การบำบัดปรอทในน้ำเสียจากถังคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยการแลกเปลี่ยนประจุ

นางสาวดรุณี พงษ์ภัทรินทร์

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TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ION EXCHANGE

Miss Darunee Pongpattarrine

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 ION EXCHANGE
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Field of Study	Environmental Management
Thesis Advisor	Assistant Professor Manaskorn Rachakornkij, Ph.D.
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ดรุณี พงษ์ภัทรินทร์ : การบำบัดปรอทในน้ำเสียจากถังคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยการแลกเปลี่ยนประจุ. (TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ION EXCHANGE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.มนัสกร ราชากรกิจ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.จินต์ อโณทัย, 118 หน้า.

การศึกษานี้เป็นการศึกษาเรื่องการบำบัดน้ำเสียที่ปนเปื้อนปรอทจากถังเก็บคอนเดนเสทของอุตสาหกรรมปิโตรเคมีด้วยกระบวนการแลกเปลี่ยนไอออนด้วยเรซิน เพื่อเป็นการหาวิธีเพื่อลดปริมาณปรอทที่ปนเปื้อนอยู่ในน้ำทิ้งจากถังเก็บคอนเดนเสทให้ได้ตามระดับตามมาตรฐานของน้ำทิ้งจากโรงงานอุตสาหกรรมที่กำหนดให้มีปรอทปนเปื้อนไม่เกิน 5 ppb พร้อมทั้งหาสภาวะที่เหมาะสมในการบำบัดโดยใช้การแลกเปลี่ยนไอออนด้วยเรซิน ประสิทธิภาพในการบำบัด และการออกแบบเพื่อนำเรซินไปใช้งานจริงในระดับอุตสาหกรรมโดยการศึกษาครั้งนี้ทำการทดลองกับเรซิน 2 ชนิด คือ เรซินแลกเปลี่ยนชนิดกรดอ่อน (Duolite C433) และ เรซินที่แลกเปลี่ยนจำเพาะเจาะจงกับปรอท (Amberlite IRC718) การทดลองแบบกะได้มีการศึกษาถึงปัจจัย ได้แก่ เวลาเข้าสู่สมดุล ค่าพีเอช ชนิดประจุแลกเปลี่ยน และสมการไอโซเทอม แล้วนำภาวะที่เหมาะสมมาศึกษาต่อในการทดลองแบบต่อเนื่อง ได้ทำการทดลองศึกษาความสูงของชั้นเรซินที่เหมาะสมซึ่งผลการศึกษาพบว่า เรซินชนิดที่จำเพาะต่อปรอท (Amberlite IRC718) มีความสามารถในการบำบัดปรอทในน้ำเสียให้มีปรอทลดต่ำกว่า 5 ppb จนเหลือ 2.5 ppb เพราะเรซินชนิดนี้มีความจำเพาะเจาะจงกับปรอทมากกว่าแคลเซียมถึง 43,000 เท่า ซึ่งสภาวะที่เหมาะสมได้แก่ ที่เวลาสมดุล 3 ชั่วโมง ค่าพีเอชที่เหมาะสมเท่ากับ 2 โปรตอนเป็นประจุแลกเปลี่ยนที่ให้ประสิทธิภาพดีกว่าโซเดียมไอออน และปริมาณเรซินที่เหมาะสมคือ 200 กรัมต่อลิตร สมการ Freundlich isotherm ไม่สามารถอธิบายการการแลกเปลี่ยนประจุได้ เนื่องจากในน้ำเสียจริงมีการรบกวนจากไอออนชนิดอื่นๆที่อยู่ในน้ำเสีย ส่งผลให้เกิดการแลกเปลี่ยนประจุแบบแข่งขันเกิดขึ้นและผลการทดลองแบบต่อเนื่องพบว่า การแลกเปลี่ยนไอออนเกิดขึ้นอย่างรวดเร็ว ซึ่งอัตราส่วนของน้ำที่กรองผ่านคอลัมน์ต่อปริมาตรเรซินที่ใช้มีค่าน้อยมาก แม้ว่าจะเพิ่มชั้นความสูงของเรซินแล้ว และประสิทธิภาพในการดูดซับของเรซินมีน้อย อย่างไรก็ตามเรซิน IRC718 มีประสิทธิภาพในการบำบัดปรอทให้ตามมาตรฐานได้

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ดรุณี พงษ์ภัทรินทร์
ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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DARUNEE PONGPATTARRINE: TREATMENT OF MERCURY IN WASTEWATER FROM CONDENSATE TANK OF PETROCHEMICAL INDUSTRY BY ION EXCHANGE. ADVISOR: ASST. PROF. MANASKORN RACHAKORNKIJ, Ph.D., CO-ADVISOR: ASSOC.PROF. JIN ANOTAI, Ph.D., 118 pp.

This study focuses on treatment of mercury in wastewater from condensate tank of petrochemical industry by ion exchange process in order to reduce mercury concentration in the wastewater to meet the regulatory requirement on effluent mercury level (5 ppb). In this study, optimal condition for ion exchange process, treatment efficiency, resin regeneration, design criteria for application in real operation and economic aspect were studied. Two types of resin were employed; weak acid cation exchange resin (Duolite C433) and mercury specific cation exchange resin (Amberlite IRC718). Batch study was carried out to determine equilibrium time, effect of pH, effect of exchange ion as well as adsorption isotherm. The optimal condition obtained from the batch test would be applied in the column study with varied bed depths. The results showed that Amberlite IRC718 had the capacity to reduce the mercury concentration in the wastewater down to 2.5 ppb. This is due to the fact its selectivity for mercury ions is 43,000 times higher than that for calcium ions. The optimal conditions was found at equilibrium time of 3 hours, pH 2, and resin dose of 200 grams/liter. Freundlich isotherm was unable to describe the ion exchange mechanism because of interference caused by competitive ion exchange with other ions in real wastewater. The continuous test showed that ion exchange process occurred rapidly. Although volume of resin in column was doubled, the ratio between volume of wastewater flowing through the column and volume of resin was still very low. The adsorption capacity of resin was low. This study concluded that Amberlite IRC718 was effective in reducing mercury level in the condensate wastewater to meet the 5 ppb standard.

Field of Study : Environmental Management Student's Signature Darunee Pongpattarrine

Academic Year : 2010 Advisor's Signature ....

Co-advisor's Signature..........................

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LIST OF ABBREVIATIONS

°C	Degree celsius
µl	Microliter
µg/L	Microgram per liter
µm	Micrometer
AAS	Adsorption spectrophotometer
BOD	Biological oxygen demand
BV/h	Bed volume per hour
cm	Centimeter
COD	Chemical oxygen demand
Conc	Concentration
DI	Deionized water
eq/l	Equivalent per liter
FOG	Fat oil and grease
g	Gram
g/cm^3	Gram per cubic centimeter
g/ml	Gram per milliliter
g/mole	Gram per mole
HCl	Hydrochloric acid
Hg	Mercury
$Hg(NO_3)_2$	Mercury(II) nitrate
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
K	Kelvin
kg	Kilogram
$KMnO_4$	Potassium permanganate
$K_2S_2O_8$	Potassium persulfate
L	Liter
M	Molar
meq/ml	Milliequivalent per milliliter
mg	Milligram

mg/L	Milligram per liter
ml/hour	Milliliter per hour
min	Minute
ml	Milliliter
mΩ	Milliohm
MW	Molecular weight
NaOH	Sodium hydroxide
NH_2OH HCl	Hydroxylamine hydrochloride
pH	Power of hydrogen
ppb	Part per billion
TDS	Total dissolve solids
TOC	Total organic carbon
TSS	Total suspended solid

CHAPTER I

INTRODUCTION

1.1 Problem and inspiration

A petrochemical production plant uses crude oil from the condensate tank of petroleum refinery as a raw material to produce aromatic products. The wastewater drained from this condensate tank contaminates mercury as high as 2,000 ppb; therefore, it has to be properly treated before discharging to receiving waters. Existing treatment units for mercury removal at this factory are shown in Figure 1.1.

1. Oil is firstly removed by flotation in a surge tank to prevent adverse impact in the following units.

2. Skimmed wastewater is transferred to an acid buffer tank to lower the pH to 3 to 4 by sulfuric acid (H_2SO_4) to increase adsorptive of mercury onto activated carbon surface.

3. Acidified wastewater is then passed through a series of activated carbon columns in which mercury is adsorbed and removed from the water.

4. Treated water is adjusted to pH 7 in an acid buffer tank and transferred to combined treatment facilities to remove residual organic pollutants in terms of BOD and COD.

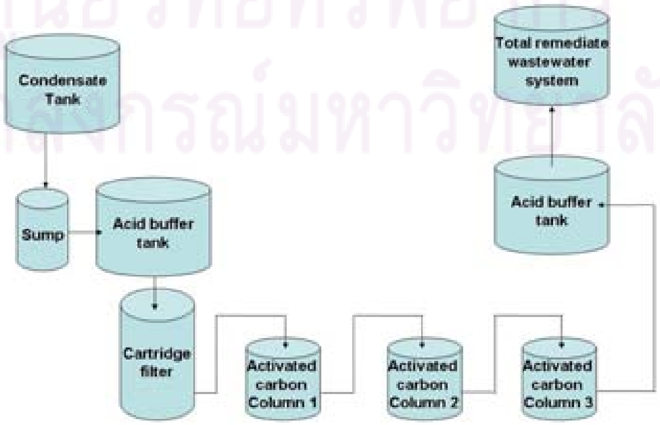


Figure 1.1 Treatment diagram for mercury removal.

At this moment, it is found that this mercury treatment system is not quite stable, i.e., treated effluent still periodically contains high mercury contents in the range of 6 to 150 μg/L which are higher than the industrial effluent standard of 5 μg/L. Hence, there is an urgent need to improve or retrofit this mercury removal unit in order to ensure that effluent mercury always complies with the standard.

1.2 Objectives of the study

Main-objective

1. To investigate the feasibility of using ion exchange process to remove mercury from condensate discharge of petrochemical production industry.
2. If ion exchange technology is feasible, to determine the optimum conditions, design criteria, and economic aspect of the ion exchange column for field practice.

Sub-objectives

1. To compare mercury removal efficiencies of ion exchange process to existing activated carbon adsorption.
2. To characterize ion exchange behavior between mercury selective and non selective cationic exchange resins both in isotherm batch test and column test.
3. To determine regeneration ability of spent resins and their exchange capability after regeneration for long-term usage.

1.3 Hypotheses

1. Ion exchange process, particularly with mercury selective exchange resins, can remove mercury in selective manner.
2. Operating conditions such as solution pH and flow rate have significant impact on mercury exchange behavior.

1.4 Scopes of the study

1. The real wastewater from the condensate tank before 5-μm filtration of a refinery plant would be used in this study.

2. Two types of ion exchange resins would be used which are Duolite C433 (an ordinary weak acid cationic resin) and Amberlite IRC718 (a specific resin with mercury selectivity).

3. Water characteristics analyzed in this study would include pH, soluble solids, TOC, total and soluble mercury, FOG, COD, and chloride.

4. Experiments would be conducted at room conditions.

5. Targeted pollutant is mercury with the concentration limit of 5 μg/l.

1.5 Expected outcomes

In order to remove mercury to meet the standard level and remove mercury from the environment. In addition, the optimum condition from this experiment can be applied in the real operation such as pH, equilibrium time, and resin dose. From the optimum parameters, they can apply to the design criteria such as the adsorbent volume for real operation.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Theoretical backgrounds of mercury

Today, heavy metals have been increasingly used for industrial purposes such as in metal plating industry, petroleum industry, etc. In the petrochemical production industry, mercury has been used as an additive in the raw materials for production. Mercury will contaminate in the bottom residue and can pollute the environment in large amount if improperly managed. Demand of mercury has also been increasing rapidly in several other manufacturers including paint, laboratory chemicals, preservatives, and chemical test kits as well as in mining industry. As a result, a large amount of mercury possibly reaches and contaminates the aquatic environment through improperly/inadequate treated discharges. (Gupta, Singh, and Rahman, 2004) In 2003, the USEPA and EPRI reported that coal-fired utilities of commercial boilers release a large amount of mercury to the atmosphere, i.e., around 50 to 55 tons of total mercury per year in the U.S. alone. At the mean times, scrubbing waters at pH 5 could contained up to 500 µg/L of mercury (II) which exceeded the standards for mercury in treated effluent and drinking water of 10 and 2 µg/L, respectively. (Ritter and Bibler, 1992; DeVito, 1997; Kudlac and Amrhein, 2000; National primary drinking water standards EPA, 2001 cited in Nam, Salazar, and Tavlarides, 2003). Mercury(I) chloride is mainly produced by gold mining. The step of extraction gold by cyanide can create mercury(II) cyanides ($Hg(CN)_2^0$, $Hg(CN)_3^-$, and $Hg(CN)_4^{2-}$) while mercury(I) chloride, mercury(II) sulfate, mercury(II) sulfide, and mercury(II) selenide are produced by sulfide ore roasting. Its fume will attach on the fly ash, dust, and slag which are created from this step. (Potential export of mercury compounds from the United States for conversion to elemental mercury, 2010)

2.1.1 General information of mercury

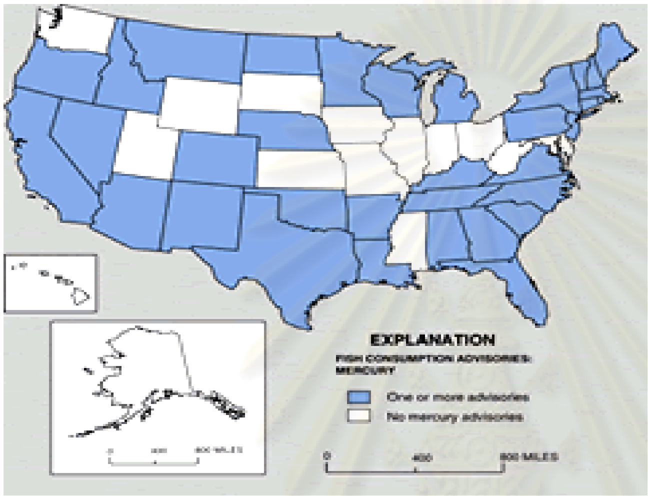
Mercury is an element and uses “Hg” as its symbol. It is atomic number and atomic weight are 80 and 201, respectively. Mercury is the element which has characteristic in silver white metal with the melting and boiling points of −38.83 and 356.73 °C, respectively, so it stays in liquid form at room temperature. (ATSDR, 2010 : online) Density of mercury at standard conditions is 13.534 g/cm^3. Mercury has moderate vapor pressure and its vapor is toxic, odorless, colorless and hazard to human and environment so human can expose the toxic mercury fume accidentally. Mercury is the major pollutant in water. Beside, the heavy metal such as mercury is the chemical which is not easily to be degraded or removed by biological treatment. From this reason, the chemical process such as chemical precipitation, membrane filtration, electroflotation, ion exchange, and reverse osmosis are the alternative ways. (Gupta et al., 2004)

2.1.2 Source of mercury

2.1.2.1 Natural source: such as volcano eruption, natural mercury deposits, and volatilization from the ocean.

2.1.2.2 Human activity: such as chemical manufacture, electroplating industry, battery recycling, waste treatment, coal combustion, chlorine alkali processing, waste incineration, oil refinery, paint industry, pulp and paper, metal processing and mining. (Anirudhan, Divya, and Ramachandran, 2008; Krabbenhoft and Rickert USGS, 2009 : online). Coal burning power is the source which emits mercury in the large amount in the US and accounts for 50% of mercury release via human activity. In addition, burning hazardous waste and improper treatment of mercury waste from laboratory are other routes to increase the amount of mercury in the environment. Mercury can spread to the environment via air, soil and water. Mercury will not stay in the environment as a pure element but stay as in compound. Particle bound mercury can deposit back to the land via dry and wet depositions. (Potential export of mercury compounds from the United States for conversion to elemental mercury, 2010).

Mercury contaminate to the aquatic system, most in oxidized forms, was concerned in late 1980's because the aquatic lives such as fish was examined with high mercury level in the 33 states of US as shown in Figure 2.1. Mercury can bind to chlorine, sulfur and oxygen into inorganic form which is called salts and bind with methyl group into organic form. (ATSDR, 2010 : online)



Blue area = one or more mercury contaminate in aquatic environment

White area = No report

Figure 2.1 Mercury contamination areas in the United States. (US EPA fish consumption database) (Krabbenhoft and Rickert USGS, 2009 : online).

2.1.3 Mercury cycle in the environment

Mercury cycle

Step 1: Mercury will combine with the water vapor in the air. Mercury will stay in the inorganic form (Hg^{2+}), and then fall to the land as rainfall.

Step 2: Inorganic mercury can diffuse and deposit to the soil particle, or discharge to the water source such as river, lake or ocean by runoff.

Step 3: Mercury diffuses to the soil particles and entering to the food chain via bacteria and plankton

Step 4: In the food chain, mercury can adsorb to the muscle tissue of fish so human will receive the mercury upon ingesting the fish. The mercury can enter to fish by following steps:

- Bacteria that has sulfate in the metabolism will uptake mercury inorganic form to their cell.

-Metabolism of bacteria transfers mercury inorganic form into methylmercury compound. From this step, it increases toxic to the human because methylmercury is more hazard than inorganic mercury and human metabolism takes a long time to degrade mercury in this type.

- Bacteria which contaminate with mercury can release mercury to water or uptakes by the next level of consumer such as plankton, zooplankton, herbivore, carnivore and human. Human is the last consumer so the level of mercury will accumulates at the highest concentration when human ingests because the bioaccumulation and biomagnifications process.

