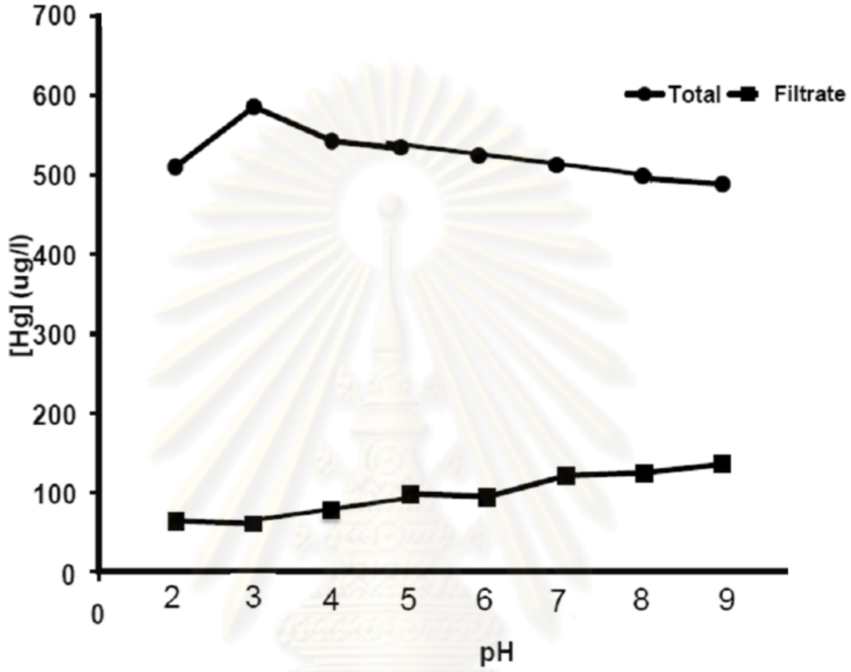

Figure 4.2 Effect of pH in mercury solubility in water (after filtrate with 6 micron filter paper)

4.3 Adsorption of mercury in wastewater

4.3.1 Batch Test

4.3.1.1 Equilibrium Time

Equilibrium time played an important role in determination of adsorption isotherm. In this part, two types of activated carbons, MERSORB $^{®}$LW and CGC-12, were tested. Results in clearly showed that of the adsorption process began to reach an equilibrium in 12 hours; therefore, 24 hours was selected as a equilibrium time for the following experiments.

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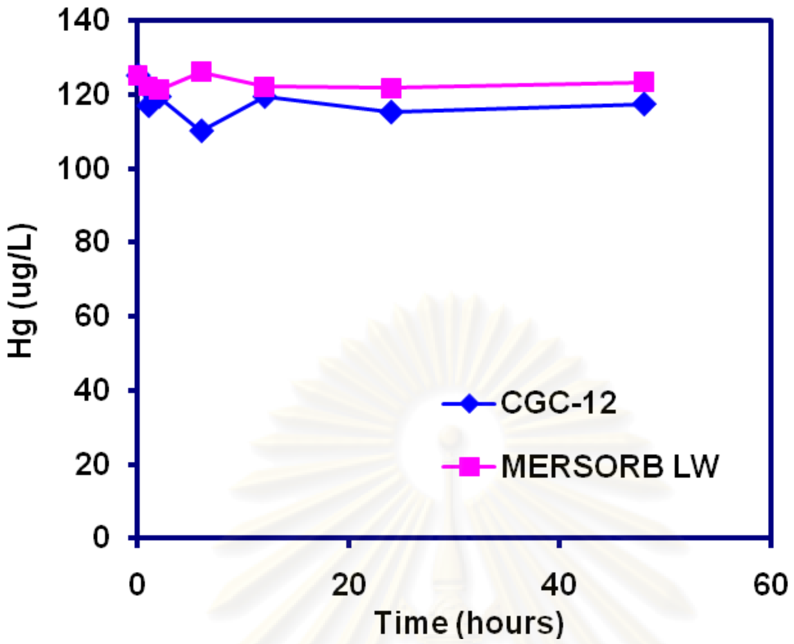

Figure 4.3 Adsorption of mercury by activated carbon 1 g/L

4.3.1.1.2 Effect of pH

The pH condition has a great impact on mercury ions in water and surface charge of activated carbons. In this research, three pH conditions which are 2, 5, and 7 were investigated. The previous research showed that pH 5 is the most suitable condition for activated carbon adsorption. On the other hand, pH 2 was used as a present condition in the mercury treatment units of petrochemical industry. Wastewater used in this test came from the second collection; therefore, the concentrations of mercury were much lower than the first collection. At pH 2, the results showed that the effective adsorbents were in the order of CGC-12, NORIT GAC 1240, and MERSORB ®LW respectively. It is contrast to at pH 5 which was the performances of NORIT GAC 1240 and MERSORB ®LW better than CGC-12 as shown in Figure 4.4.

However, the initial concentration of mercury in both adsorption tests were different; therefore, direct comparison of adsorption capacities cannot be made. It was essential to compare in terms of adsorption isotherms as shown in Figure 4.5. The results indicated that all adsorption isotherm curves were concave. That is, mercury adsorption by all three adsorbents were unfavorable. Other contaminants in the wastewater which were much more than mercury concentration might have competed with mercury for adsorption at the surfaces of activated carbons.

Nonetheless, the previous studies reported that the average concentrations of total and filtrate mercury were 300 and 100 µg/L respectively. In case of low mercury concentrations, mercuric(II) nitrate ($Hg(NO_3)_2$) was be added to wastewater in order that the final concentration of mercury after filtrate with 6 micron filter paper was approximate 100 µg/L. The adsorption capacities of CGC-12 and NORIT GAC 1240 were similar and higher than MERSORB ®LW at pH 2. Contrast to at pH 5, the performances of NORIT GAC 1240 slightly higher than CGC-12 and the MERSORB ®LW had the lowest adsorption capacities, as shown in Figure 4.6. Figure 4.7 presented the adsorption isotherms at pH 2 were better than at pH 5 which were controversial to the adsorption tests of low mercury concentrations. Two adsorption of high mercury concentrations were investigated to confirm that the trends of adsorption capacities of activated carbons at ph 2 were higher than at pH 5 and NORIT GAC 1240 performed the best adsorption capacities, then CGC-12 and MERSORB ®LW respectively as shown in Figure 4.8 to Figure 4.11 (in the third test, CGC-12 cannot be purchased).

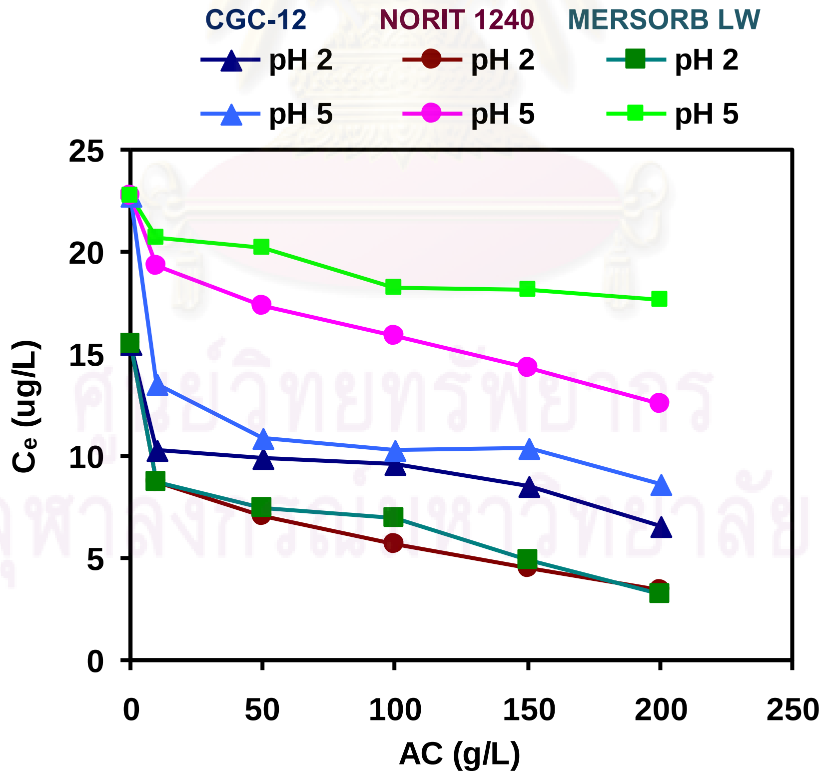

Figure 4.4 Concentrations of mercury in wastewater at equilibrium and the quantities of activated carbons