- In this step, mercury can change their form to Hg(0), Hg(II) or CH_3Hg by reduction, demethylation and methylation.

Step 5: Mercury from the land and water can volatile to the atmosphere. (Krabbenhoft and Rickert USGS, 2009 : online).

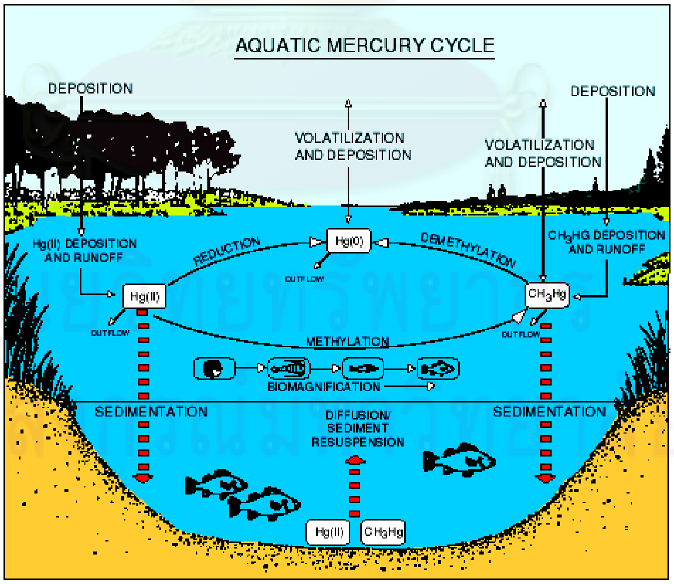


Figure 2.2 Fate of mercury in the environment.

(Krabbenhoft and Rickert USGS, 2009 : online)

The mercury can form to the compound in several forms. From the data in the US, the amount of mercury compound produces in the United States (order from large to small amount)

1) Mercury(I) chloride $HgCl$:

-Source: Gold mining as major source, chemical and pharmaceutical as minor source.

It accounts for 25 metric tons of elemental mercury in 2004 so the mercury(I) chloride is generated the most in the United States.

2) Mercury(II) sulfate $HgSO_4$:

-Source: Chemical manufacturing and waste treatment. It accounts for 260.8 kg in 2004.

3) Mercury (II) nitrate $Hg(NO_3)_2$:

-Source: Chemical manufacturing. It accounts for 88.7 kg in 2004.

4) Mercury (II) chloride $HgCl_2$:

-Source: Chemical manufacturing. It accounts for 76.8 kg in 2004

5) Mercury (II) acetate $Hg(CH_3COO)_2$:

-Source: Chemical manufacturing. It accounts for 41.3 kg in 2004

6) Mercury (II) oxide HgO:

-Source: Chemical manufacturing and battery recycling. It accounts for 32.5 kg in 2004.

7) Mercury (II) iodide HgI_2:

-Source: Chemical manufacturing. It accounts for 11.3 kg in 2004

8) Mercury (II) thiocyanate $Hg(SCN)_2$:

-Source: Chemical manufacturing. It accounts for 6.4 kg in 2004

9) Mercury(I) chloride $HgCl$:

-Source: Chemical manufacturing. It accounts for 1.3 kg in 2004

10) Phenyl mercury(II) acetate $C_8H_8HgO_2$:

-Source: Chemical manufacturing. It accounts for 0.2 kg in 2004

11) Mercury(II) selenide ($HgSe$) and thimerosal ($C_9H_9HgNaO_2S$):

-Source: Chemical manufacturing, mining waste and waste treatment.

The mercury released is unknown. (Potential export of mercury compounds from the United States for conversion to elemental mercury, 2010)

2.1.4 Toxicity of mercury

From the report, the American people receive mercury by ingesting the fish and shellfish in the organic form (methyl mercury). The toxicity and severity in each person depend on following factors:

2.1.4.1 Form of mercury: such as organic, inorganic and complex form. The organic form of mercury is the most toxicity, when compares to the other forms because methylmercury (CH_3Hg) can absorbed rapid by muscle tissue and excretes slow from the body. While, the elemental mercury Hg (0) is less toxic than organic mercury but it stays in the environment higher than other form because it brings to apply such as thermometer, electrical switch and etc.

2.1.4.2 Health status of people: patients are sensitive to mercury more than normal people because their immunity are low protection such as white blood cells are destroyed by HIV virus, so this people cannot persist to any pollutants same as normal people.

2.1.4.3 Age of receptor: In the baby, elder people and pregnant women can get the toxicity from mercury higher than adult because they are sensitive and immune of the body is incomplete to work, so they have more risk.

2.1.4.4 Duration of exposure: If the duration in exposure are long, it has a chance that body will get the high mercury concentration and more affect to the body such as damages the gastrointestinal tract, kidney failure and effect in fetus.

2.1.4.5 Dose of pollutant: If the body gains the high dose of mercury, it will be affect to the body higher than low dose such as headache nausea in low dose but muscle weakness, dysfunction in organ and death in high exposure. (USGS fact sheet 146-00, 2000 : online).

2.1.4.6 Route of exposure: It can be divided into 3 types.

2.1.4.6.1 Ingestion: mercury will affect in gastrointestinal tract and cause the Minamata disease and Acrodynia which is the disease in children, when they ingest mercury from broken thermometer. The symptoms are pink discoloration of the hands and feet, irritability and photophobia.

2.1.4.6.2 Dermal contact: mercury will affect in itchy and irritate the skin.

2.1.4.6.3 Inhalation: mercury will affect in difficult in breathe and destroy lung tissue in high exposure. (Ed Rook et al., 2001)

Mercury can transform by metabolism of human into several forms: (Seiler Han, Sigel, and Sigel, 1994)

1) Oxidation of metallic mercury to divalent mercury.
2) Reduction of divalent mercury to metallic mercury.
3) Methylation of inorganic mercury.
4) Demethylation of methylmercury to divalent inorganic mercury.

2.1.5 Effect of mercury to human health

The effect of mercury to the human health is different based on type of mercury

2.1.5.1 Effect of elemental mercury

Target organ is brain of adult and baby. The harmful from this type will come from breakage of product which uses elemental mercury in the component such as thermometer. Elemental mercury can vapor and attach to lungs which affect to the emotion such as mood swing, nervousness, excessive shyness and aggressive, weakness of muscle, headache, kidney and respiratory failure, death in high exposure dose. The symptoms are grouped to chronic effect and non carcinogen.

2.1.5.2 Effect of methylmercury

Target organ is brain and kidney. This type of mercury will affect to fetus or baby greater than adult by the pregnant gain methylmercury so it affects to the brain and nerve development of fetus. The methyl mercury is called “neurotoxicant”. It affects to blood both suddenly and permanent The results are baby has the problem in thinking, language, memory, muscle weakness, insensitive to dangerous and affect to central nervous system.(Mercury Study Report to Congress Volume V: Health Effects of Mercury and Mercury Compounds, 1997) Methylmercury is a non-carcinogen. The chronic effects are kidney failure, irregular movement, insensitive or sensory dysfunction and autism. (Doull et al., 1980; Mondal and Das, 2003; US EPA, 2010 : online)

2.1.5.3 Effects of other mercury compounds (inorganic and organic)

It enters to body by ingestion, then absorb to gastrointestinal tract. If exposure in high level, it will create mood swing, loss of memorization, muscle weakness, irritate skin.

2.1.6 Metabolism of mercury in the body

Normally, elemental mercury will adsorb to lung 80%, while liquid mercury will ingest 1%. Inorganic mercury absorb to kidneys, while two types (elemental and methyl mercury) can transfer between blood brain and barrier of placenta. Due to this process, fetus may have high mercury level in blood since they still in placenta. In the case of high exposure, mercury can accumulates in the hair, fat tissue, and breast milk so baby obtains mercury in high concentration via nursing. (Utah, 2010 : online)

2.1.7 Advantage of mercury

Although, mercury is harmful to human health and environment, it still has several advantages such as use in part of component in thermometer, electrical switch, fluorescent lamp, use as dental amalgam, produce chlorine gas, soda. Furthermore, it can use in cosmetic and pharmaceutical ways, for example; skin lightening cream, antiseptic cream and ointment. (US EPA, 2010 : online; ATSDR, 2010 : online).

2.1.8 Mercury in crude oil

The mercury can stays in the crude oil and condensate gas in several forms such as

2.1.8.1 Elemental form (Hg^o) can soluble in organic solvent such as crude oil and water. The mercury should be removing from crude oil because it will form complex with iron and become to iron oxide which may corrode the pipe.

2.1.8.2 Organic mercury (R-Hg-R, R= CH_3 C_2H_5) such as dialkyl mercury, dimethyl mercury, diethylmercury commonly found in organic phase, so it can highly soluble in crude oil. It is more toxic than inorganic mercury. (Zettlitzer, Eiden, and Falter, 1997).

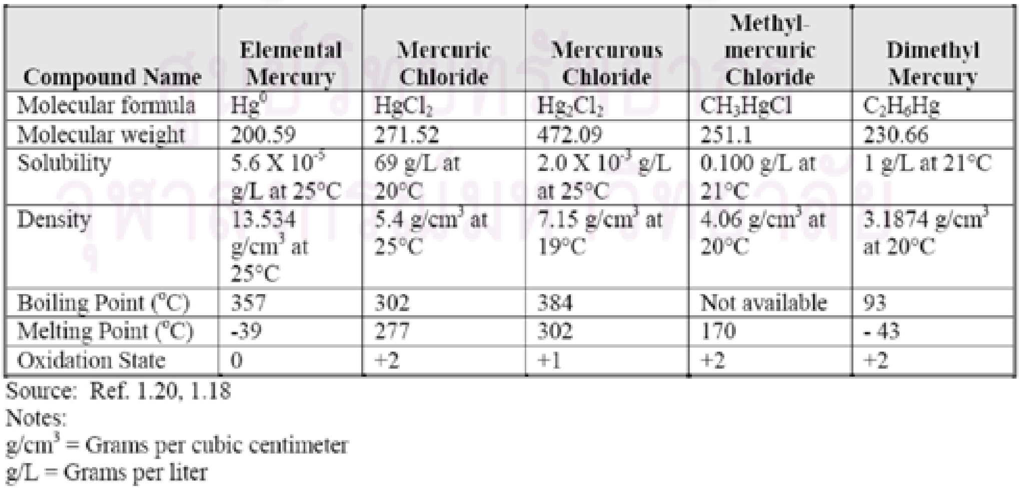
2.1.8.3 Inorganic mercury (R-Hg-X, X= halide, sulfate or –S-R) is the mercury form complex with chlorine, sulfur, or oxygen such as monoalkyl or monoaryl mercury. It can dissolve in polar solvent. For example, mercuric chloride such as monomethylmercury halides prefers to soluble in water than elemental mercury 10 times.

2.1.8.4 Complexed form (HgK and HgK_2,K = organic sulfide, thiol, thiophene or mercaptan) Mercury in this type can found in some crude oil and condensate gas.

2.1.8.5 Suspended mercury compound such as mercuric sulfide (HgS). It is insoluble in crude oil and water because it is suspended solid. (Wilhelm and Bloom, 2000)

The physical and chemical properties of several mercury compounds. It can be seen that different types of mercury compounds have different properties including solubility, density, boiling point, melting point, etc as shown in table 2.1.

Table 2.1 Physical and chemical properties of some mercury compounds.
(US EPA, 2007)



Compound Name	Elemental Mercury	Mercuric Chloride	Mercurous Chloride	Methyl-mercuric Chloride	Dimethyl Mercury
Molecular formula	Hg^0	$HgCl_2$	Hg_2Cl_2	CH_3HgCl	C_2H_6Hg
Molecular weight	200.59	271.52	472.09	251.1	230.66
Solubility	$5.6 X 10^{-5}$ g/L at 25°C	69 g/L at 20°C	$2.0 X 10^{-3}$ g/L at 25°C	0.100 g/L at 21°C	1 g/L at 21°C
Density	13.534 g/cm^3 at 25°C	5.4 g/cm^3 at 25°C	7.15 g/cm^3 at 19°C	4.06 g/cm^3 at 20°C	3.1874 g/cm^3 at 20°C
Boiling Point (°C)	357	302	384	Not available	93
Melting Point (°C)	-39	277	302	170	- 43
Oxidation State	0	+2	+1	+2	+2

Source: Ref. 1.20, 1.18
Notes:
g/cm^3 = Grams per cubic centimeter
g/L = Grams per liter

2.2 Principle of ion exchange

Ion exchange comes from the principle that one ion is removed and another ion is replaced. The ion exchange reaction creates the several changes such as ionic state of a resin, properties of swelling of water, ion hydration and co-ion uptake.(Harland, 1994) The resin is the small porous materials which has insoluble in water and organic solvent properties. The materials are used to produce the resin based on polystyrene and polyacrylate. The monomers is crosslinked together and create the porous. The more crosslink will create more porous and adsorptive capacity so ion can absorb to the resin in good performance. This enhances physical strength and less swelling in water. The resin is also called "absorber." Normally, it has 50% of water and gel component. The ion which is good in absorb should have a high molecular weight. (Eckenfelder and Wesley, 2000). The rate of adsorption is controlled by rate of diffusion. The structure of the pore is shown in Figure 2.3.

Figure 2.3 Structure of macropore and micropore in the resin.
(Neumann and Fatula, 2009)

Due to the bead of resin has lots of small pore, it increases surface area and capacity in adsorption. The monomer unit of resin polymer composes of polymer backbone, functional groups which attaches with exchange ion either cation or anion. When the functional group bond to ion, they can bind together with weak electrostatic forces, so the ion can easy exchange as shown in Figure 2.4.

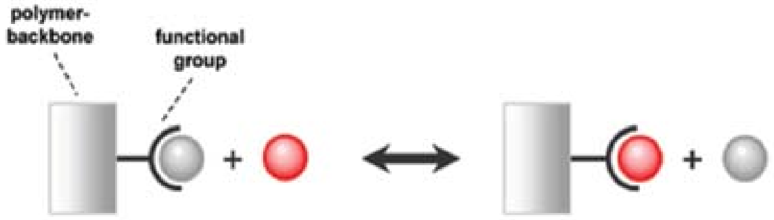


Figure 2.4 Structure of monomer of the resin: white ball is original ion of resin, red ball is exchange ion. (Neumann and Fatula, 2009)

2.2.1 Type of ion exchange resin

Ion exchange resin can be classified into several groups according to categorizing criteria.

2.2.1.1 Based on type of ion which exchange in the process, ion exchange resins can be separated into 2 types:

2.2.1.1.1 Cation exchange resin: The type of resin which interchange positive ion. It has acid functional group to exchange with another ion such as carboxylic (-COOH), sulfonic(-SO_3H), phosphonic group (-$PO(OH)_2$).

2.2.1.1.2 Anion exchange resin: The type of resin which interchange negative ion. It has basic functional group to exchange with another ion such as amine. (Eckenfelder and Wesley, 2000; Neumann and Fatula, 2009)

2.2.1.2 Based on activity of functional group: it can separate into 4 types:

2.2.1.2.1 Strong acid cation exchange resin: This type acts as strong acid so ionization well and independent on pH, for example, acid (R-SO_3H) and salt (R-SO_3Na)

2.2.1.2.2 Weak-acid cation resin: This type acts as weak acid so ionization weak and dependent on pH. Because of weak acid cation resin, it operates well in pH range 5 to 10, for example, carboxylic group (-COOH) or Duolite C433 resin which is used in this research.

2.2.1.2.3 Strong base anion resin: This type acts as strong base so ionization well and independent on pH, for example, hydroxide group (-OH).

2.2.1.2.4 Weak-base anion resin: This type acts as weak base so ionization weak and dependent on pH.

Apart from ordinary ion exchange resins, heavy metal selective chelating resin is also produced for specific purpose. This resin acts similar to weak acid cation resin, but it has high affinity to heavy metal ion by using EDTA as chelating agent to bind with heavy metal ion to create the complex compound. (Eckenfelder and Wesley, 2000)

2.2.2 Mechanism of functional group

The functional group of resin will bind with ion tightly or loosely depending on the selectivity and affinity to the ion. Resin which has the amino diacetic acid as the functional group will bind to Cu^{2+} and Hg^{2+} greater than Na^{+}. When the wastewater has the Cu^{2+}, the functional groups will affinity to copper ion greater than Na^{+} by electrostatic force and copper ion bonds to electron pair of nitrogen atom. The ion exchange occurs until the functional group saturate with copper. This point is called “equilibrium or mass action effect.” as shown in Figure 2.5.

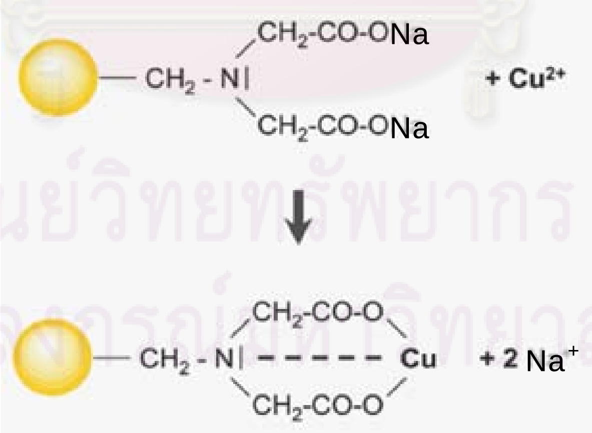


Figure 2.5 Mechanism of ion exchange resin between functional group and exchange ion. (Neumann and Fatula, 2009)

Table 2.2 The affinity of cation and anion exchange from most to least preference (Clifford, 1986)

Affinity	**Cation exchange**	**Anion exchange**
Most	Ra^{2+}	$HCRO_4^-$
	Ba^{2+}	CrO_4^{2-}
	Sr^{2+}	ClO_4^-
	Ca^{2+}	SeO_4^{2-}
	Ni^{2+}	SO_4^{2-}
	Cu^{2+}	NO_3^-
	Co^{2+}	Br^-
	Zn^{2+}	HPO_4^-
	Mn^{2+}	$HAsO_4^-$
	UO_2^{2+}	SeO_3^{2-}
	Ag^+	CO_3^{2-}
	Cs^+	CN^-
	K^+	NO_2^-
	NH_4^+	Cl^-
	Na^+	$H_2PO_4^-$
	Li^+	$H_2AsO_4^-$
		HCO_3^-
		OH^-
		CH_3COO^-
Least		F^-

2.2.3 Factor affect on adsorbability

2.2.3.1 Solubility of substance which is inversely correlated with adsorbability. (Chiarle, Ratto, and Rovatti, 1999; Eckenfelder and Wesley, 2000)

2.2.3.2 Structure of adsorbed substance such as branch structure will absorb greater than straight structure.

2.2.3.3 Substituent group, hydroxyl and sulfonic reduce adsorbability whereas the nitro group increase adsorbability.

2.2.3.4 Size of substance, i.e., larger size can absorb more than small size.

2.2.4 Factors affect ion exchange capacity

2.2.4.1 Size and charge of exchange ion (Mondal and Das, 2003): the larger size and more charge ion has selectivity to exchange more than small size and less charge ion.

2.2.4.2 Type of activity of functional group (Jiang et al., 2006): strong acid and strong base exchange in depend on pH, while weak acid and weak base exchange depend on pH

2.2.4.3 Concentration of exchange ion in solution: More ions in solution enhance more exchange ion.

2.2.4.4 Temperature (Pehlivan and Altun, 2006): High temperature will catalyst ion exchange occurs rapidly.

2.2.4.5 Contact time (Donia, Atia, and Heniesh, 2008): Long contact time can support exchange ion until saturate, so the resin could use in full capacity.

2.2.4.6 Amount of resin (in batch operation): More amount of resin can reduce the pollutant concentration, so it increases exchange capacity.

2.2.4.7 pH of wastewater (Shi et al., 2009): pH of wastewater has the effect in form of ion and the exchange capacity will depend on form of ion.

2.2.4.8 Flow rate of treat solution (in column operation): Low flow rate will support the effective of exchange capacity.

2.2.4.9 Resin depth (in column operation) (Rivas et al., 2010): More amount of resin depth will support the more exchange ion.

2.2.5 Regeneration process

The regeneration process is the method for exchange the former ion (such as Hg^{2+}) with original ion of resin (such as H^+). The chemical substance which uses in the regeneration is called “regenerant.” The regenerant can be acid, salt brine or alkaline solution. In this research, the regenerant is HCl which will provide the proton (H^+) to the resins and force the release of mercury ion (Hg^{2+}).

2.3 Technology for remove mercury

When mercury contaminate to water source the basic techniques commonly use

2.3.1 Precipitation treatment process

This technique can remove mercury by adding chemical substance into the solution to transform mercury from soluble form to insoluble form (such as HgS). (Potential export of mercury compounds from the United States for conversion to elemental mercury, 2010)

2.3.1.1 Sulfide precipitation

This method can remove mercury in inorganic form by using sodium sulfide or other sulfide compounds. This added compound will convert mercury from soluble into insoluble form of HgS as shown in the following equation:

$$Hg^{2+} + S^{2-} \rightleftharpoons HgS_{(s)} \quad (1)$$

After the precipitation, the remove of solid particles will follow which can be accomplished by centrifuging, filtration, or sedimentation.

Disadvantages:

- This technique depend on the influence of pH by the removal efficiency is reduced at pH > 9 so the optimum pH for operation is neutral pH. (Patterson, 1985 cited in Osantowski et al., 1997)

- This technique cannot reduce mercury to 10 to 100 µg/L level.

- This technique cannot treat the mercury concentration below 10 µg/L.

- It needs to remove solid residue which increases treatment cost.

- From the stoichiometric equation, the sulfide product is a toxic substance to human and environment.

- Products need further remediation before suitable for final dispose; hence, increasing the overall cost. In addition, after landfilling, mercury-containing leachate may contaminate to water source. (Hansen and Stevens, 1992 cited in Osantowski et al., 1997)

Efficiency of removal: 95-99.9% in well operation and maintenance.

2.3.1.2 Coagulation/co-precipitation

This technique combines the co-precipitation and adsorption together relying on ion attachment onto solid surface. Coagulant normally used is aluminum sulfate (alum), iron salts (ferrous or ferric salts) (Patterson and Ford, 1992) and lime. Removal efficiency depends on the structure of solid, pH of coagulant surface and solubility of mercury compounds. (Potential export of mercury compounds from the United States for conversion to elemental mercury, 2010)

Disadvantages:

-This technique is complicated and requires several steps.

-High cost for the large scale.

Removal efficiency: 94-98% for alum and iron
70% for lime (Patterson, 1985)

2.3.2 Adsorption process

This process uses adsorbent to adsorb the mercury. This technique has an ability to catch mercury from liquid or gas phase. The popular adsorbent used is activated carbon. Nonetheless, new alternative adsorbent materials are also available including bicarbonate-treated peanut hull carbon (BPHC), modified *Hardwickia binata* bark (MHBB), coal fly ash, and the forager sponge. (Namasivayam and Periasamy, 1993)

2.3.2.1 Activated carbon

2.3.2.1.1 Granular activated carbon (GAC): GAC is the most common for use. This carbon can be applied in a continuous-flow manner as shown in Figure 2.6.

- Downflow in series: Columns connect in the series and wastewater flows from the top of one column to the bottom and sequentially to next columns.

- Moving bed: Activated carbon will be subjected to adsorption. The limitation is amount of organic in the wastewater should be low because this type carbon cannot backwash.

- Downflow in parallel: Columns stay in parallel and the effluent after treated will mix with effluent from another column until reaching the desired concentration.

- Upflow expanded in series: This type performs similar to the downflow but the wastewater flow in the opposite direction. The wastewater is pumped from the bottom of the column, treated with activated carbon, and the effluent will flow out from the top. It is suitable for wastewater containing high suspended solids.

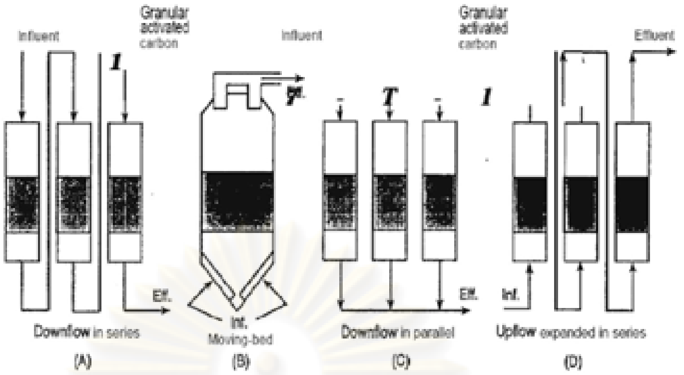


Figure 2.6 Type of granular activated carbon column design.
(Calgon Carbon Corporation, n.d.)

2.3.2.1.2 Powder activated carbon (PAC): PAC is often added directly to the slurry and not popular to regenerate for reuse because of poor recovery.

Removal efficiency: 80%

2.3.2.2 Xanthate adsorbent

Starch xanthate could reduce mercury from 10 mg/L to 23 µg/L (Campanella et al., 1986), from 100 to 0.001 mg/L (Tiravanti et al., 1987) and from 6.3 mg/L to 0.01 mg/L (Macchi et al., 1985) However, this technique needs additional treatment such as sedimentation, filtration.

2.3.2.3 Other adsorbents

2.3.2.3.1 Bicarbonate-treated peanut hull carbon adsorbent (BPHC) (Namasivayam and Periasamy, 1993)

2.3.2.3.2 Modified *Hardwickia Binata* bark adsorbent (MHBB) (Anon, 1986)

2.3.2.3.3 Coal Fly Ash Adsorbent (Sen and De, 1987)

2.3.2.3.4 Forager Sponge Adsorbent

All of these methods are not popular to use because low efficiency

2.3.3. Ion exchange process

Ion exchange process is the reversible interchange of ion between the solid and solution phase. If ion exchanger is M^-A^+. A^+ is the exchange ion and B^+ has in the solution phase, so the ion exchange will occur by A^+ and B^+ exchange together. Finally, B^+ will attach with M^- which has opposite charge. A^+ and B^+ are called counter ion. M^- is called insoluble fixed anionic complement of the ion exchanger or called fixed anion. In the solution phase, the ion which has same charge as in fixed ion is called co-ions. From the above, cation will exchange, so it is called cation exchange. The reaction presents as in following equation.

$$\begin{array}{ccccccc} M^-A^+ & + & B^+ & \rightleftharpoons & M^-B^+ & + & A^+ \\ \text{solid} & & \text{solution} & & \text{solid} & & \text{solid} \end{array}$$

While, the anion exchange occurs by anion A^- in the solid phase will exchange with B^- in the solution phase. Finally B^- attaches with M^+ by electrostatic force(weak force in order to easy exchange) and A^- will present in the solution phase instead. The reaction presents as in following equation.

$$\begin{array}{ccccccc} M^+A^- & + & B^- & \rightleftharpoons & M^+B^- & + & A^- \\ \text{solid} & & \text{solution} & & \text{solid} & & \text{solid} \end{array}$$

The ion exchange reaction between counter ion will occur until two ions exchange in equivalents amounts. (Harland, 1994)

The resin, which has the iminodiacetic acid and thiol group(-SH) as functional group, specific to mercury(II) rather than calcium and magnesium hence, resin has functional group like this suits for mercury removal. In generally, the ion exchange resin perform as continuous system by use column for industrial scale, while the batch test often perform in laboratory scale in order to find the optimal condition for best operation.

The ion exchange treatment has the cycle in several steps.

2.3.3.1 Service step: resin will contact with the mercury in wastewater and ion exchange reaction occur depend on the affinity of functional group. The example of affinity of commercial resin as shown : (Calmon, 1981)

Amberlite IRC-718:

$Hg^{2+}>Cu^{2+}>Pb^{2+}>Ni^{2+}>Zn^{2+}>Cd^{2+}>Co^{2+}>Fe^{2+}>Mn^{2+}>Ca^{2+}$

The ion exchange will occur until the concentration of effluent reach to breakthrough. The operation is stopped. In the column operation, breakthrough is the point that exchange resin saturate with the ion and the concentration of contaminant is higher than the desire concentration. When the experiment reach to this point, operation is stopped and regeneration resin is occurred.

2.3.3.2 Backwash step: This step occurs by use distilled water to make the resin disperse and remove any particle which clog to the column by use flow rate greater than the service step.

2.3.3.3 Regeneration step: This step occurs by use dilute acid such as HCl or H_2SO_4 or any solution that suits for regeneration. This chemical substance is called regenerant. The objective of this step returns the resin to the original form and adsorb ion will release.

2.3.3.4 Rinse step: This step occurs by use distilled water to wash the column so as to flush the residual regenerant from column. After that, resin readies to use in next cycle. (Eckenfelder and Wesley, 2000)

In the anion exchange resin, (Sorg, 1979) reported that chloride content in the wastewater can increase the efficiency of removal mercury in complex mercuric chloride form. While anion content should be low, if cation exchange perform.

Advantages:

- The operation is stable and easy to perform.
- The removal efficiency is high near 100%
- Resins which use in the ion exchange have several type ,so resins have capacity to treat various chemical substance.

Disadvantages:

- Unsuitable for high total dissolve solid in wastewater.
- Efficiency of removal depends on quality of effluent.
- Spent regenerant cannot reuse again.

Removal efficiency: 95-99.9%

2.3.4. Other treatment processes

2.3.4.1 Chemical reduction: This technique uses the reduction process to reduce soluble ionic mercury to solid element mercury which can be easily separated from wastewater. Several reducing agents can be used such as aluminum, zinc, and iron, hydrazine, stannous chloride, and sodium borohydride.

Disadvantages:

- This treatment process requires extra polishing steps, so increasing treatment cost.

- This technique cannot reduce the mercury to below 100 µg/L.

Removal efficiency: 92-98%

2.3.4.2 Membrane Separation

2.3.4.2.1 Ultrafiltration
2.3.4.2.2 Charged filtration
2.3.4.2.3 Crossflow microfiltration
2.3.4.2.4 Magnetic filtration
2.3.4.2.5 Reverse osmosis

2.3.4.3 New mercury treatment technologies such as

2.3.4.3.1 Macrocycle technology
2.3.4.3.2 Biological treatment system:
2.3.4.3.3 Membrane extraction:

Disadvantages: Bacteria cell takes time and needs optimum condition to grow, it cannot resist in extremely condition.

The summary of the performance of various treatment techniques in removing mercury in water. It shows the ion exchange can reduce mercury down to 0.5-5.0 µg/L level which is the lowest concentration among all other technology. So, ion exchange technology is a very promising method to remove mercury; thus, it is selected in this research. There are several kinds of mercury-specific exchange resins commercially available in global market as shown in table 2.3. Nonetheless, Amberlite IRC-718 is selected due to its availability in local market and relatively low cost. In addition, the Duolite C433 which is a non selective resin is also used for comparison purpose. The objective in this study is to characterize the adsorption behavior of both resins regarding on mercury adsorption in both batch and column reactors.

Table 2.3 Summary of effluent mercury concentration from various treatments.

Mercury removal technology	**Mercury concentration of effluent (μg/L)**
1. Sulfide precipitation	10 to 100
2. Co-precipitation	0.5 to 5.0
3. Activated carbon adsorption	0.5 to 20
4. Starch xanthate adsorption	5 to 20
5. Ion exchange	0.5 to 5.0
6. Reduction	10 to >100
7. Membrane separation	Efficiency of removal mercury 80-90%

Table 2.4 Summary of the efficiency in mercury removal in each technology. (US EPA, 1997)

Treatment Methods	**Initial Concentration (μg/l)**	**Achievable Concentration (μg/l)**	**Removal (%)**
Sulfide precipitation (+filtration)	300-50,000	10-100	95-99.9%
Co-precipitation+ coagulation	50-500	0.5-5.0	94-98%
Activated carbon adsorption	10-10,000	0.5-20	>80%
Xanthate adsorber adsorption	10-100	5-20	80%
Ion exchange	200-70,000	0.5-5.0	95-99.9%
Chemical reduction	1,800-5,000	10- >100	95-98%

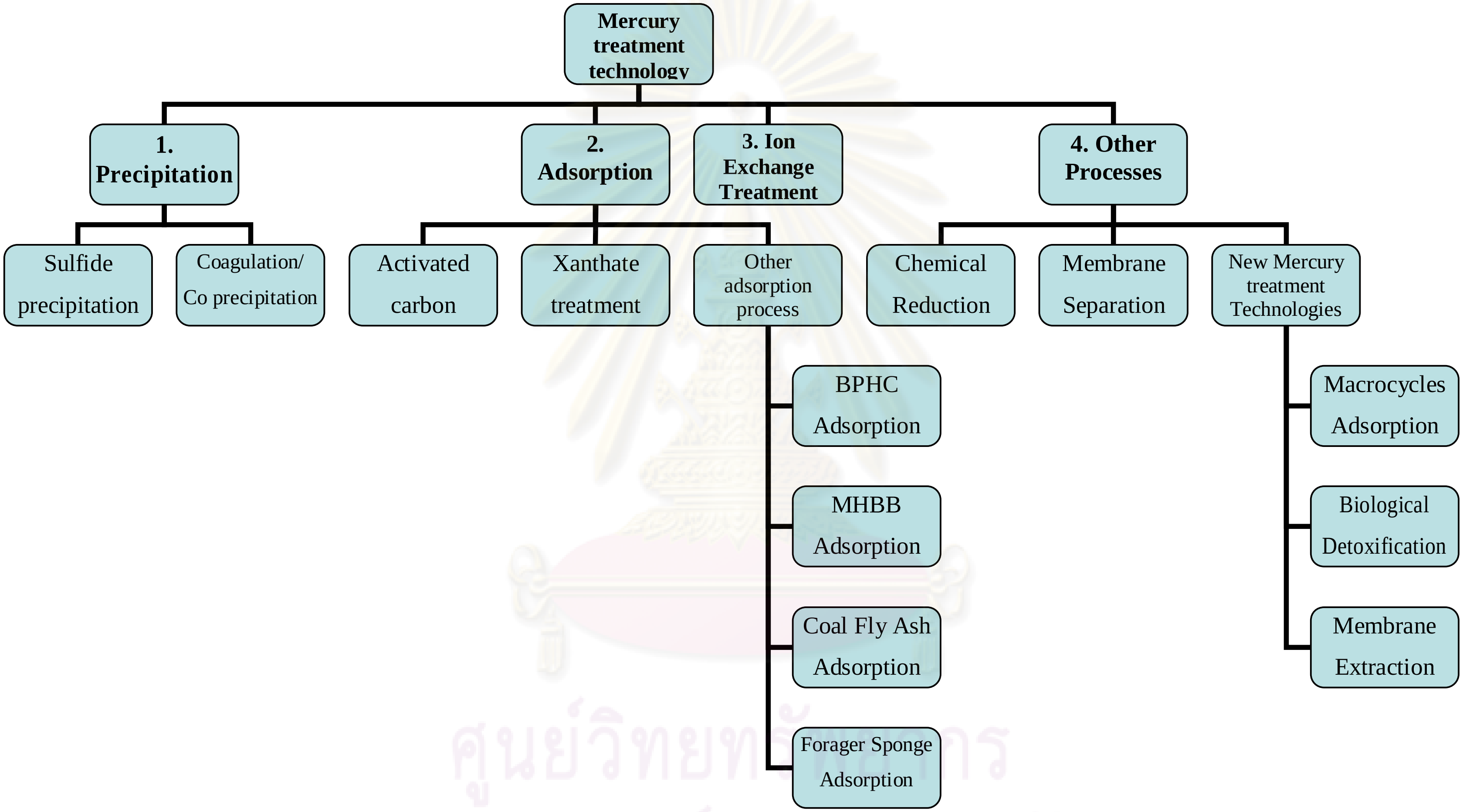


Figure 2.7 The diagram of available technology for treatment mercury. (Mercury Study Report to Congress Volume V: Health Effects of Mercury and Mercury Compounds, 1997)

2.4 Property of selected cationic exchange resins (use information from technical sheet of Rohm and Haas company).

In this research, the resins are used in 2 types

2.4.1 Duolite C433 resin

It is the weak acid cation exchange resin (use as reference) (Habova, Melzoch, and Rychtera, 2004).