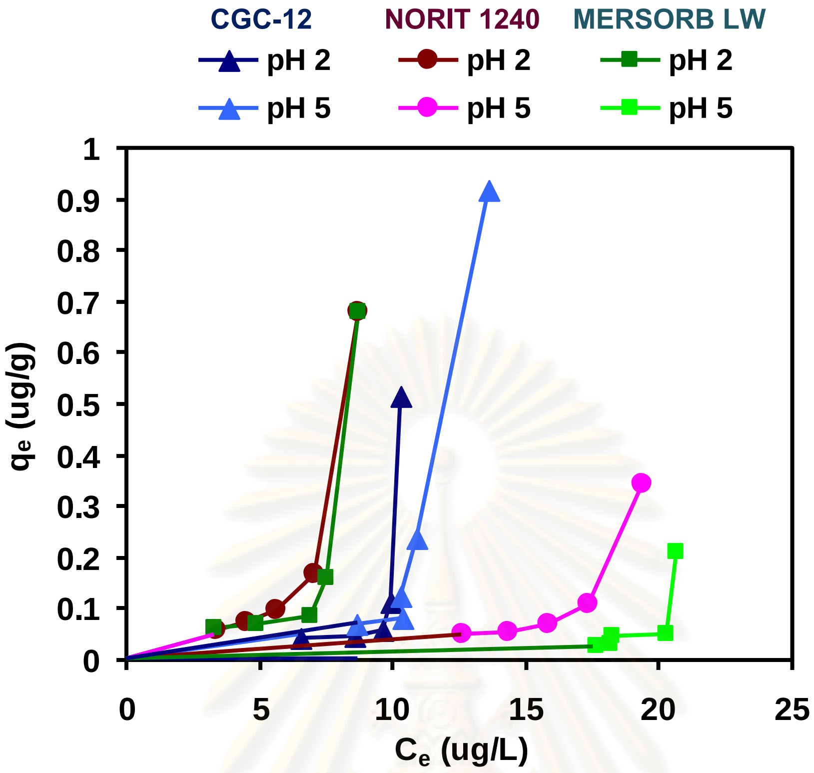

Figure 4.5 Adsorption isotherm of Figure 4.4

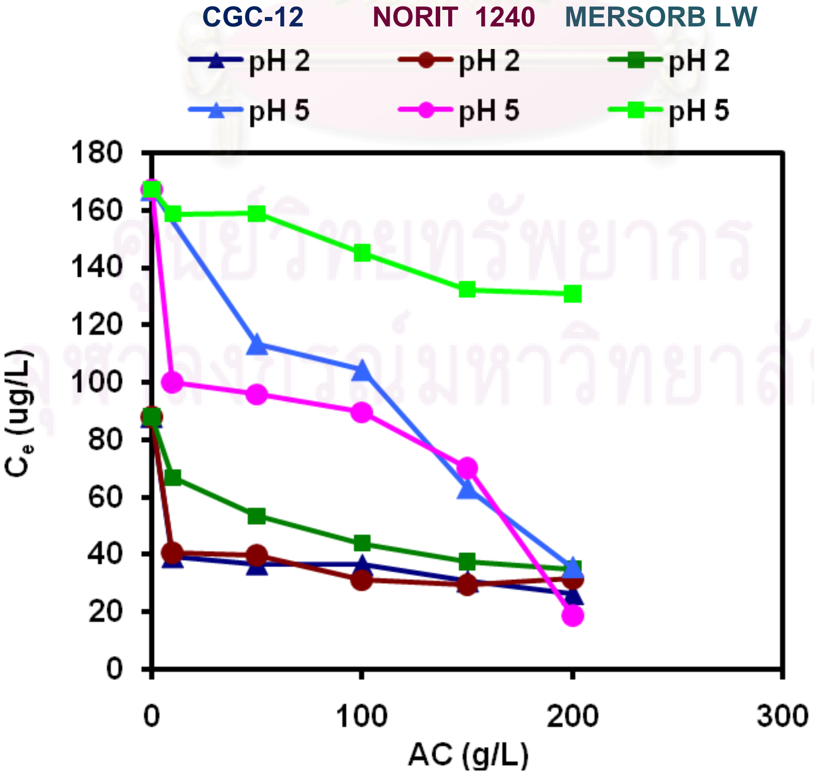

Figure 4.6 Concentrations of mercury adding $Hg(NO_3)_2$ 100 μg/L at equilibrium time and the quantities of activated carbons used in the first adsorption test

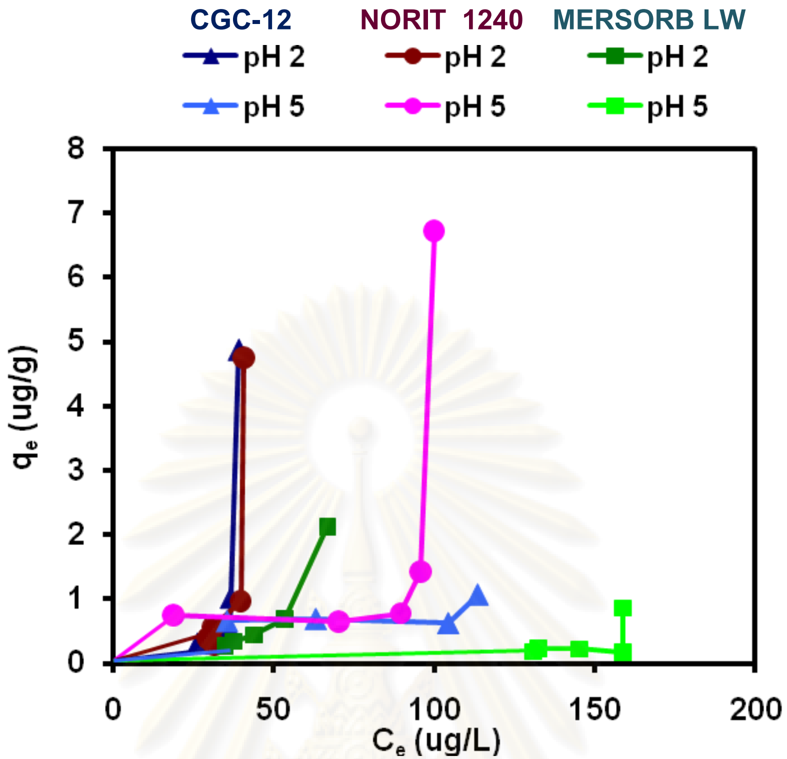

Figure 4.7 Adsorption isotherm of Figure 4.6

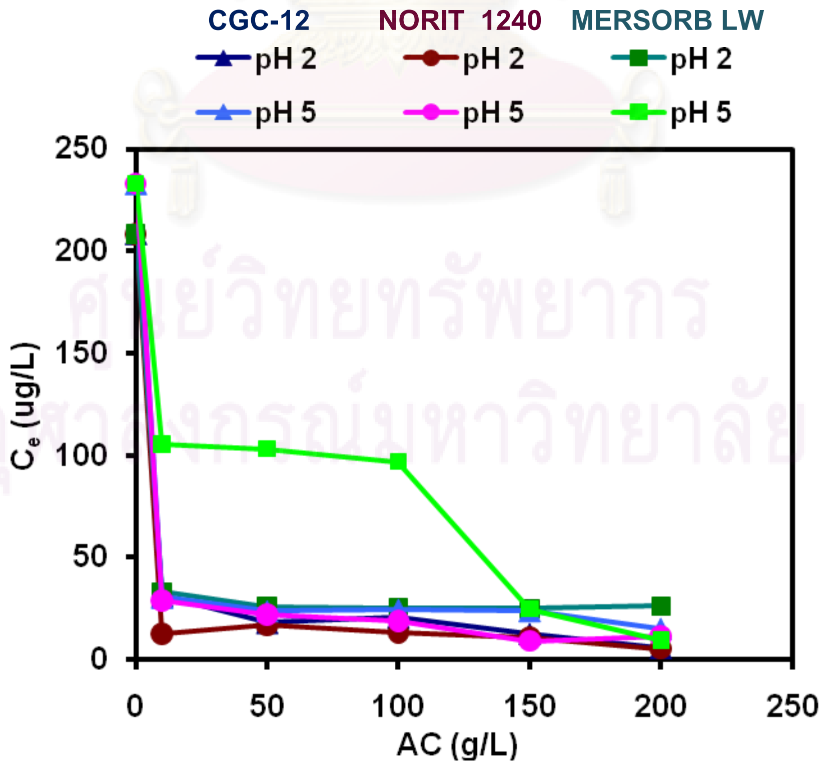

Figure 4.8 Concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the second adsorption test

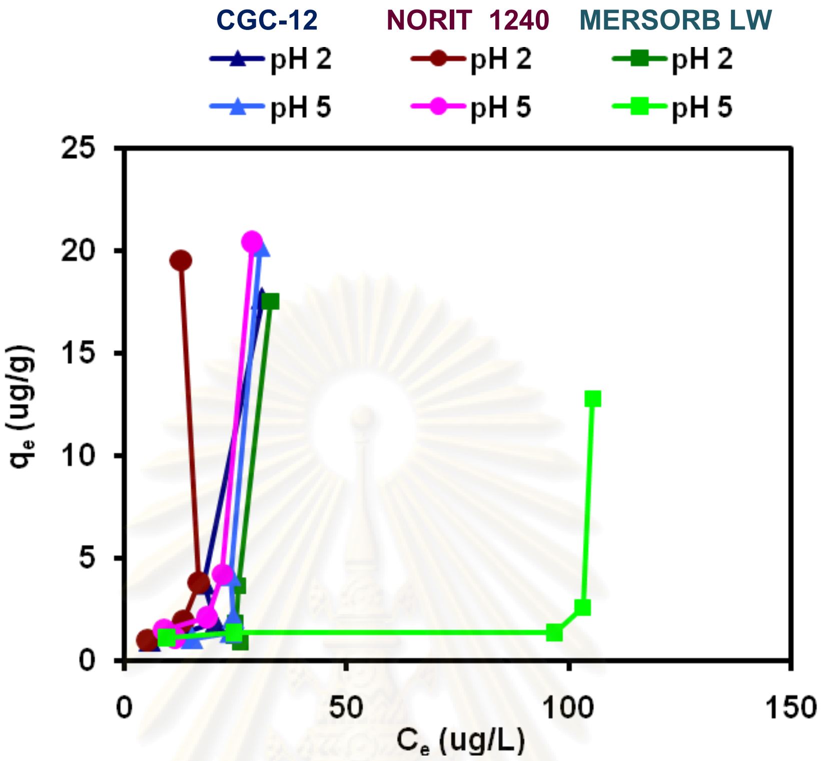

Figure 4.9 Adsorption isotherm of Figure 4.8

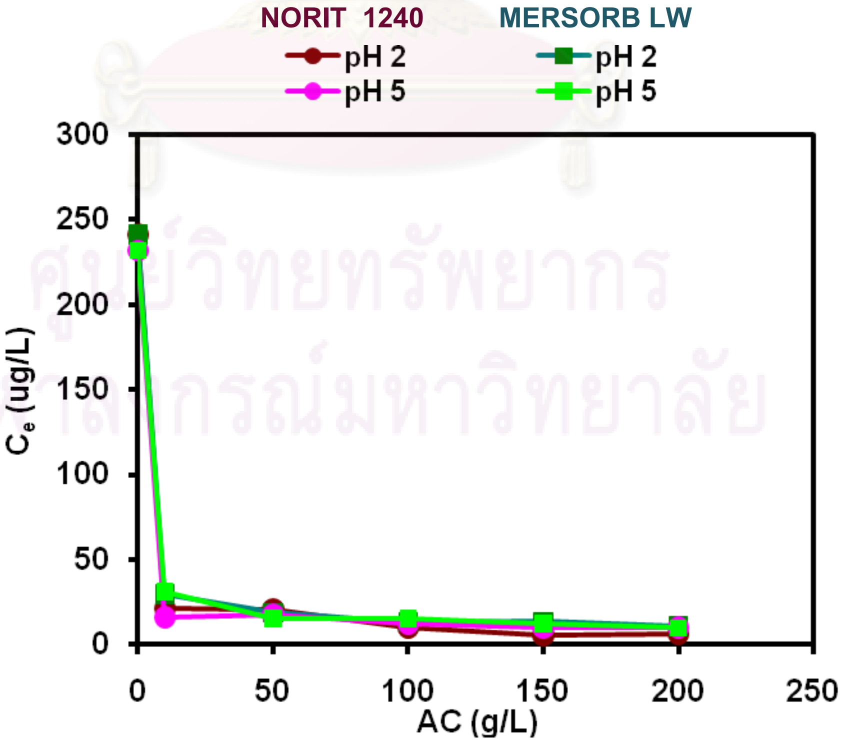

Figure 4.10 Concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the third adsorption test