Properties

- Functional group is the carboxylic group(-COO)
- The matrix is polyacrylic acid crosslinked with divinyl benzene. (-CH2-CH-COOH-)n. The structure is shown in Figure 2.8. (Gupta et al., 2004)
- moist golden translucent beads form
- The total exchange capacity is 4.2 eq/l H^+ form.
- The operating pH range is 5-10
- The operating temperature limit 120°C.
- It has affinity to bind with any 2+ ion.
- Flow rate for service run is 5-40 BV/h
- Flow rate for regeneration is 4-8 BV/h by use 2-5% HCl.

Remark: BV = bed volume, volume of column

This resin is used in this study because specific selectivity to certain ions or groups of ions and often bind to inorganic chemical.(Matsumota, Weber, and Kyles, 1989; Allen and Brown, 1995; Lai, Lo, and Lin, 1994) It can bind with any divalent caions including Hg^{2+} but does not have specific affinity to Hg^{2+}.

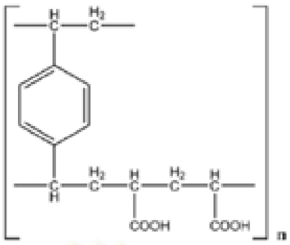


Figure 2.8 Structure of Duolite C433 resin.

After, resins are saturated with mercury ,so resin will be backwashed with DI water 15 mΩ by flow rate higher than flow of regeneration. The process for regenerate by use flow rate of 5% HCl (regenerant) at flow rate of 8 BV/h or 400 ml/h or 6ml/min, time 60 minutes. After that, resin will be rinsed with DI water 15 mΩ at flow rate 1,000 ml/h time 30 minutes. Then, measure the pH in range 4-5 in order to ensure that resin has not residual regenerant. Finally, resin will be dried at room temperature.

2.4.2 Amberlite IRC-718 resin

It is the commercial chelating cation exchange resin.

Properties

- Functional group is iminodiacetic acid.(Park and Cha, 1998)
- The matrix is styrene-divinyl benzene. The structure is shown in Figure 2.9. (Doreen, 1993)
- Hydrated, opaque beads form
- The total exchange capacity is 1.1 meq/mL H^+ form.
- The operating pH range is 1.5-14.0
- The operating temperature limit 70°C.
- It has affinity to bind with heavy metal ion than sodium, potassium, calcium and magnesium. It selects to Hg^{2+} ion than calcium 43,000 times at pH 2.
- Flow rate for service run is 8-32 BV/h
- Flow rate for regeneration is 2-4 BV/h by use 5-15% HCl

This resin is a chelating resin with good stability, high capacity in adsorption, greater selectivity with heavy metals, less swelling and can perform in wide range of pH. From these advantages, it enhances to recover heavy metal easily. (Voutsa et al.,1988; Agrawal and Sahu, 2006) Its structure is macroporous (macrorecticular) which enhances its resistivity to osmotic shock and short diffusion paths. This effect can be observed in the improvement of kinetic process. (Malla, Alvarez, and Batistoni, 2002) This resin is used to perform in this research because it has higher affinity to Hg^{2+} 43,000 times than Ca^{2+}, the most found divalent cation in typical wastewater, at pH 2 and it can also form chelates with the ion which enhances resin binding and heavy metal stability. (Agrawal and Sahu, 2006)

Sorption characteristic and efficiency of removal depend not only on pH, time, amount of resin, but also on size of the chelate ring, metal atom, number of donor atoms/bonding site on the reagent, type of donor atoms (hard or soft), oxidation state of the metal ion, nature of the solvent and etc. (Park, Chung, and Cha, 2000) Therefore, it is important to determine the optimum conditions for ion exchange which varies from wastewater to wastewater. In addition, sorption equilibrium and transfer process of metal ions between the liquid phase (wastewater) and solid phases (resin) are also needed to be clarified. (Rawat and Muktawat, 1981; Masaaki et al., 1984; Khan and Singh, 1987; Rawat, Ahamd, and Agarwal, 1990; Heonles et al., 1997)

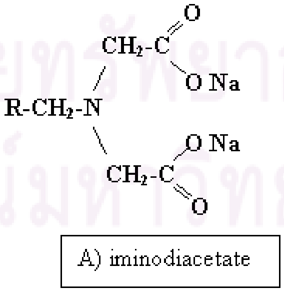


Figure 2.9 Structure of Amberlite IRC-718 resin. (Leinonen, 1999)

After, resins are saturated with mercury, so resin will be backwashed with DI water 15 mΩ by flow rate greater than flow of regeneration. The process for regeneration by use 10% HCl as regenerant (for this experiment) at flow rate of 4

BV/h or 200 ml/h or 3ml/min, time 60 minutes. After that, resin will be rinsed with DI water 15 mΩ at flow rate 1,000 ml/h time 30 minutes. Then, measure the pH in range 4-5. Finally, resin will be dried at room temperature.

2.5 Adsorption isotherm

2.5.1 Adsorption isotherm model in batch reactor

2.5.1.1 Freundlich model

Freundlich equation is a model for non ideal adsorption between heterogeneous surface. (Kitsanguan, 2007) Freundlich adsorption equation is shown as follows: (Eckenfelder and Wesley, 2000; Gupta et al., 2004)

$$\frac{X}{M} = KC_e^{\frac{1}{n}} \tag{a}$$

where: q_e = amount adsorb per unit weight of adsorbent

C_e = concentration of substance in equilibrium solution per milliliter

K and n = Freundlich constants depending on the adsorbent, temperature and substance to be adsorbed and are the indicators of sorption capacity and adsorption intensity, respectively.

Logarithm of equation "a" yields a linear form of Freundlich isotherm as shown below: (Osantowski et al., 1997)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{b}$$

The Freundlich parameters "k" and "n" can be determined from the intercept and slope of the plot between log X/M and log C_e.

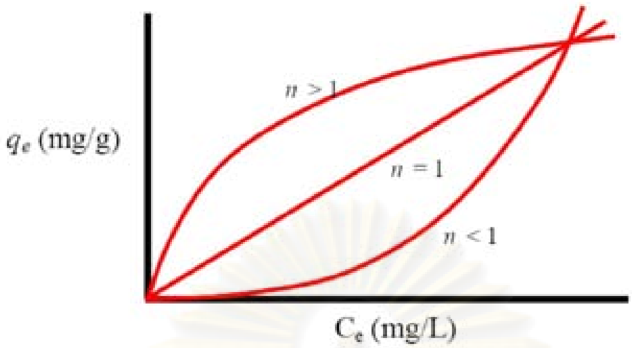


Figure 2.10 Freundlich isotherm plotting between C_e and q_e presenting n value. (Akewaranugulsiri, 2008)

2.5.1.2 Langmuir model

This model is based on an equilibrium phenomenon between condensation and evaporation of adsorbed molecules. The Langmuir adsorption equation in a non-linear form is shown below: (Benamor et al., 2008)

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad \text{(c)}$$

Where: q_m = maximum sorption capacity

q_e = sorption capacity

b = a coefficient in the Langmuir equation representing an affinity of the adsorbent for the adsorbate,

C_e = equilibrium concentration of adsorbate in the impregnation solution

The linear form of equation “c” can be presented as follows: (Kitsanguan, 2007)

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{bq_m}\right)\frac{1}{C_e} \qquad \text{(d)}$$

2.5.2 Adsorption kinetics in column reactor (Bohart and Adams relationship)

It uses for analyze the activity of continuous operation is shown as follow.

$$\ln\left(\frac{C_0}{C_B}-1\right)=\ln(e^{KN_0X/v}-1)-KC_0t$$

Because $e^{KN_0X/v}$ is greater than unity, so this equation can transform to

$$t=\frac{N_o}{C_0v}\left[X-\frac{v}{KN_0}\ln\left(\frac{C_0}{C_B}-1\right)\right]=\frac{N_0}{C_0}\left[EBCT-\frac{1}{KN_0}\ln\left(\frac{C_0}{C_B}-1\right)\right]$$

Bed depth prevents the excess concentration of effluent at t = 0, so critical depth can calculate from:

$$X_0=\frac{v}{KN_0}\ln\left(\frac{C_0}{C_B}-1\right)$$

Critical empty bed contact time ($EBCT_0$) can calculate from:

$$EBCT_0=\frac{1}{KN_0}\ln\left(\frac{C_0}{C_B}-1\right)$$

When plot linear graph t versus X or EBCT.

Adsorptive capacity N_0 calculate from slope and rate constant K from intercept as follow:

$$K=-\frac{1}{C_0b}\ln\left(\frac{C_0}{C_B}-1\right)$$

t = service time

v = linear flow rate

X = bed depth

K = rate constant

N_0 = adsorptive capacity

C_0 = influent concentration

C_B = allowable effluent concentration

EBCT = empty bed contact time (Eckenfelder and Wesley, 2000)

2.5.3 Scale-up approach

This method used for design column in laboratory scale for real operation. Fornwalt and Hutchins (1966) created for carbon adsorption column. The advantage of this method was simple and requires a few experimental data. This method referred that liquid flow rate in term of bed volume per unit time (Q_b) and contact time (T_c) equaled to ε/Q_b equaled in between test and design column. It could be assumed that volume of liquid treated per unit mass of adsorbent ($\hat{V}_B$) equaled between test and design column. In generally, Q_b was 0.2-3.0 bed volume per hour and it could calculate from breakthrough volume, the solute concentration, the maximum solid-phase concentration. The equation for this design procedure could show as follow. (Reynolds and Richards, 1995)

The contact time was computed from

$$T_C = \frac{\varepsilon}{Q_b}$$

Where, ε = pore fraction

The bed volume of design column equaled to

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

Where, Q = design liquid flow rate

Mass of adsorbent for design column (M) equaled to

$$M = (BV)(\rho_s)$$

Where, ρ_s = adsorbent bulk density

The volume of liquid treated per unit mass of adsorbent, $\hat{V}_B$ equaled to

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

Where, V_B = breakthrough volume for allowable effluent solute concentration

M = mass of adsorbent in test column

The mass of adsorbent exhausted per hour for design column (M_t) equaled to

$$M_t = \frac{Q}{\hat{V}_B}$$

Where, Q = design liquid flow rate

The breakthrough time (T) computed from

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

Where, M = mass of adsorbent in design column

The breakthrough volume (V_B) computed from

$$V_B = QT$$

2.6 Literature Reviews

Related articles:

2.6.1 Resin treats Mercury

2.6.1.1 This research reported that weakly acidic and polystyreneldivinylbenzene cation resin with thiol (SH) functional groups could reduce mercury from 200 to 70,000 µg/L to 1 to 5 µg/L with a pretreatment with 0.2 µm filter.The wastewater came from defense facility wastewater. Efficiency removal accounted for 99.5% (Ritter and Bibler, 1992)

2.6.1.2 This paper removed mercury by using Amberliter IRC 718 (similar to this study). This resin selectively removed mercury with high efficiency at low pH. They studied effect of pH by use synthetic wastewater which added concentration of $HgSO_4$ same as smelter wastewater and vary pH 1.3, 1.5, 1.7. In the column operation, they tested with synthetic wastewater contained $ZnSO_4$, $HgSO_4$, $FeSO_4$ or $Fe_2(SO_4)_3$, , $CdSO_4$, $Pb(NO_3)_2$ and NaF with 2 g of resin at 12 BV/h. While, they use smelter wastewater as real wastewater with 8 g of IRC-718 flow rate 19-20 BV/h. The results showed that when increased pH from 1.3 to 1.7, the desorption of Hg from resin decreased from 4.8% to 1.5% as shown in Figure 2.11

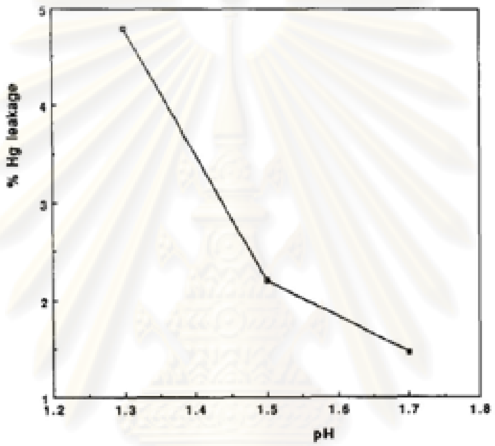


Figure 2.11 Effect of pH on Hg leakage from IRC-718. Feed: 210 bv of 9.5 mg/l Hg(II) in sulfuric acid. Flow 12 bv/h.

When the Amberlite IRC 718 was used, mercury could be reduced from 11,800 µg/L to 15 - 35 µg/L without any pretreatment. The removal efficiency was high because the iminodiacetic acid functional group was highly selective to mercury(II) rather than other ions in the wastewater. Removal efficiency accounted for 99.8%. (Becker and Eldrich, 1993)

2.6.1.3 This research studied adsorption characteristic of Duolite C433 to Hg^{2+}, Pb^{2+}, and Cd^{2+} in synthetic wastewaters at different temperature. The results showed that when increased the adsorption time, the removal capacity of heavy metals (Hg^{2}, Pb^{2+} and Cd^{2+}) increased until reaching a plateau at 90 minutes for mercury and lead, and 75 minutes for cadmium as shown in Figure 2.12 Adsorption isotherm test showed that resin could adsorb mercury better as the temperature increased up to 40°C but declined when further increased to 50°C. Adsorption behavior could be sufficienctly explained by Freundlich isotherm. From the thermodynamic point of view, it was found that the ΔG^0 for adsorption was negative meaning the adsorption reaction could occur spontaneously under the studied conditions. The ΔS^0 was positive meaning an increase in disorder degree when sorption happened at the solid/solution interface. It also increased with temperature and, thus, the reason why the adsorption efficiency increased as the temperature increased. (Gupta et al.,2004)

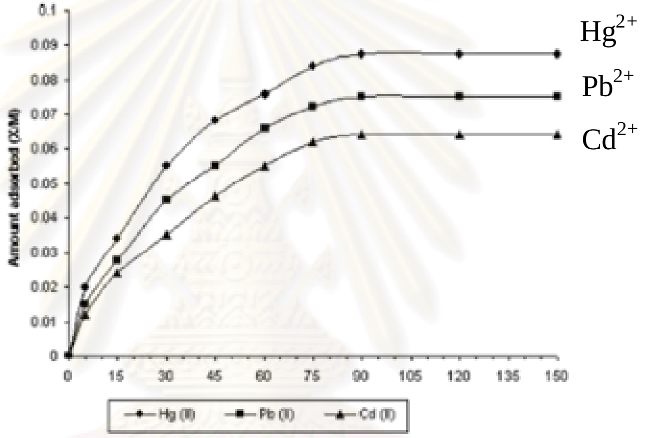


Figure 2.12 Effect of equilibrium time on the sorption of Hg(II), Pb(II), and Cd(II) on Duolite C-433.

2.6.1.4 This research studied about the specificity of ion exchange resin to remove heavy metal included lead(II) Pb^{2+}, mercury(II) Hg^{2+}, cadmium(II) Cd^{2+}, nickel(II) Ni^{2+}, vanadium(IV,V) V^{4+} , V^{5+}, chromium(III,VI) Cr^{3+}, Cr^{4+} , copper(II) Cu^{2+}, Zinc(II) Zn^{2+}. The researcher compared the ion exchange resin method with other methods such as conventional method : precipitation. This did not suitable for low concentration of mercury because these ions were precipitated as hydrated metal oxides or hydroxides, sulfides or xanthiogenates using calcium oxide. While, flocculation or coagulation would created the large amount of sediment heavy metal. It needed treatment these sediment in the final step, which created more cost. In sometimes, all of heavy metal did not precipitate with coagulant because in the water after treatment still had ion of heavy metal in 2-3 mg/dm^3. (Fabiani, 1992 cited in Dą browski et al., 2004) Whereas, ion exchange resin could remove ion by selective manner, so the removal efficiency would higher than other method. The advantage was easy method and can remove heavy metal especially in mercury. Even though, it had traces of impurities from solutions. Mercury appeared in the form Hg^{2+} and Hg^{2+}_2. Ion exchange resin suited for low concentration of mercury in the large volume of wastewater. Besides, resin had several types such as strong and weak acid cation exchange resin and strong and weak basic anion ion exchange resin so it can worked in wide range of pH.(Gardiner and Munoz, 1971 cited in Dą browski et al., 2004) such as Imac TMR (Akzo Zout) was selective removal of Hg(II) ions. It was a styrenedivinylbenzene copolymer with thiol(-SH) and sulphonic as functional groups. Because of thiol group, mercury could remove in high amount. The residual mercury concentration in effluent was 0.5-5 ppb, meanwhile the precipitation treatment by sulfide could achieve to 1-3 ppb. Dowex A-1 was the resin that had iminodiacetic acid as functional group. This group had high affinity to Hg(II) ions (Rengan, 1997 cited in Dą browski et al., 2004)

2.6.2 Resin treats other heavy metal

2.6.2.1 The general method for treat heavy metal are ion exchange and chemical precipitation but the advantages of ion exchange which was over the chemical precipitation were selectivity, produced less amount of sludge. This paper used Purolite C100 for treatment the Ce^{4+}, Fe^{3+} and Pb^{2+}. These metals contaminated to the wastewater from metal industry. Purolite C100 was Polystyrene-divinyl benzene and sulfonic acid as functional group. The objective of this study analyzed the influence of charge in the wastewater (Ce^{4+}, Fe^{3+} and Pb^{2+}), which affect to the efficiency in the remove of heavy metal of Purolite C100 resin. This resin was added into the synthetic wastewater composed of Ce^{4+}, Fe^{3+} and Pb^{2+} and shake this flask 24 hours or until it was equilibrium. The results showed that the Ce^{4+} could adsorb maximum then Fe^{3+} and Pb^{2+} respectively because of the charge density of cations and the diameter of hydrated cations. When the diameter of hydrated cations was less, the adsorption capacity was greater the large in the diameter. (Abo-Farha et al., 2009)

2.6.2.2 The copper ion was found in the wastewater such as mining, plating baths, coal burning, wire manufacturing, steel manufacturing, fertilizer, pigments, printing circuits and paints. The wastewater from this factory could contaminate to the food cycle so the technology for removal copper(II) ion was interested. The ion exchange resin was the popular method because the chemical reaction by ion exchange could occur rapid and easy in operation. However, the efficiency would go the best. It depended on the specificity of resin to the ion. The chelating resin suited for removal heavy metal because multi-adsorbing function. This paper would focus on the synthesis of resin from melamine–formaldehyde hydrogel modified with nitrilotriacetic acid (NTA) because Gurnule et al., 2002 stated that the melamine-formaldehyde had the properties in removal Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II) and Fe(III). The synthesis resin method used melamine, NTA, acetone and guaiacol by using the high temperature as catalyst to support the chemical reaction. After that the synthesized resin was used to remove copper(II) ion in the synthesis wastewater by vary temperature, pH and initial concentration. The results showed that the grains of MF–NTA gel resin were white and insoluble in water, acetone and ethanol. Beside, it could resist in dilute acid or base. When the adsorption of copper (II) ion occurred the resin would change in color from white to light blue. The resin had high performance between pH 3-6 by the maximum was pH 6. The efficiency would decrease, when the pH higher than 6 because hydroxide precipitation. When the temperature and dose was high, the adsorption capacity would high together. The resin could form stable in normal temperature and high specificity toward the copper(II) ion. (Baraka, Hall, and Heslop, 2007)

2.6.2.3 The vanadium (V) was the transition metal which had the strong toxicity. It came from the ceramic, glass, and textile industry. In previous study, Qian et al.,2004; Manohar et al., 2005 and Dogan et al.,2006 used the chitosan, chemically modified silica and aluminum-pillared bentonite, but the efficiency in removal were not satisfied. Cho et al., 2007 found the ion exchange fiber had high adsorption rate but limit in the pressure drop, so the hybrid ion exchanger (HIE) between the ion exchange fibers with ion exchange resin by hot-melting adhesive was selected in order to increase the stability, efficiency and remove limitation. Then, pH, initial concentration and temperature were the analyzed parameters. The polyolefin fiber (PONF) was used as ion exchange fiber and Amberlite IRA-96 was used as ion exchange resin. These two components were linked with hot-melting adhesive method. Then, HIE was reacted with vanadium oxide (V_2O_5) solution by vary three parameters. The results showed that acidic pH (pH 3) was supported the adsorption greater than basic pH (pH 7). When increased temperature and initial concentration, the adsorption efficiency was increased especially high temperature because it activated the reaction to go faster by adsorption went to the equilibrium in 200 minutes (313 K or 40°C) compare to 300 minutes in room temperature. (Yeom, Lee, and Hwang, 2009)

2.6.3 Technology for remove mercury

2.6.3.1 In normally, the chemical materials such as chemical agent or resin were used to remove mercury but the natural materials which consisted of lignocellulosic materials such as wheat straw, peanut shell, moss peat, bagasse fly ash, tree fern, and gram husk and coconut coir pith. All of them had the properties to remove heavy metal such as mercury because of adsorption capacity from lignin and pectin. The coconut coir pith (CP) was selected to study the properties because it was easy to find and low cost. In this study, the researchers modified the CP with carboxylate as functional group and analyzed the properties to treat mercury. The modified CP was made from the chemical reaction by adding the reagent such as of $K_2S_2O_8$ and $Na_2S_2O_3$. After that, the modified CP was shaken with synthetic wastewater which consisted of $HgCl_2$ and analyzed data by AAS. The results showed that the adsorption increased when the pH increased because of protonation of functional group. When temperature and amount of adsorbent increased, the adsorption capacity would increase together. The adsorption behavior followed with first order kinetic and Freundlich isotherm. (Anirundhan, Divya, and Ramachandran, 2008)

2.6.3.2 Mercury was the toxic metal. It was produced from chloro-alkali, paper, pulp, oil refinery, paint, pharmaceutical and batteries. The method for treatment of mercury was studied. The biological method could remove mercury by use enzyme from the bacteria which could resist in extreme condition. The enzyme that had special property was papain. Dutta et al., 2009 stated that papain was proteolytic enzyme which had sulfhydryl group in active site. The functional group in this active site would support the enzyme could bind with metal ion. Due to the enzyme did not stable and denature in extreme condition such as high temperature or high metal concentration, so the immobilization was an alternative way to protect enzyme for using many cycles. In this study, the researcher would use alginate which was the algae for immobilization with this enzyme, so it was called AIP. The parameters were studied such as concentration of papain, concentration of sodium alginate, concentration of calcium chloride, temperature and pH.

The results showed that optimum condition were 70°C and pH 5. The temperature had large influence in diffusivity. The diffusivity increases with an increase in temperature. However,this bead could operate in the temperature 4–70°C and pH 2–12. The mercury removal would saturate in 8 minutes, when vary mercury concentration from 1-30 mg/l. The conclusion was best mercury removal (98.88%) was obtained when mercury (II) concentration equaled to 10 mg/L with 5 g AIP at pH 7 and 35 °C for 8 minutes. (Bhattacharyya et al., 2010)

2.6.3.3 The mercury was the toxic heavy metal for environment, so it was important to find the method for treatment such as adsorption. From Tharin et al.,1974; Manchon-Vizuete et al.,2005 found the properties of waste tired rubber that could immobilized mercury ion contaminated in soil. Due to the components of production of rubber were zinc oxide, carbon black and cross link sulfur, these components had affinity to mercury. From this reason, the researchers would apply the waste tired rubber in order to treat mercury contaminated in wastewater. This research would study the size of waste tired rubber and component of carbon black, sulfur crosslink and amount of zinc oxide which might affect to the adsorption properties. The pretreatment of waste tired rubber started with waste rubber, stearic acid and ZnO, then vulcanization so as to get the suitable materials. The $HgCl_2$ acted as synthetic wastewater reacted with vary size of rubber by perform in 8 hours at 30°C. After that, vary crosslink density and components of rubber and pH variation.

The results showed that the smaller size of rubber had the well performance in sorption better than the larger size because of the surface area. When the amount of crosslink sulfur was high, the sorption capacity would high together because Hg(II) could inserted between the crosslink in vulcanizing reaction, but not in the zinc oxide. While the high amount of carbon black, it would affect the less efficiency in mercury adsorption because it inhibited the diffusion of Hg(II) to rubber. (Danwanichakul et al., 2008)

2.6.3.4 The conventional technology to remove mercury such as stabilization and solidification could not reduce the leachability of mercury by mercury leached from cement or some of them were precipitated as HgO and volatized from cement. So, the alternative way to solve this problem was binding the –SH (thiol) group to the support matrixes such as silica, alumina and clay so as to enhance adsorption capacity to mercury. The mechanism was thiol group would bind strongly and affinity to mercury and form HgS as precipitation and stabilization on the matrixes surface. The objective of this study analyzed the cost effective method to treat the mercury in solid wastes by use the 3-mercaptopropyltriethoxysilane was used to graft the –SH to the natural clinoptilolite zeolites and the mercury adsorption capacity of the thiol-functionalized zeolite in aqueous solutions was investigated. The thiol-functionalized zeolite (TFZ) was prepared from the mixing between zeolite and 3-mercaptopropyltriethoxysilane and was washed with toluene and ethanol. Then, TFZ was tested in the adsorption isotherm by vary the $Hg(NO_3)_2$ were 10mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100mg/L. The solidification and stabilization was performed by TFZ mixed with Hg concentration from 100-1,000 mg/kg. Then, it was shaken at room temperature and pH 6 in order to analyze the stabilization. The waste from this test would set with Portland cement to test the solidification. The results showed that Freunlich isotherm could describe the adsorption behavior better than Langmuir isotherm and adsorption capacity was increased in ten times. The optimum condition pH was 5.0 and optimum condition for solidification and stabilization was 1,000 mg Hg/kg waste, 5% TFZ dosage and 100% cement dosage. The stabilization efficiency and solidification efficiency equaled to 98% and 99.89% respectively. (Zhang et al., 2009)

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Weak acid cation exchange resin (Duolite C433)

This is a commercial weak acid cation exchange resin. It can bind to any divalent cation ion but non selective to divalent mercury ion. It was purchased from Rohm and Haas company, United States of America.

This resin is used in this study because specific selectivity to certain ions or groups of ions and often bind to inorganic chemical.(Matsumota et al., 1989; Allen and Brown, 1995; Lai et al., 1994) It can bind with any divalent caions including Hg^{2+} but does not have specific affinity to Hg^{2+}.

3.1.2 Chelating cation exchange resin (Amberlite IRC718)

This is a commercial chelating cation exchange resin. It can selective to divalent mercury ion. It was purchased from Rohm and Haas company, United States of America.

3.1.3 Wastewater from petrochemical industry was sampling from sampling point 1 that was raw wastewater as shown in Figure 3.1.

3.1.4 5% $KMnO_4$

Potassium permanganate ($KMnO_4$, MW 158.034 g/mol) was purchased from Univar, Ajax Finechem (Australia and New Zealand). The 5% $KMnO_4$ was prepared from 5 g of $KMnO_4$ mixed with 18 mΩ distilled water 100 ml.

3.1.5 Mix acid

This reagent was prepared from mixed between conc HNO_3 (65% nitric acid) 125 ml, conc H_2SO_4 (96% sulfuric acid) 250 ml and 18 mΩ distilled water 125 ml. The two acids were purchased from Carlo Erba, Italy.

3.1.6 5% $K_2S_2O_8$

Potassium persulfate ($K_2S_2O_8$, MW 270.322 g/mol) was purchased from Unilab, Ajax Finechem (Australia and New Zealand. The 5% $K_2S_2O_8$ was prepared from 5 g of $K_2S_2O_8$ mixed with 18 mΩ distilled water 100 ml.

3.1.7 10% NH_2OH HCl

10% hydroxylamine hydrochloride (NH_2OH HCl, MW 69.5 g/mol) was purchased from Carlo Erba, Italy. The 10% NH_2OH HCl was prepared from 10 g of NH_2OH HCl mixed with 18 mΩ distilled water 100 ml.

3.1.8 Other reagents

Sodium hydroxide (NaOH, MW 40.00 g/mol) were purchased from Carlo Erba, Italy.

3.2 Equipments

The equipments used in the experiment are following

3.2.1 Hot plate stirrer

3.2.2 pH meter

3.2.3 Water bath

3.2.4 Piston pump

3.2.5 Cold vapor atomic adsorption spectrophotometer from Perkin Elmer (A Analyst 800), United States of America.

3.3 Methodology

3.3.1 Characterization of raw wastewater

To evaluate the performance of the existing treatment units for mercury as shown in figure 3.3 water samples from several points of the treatment system would be collected and analyzed:

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

This point would examine pH, total suspended solid (TSS), total dissolve solids (TDS), biological oxygen demand (BOD), total organic carbon (TOC), total and soluble mercury concentration, fat oil and grease (FOG), chemical oxygen demand (COD), arsenic concentration and chloride concentration. Sample at this point would be used in this study.

Point 2: After cartridge filter (representing a filtered wastewater before mercury removal)

This point would examine pH, total suspended solids (TSS), total mercury concentration and arsenic concentration.

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

This point would examine pH, total organic carbon (TOC), total mercury concentration and arsenic concentration.

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

This point would examine pH, total organic carbon (TOC), total mercury concentration and arsenic concentration.

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

This point will examine pH, total organic carbon (TOC), total mercury concentration, chemical oxygen demand (COD) and arsenic concentration.

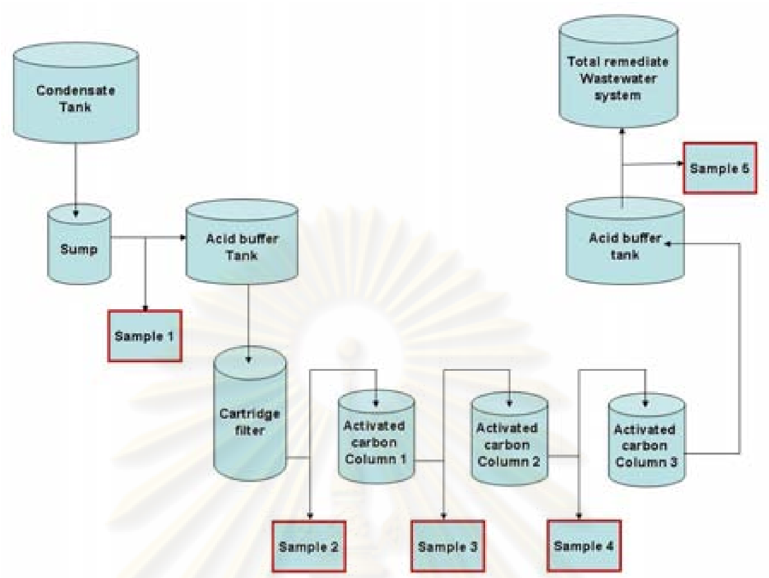


Figure 3.1 Flow diagram of existing mercury treatment system of a refinery plant and sampling points

3.3.2 Effect of pH to solubility of mercury

The real wastewater would divide two types. The first types was not filtrate as total form of mercury and the second types was filtrate through 6 μm filter paper as soluble form. Then, two types was varied pH 2-9 in order to check the solubility in each pH.

3.3.3 Batch test: the 3 factors would analyze as follow

3.3.3.1 Determination for the adsorption equilibrium time

The real wastewater of 150 ml and 10 mg of resin (either C433 or IRC718) would be added to a 250-ml Erlenmeyer flask. Then, the flasks would be swirled at 30°C on the shaker. At predetermined time of 0, 5, 10, 15, 30, 45, 60, 90, 120 and 180 minutes, a 15-ml sample would be taken by using a syringe. The sample would be immediately filtered by a 0.45-μm filter paper and determined for mercury content. Solution pH would be monitored through out the experiment.

Expected outcome : Time profile of mercury adsorption, equilibrium time

3.3.3.2 Determination effect of initial pH

In this part, pH of the real wastewater would be adjusted (within the typical range as suggested by manufacturer) by using NaOH or HCl and determined for adsorption behavior of cationic resins (both C433 and IRC718). The used amount of resin was between 0, 1, 5, 10, 15, 20 grams with real wastewater 100 ml. The studied pH would be 2, 5 for C433 and IRC718 resin. Ion exchange adsorption would be allowed to reach equilibrium (using the equilibrium time from previous section) and then determined for remaining mercury concentration. Solution pH would be monitored through out the experiment. It was important to note that the solution pH would change with time due to the release of H^+ as a result from mercury exchange. Hence, determination of optimum pH had to be considered carefully. (Chiarle et al.,1999; Mondal and Das, 2003; Pehlivan and Altun, 2006; Donia, Atia, and Heniesh, 2008)

Expected outcome : optimum pH ($pH_{opt, real}$ vs $pH_{opt, syn}$)

3.3.3.3 Effect of type of exchange ion

The real wastewater spike with 100 ppb Hg from $Hg(NO_3)_2$ would adjust to optimum pH, used the amount of resin between 0, 1, 5, 10, 15, 20 grams with real wastewater 100 ml and then shake in the Erlenmeyer flask by tested the resin between sodium form (Na^+) and proton form(H^+). After that, the flask would shake in equilibrium time. Then, take the sample to digest and analyzed Hg concentration.