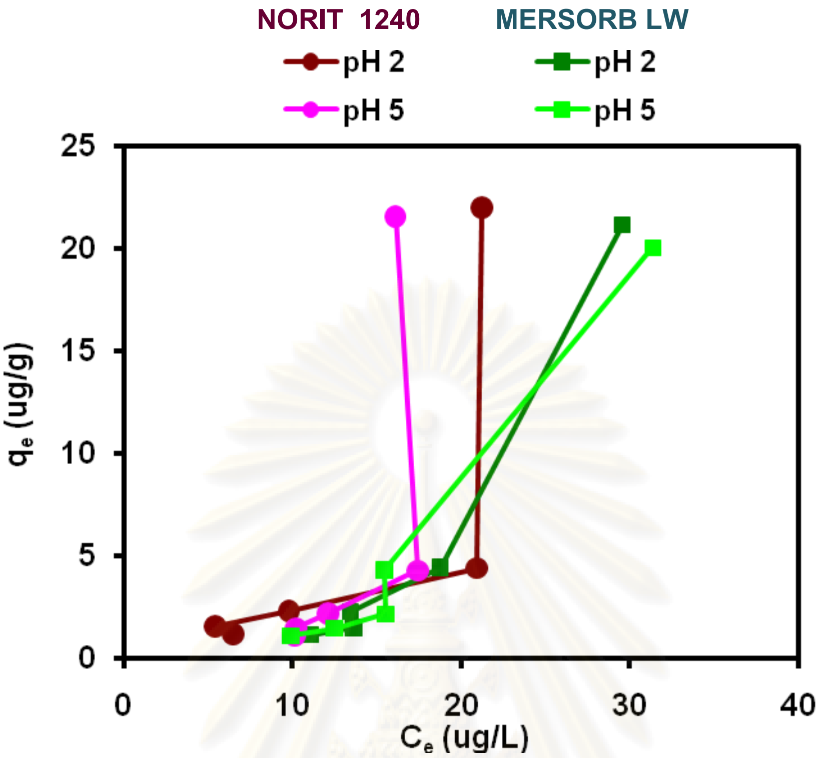

Figure 4.11 Adsorption isotherm of Figure 4.10

In the third test, the adsorptions of mercury at pH 7 were studied, because some research reported that activated carbons can adsorb mercury effectively at pH 7 condition. The results indicated that CGC-12 and NORIT 1240 had the closed adsorption capacities and higher than MERSORB ®LW as shown in Figure 4.12. In addition to, there were some small precipitants suspended in the wastewater after filtrate with 6 micron filter paper. They seemed to be homogeneous, but they precipitated later and they may cause of the concentrations of mercury in the clear part of wastewater remarkable decreased. This situation cannot be found in the wastewater at pH 2 and 5 conditions. From this noticeable information, it showed that some metals contaminating in the wastewater can precipitate at pH 7. Occurred precipitants were smaller than 6 micron and can adsorb mercury at the surfaces. The results indicated that adsorption tests at pH 7 were not appropriate for the research, because precipitants can clog at the internal pores of activated carbons resulting in the adsorption capacities declined. In the practical way, the coagulation and flocculation processes were required to increase the rates of precipitation. The mercury contaminated sludge must be managed safely. All of the results from the batch adsorption tests showed that NORIT GAC 1240 were the most suitable adsorbents for mercury adsorptions. The optimal condition for mercury adsorption was pH 2. However, the adsorption tests were non-favorable.

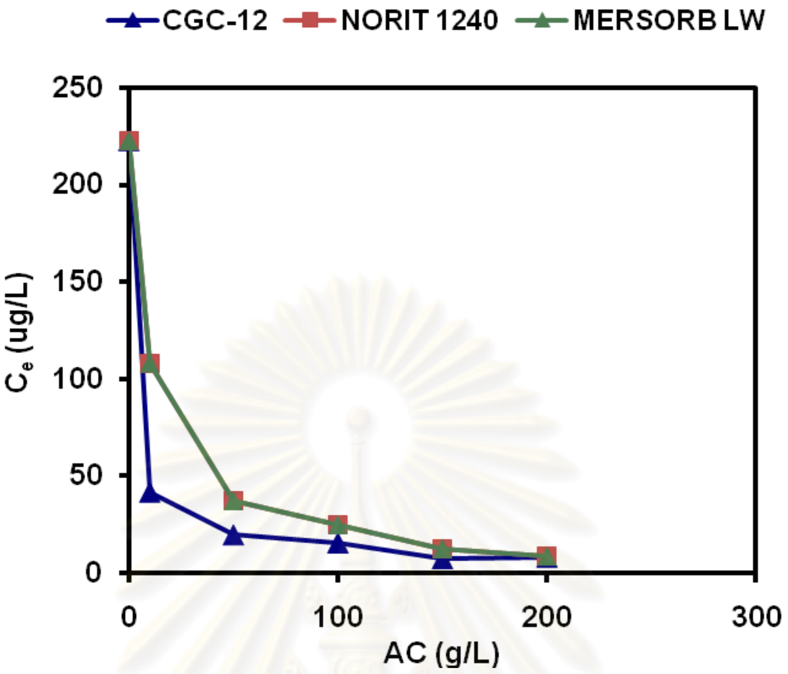

Figure 4.12 Concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the pH 7 condition

4.3.1.3 Adsorption isotherms

Results indicated that adsorptions of mercury were non-favorable. Therefore, Freundlich adsorption isotherm is the only assumption using for describing the adsorption process, since other adsorption isotherms such as Langmuir and BET cannot be fitted. From Freundlich isotherms as shown in Figure 4.13 to Figure 4.16, the Freundlich constants were calculated in the Table 4.3. R^2 from the Table 4.3 showed that Freundlich adsorption isotherm cannot explain the adsorption of mercury by activated carbons, because most R^2 were low. Other contaminants in the wastewater which were much more than mercury can interrupt the adsorption of mercury and result in the adsorption processes differ from adsorption theories. In addition, there are triplicate adsorption studies for wastewater adding 100 µg/L $Hg(NO_3)_2$. Each isotherm from three adsorption experiments is different due to the unique characteristics of wastewater from different collections.

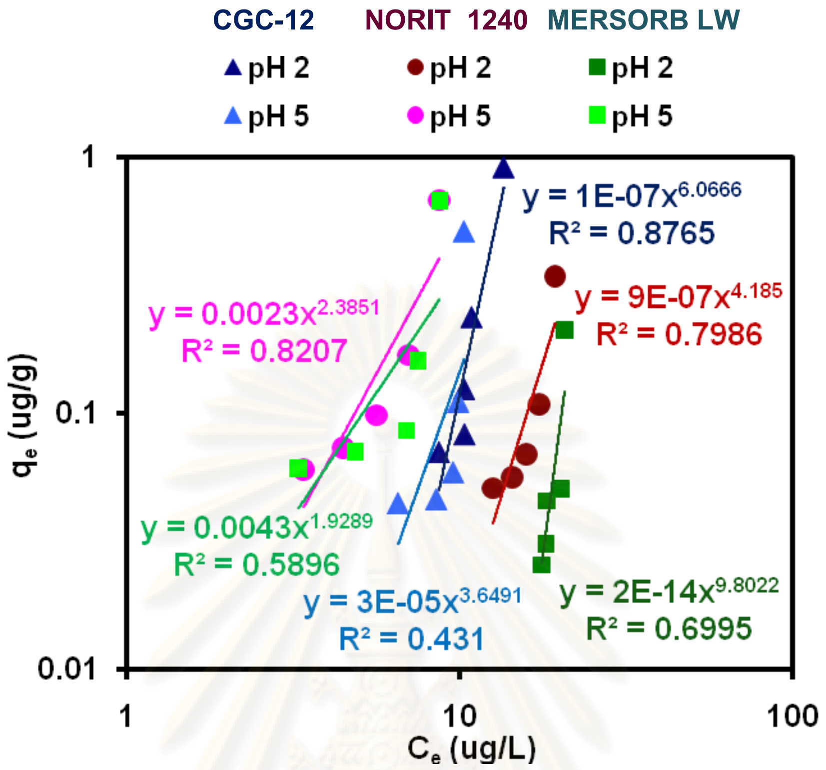

Figure 4.13 Freundlich isotherm from adsorption of mercury in wastewater

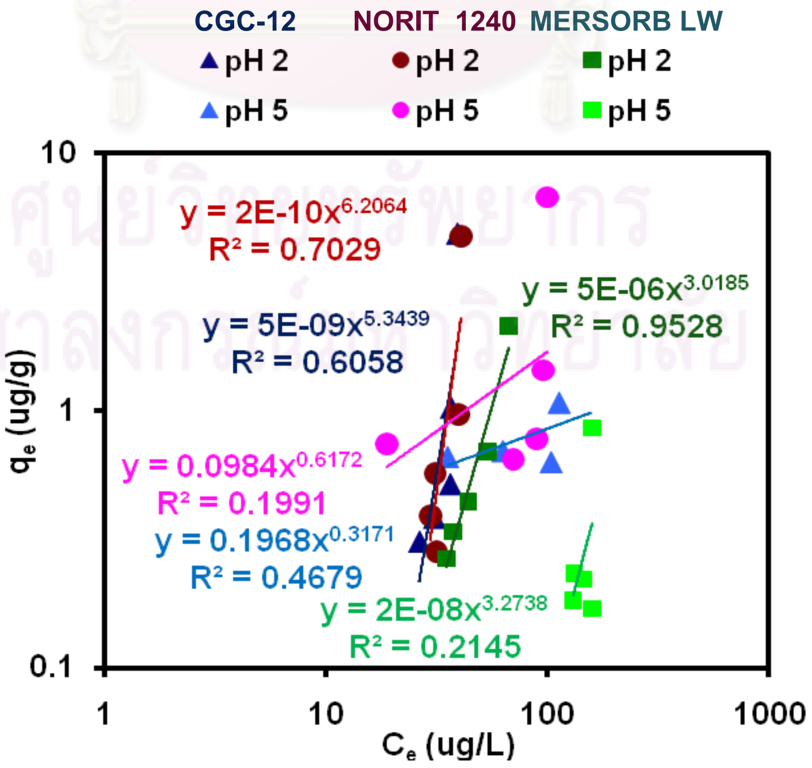

Figure 4.14 Freundlich isotherm from adsorption of mercury in wastewater adding $Hg(NO_3)_2$ 100 µg/L in the first test

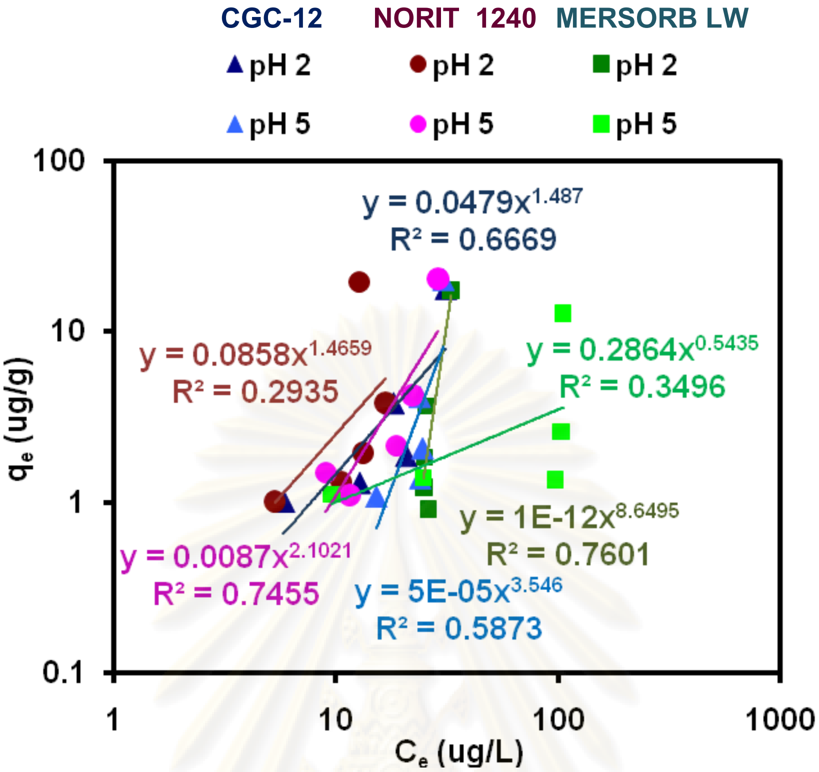

Figure 4.15 Freundlich isotherm from adsorption of mercury in wastewater adding $Hg(NO_3)_2$ 100 µg/L in the second test