3.3.3.4 Determination of adsorption isotherm

Adsorption isotherm of both resins in real wastewaters would be determined by varying the amount of resins were 0, 1, 5, 10, 15, 20 grams per wastewater 100 ml. (precise quantity of resins required would be specified after the exchange characteristics of the resin had been clarified in two previous sections). Sampling and analytic procedures would be similar to Section 2.1. Obtained data would be used to determine the adsorption isotherm. (Shi et al., 2009; Rivas et al., 2010)

Expected outcomes :

- Adsorption isotherm
- Adsorption capacity (Q_{real} vs Q_{syn})
- Effect of wastewater characteristic on Q

3.3.4 Column test :

The size of the column for existing conditions

Column size = 57 cm ϕ × 258 cm height (total)

Adsorbent volume = 658 L

Flow rate = 8 m^3/day = 5.56 L/min

V_{flow} = 2.18 cm/min

EBCT = 2.0 hours

The size of the column for using in this study as shown in Figure 3.2

Column size = 5 cm ϕ × 22.5 cm height (can increase to 67.5 cm height)

Adsorbent volume = 0.44 L

Flow rate = 3.67 mL/min

V_{flow} = 0.19 cm/min

EBCT = 2.0 hours, 4.0 hours and 6.0 hours.

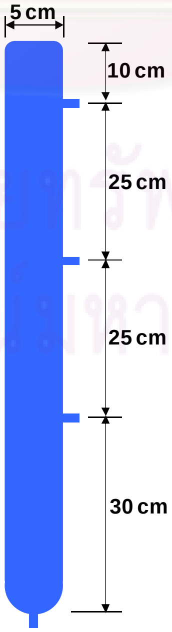


Figure 3.2 Column size 5 cm ϕ × 90 cm height use for this experiment.

3.3.4.1 Effect of resin depth

Information obtained from the batch test would be applied as an optimal condition in the column test. The depth of resin in the column would be varied volume of resin 440 ml and 880 ml, flow rate 200 ml/min and hydraulic retention time 2 and 4 hours, whereas the flow rate would be kept constant. The test would be operated at a fixed flow rate and ran until the breakthrough happens i.e., 5 to 40 BV/hr for C433 and 8 to 32 BV/hr for IRC718. The test will be operated at a fixed bed depth and run until the breakthrough happens, i.e., effluent mercury concentration reaches 5 μg/l (industrial effluent standard for mercury in Thailand). The real wastewaters would be studied to determine the effect of wastewater characteristics on adsorption behavior in column operation. Data obtained from this part would be used to characterize the column adsorption behavior by using Bohart and Adams equation. Then, results from the continuous test would be applied in the design for the real operation. (Jiang et al., 2006; Donia et al., 2008)

Expected outcomes :

- Breakthrough curve ([Hg] = 5 ug/l) + Graph breakthrough
- Column adsorption behavior
- Criteria for design (using Bohart and Adam) + graph

3.3.4.2 Determination for resin regeneration ability (Atia, Donia, and El-Nomany, 2009)

Regeneration ability of each exchange resin would be determined in order to verify its reliability in mercury removal under field practice. Spent resin from Sections 3.1 would be regenerated according to the procedure recommended by the manufacturer and retested for its adsorption behavior between regenerated and new resin by batch study.

The IRC718 resin from the continuous test was used in the regeneration test in duplicate by regent IRC718 in column with 10% HCl, flow rate 200 ml/hour, 2 hours and rinse resin with 18 mΩ DI water, flow rate 1,000 ml/hour, 1 hour for first time, while 15% HCl in 3 hours, same condition was used in order to ensure this test. Then, sample would take in every 50 ml of effluent for acid regeneration, while rinse with DI water would take in 3 periods composed of 50 ml in first period, when water passed through column in 500 ml and 50 ml in last period. The regenerate resin would test for efficiency in reuse by did the batch test and compared with new resin (resin which did not use before). The optimal resin dose would test with real wastewater and mass balance of mercury and percentage of recovery was calculated as follow

Mass balance of mercury (μg) = [Hg] in regenerant (μg/l) x Volume of regenerant (L)

$$\text{\% of recovery} = \frac{\text{Concentration of mercury in regenerant}}{\text{Concentration of mercury in exhausted resin}} \times 100$$

Expected outcomes:

From batch test:

-Time-profile of the Hg adsorption and equilibrium time

-optimum pH ($pH_{opt, real}$ vs $pH_{opt, syn}$)

-Adsorption isotherm

-adsorption capacity (Q_{real} vs Q_{syn})

-effect of wastewater characteristic on Q

From column test

-Breakthrough curve

-Column adsorption behavior

-Criteria for design (using Bohart and Adam)

3.5 Analytical methods

The sample digestion would be followed with standard method EPA 7470A mercury in liquid waste (Hydride generation technique) as shown in Figure 3.3. Then, Hg^{2+} concentration in the wastewater from the experiments was analyzed by using Cold vapor adsorption spectrophotometer (AAS).

The standard method EPA 7470A mercury in liquid waste (Hydride generation technique)

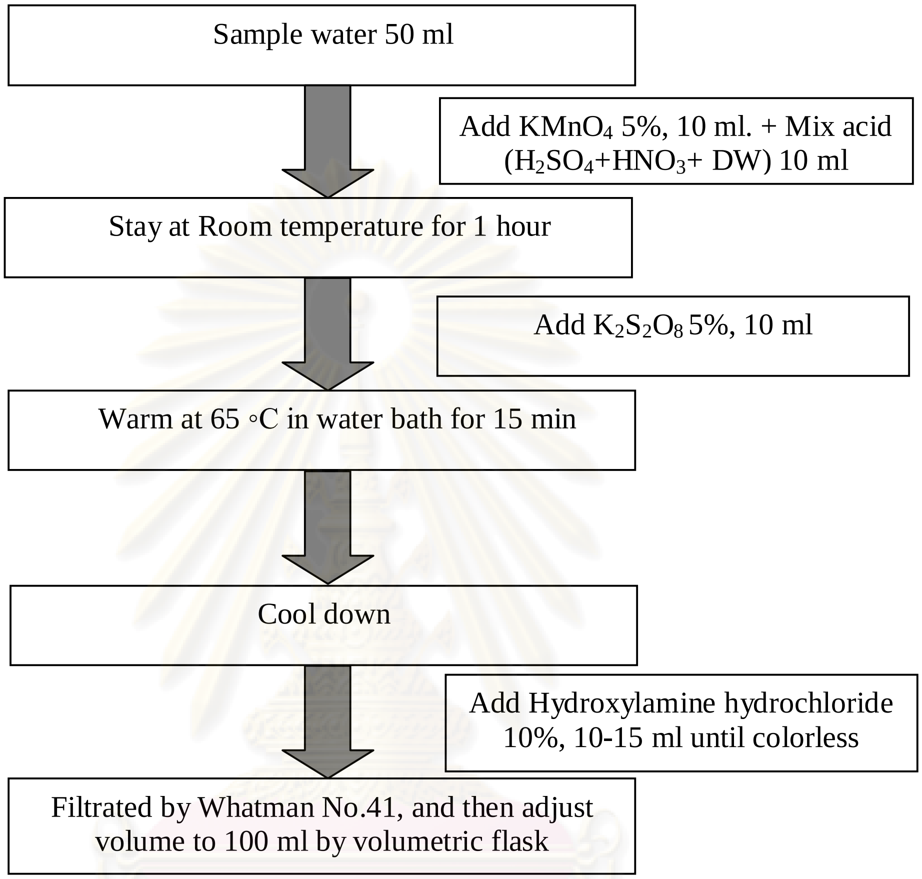


Figure 3.3 The diagram of standard method EPA 7470A mercury in liquid waste (Hydride generation technique)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Wastewater characteristics in 5 sampling points

The real wastewater properties was analyzed into 9 properties such as pH, total suspended solid (TSS), total dissolved solid (TDS), fat oil and grease (FOG), chemical oxygen demand (COD), total organic carbon (TOC), mercury concentration in total and soluble form(flirtation through 6 µm), arsenic concentration and chloride concentration. In this study, the wastewater was sampling from 5 points as shown in Figure 4.1 and the characteristics of raw wastewater were shown in the table 4.1.

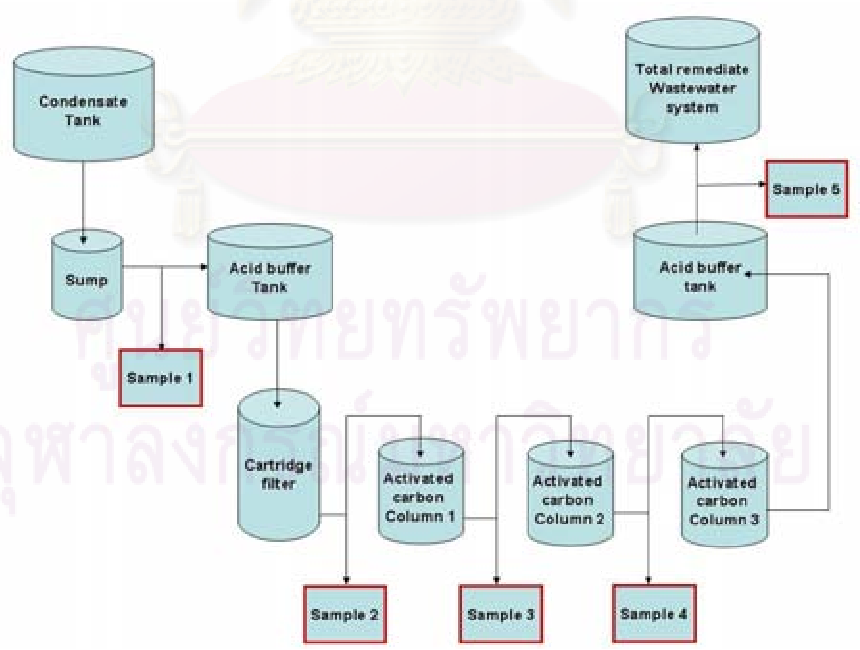


Figure 4.1 Flow diagram of existing mercury treatment system of a refinery plant and sampling points

Table 4.1 Characteristics of real wastewater in each sampling point

Sampling date	**7 June 2010**					**30 September 2010**	**24 December 2010**	**2 March 2011**
Parameters	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**	**Point 1**		
pH	5.01	2.43	2.39	2.46	6.01	4.40	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
BOD (mg/l)	-	-	-	-	-	298	300	308
TOC (mg/l)	1,394	-	5,116	5,218	1,692	922.80	2,097	1,002
Hg (µg/l): - Total	459	572	372	411	130	85	73.20	22.5
-6 µm Filtrate	125	-	-	-	-	18	1.30	4.8
As (mg/l)	167	174	161	168	99	-	-	52
Chloride (mg/l)	926	-	-	-	-	-	-	-

From the results in table 4.1, it showed the raw wastewater (point 1) had the acidic pH, TDS, COD and TOC in high amount which might be interfere in ion exchange process. The COD was high amount, it pointed that wastewater had organic carbon in high too. If it could ionize, it had a high effect in ion exchange process. It might competitive with mercury ion which had low concentration (459 µg/l) when compared with COD level. Total mercury concentration was 459 µg/l and filtrate mercury concentration was 125 µg/l. It showed that most of mercury ion attached with the suspended solid, so the filtration was the pretreatment to reduce mercury concentration. Even though, arsenic and chloride concentration were high, but arsenic did not interfere the ion exchange because arsenic presented in arsenate (AsO_4^{3-}) and arsenite (AsO_2^-), while ion exchange process occurred with cation in acidic to neutral pH. (Mohan and Pittman, 2007) Chloride was the negative charge, anion which interfered the ion exchange process by chloride ion could form chlorocomplexes with mercury ion. (Becker and Eldridge, 1993) Fatty oil and grease was low concentration and it did not coat the adsorbents.

In point 2-4, the pH was acid around 2 because wastewater was adjusted pH in acid buffer tank to pH 2 in order to prompt in adsorption with activated carbon. The total suspended solid was reduced by filtration through cartridge filter, but the mercury concentration was high. The reason might come from adjustment pH to 2; it might increase the solubility of mercury ion. After that, total organic carbon was increased three times, when it passed through activated carbon column 1. The characteristic of wastewater was same, when it passed through activated carbon column 2. While, the total organic carbon and mercury concentration were significantly reduce, when it passed through activated carbon column 3. From the results, it showed the variation of characteristics of wastewater that might come from variation of raw wastewater and residue of wastewater in each treatment process.

In point 5, the pH was around 6 because wastewater was adjusted to neutral pH in order to ready in remove COD and BOD in total remediate wastewater system. Wastewater was adsorbed with 3 activated carbon columns, however; they could not reduce mercury concentration lower than 5 ppb, so it needed to treat with ion exchange process. The efficiency of treatment wastewater was not meet to the standard. The reasons were this process had exhausted activated carbon and flow rate was high and it had the effect in adsorption of activated carbon.

However, the pretreatment such as skimmed oil and using the filtration in order to remove total suspended solid (TSS). It suited for pretreatment of wastewater prompt to treatment by ion exchange process. The pretreatment would decrease the problem from oil coated resin and resin was clog by TSS.

This experiment was not only one sampling, but wastewater was tested in three times. They composed of the second sampling (30 September 2010) mercury concentration 85 mg/l for total form and 18 mg/l in soluble from. The third sampling

(24 December 2010) mercury concentration 73.2 mg/l for total form and 1.3 mg/l in soluble from. The fourth sampling (2 March 2010) mercury concentration 22.5 mg/l for total form and 4.8 mg/l in soluble from. From the several sampling, mercury concentration was not stable, so the spike $Hg(NO_3)_2$ for the wastewater which had the soluble form less than 100 µg/l was needed in order to adjust the condition suited for apply in real operation.

From the analysis of multi elements (table 4.2), the results showed that Fe and Ni were high 88.046 and 50.910 mg/l respectively, when compared with the mercury concentration, so it was very higher than mercury. Fe was the elements that affinity than Hg (see appendix A table A.1), so the competitive ion exchange might occur. Even though, Ni was lower affinity than Hg, but the concentration was high in mg/l level, so the competitive in exchange ion might occur as in Fe.

Table 4.2 The chemical characteristics of real wastewater

Elements	**Concentration (mg/l)**
Ag	0.007
Al	0.392
B	No data
Ba	0.041
Bi	No data
Ca	23.798
Cd	0.014
Co	0.022
Cr	0.141

Elements	Concentration (mg/l)
Cu	No data
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	No data
Sr	0.217
Tl	ND
Zn	0.937

4.2 Effect of pH to solubility of mercury

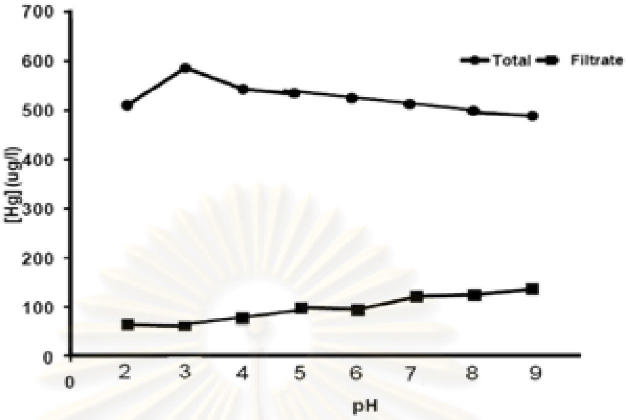


Figure 4.2 The effect of pH 2-9 to the solubility of mercury

Due to the pH was the factor that controls the precipitation and formation of complexes, so the effect of pH to the solubility of mercury (II) ion was needed. From the literature reviews of activated carbon and resin stated that optimal condition was between acidic to neutral pH, so the solubility was test pH 2-9. (Walton, 1964; technical data sheet of Rohm and Haas company; and Tonini et al., 2003)

From the Figure 4.2, the results showed that when pH was increased, the solubility of mercuric ion in wastewater was slightly increased. The reason was when pH of wastewater increased, hydroxide ion was presented solubility was rose. Due to it was not significantly different between each pH, so the comparison between each pH could perform by less error. However, the solubility would depend on the characteristic of wastewater. The variation in wastewater might affect in the solubility.

4.3 Equilibrium time

From the study, the mercury concentration would reduce in first hour, then, it did not dramatically decrease between second to third hours. From the results, the equilibrium time of ion exchange process by two resins (C433 and IRC718) were 3 hours and it took time less than adsorption by activated carbon which was 12 hours, so the equilibrium time was 3 hours as shown in Figure 4.3 The results correlated with theory because ion exchange was the reaction which occurred at surface of adsorbent, while the adsorption needed to diffuse into meso-porous and micro-porous of activated carbon by using the micro-porous diffusion mechanism. This process was slow because it was controlled by Brownian motion (Lara et al., 2007). However, the equilibrium time which used for next study equaled to 24 hours as in activated carbon adsorption in order to easy to compare in treatment efficiency.

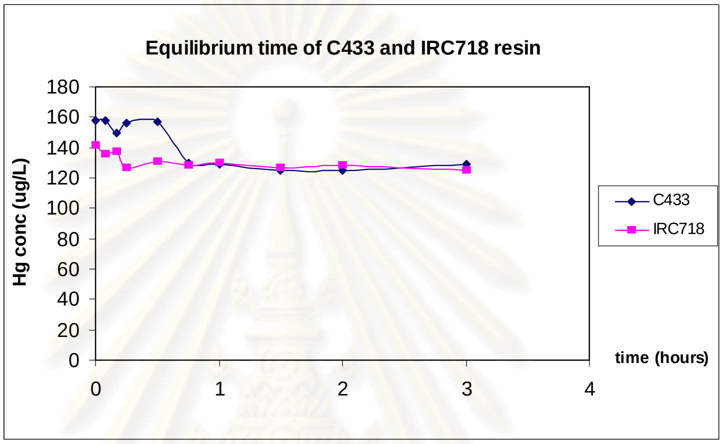


Figure 4.3 The result of equilibrium time by use C433 and IRC718 resin in sodium form, 10g/l between 0-3 hours.

4.4 Effect of pH to ion exchange reaction

In this study, the selected pH of wastewater was 2 and 5 because pH 2 was the optimum pH from recommendation in technical data sheet of IRC718 resin and pH 5 was the optimal pH for C433, so the study in two pH was performed in order to compare the efficiency in mercury removal. Beside, it was easy to compare the efficiency in treatment of mercury in wastewater with activated carbon.

The results showed that IRC718 at pH 2 could reduce the mercury concentration from 22.77 µg/l to 2.5 µg/l, while C433 could reduce mercury to 14.764 µg/l. The percentage of removal equaled to 89% and 35.2% respectively. IRC718 at pH 5 could reduce the mercury concentration from 15.493 µg/l to 4.363 µg/l, while C433 could reduce mercury to 14.094 µg/l. The percentage of removal equaled to 71.8% and 0.09% respectively. The graph was as shown in Figure 4.4.

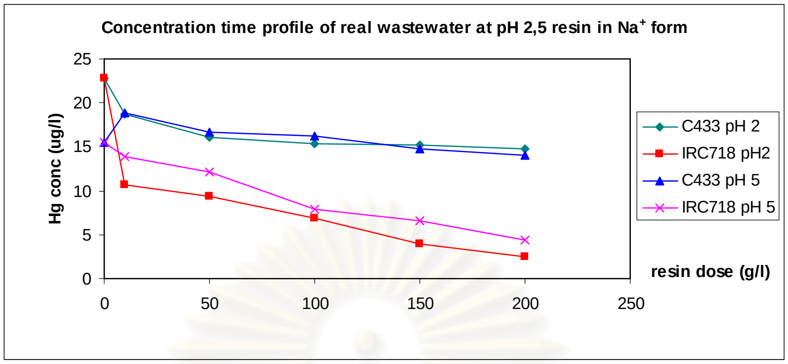


Figure 4.4 Mercury concentration of real wastewater at pH 2 and 5 at equilibrium time (24 hours), resin in Na^+ form

From the results, it showed that IRC718 had the well performance in reduce mercury concentration higher than C433. In addition, IRC718 could reduce to meet the standard of mercury in wastewater drainage of Thailand (5 ppb). pH 2 worked better than pH 5. The efficiency in remove mercury of IRC718 at pH 2 and pH 5 account for 89% and 71.84% respectively. The reason was the selectivity to Hg^{2+} of IRC718 at pH 2 was 43,000 times based on Ca^{2+}, when pH increased (pH 4) the selectivity reduced to 2,800 times (Technical data sheet from Rohm and Haas, USA). Moreover, functional group of IRC718 could bind with the mercury ion which enhances resin binding and heavy metal stability at pH 2. (Agrawal and Sahu, 2006) While, C433 was the resin which used for hardness reduction such as Ca^{2+} and Mg^{2+} and it was non selective to mercury ion.

The wastewater which use in this experiment was from the second sampling. It had the low mercury concentration, so the spike with 100 ppb of $Hg(NO_3)_2$ was needed.

The results of real wastewater with spiked 100 ppb $Hg(NO_3)_2$ was shown as in Figure 4.5. The results were same as in non spike real wastewater. IRC718 at pH 2 could reduce the mercury concentration from 88.080 µg/l to 19.763 µg/l, while C433 could reduce mercury to 71.443 µg/l. The percentage of removal equaled to 77.56% and 18.8% respectively. IRC718 at pH 5 could reduce the mercury concentration from 167.250 µg/l to 77.635 µg/l, while C433 could reduce mercury to 112.271 µg/l. The percentage of removal equaled to 53.5% and 32.8% respectively. ,so it ensure that pH 2 was the optimal condition for treatment mercury by IRC718 as pH of solution decreased, the selectivity for Hg^{+2} over all other metals increased strongly. (Becker and Eldridge, 1993)

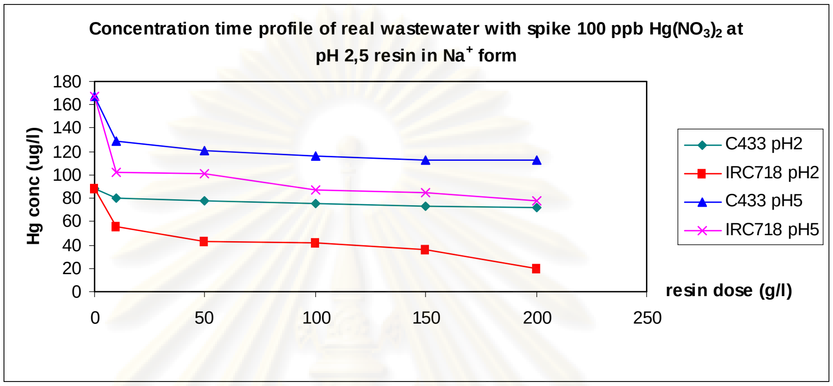


Figure 4.5 Mercury concentration of real wastewater at pH 2 and 5 at equilibrium time (24 hours), resin in Na^+ form with spike 100 ppb $Hg(NO_3)_2$

Owing to, the initial mercury concentration was different in pH 2 and 5, so the comparison from the profile curve could not perform and it needed to compare by isotherm graph.

When plot the isotherm with Freundlich isotherm, the graph showed that mercury ion exchange with resin in non-favourable. It meant mercury ion tended to stay in wastewater more than exchange in resin. The reason might from high concentration of other ions would competitive or interfere in ion exchange process, so it needed to use resin more than usual to treat mercury in wastewater as shown in Figure 4.6 and Figure 4.7.

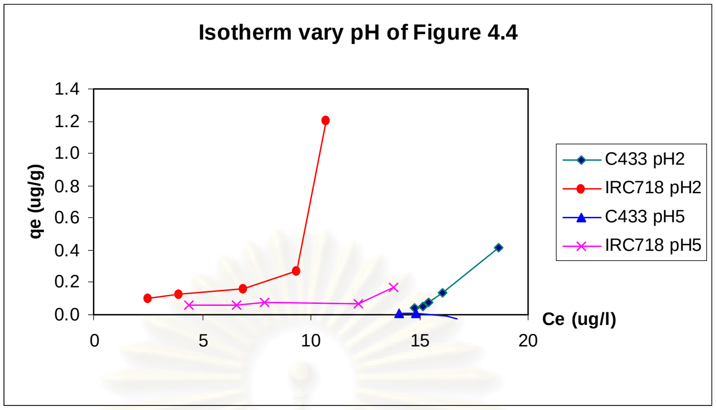


Figure 4.6 Isotherm of Figure 4.4

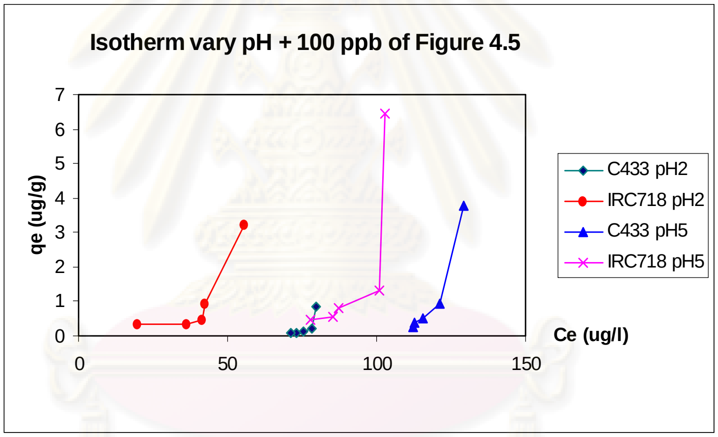


Figure 4.7 Isotherm of Figure 4.5

4.5 Effect of type of exchange ion

The ion exchange resin could work in sodium form (Na^+) and proton form (H^+), so the type of exchange ion was studied. The results showed that H^+ form had the efficiency in reduce mercury concentration more than Na^+ form for IRC718, but Na^+ form had the efficiency in reduce mercury concentration more than H^+ form for C433 as shown in Figure 4.8 and isotherm graph was shown in Figure 4.9.

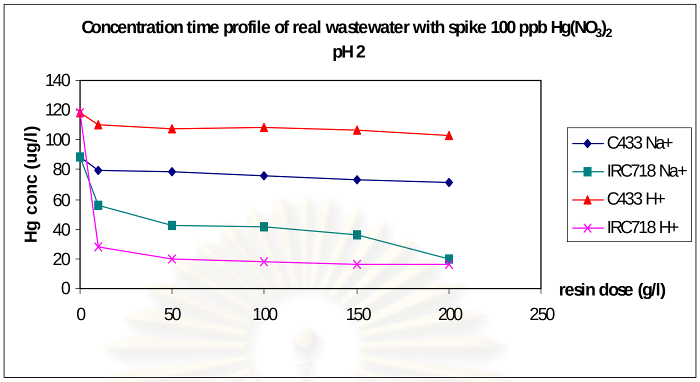


Figure 4.8 Effect of type of exchange ion to mercury concentration of real wastewater with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours) pH 2, resin in Na^+ and H^+ form

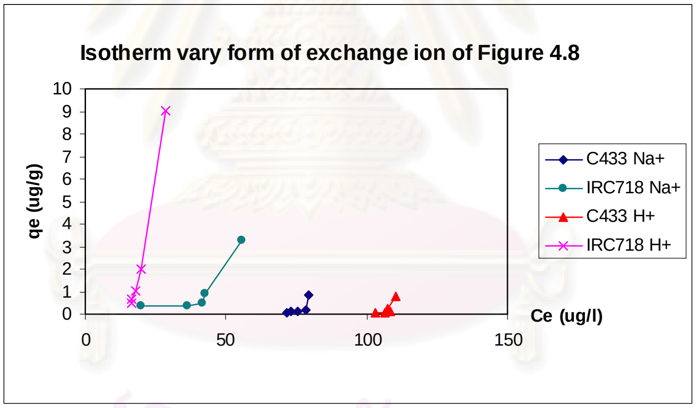


Figure 4.9 Isotherm of Figure 4.8

These results did not accurate, so the study for test H^+ form between two resins was studied two times. The results showed that mercury concentration from 118.450 µg/l reduced to 16.395 µg/l for IRC718 and 103.118 µg/l for C433 at the first time. The percentage of removal equaled to 86.1% and 12.9% respectively. While 214.400 µg/l reduced to 15.794 µg/l for IRC718 and 181.155 µg/l for C433 at the second time. The percentage of removal equaled to 92.6% and 15.5% respectively. The results were shown as in Figure 4.10 and Figure 4.12. The two tests ensured that IRC718 exchange ion in H^+ form had the efficiency in treatment of mercury better than Na^+ form which correlated with the degree of exchange depended on size and charge of ion which small ion had the degree and selectivity in exchange better than large ion. (Eckenfelder and Wesley, 2000 and Clifford, 1986). The isotherms in two tests were shown in Figure 4.11 and Figure 4.13.

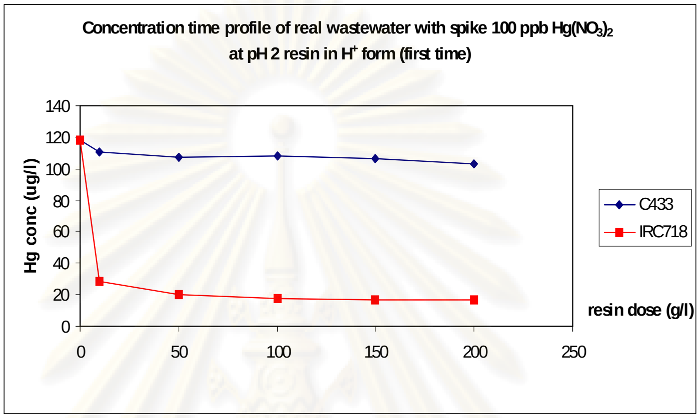


Figure 4.10 Mercury concentration of real wastewater with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours) pH 2, resin in H^+ form (first time)

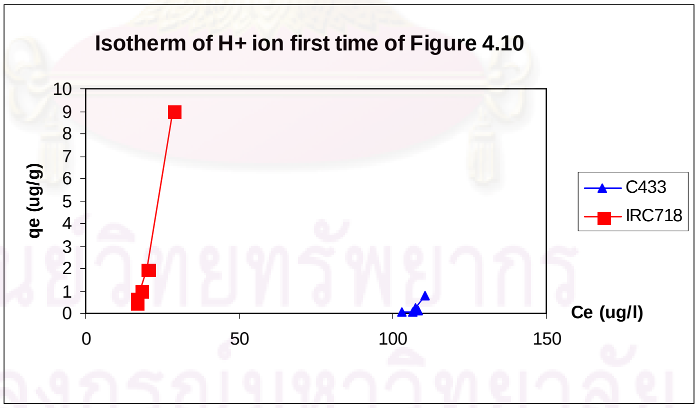


Figure 4.11 Isotherm of Figure 4.10.

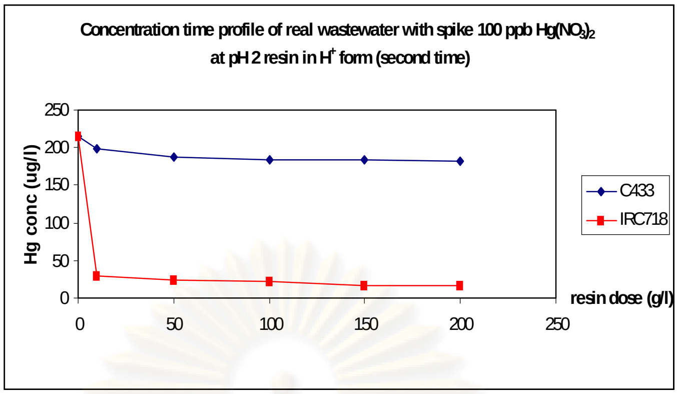


Figure 4.12 Mercury concentration of real wastewater with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours) pH 2, resin in H^+ form (second time)

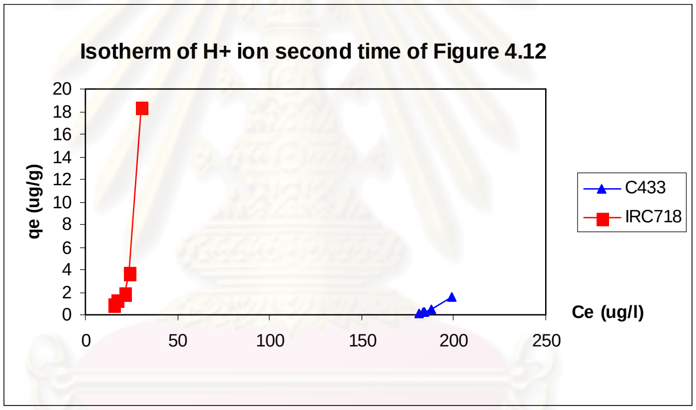


Figure 4.13 Isotherm of Figure 4.12

4.6 Isotherm equilibrium and isotherm constant

From the previous results (equilibrium time, effect of pH and effect of type of exchange ion) , the isotherm tended to non-favourable, so the Freundlich isotherm was the only isotherm that suited for interpretation because the maximum adsorption capacity could not calculate, so the Langmuir isotherm and BET isotherm could not use. The Freundlich isotherm graph was non-favorable form as shown in Figure 4.14 to Figure 4.17. After that, the isotherm constant such as K (sorption capacity), n (adsorption intensity) and R^2 were calculated.