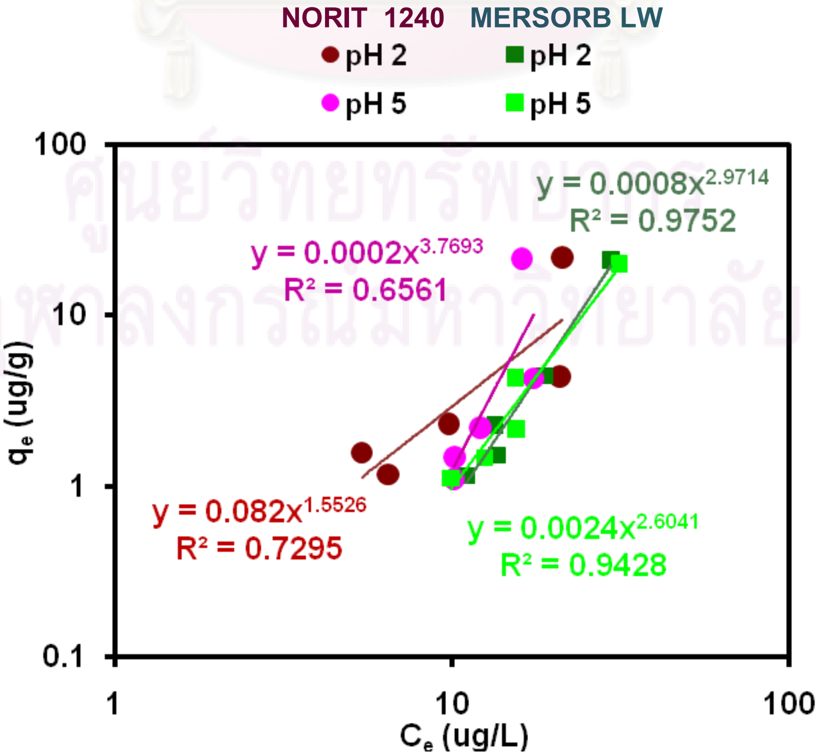

Figure 4.16 Freundlich isotherm from adsorption of mercury in wastewater adding $Hg(NO_3)_2$ 100 µg/L in the third test

Table 4.3 Freundlich constants

Wastewater	pH	Activated carbon	K	1/n	R^2
Raw wastewater	2	CGC-12	1×10^{-7}	6.0666	0.8765
		NORIT GAC 1240	9×10^{-7}	4.185	0.7986
		MERSORB ®LW	2×10-14	9.8022	0.6995
	5	CGC-12	3×10^{-5}	3.6491	0.4310
		NORIT 1240	0.0023	2.3851	0.8207
		MERSORB ®LW	0.0043	1.9289	0.5896
Wastewater + $Hg(NO_3)_2$ 100 µg/L in the first test	2	CGC-12	5×10^{-9}	5.3439	0.6058
		NORIT GAC 1240	2×10^{-10}	6.2064	0.7029
		MERSORB ®LW	5×10^{-6}	3.0185	0.9528
	5	CGC-12	0.1968	0.3171	0.4679
		NORIT GAC 1240	0.0984	0.6172	0.1991
		MERSORB ®LW	2×10^{-8}	3.2738	0.2145
Wastewater + $Hg(NO_3)_2$ 100 µg/L in the second test	2	CGC-12	0.0479	1.487	0.6669
		NORIT GAC 1240	0.0858	1.4659	0.2935
		MERSORB ®LW	1×10^{-12}	8.6495	0.7601
	5	CGC-12	5×10^{-5}	3.546	0.5873
		NORIT GAC 1240	0.0087	2.1021	0.7455
		MERSORB ®LW	0.2864	0.5435	0.3496
Wastewater + $Hg(NO_3)_2$ 100 µg/L in the third test	2	NORIT GAC 1240	0.0820	1.5526	0.7295
		MERSORB ®LW	0.0008	2.9714	0.9752
	5	NORIT GAC 1240	0.0002	3.7693	0.6561
		MERSORB ®LW	0.0024	2.6041	0.9428

4.3.1.2 Column Test

Results from the batch adsorption section indicated that NORIT GAC 1240 had more efficient than other adsorbents for adsorbing mercury in wastewater at the pH 2. The optimal conditions from the batch test were be used in the column adsorption test. In addition to NORIT GAC 1240, MERSORB $^{®}$LW were tested the performance at pH 2, volume 880 ml, filtration flow rate 220 ml/hr , and empty bed contact time 4 hr. The results of adsorption test of MERSORB $^{®}$LW were shown at Figure 4.17. Although MERSORB $^{®}$LW can treat wastewater 9.5 L, 741 L of MERSORB $^{®}$LW were used for treating wastewater 8 m^3 per day which was not suitable for cost analysis, because it is expensive and has to import this activated from abroad.

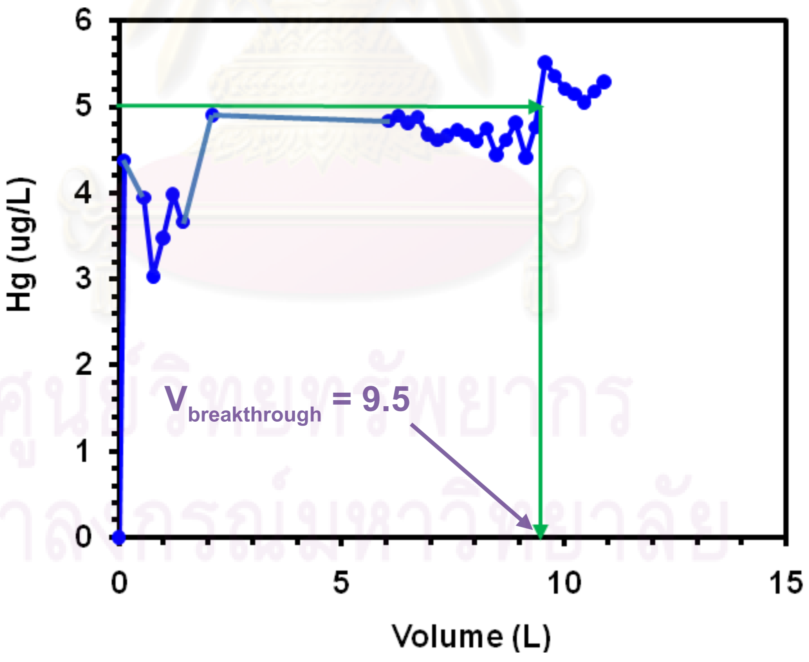

Figure 4.17 Breakthrough curve at pH 2 of adsorption of mercury by MERSORB $^{®}$LW volume 880 ml filtration flow rate 220 ml/hr (HRT = 4 hr, $[Hg_0]$ = 118.5 ug/L)

In the column test of NORIT GAC 1240, the flow rate at 220 ml/h and volume of activated carbon 440 ml resulting in the empty bed contact time (EBCT) equal to 2 hours which was the same as the real treatment units of the petrochemical industry. However, the flow rate of the test column and the real column was different significantly

(0.18 and 2.18), because the physical of test column was smaller than the column in the treatment units 11.4 times. Flow rate difference affected the efficiency of activated carbon adsorption, especially kinetics. Due to the test column had same empty bed contact time (EBCT) as the real column, the results from the experiments can be applied. The adsorption of NORIT GAC 1240 continued until the inlet concentration of mercury equal to the outlet concentration approximately 45 days.

pH solution was one of the essential factors for activated carbon adsorption. At the beginning state of adsorption, pH solution was about 9 which higher than the pH 2 of the prepared wastewater as shown in Figure 4.18. The high pH results from the alkaline of activated carbon and the remaining demineralized water was applied for preventing activated carbon adsorption from the air bubbles between the pores of activated carbon. Air bubbles occurred when wastewater pass through the column slowly. These air bubbles may interrupt the contacts between wastewater and the surfaces of activated carbon. Then, the pH solution decreased until 2; therefore, the variations of adsorption efficiency due to improper pH took place only the first state. Although pH solution was not suitable for adsorption at the beginning step, the outlet concentration of mercury was still less than 5 ppb, because NORIT GAC 1240 was quite fresh. After the activated carbon reached a new equilibrium when adsorption process was appropriate at pH 2 then the adsorption capacity rose.

Temperatures of the treated wastewater about 28.2 ˚C were closed to room temperature as shown in Figure 4.19. The temperature changes relied on the room temperature which was according to the real situation at the petrochemical plant; therefore, it was not necessary to adjust effect of temperature from the adsorption process

Results from activated carbon adsorption at EBCT 2 hour presenting in Figure 4.20 indicated that total mass of mercury adsorbed on activated carbon 440 ml or 220 g (density of NORIT GAC 1240 is 0.5 g/ml) equal to 24,485 μg. The maximum adsorption capacity of NORIT GAC 1240 was 111.3 μg Hg/g. This value was closed to the maximum adsorption capacity from batch test as shown in Table 4.2; therefore, it may conclude that NORIT GAC 1240 was specific enough to mercury, so other contaminants cannot replace adsorbed mercury on the surfaces of activated carbon. On the other hand, activated carbon in batch test contacted to certain wastewater all the time until reach the equilibrium, the competition between mercury and other contaminants on the surfaces of activated carbon depended on the concentration and the selectivity of activated carbon. However, there is fresh wastewater always run into the column causing the patterns of the contact and adsorb were changed. It was mean that the contaminants which adsorb on the surface of activated carbon well can replace other adsorbed compounds which were less specific to activated carbon.

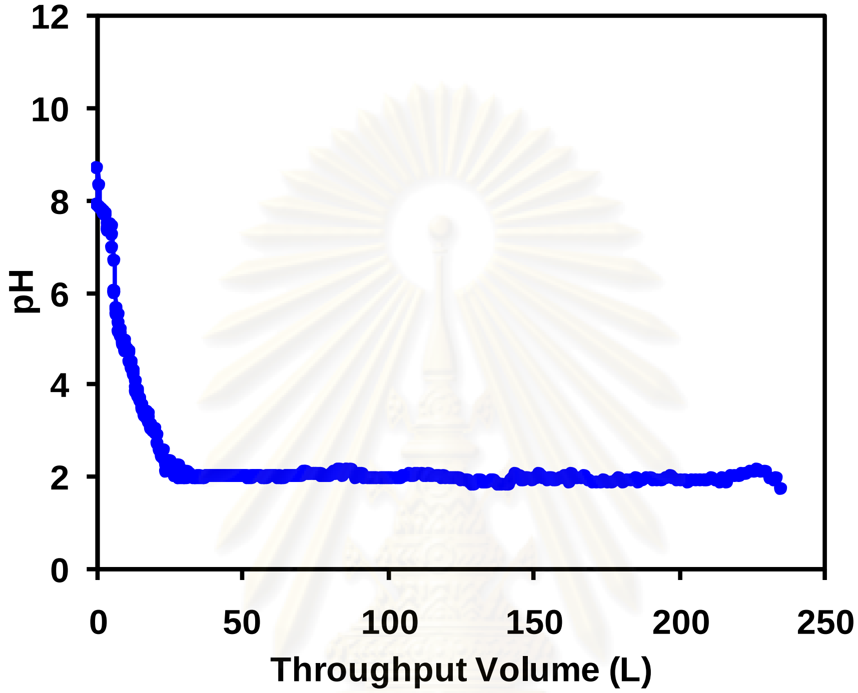

Figure 4.18 pH of treated wastewater from column adsorption of NORIT GAC 1240 volume 440 mL and filtration flow rate 220 mL/h (HRT = 2 hours) at pH solution 2

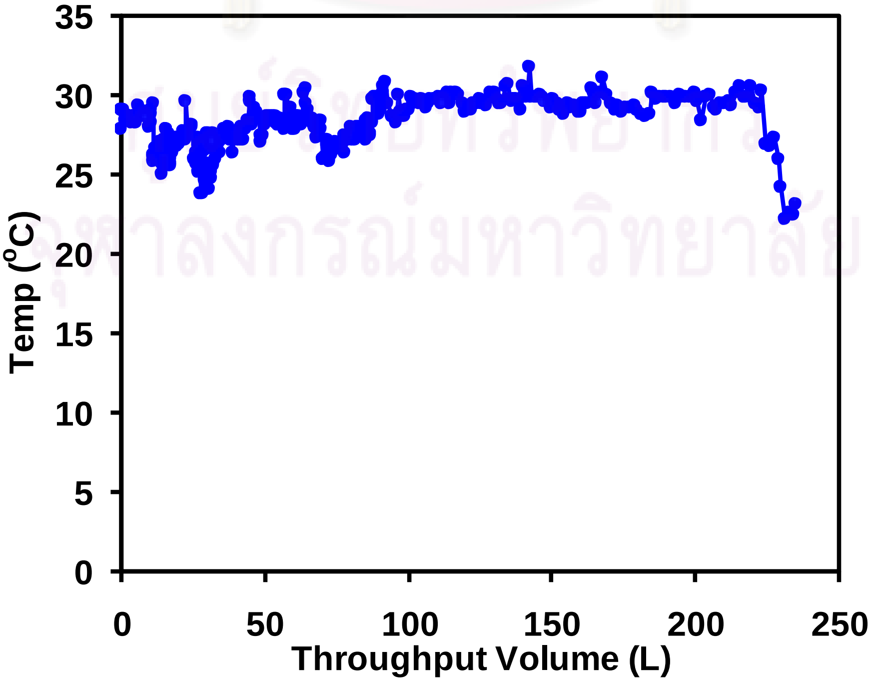

Figure 4.19 Temperature of treated wastewater from column adsorption of NORIT GAC 1240 volume 440 mL and filtration flow rate 220 mL/h (HRT = 2 hours) at pH solution 2

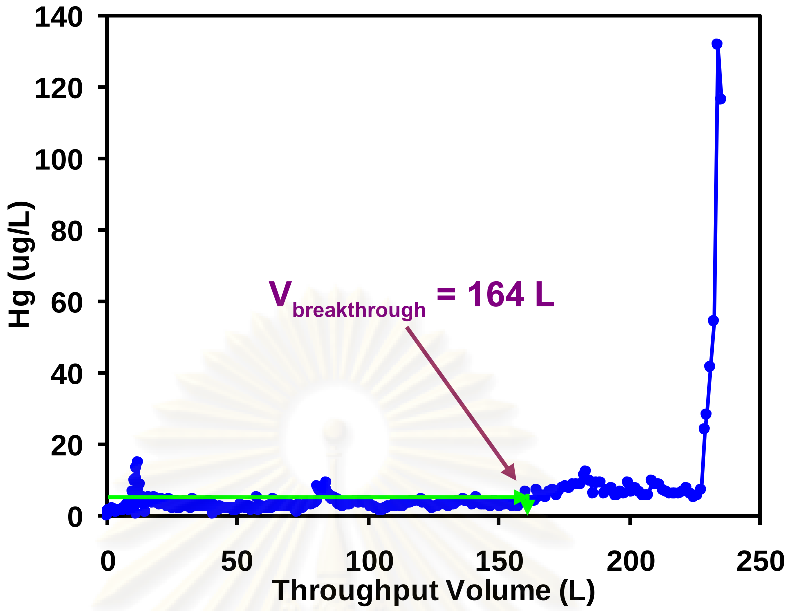

Figure 4.20 Breakthrough curve at pH 2 of adsorption of mercury by NORIT GAC 1240 volume 440 ml filtration flow rate 220 ml/hr (HRT = 4 hr, $[Hg_0]$ = 103.82 ug/L)

It can be seen from the data in Table 4.20 that volume of treated wastewater until reach a breakthrough at 5 μg/L was 164 L. The adsorption capacity of NORIT GAC 1240 when reach the breakthrough was 76.5 μg Hg/g activated carbon and activated carbon in the column was used 68.7 %. The proportion of volume of treated wastewater before breakthrough and exhausted activated carbon was 372.7.

Table 4.4 Adsorption capacity of NORIT GAC 1240 at volume 440 mL, pH 2, and EBCT 2 hours

$[Hg]_{in, avg}$ (μg/L)	$Hg_{adsorbed}$ (μg)		Adsorption Capacity (μg Hg per g AC)		
	Total	Breakthrough	Total	Breakthrough	%Total
103	24,485	16,838	111.3	76.5	68.7

4.3.3 Comparison between activated carbon adsorption and ion exchange

This part compared the results of mercury treatment by activated carbon adsorption and ion exchange (Pongpattharin, 2011) in the same conditions. At the same initial concentration of mercury in raw wastewater at pH 2 and 5, the results were presented in Figure 4.21 and 4.22 respectively. Figure 4.21 provided resin IRC 718 can remove mercury better than activated carbon CGC-12 and followed by NORIT 1240 and resin C 433, and MERSORB LW had the lowest capacity. At pH solution 5, activated carbon NORIT 1240 and MERSORB LW had a higher capacity than resin IRC 718, CGC-12 and resin C 433, respectively as shown in Figure 4.42. However in case of high concentration of mercury (approximate 100 μg/L) which was closed to the average mercury concentration in the condensate tank, NORIT GAC 1240 was the best performance at pH 2. From Figure 4.43 comparing the isotherms of NORIT GAC 1240 and resin IRC 718 at pH2 which was the optimum condition for both NORIT GAC 1240 and resin IRC 718, it may implied that NORIT GAC 1240 had a better tendency to remove mercury than resin IRC 718 and it was according to the results from the column adsorption test.

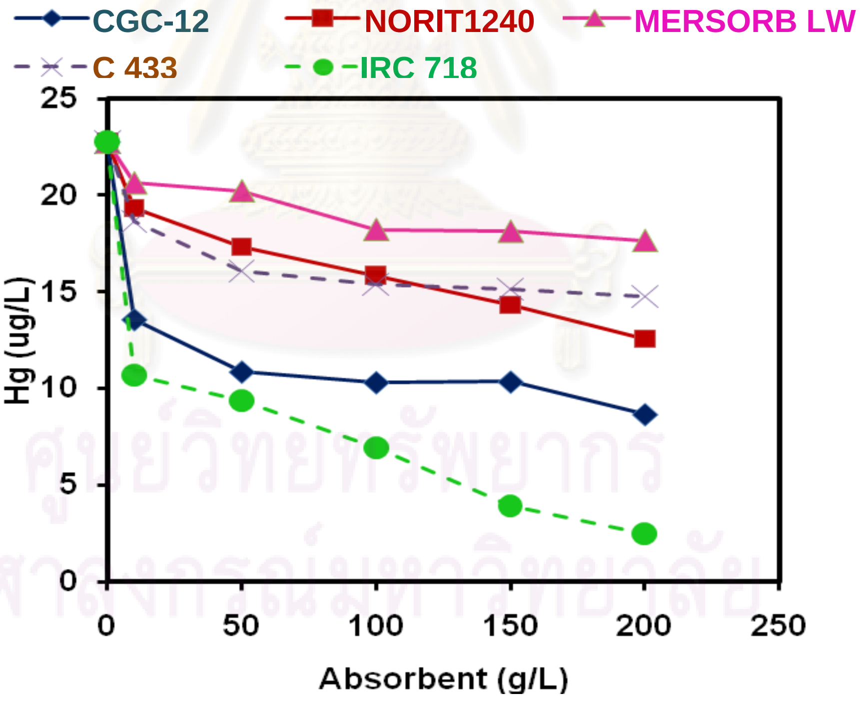

Figure 4.21 Comparison of mercury removal between activated carbon and resin at pH 2

(—: NORIT GAC 1240; - - : resin IRC 718)

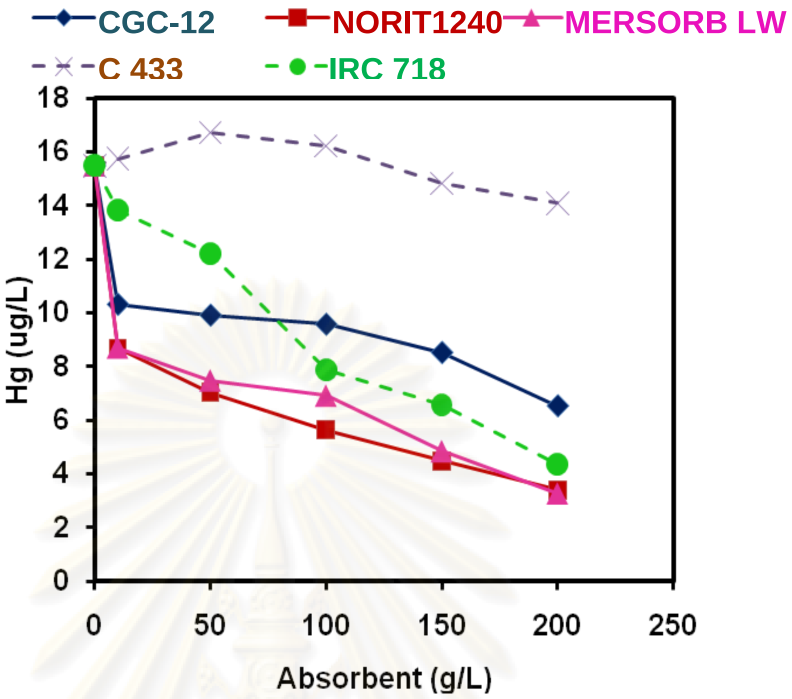

Figure 4.22 Comparison of mercury removal between activated carbon and resin at pH 5 (: NORIT GAC–1240; - - : resin IRC 718) (ion exchange data came from Pongpattharin, 2011)

4.4 Economic Consideration

The results from column test can be applied to design the real activated carbon columns in field practice for petrochemical industry. Several approaches are typically applied for this scale-up purpose such as Bohart-Adams expression, scale-up approach, and kinetics approach which using Thomas expression (Reynolds and Richards, 1996). Since this study performed with only one column condition, the Bohart-Adams could not be used. For kinetics approach using Thomas expression as shown in Equation (4.1), it was found that the adsorption data obtained from column test could not fit with the linearized form of Thomas expression as shown in Equation (4.2) (illustration was not shown). This is possibly due to the fact that mercury was considering as a trace substance in this wastewater (in µg/L scale) as compared to other adsorbate species (in mg/L scale); therefore, the adsorption behavior of mercury might not follow the theoretical derivation, because of the interference from major species. For scale-up approach, it is very convenient to apply in this case since the empty bed contact time (EBCT) of the tested column was similar to those of the existing columns of the studied plant.

$$-\cong\frac{\qquad}{-\quad .}\qquad (4.1)$$

$$\ln\left(\frac{}{} - 1\right) = \frac{}{} - \frac{k_1C_0V}{Q} \qquad (4.2)$$

Applying scale-up approach to activated carbon column of petrochemical plant which had activated carbon 658 L and flow rate 8 m^3/d, and EBCT 2 hours, the results showed that activated carbon can be used for mercury adsorption 30.7 day until breakthrough and then replace the new activated carbon in case of single adsorption column. The cost of activated carbon for replacing in the real column was 300 Baht/m^3 wastewater. This price was calculated from cost of activated carbon and disposal of spent activated carbon (price of NORIT GAC 1240 = 110 Baht/L and disposal of spent activated carbon = 4,000 Baht/ton)

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

These findings enhanced our understanding of adsorption of mercury in wastewater of petrochemical industry as follows:

1. Wastewater from condensate tank contained various organic and inorganic compounds which were much more abundant than mercury concentration. These compounds might compete for adsorption surfaces of activated carbons and interrupt adsorption process and cause activated carbon adsorb mercury down to 5 μg/L abided by the industrial effluent standard more difficultly.
2. Mercury removal efficiency from petrochemical industry by NORIT GAC 1240 which was an activated carbon used in the mercury treatment unit of this plant was higher than a sulfur impregnated activated carbon, MERSORB LW, which was specific to mercury and a high purity grade of activated carbon CGC-12 which used for solvent recovery.
3. Mercury adsorption by activated carbon reached an equilibrium within12 hours and the optimum condition was pH 2 and the adsorption was unfavorable resulting in using plenty of activated carbons in the process.
4. The evidence from this study suggests that optimum conditions from batch adsorption tests and design criteria from column adsorption tests were useful options for application in the mercury treatment units of petrochemical industry.
5. Ratio of treated wastewater to amount of NORIT GAC 1240 was 372.7 which was much higher than ion exchange by IRC 718. In case of real column in the treatment unit which contained activated carbon 658 L can operate 30.7 days until reached breakthrough point. The cost of mercury adsorption process was 295 Baht/m^{3}wastewater (NORIT GAC 1240 = 110 Baht/L).

5.2 Recommendations

The optimal of bed depth and flow rate is the significant parameter of column test that influences on the performance of activated carbon adsorption. Increasing bed height of activated carbon causes increase in number of binding sites broadening the mass transfer zone. The flow rate relates to speed of adsorption zone. Increasing flow rate resulting in decrease in the time required to reach the specific breakthrough concentration and cause insufficient time for adsorption and diffusion limitations of adsorbate on the activated carbon in column. The effects of variations of bed depth and flow rate are concern; therefore, the continued works should be performed as follows.

1. Vary filtration flow rates
2. Vary bed depths of activated carbon

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APPENDICES

APPENDIX A

Mercury Digestion

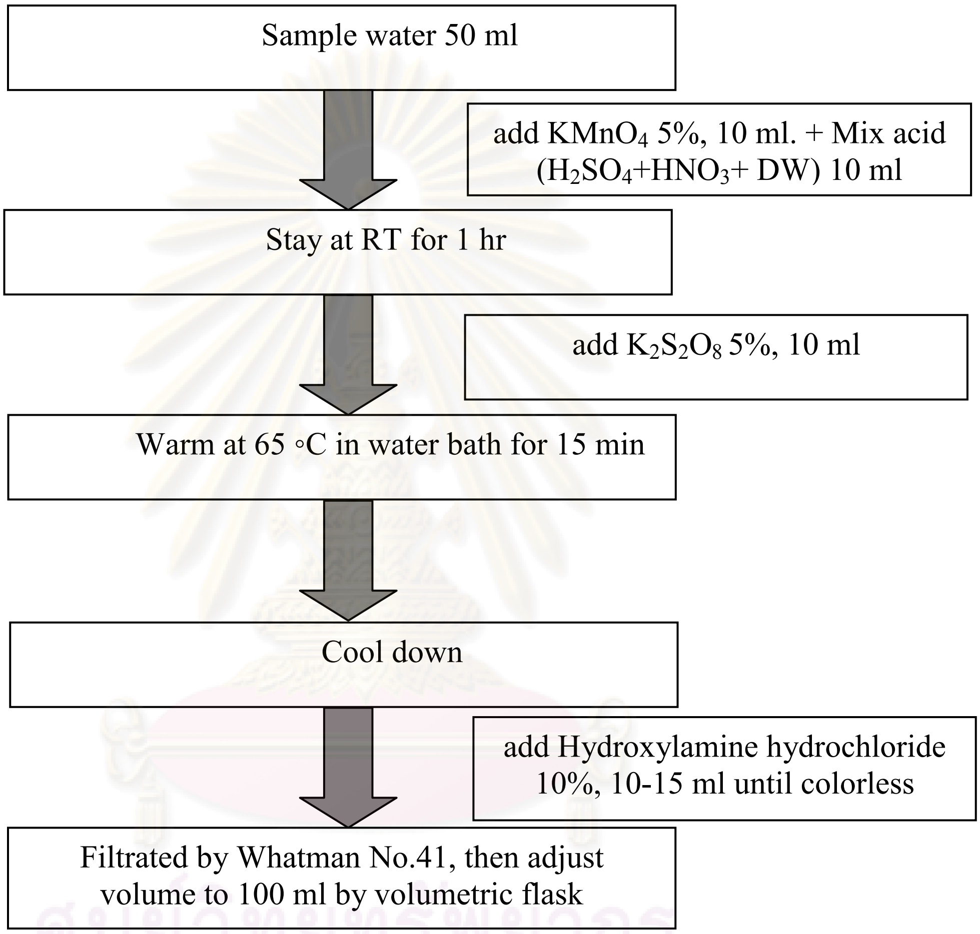

Figure A1 Digestion method of EPA 7470A for mercury in liquid waste

APPENDIX B

Table B1 Data from Effect of pH in mercury solubility in water (after filtrate with 6 micron filter paper)

Wastewater	**Hg concentration (μg/L)**
Deionized water	< 1.000
Raw wastewater	77.300
Raw wastewater pH 2	510.3
Raw wastewater pH 3	585.4
Raw wastewater pH 4	542.3
Raw wastewater pH 5	531.2
Raw wastewater pH 6	513.6
Raw wastewater pH 7	503.8
Raw wastewater pH 8	499.35
Raw wastewater pH 9	488.6
Filtered wastewater	< 1.000
Filtered wastewater pH 2	64.3
Filtered wastewater pH 3	61.4
Filtered wastewater pH 4	81.15
Filtered wastewater pH 5	97.8
Filtered wastewater pH 6	94.7
Filtered wastewater pH 7	120.8
Filtered wastewater pH 8	124.7
Filtered wastewater pH 9	135.9

Table B2 Data from adsorption of mercury by activated carbon 1 g/L

Table B2 Data from adsorption of mercury by activated carbon 1 g/L

Time (hr)	**Hg Concentration (µg/l)**		**pH**	
	CGC-12	MERSORB ®LW	CGC-12	MERSORB ®LW
0	131.4	125.1	5.08	5.07
1	122.8	122.2	5.10	5.06
2	125.4	121.3	5.09	5.02
6	115.7	126.1	5.10	5.00
12	125.4	122.1	4.99	4.93
24	121.0	121.7	4.96	4.87
48	123.3	123.4	4.90	4.79

Table B3 Data from concentrations of mercury in wastewater at equilibrium and the quantities of activated carbons at initial pH solution 2

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	15.49	15.49	15.49	2	2	2
1	10.32	8.70	8.71	2.3	4.71	4.71
5	9.92	7.03	7.49	5.94	4.41	4.41
10	9.58	5.64	6.93	7.61	6.27	6.27
15	8.52	4.47	4.85	8.35	7.23	7.23
20	6.54	3.40	3.28	8.87	7.65	7.65

Table B4 Data from adsorption isotherm of Figure 4.4 at initial pH solution 2

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	15.49	10.32	8.70	8.71	0.52	0.68	0.68
5	15.49	9.92	7.03	7.49	0.11	0.17	0.16
10	15.49	9.58	5.64	6.93	0.06	0.10	0.09
15	15.49	8.52	4.47	4.85	0.05	0.07	0.07
20	15.49	6.54	3.40	3.28	0.04	0.06	0.06

Table B5 Data from concentrations of mercury in wastewater at equilibrium and the quantities of activated carbons at initial pH solution 5

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	22.77	22.77	22.77	5	5	5
1	13.58	19.34	20.65	6.83	5.71	5.16
5	10.87	17.33	20.24	8.28	7.32	5.97
10	10.32	15.86	18.23	9.19	8.51	6.55
15	10.35	14.34	18.14	9.5	8.82	6.7
20	8.67	12.58	17.66	9.64	8.84	6.8

Table B6 Data from adsorption isotherm of Figure 4.4 at initial pH solution 5

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	22.77	13.58	19.34	20.65	0.92	0.34	0.21
5	22.77	10.87	17.33	20.24	0.24	0.11	0.05
10	22.77	10.32	15.86	18.23	0.12	0.07	0.05
15	22.77	10.35	14.34	18.14	0.08	0.06	0.03
20	22.77	8.67	12.58	17.66	0.07	0.05	0.03

Table B7 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the first adsorption test at initial pH solution 2

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	88.08	88.08	88.08	2	2	2
1	39.28	40.61	66.86	2.02	2.03	2.03
5	36.81	39.78	53.47	2.12	2.12	2.27
10	36.46	31.07	43.92	2.66	2.52	3.02
15	30.81	29.53	37.57	3.87	2.81	3.48
20	26.37	31.54	34.93	4.23	2.92	3.74

Table B8 Data from adsorption isotherm of Figure 4.7 at initial pH solution 2

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	88.08	39.28	40.61	66.86	4.88	4.75	2.12
5	88.08	36.81	39.78	53.47	1.03	0.97	0.69
10	88.08	36.46	31.07	43.92	0.52	0.57	0.44
15	88.08	30.81	29.53	37.57	0.38	0.39	0.34
20	88.08	26.37	31.54	34.93	0.31	0.28	0.27

Table B9 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the first adsorption test at initial pH solution 5

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB $^{®}$LW	CGC-12	NORIT GAC 1240	MERSORB $^{®}$LW
0	167.25	167.25	167.25	5	5	5
1	214.53	99.99	158.69	6.23	5.06	5.04
5	113.55	95.82	158.77	6.17	5.84	5.13
10	104.40	89.58	145.23	6.69	6.64	5.73
15	63.16	70.24	132.39	6.91	6.73	6.01
20	35.51	18.87	130.76	6.84	7.57	6.5

Table B10 Data from adsorption isotherm of Figure 4.7 at initial pH solution 5

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB $^{®}$LW	CGC-12	NORIT GAC 1240	MERSORB $^{®}$LW
1	167.25	214.53	99.99	158.69	-4.73	6.73	0.86
5	167.25	113.55	95.82	158.77	1.07	1.43	0.17
10	167.25	104.40	89.58	145.23	0.63	0.78	0.22
15	167.25	63.16	70.24	132.39	0.69	0.65	0.23
20	167.25	35.51	18.87	130.76	0.66	0.74	0.18

Table B11 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the second adsorption test 2 at initial pH solution2

Dose (g)	Hg Concentration (µg/L)			pH		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	208.20	208.20	208.20	2	2	2
1	31.08	12.75	32.98	2.02	2.03	2.01
5	18.06	16.71	25.56	2.13	2.05	2.11
10	20.60	13.24	25.03	2.30	2.30	2.6
15	12.72	10.58	24.83	2.61	2.29	3.11
20	5.80	5.30	26.14	2.89	2.38	2.96

Table B12 Data from adsorption isotherm of Figure 4.9 at initial pH solution 2

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	208.20	31.08	12.75	32.98	17.71	19.55	17.52
5	208.20	18.06	16.71	25.56	3.80	3.83	3.65
10	208.20	20.60	13.24	25.03	1.88	1.95	1.83
15	208.20	12.72	10.58	24.83	1.30	1.32	1.22
20	208.20	5.80	5.30	26.14	1.01	1.01	0.91

Table B13 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the second adsorption test 2 at initial pH solution5

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	233.20	233.20	233.20	5	5	5
1	30.47	28.76	105.41	4.89	4.97	4.96
5	23.85	22.08	103.15	5.70	5.66	5.29
10	24.57	18.68	96.80	6.25	5.45	5.44
15	23.98	9.01	24.75	6.70	5.89	5.35
20	15.22	11.48	9.57	6.52	6.36	6.14

Table B14 Data from adsorption isotherm of Figure 4.9 at initial pH solution 5

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	233.20	30.47	28.76	105.41	20.27	20.44	12.78
5	233.20	23.85	22.08	103.15	4.19	4.22	2.60
10	233.20	24.57	18.68	96.80	2.09	2.15	1.36
15	233.20	23.98	9.01	24.75	1.39	1.49	1.39
20	233.20	15.22	11.48	9.57	1.09	1.11	1.12

Table B15 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the third adsorption test at initial pH solution 2

Dose (g)	**Hg Concentration (µg/l)**		**pH**	
	NORIT GAC 1240	MERSORB ®LW	NORIT GAC 1240	MERSORB ®LW
0	241.20	241.20	2	2
1	21.25	29.56	2.02	2.07
5	20.90	18.78	2.51	3.21
10	9.80	13.44	3.38	3.55
15	5.41	13.62	4.58	3.95
20	6.48	11.04	3.99	4.06

Table B16 Data from adsorption isotherm of Figure 4.11 at initial pH solution 2

Carbon dose (g)	Initial concentration	C_e		q_e	
		NORIT GAC 1240	MERSORB ®LW	NORIT GAC 1240	MERSORB ®LW
1	241.20	21.25	29.56	22.00	21.16
5	241.20	20.90	18.78	4.41	4.45
10	241.20	9.80	13.44	2.31	2.28
15	241.20	5.41	13.62	1.57	1.52
20	241.20	6.48	11.04	1.17	1.15

Table B17 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used in the third adsorption test at initial pH solution 5

Dose (g)	Hg Concentration (µg/l)		pH	
	NORIT GAC 1240	MERSORB ®LW	NORIT GAC 1240	MERSORB ®LW
0	231.80	231.80	5	5
1	16.11	31.36	5.48	5.44
5	17.46	15.44	5.96	5.78
10	12.11	15.52	6.47	5.95
15	10.19	12.49	6.61	6.07
20	10.14	9.91	6.69	6.43

Table B18 Data from adsorption isotherm of Figure 4.11 at initial pH solution 5

Carbon dose (g)	Initial concentration	C_e		q_e	
		NORIT GAC 1240	MERSORB ®LW	NORIT GAC 1240	MERSORB ®LW
1	231.80	16.11	31.36	21.57	20.04
5	231.80	17.46	15.44	4.29	4.33
10	231.80	12.11	15.52	2.20	2.16
15	231.80	10.19	12.49	1.48	1.46
20	231.80	10.14	9.91	1.11	1.11

Table B19 Data from concentrations of mercury adding $Hg(NO_3)_2$ 100 µg/L at equilibrium time and the quantities of activated carbons used at initial pH solution 7

Dose (g)	**Hg Concentration (µg/l)**			**pH**		
	CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
0	222.60	222.6	222.6	7	7	7
1	41.67	35.71	108.06	7.41	6.77	6.96
5	19.63	23.79	37.17	7.81	7.01	6.86
10	15.57	16.32	24.80	7.81	7.48	6.8
15	7.37	11.25	12.62	7.92	7.56	6.78
20	8.28	13.22	8.61	7.83	7.65	6.73

Table B20 Data from adsorption isotherm of Figure 4.11 at initial pH solution 7

Carbon dose (g)	Initial concentration	C_e			q_e		
		CGC-12	NORIT GAC 1240	MERSORB ®LW	CGC-12	NORIT GAC 1240	MERSORB ®LW
1	222.60	41.67	35.71	108.06	18.09	18.69	11.45
5	222.60	19.63	23.79	37.17	4.06	3.98	3.71
10	222.60	15.57	16.32	24.80	2.07	2.06	1.98
15	222.60	7.37	11.25	12.62	1.43	1.41	1.40
20	222.60	8.28	13.22	8.61	1.07	1.05	1.07

Table B21 Data from breakthrough curve at pH 2 of adsorption of mercury by MERSORB$^{®}$LW volume 880 ml filtration flow rate 220 ml/hr (HRT = 4 hr, [Hg$_0$] = 118.5 ug/L)

Volume(L)	Hg (ppb)
0.00	118.46
0.11	4.37
0.33	7.74
0.55	3.94
0.77	3.03
0.99	3.48
1.21	3.98
1.43	3.66
1.65	7.45
1.87	5.69
2.09	4.90
2.31	7.44
2.53	5.23
2.75	5.59
2.97	5.81
3.19	5.94
3.41	6.19
3.63	5.78
3.85	5.87
4.07	5.93
4.29	6.20
4.51	6.53
4.73	6.36
4.95	6.26
5.17	5.91
5.39	6.34
5.62	5.83
5.84	6.23
6.06	4.83
6.28	4.90

Table B21 (continued)

Volume(L)	Hg (ppb)
6.50	4.82
6.72	4.88
6.94	4.68
7.16	4.61
7.38	4.67
7.60	4.74
7.82	4.67
8.04	4.60
8.26	4.75
8.48	4.44
8.70	4.62
8.92	4.81
9.14	4.42
9.36	4.76
9.58	5.51
9.80	5.36
10.02	5.21
10.24	5.15
10.46	5.05
10.68	5.18
10.90	5.29

Table B22 Data from breakthrough curve at pH 2 of adsorption of mercury by NORIT GAC 1240 volume 880 ml filtration flow rate 220 ml/hr (HRT = 4 hr, $[Hg_0]$ = 118.5 ug/L)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
0.00	118.46	7.89	27.9
0.22	1.10	8.68	29
0.66	1.31	8.32	29.1
1.10	1.15	7.85	29
1.54	1.31	7.81	28.8
1.65	1.52	7.78	28.8
1.87	1.82	7.77	28.4
2.09	1.61	7.73	28.7
2.31	1.59	7.77	28.5
2.53	1.34	7.72	28.7
2.75	1.67	7.69	28.7
2.97	1.40	7.67	28.6
3.19	1.12	7.65	28.6
3.41	0.89	7.4	28.4
3.63	1.76	7.33	28.3
3.85	1.43	7.35	28.5
4.07	1.68	7.45	28.4
4.29	1.74	7.45	28.4
4.51	1.46	7.47	28.7
4.73	1.44	7.48	28.7
4.95	1.51	7.41	28.3
5.17	1.52	7.23	28.3
5.39	1.59	6.96	28.6
5.62	1.29	6.7	28.6
5.84	1.66	5.99	29.3
6.06	1.78	6.02	28.7
6.28	1.55	5.96	28.7
6.50	2.01	5.67	28.9
6.72	2.23	5.59	29.1
6.94	1.95	5.53	29.1

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
7.16	2.21	5.52	28.8
7.38	2.69	5.3	28.9
7.60	2.73	5.14	28.9
7.82	2.68	5.18	28.8
8.04	2.95	5.09	28.8
8.26	3.10	5.03	28.9
8.48	2.93	5.03	28.6
8.70	1.62	4.9	28.9
8.92	1.96	4.89	28.9
9.14	3.59	4.87	28.8
9.36	3.33	4.96	28.8
9.58	6.73	4.78	28.9
9.80	2.05	4.84	28.8
10.02	2.03	4.73	28
10.24	9.95	4.78	28.8
10.46	3.65	4.74	28.3
10.68	3.07	4.72	29.1
10.90	10.37	4.7	29.4
11.12	4.35	4.65	25.8
11.34	13.45	4.47	26.2
11.56	0.54	4.5	26.1
11.78	14.64	4.46	26.4
12.00	3.53	4.42	26.6
12.22	7.07	4.36	26.6
12.44	3.54	4.29	26.5
12.66	8.88	4.24	26.50
12.88	4.25	4.18	26.00
13.10	4.53	4.07	26.80
13.32	3.76	3.93	27.00
13.54	3.56	3.82	26.90
13.76	4.12	3.86	26.90

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C$^{\circ}$)
13.98	5.08	3.76	26.50
14.20	3.54	3.85	25
14.42	1.00	3.75	25.7
14.64	1.00	3.67	26.5
14.86	3.27	3.66	27.2
15.08	4.28	3.62	27
15.30	4.17	3.55	27
15.52	4.39	3.5	27.8
15.74	4.39	3.45	27.2
15.96	5.04	3.43	27.8
16.18	4.52	3.38	27.6
16.40	4.64	3.3	27.6
16.63	4.54	3.34	27
16.85	4.46	3.29	26.9
17.07	4.09	3.43	25.6
17.29	3.59	3.35	25.7
17.51	4.43	3.34	26
17.73	4.60	3.27	26.3
17.95	4.07	3.19	26.6
18.17	4.97	3.16	27
18.39	4.15	3.12	26.8
18.61	3.84	3.08	26.8
18.83	4.08	3.04	27.2
19.05	3.91	3.02	27
19.27	3.93	3.01	27.3
19.49	3.59	2.99	26.8
19.71	3.63	2.94	26.7
20.15	3.36	3.02	26.9
20.59	2.93	2.89	26.9
21.03	4.84	2.69	27.1
21.47	3.49	2.56	27.7

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C$^{\circ}$)
21.91	3.38	2.54	27.3
22.35	3.76	2.43	27.1
22.79	3.83	2.56	29.6
23.23	2.78	2.38	27.4
23.67	4.51	2.26	27.7
24.11	4.34	2.11	27.9
24.55	4.28	2.2	28.1
24.99	3.87	2.18	28
25.43	2.31	2.34	26
25.87	3.21	2.24	26.2
26.31	3.01	2.15	26.4
26.75	3.10	2.11	26.7
27.19	3.45	2.11	27.3
27.64	3.27	2.12	27.1
28.08	2.18	2.26	23.8
28.52	3.37	2.18	23.8
28.96	3.57	2.13	24.6
29.40	3.78	2.09	25.2
29.84	3.95	2.08	25.7
30.28	4.20	2.07	25.4
30.72	4.13	2.06	24.1
31.16	3.01	2.09	24.7
31.60	4.34	2.04	25.2
32.04	4.29	2.01	25.6
32.48	4.18	2.03	25.7
32.92	4.47	2.01	25.9
26.53	3.83	2.02	25.7
26.75	3.88	2.08	25.1
27.19	2.23	2.02	25.6
27.64	3.44	1.99	25.6
28.08	3.03	1.98	26.8

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
28.52	3.20	1.98	26.4
28.96	2.86	1.95	26.5
29.40	2.92	1.98	26.7
29.84	2.98	2	26.7
30.28	2.53	1.97	27.6
30.72	2.49	1.96	27.6
31.16	2.43	1.98	27.5
31.60	2.53	2.04	26.6
32.04	2.15	2	27.2
32.48	2.54	2	27.6
32.92	2.99	1.99	27.4
33.36	2.75	1.98	27.4
33.80	2.71	1.98	26.6
34.24	2.64	1.97	26.4
34.68	2.94	2.02	27
35.12	2.50	1.98	27.2
35.56	2.92	1.99	27.3
36.00	2.64	1.98	27.9
36.44	2.79	1.97	27.6
36.88	2.74	1.98	27.6
37.32	2.34	1.98	28
37.76	2.81	1.99	27.6
38.20	2.77	2	27.1
38.65	3.02	1.99	26.4
39.09	3.27	2	27.5
39.53	4.04	2.01	27.7
39.97	2.41	1.99	27.1
40.41	3.21	2	27.5
40.85	0.72	2.01	27.7
41.29	1.54	1.99	27.1
41.73	1.56	2	28

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C$^{\circ}$)
42.17	1.75	2	27.2
42.61	1.44	2.03	27.2
43.05	1.64	2.02	27.8
43.49	2.52	2.03	27.8
43.93	1.89	2.02	28.4
44.37	1.83	2.03	28.4
44.81	1.95	2.02	29.8
45.25	2.01	2.02	29.6
45.69	1.96	2	28.1
46.13	1.83	2.01	28.6
46.57	1.85	2.03	29.2
47.01	1.86	2.02	28.9
47.45	1.88	2.03	28.9
47.89	1.81	2.03	28.7
48.33	1.38	2.03	27
48.77	1.87	2.03	27.5
49.21	1.75	2.03	28.5
49.66	1.44	2.02	27.5
50.10	1.87	2.02	28.2
50.54	1.91	2.02	28.1
50.98	3.15	2.02	28.6
51.42	2.14	2.01	28.6
51.86	2.35	2.01	28.5
52.30	2.49	1.95	28.4
52.74	2.39	1.96	28.6
53.18	2.39	1.97	28.6
53.62	2.27	1.99	28.6
54.06	2.63	2.01	28.3
54.50	2.46	1.99	28.1
54.94	2.33	1.99	28.3
55.38	1.65	1.99	28.5

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
55.82	1.86	2	28.2
56.26	2.30	1.99	28.3
56.70	2.28	1.99	27.8
57.14	5.08	1.98	30
57.58	2.26	1.98	30
58.02	1.79	1.97	30
58.46	2.25	1.96	28.4
58.90	2.41	1.99	29.2
59.34	1.98	2.01	28.4
59.78	2.51	1.99	28.4
60.22	2.11	1.99	27.9
60.67	1.87	2	27.9
61.11	2.19	2.01	28.6
61.55	2.37	2	28.7
61.99	2.10	1.99	28.7
62.43	1.90	1.98	28.5
62.87	1.95	1.97	28.1
63.31	1.95	1.99	28.4
63.75	4.66	1.98	30.2
64.19	2.92	1.98	30.4
64.63	3.57	1.98	29.4
65.07	2.77	1.99	29.1
65.51	2.82	1.99	28.6
65.95	3.23	2	28.5
66.39	2.55	2.02	28.3
66.83	2.59	2.01	28.5
67.27	2.36	2	28.3
67.71	3.52	2	28
68.15	3.09	2.01	27.3
68.59	2.49	2.01	27.6
69.03	2.83	2.02	27.9

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
69.47	3.30	2.01	28.4
69.91	2.82	2.01	27.9
70.35	2.44	2.02	25.9
70.79	2.53	2.07	25.9
71.23	2.42	2.12	26.1
71.68	2.55	2.12	26.7
72.12	1.49	2.08	27.2
72.56	2.02	2.04	26.4
73.00	1.25	2.05	25.8
73.44	2.97	2.07	26.2
73.88	2.01	2.07	26.5
74.32	2.06	2.07	26.9
74.76	1.99	2.05	27
75.20	2.29	2.05	26.8
75.64	2.77	2.04	26.7
76.08	3.05	2.06	26.6
76.52	3.24	2.06	26.7
76.96	3.33	2.05	26.7
77.40	3.52	2.03	26.8
77.84	3.55	2	26.3
78.28	3.76	2.02	27.4
78.72	3.33	2.01	27.4
79.16	3.48	2.01	27.1
79.60	3.52	2.03	27.4
80.04	3.44	2.03	27.4
80.48	4.02	2.03	28
80.92	8.04	2.05	27.2
81.36	7.13	2.06	27.1
81.80	7.83	2.08	27.4
82.24	7.24	2.07	28
82.69	6.76	2.06	27.9

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C$^{\circ}$)
83.13	7.20	2.13	28
83.57	7.58	2.15	27.8
84.01	7.13	2.11	27.9
84.45	9.25	2.07	27.7
84.89	6.03	2.02	27.8
85.33	5.83	2.08	27.2
85.77	4.99	2.15	28.4
86.21	4.81	2.14	28.5
86.65	4.77	2.11	27.6
87.09	4.93	2.11	27.5
87.53	4.43	2.15	28.2
87.97	4.40	2.09	29.7
88.41	3.68	2.04	29.8
88.85	3.43	1.99	29.7
89.29	2.99	1.97	29.8
89.73	3.20	2	28.8
90.17	3.08	2.02	29
90.61	2.79	2.04	29.1
91.05	2.84	2.04	30.5
91.49	2.98	2.03	30.2
92.37	3.20	1.98	30.8
93.25	3.22	1.98	29.5
94.14	3.48	1.98	28.6
95.02	3.98	1.97	28.6
95.90	3.89	1.96	28.3
96.78	3.84	1.96	30
97.66	4.11	1.94	28.9
98.54	3.62	1.95	28.7
99.42	4.29	1.94	29
100.30	3.88	1.94	29.1
101.18	2.79	1.95	29.9

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C$^{\circ}$)
102.06	2.41	1.95	29.4
102.94	1.84	1.94	29.7
103.82	1.85	1.96	29.5
104.71	1.70	1.98	29.7
105.59	1.73	2.02	29.6
106.47	2.04	2.03	29.2
107.35	2.12	2.04	29.5
108.23	2.37	2.03	29.7
109.11	2.44	2.03	29.7
109.99	3.14	2.06	29.7
110.87	2.58	2.07	29.8
111.75	3.62	2.06	29.4
112.63	2.48	2.02	29.9
113.51	2.68	1.99	30.1
114.39	2.90	2.04	29.4
115.27	3.43	2.02	30.1
116.16	3.47	2.01	30
117.04	4.23	2	30.1
117.92	4.22	1.99	30
118.80	4.20	1.97	29.5
119.68	3.90	1.99	28.9
120.56	4.86	1.96	29
121.44	3.64	1.96	29.1
122.32	3.42	1.95	29.1
123.20	3.07	1.97	29.5
124.08	2.43	1.97	29.5
124.96	2.02	1.97	29.7
125.84	2.37	1.93	29.5
126.73	2.42	1.93	29.6
127.61	2.85	1.91	29.3
128.49	2.94	1.87	30.1

Table B22 (continued)

Volume (L)	Hg (ppb)	pH	Temperature (C°)
129.37	2.90	1.84	30
130.25	3.20	1.84	30.1
131.13	2.79	1.9	29.7
132.01	2.90	1.9	29.5
132.89	3.10	1.88	29.4
133.77	3.78	1.87	30.5
134.65	4.21	1.89	30.7
135.53	4.03	1.93	29.7
136.41	4.47	1.91	29.6
137.29	3.92	1.86	29.7
138.18	4.23	1.82	29.7
139.06	3.96	1.82	29
139.94	3.20	1.83	30.5
140.82	3.58	1.84	30
141.70	5.03	1.83	29.9
142.58	3.44	1.91	31.7
143.46	3.23	1.94	29.8
144.34	3.04	2.06	29.8
145.22	3.28	1.99	29.9
146.10	3.21	1.93	30

BIOGRAPHY

Miss Nichaya Lortpenpien was born on March 22, 1987, in Bangkok, Thailand. In year 2008, she graduated with a second class honors in Bachelor degree of Science majoring in Microbiology from Chulalongkorn University. Later, she pursued her master's degree study in the International Program in Environmental Management, National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Graduate School, Chulalongkorn University, Bangkok, Thailand since 2008-2010.