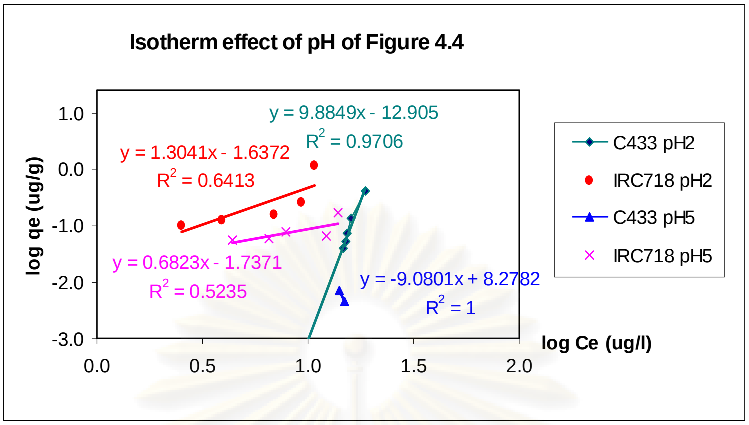


Figure 4.14 Freundlich Isotherm graph and isotherm constant of effect of pH (pH 2 and 5) at equilibrium time (24 hours), resin in Na^+ form of Figure 4.4

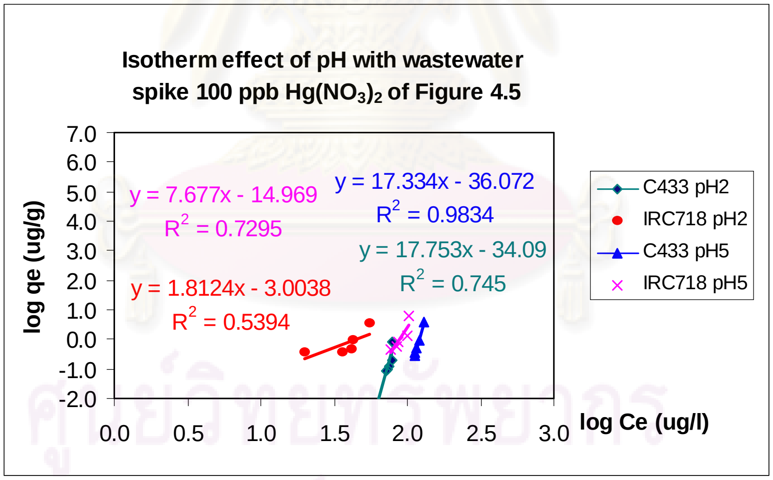


Figure 4.15 Freundlich Isotherm graph and isotherm constant of effect of pH (pH 2 and 5) with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours), resin in Na^+ form of Figure 4.5

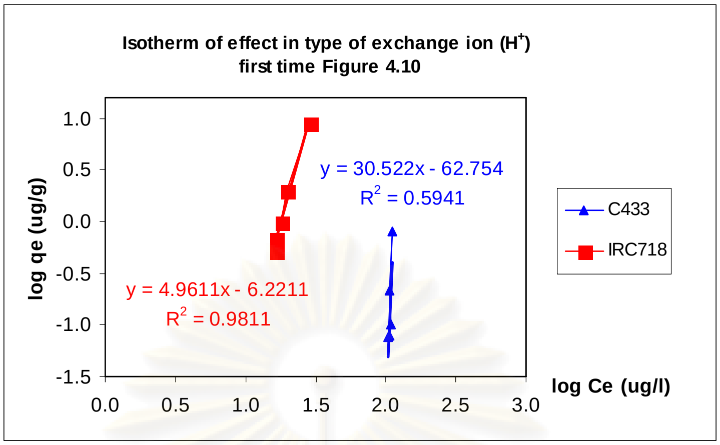


Figure 4.16 Freundlich Isotherm graph and isotherm constant of effect of type of exchange ion resin in H^+ form with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours) pH 2 (first time) of Figure 4.10

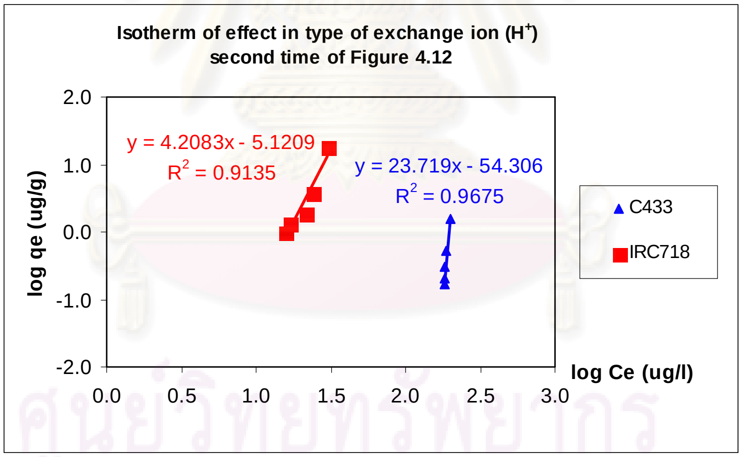


Figure 4.17 Freundlich Isotherm graph and isotherm constant of effect of type of exchange ion resin in H^+ form with spike 100 ppb $Hg(NO_3)_2$ at equilibrium time (24 hours) pH 2 (second time) of Figure 4.12

It meant the behavior in ion exchange between mercury ions and the resins were non-favorable. The mercury ions tended to stay in the wastewater more than being exchanged with resin. However, the Freundlich isotherm was unable to describe the ion exchange phenomenon well because graphs did not show good linear trend or low R^2. In addition, K (sorption capacity) and n (sorption intensity) were very low, some were minus.

The reason was wastewater had a lot of cations which had the potential to exchange with resin more than mercury ions. It could be observed from the characteristics of wastewater that high TDS (6,749 mg/l) and COD (5,769 mg/l) were present. The resins tended to exchange with other ions more which was evident very low K and n values. Even though, IRC718 resin was selective to mercury ion, but other ions were high, so the competitive in exchange was occurred.

4.7 Continuous test (Column test)

From the batch test, the optimal condition for treatment of mercury by ion exchange resin was IRC718 resin (mercury selective ion exchange resin) equilibrium time 3 hours, pH 2, exchange ion was H^+ form, so this optimal conditions would apply to use for continuous test.

From the batch test, the results showed that the efficiency in mercury removal of resin was lower than those of activated carbon adsorption of Lortpenpien (2010), so the volume of resin used 440 ml and 880 ml, which were higher amount than activated carbon. This affect in empty bed contact time (EBCT) was 2 hours and 4 hours respectively in order to ensure that contact time between mercury ion and resin was enough before breakthrough.

This test would study in effect of bed depth to the treatment of mercury concentration. IRC718 resin, volume of resin 440 ml, wastewater pH 2 with spiked 50 ppb $Hg(NO_3)_2$, hydraulic retention time (HRT) 2 hours and flow rate 220 ml/hour. The results showed that IRC718 resin was able to reduce the mercury concentration from 118.310 µg/l (influent concentration) to 4.416 µg/l (effluent concentration) with breakthrough time 375 minutes (6.50 hours), which met the mercury standard 5 ppb. Evidently, the ion exchange resin was able to treat the wastewater to meet the mercury standard in rapid manner. After that, effluent concentration increased until it was equal to the influent concentration in 2,175 minutes (36.50 hours). Breakthrough volume equaled to 1.25 liters. The breakthrough curve was shown in Figure 4.18.

The average pH equaled to 1.79 as shown in Figure 4.19. The average temperature equaled to 28.8 °C as shown in Figure 4.20.

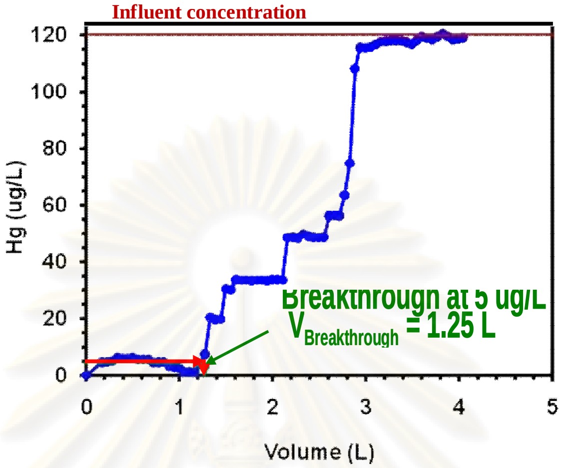


Figure 4.18 Breakthrough curve of IRC718 resin by use wastewater with spike 50 ppb $Hg(NO_3)_2$ at initial pH 2, volume 440 ml, flow rate 220 ml/hour (HRT 2 hours).

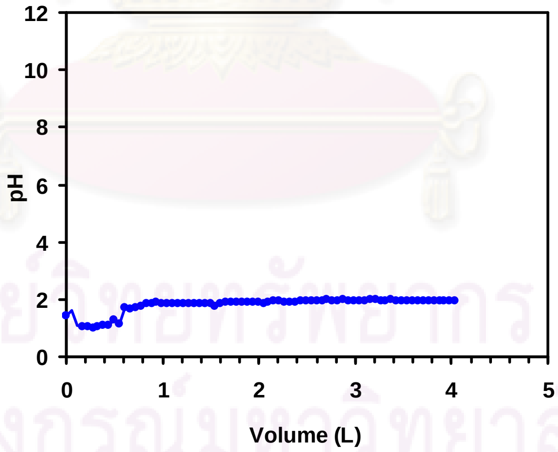


Figure 4.19 pH of effluent from the column resin of IRC718 resin by use wastewater with spike 50 ppb $Hg(NO_3)_2$ at initial pH 2 volume 440 ml, flow rate 220 ml/hour (HRT 2 hours).

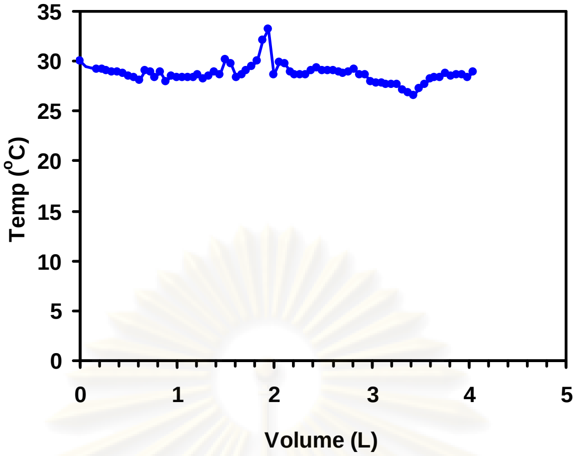


Figure 4.20 Temperature of effluent from the column resin of IRC718 resin by use wastewater with spike 50 ppb $Hg(NO_3)_2$ at initial pH 2 volume 440 ml, flow rate 220 ml/hour (HRT 2 hours).

Due to the previous study had wastewater meet to the breakthrough time in rapid manner, so the addition of volume of adsorbent was study by applied same condition as previous study but added the volume of resin two times (880 ml) and wastewater pH 2 with spiked 100 ppb $Hg(NO_3)_2$ and hydraulic retention time (HRT) 4 hours. The results showed that IRC718 resin could reduce the mercury concentration from 118.457 µg/l (influent concentration) to 3.787 µg/l (effluent concentration), breakthrough time 840 minutes (14 hours), which met the mercury standard 5 ppb. It meant the ion exchange resin could treat the wastewater to meet the standard in rapid manner same as in previous study. After that, effluent concentration would increase until equal to the influent concentration in 2,250 minutes (37.50 hours). Breakthrough volume equaled to 2.35 litres. The breakthrough curve was shown in Figure 4.21. The average pH equaled to 2.07 as shown in Figure 4.22. The average temperature equaled to 27.6 °C as shown in Figure 4.23.

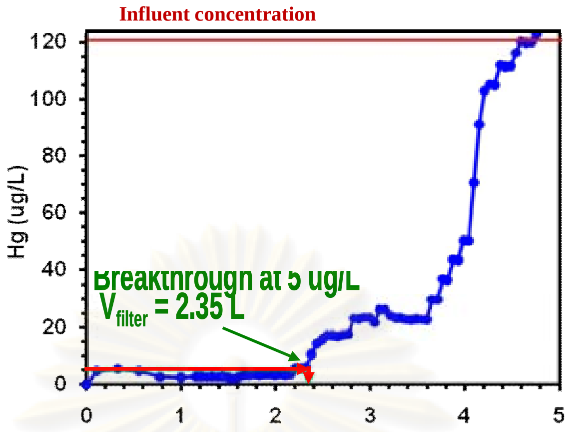


Figure 4.21 Breakthrough curve of IRC718 resin by use wastewater with spike 100 ppb $Hg(NO_3)_2$ at initial pH 2 volume 880 ml, flow rate 220 ml/hour (HRT 4 hours).

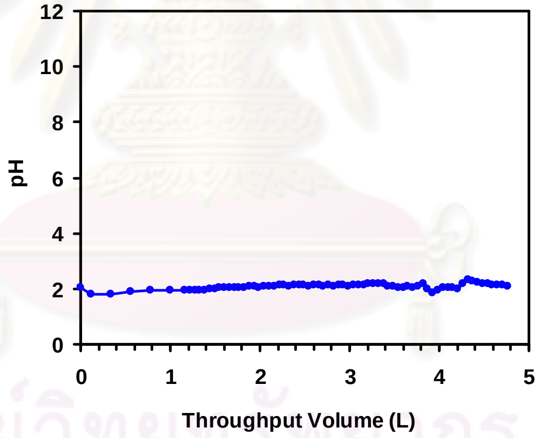


Figure 4.22 pH of effluent from the column resin of IRC718 resin by use wastewater with spike 100 ppb $Hg(NO_3)_2$ at initial pH 2 volume 880 ml, flow rate 220 ml/hour (HRT 4 hours).

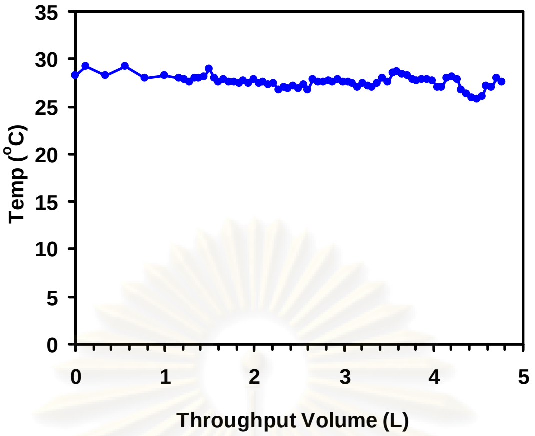


Figure 4.23 Temperature of effluent from the column resin of IRC718 resin by use wastewater spiked with 100 ppb Hg at initial pH 2 volume 880 ml, flow rate 220 ml/hour

When addition volume of adsorbent and HRT two times, the breakthrough volume was two times. The ratio between breakthrough volume and resin volume were 2.84 and 2.67. The average ratio equaled to 2.76. From the results of both continuous tests, it pointed that mass transfer zone in column was short. It affected to use resin in full capacity.

$$\text{Ratio} = \frac{\text{Breakthrough volume}}{\text{Volume of resin}}$$

IRC718 resin had the potential to apply in the real operation, it could treat the mercury concentration to meet the standard.

From two continuous tests, pH was 1.79 and 2.07 for HRT 2 and 4 hours respectively. The pH was less than 2 because the ion exchange process was occurred Hg^{2+} would exchange with H^+ in resin. Then, H^+ would stayed in wastewater, it affect in reduce the pH. From this reaction, it supported the optimal condition for continuous test in acidic pH, which pH 2 was the best condition for IRC718 to the best efficiency in treatment. The temperature was 28.8 °C and 27.6 °C for HRT 2 and 4 hours respectively. The temperature was room temperature and effect of temperature was not presented, so it could apply to use in real operation.

From the Figure 4.18 and 4.21, the calculation of exchange ion capacity of IRC718 resin was shown in table 4.3. The exchange ion capacity equaled to 0.91 and 0.74 µg Hg per gram of resin for HRT 2 and 4 hours respectively by Hg exchange come from multiply between averages of mercury concentration and volume treated in each period of time. Due to the flow rate in two continuous tests equaled, so the exchange ion capacity should be same. The maximum exchange ion capacity of IRC718 resin in H^+ form should be 0.74-0.91 µg Hg per gram of resin. While, the exchange ion capacity of IRC718 resin in H^+ form at breakthrough were same at 0.49 and 0.46 µg Hg per gram of resin for HRT 2 and 4 hours respectively. Even though, increased resin depth two times, but the exchange capacity at breakthrough were same. It pointed that the mass transfer zone was short.

The exchange capacity was lower than 1 µg Hg per gram of resin for column test as shown in table 4.3. The continuous test was lower efficiency than batch test (as shown in Figure 4.9 and 4.13). The calculation by use Freunclich isotherm equation use C_e equaled to 118.46 µg/l (initial concentration in column test). The exchange capacity would higher than 4,200 µg Hg per gram of resin. It pointed that other ions could interfere and competitive to bind with resin instead Hg^{2+}. The total dissolved solid was higher than mercury ion. The affinity of IRC718 resin with Fe^{3+} more than 325,000, Cu^{2+} more 130,000 and Hg^{2+} 43,000 based on Ca^{2+} from the technical data sheet of IRC718 resin ,so these ion would exchange with IRC718 resin better than Hg^{2+}. The Fe^{3+} and Cu^{2+} were named “X”. Another group was the ion that exchange lower than Hg^{2+} such as Fe^{2+}, Al^{3+}, Mg^{2+} and Ca^{2+} were named “Y”. In continuous test, the feed of wastewater was performed all the time, but it was not performed in batch test. Wastewater would flowed through resin all the time, it enhance most preferred ion such as Fe^{3+} and Cu^{2+} could replace Hg^{2+} which already adsorb by resin, so mercury ion would flow with the effluent as shown in Figure 4.24. This reason why the continuous test had the efficiency lower than batch test.

4.8 Regeneration test and mass balance of mercury

The used IRC718 resin from column would apply in the regeneration by using the column, 10%-15% HCl as regenerant, flow rate 200 ml/hour and 18 mΩ DI water, flow rate 1,000 ml/hour. The results were shown in table 4.4 for 10% HCl and table 4.5 for 15% HCl. The results shown that regeneration by 10% HCl 200 ml could recover mercury from resin equaled to 0.835 µg Hg/ml of resin that compared with mercury in exhausted resin equaled to 1.19 µg Hg/ml of resin. The percentage of recovery equaled to 70% (calculation shown in appendix A). After that, the 15% HCl in 200 ml as regenerant was tested and it could recover mercury equaled to 0.89 µg Hg/ml of resin or percentage of recovery equaled to 75%. However, the percentage of recovery did not satisfy, so the condition for regeneration became to 400 ml and 600 ml HCl in 2 and 3 hours respectively. The results showed that it could recover mercury from resin equaled to 1.33 and 1.43 µg/ml of resin respectively. The percentage of recovery equaled to 111% and 120% respectively. The percentage of recovery was more than 100% might come from residue of wastewater in void. The results pointed that optimal condition for regeneration was 15% HCl with 400 ml.

After that, the regeneration ability of spent resins and their exchange capability after regeneration was performed by batch test at pH 2 and contact time 24 hours. The results showed that new resin could reduce mercury from 97.5 µg/l to 4.3 µg/l, while regenerated resin could reduce mercury to 4.8 µg/l and pH was 1.92 and 1.95 respectively. The results pointed that regenerated resin had the efficiency in exchange ion same as new resin as shown in Figure 4.25.

Table 4.3 Exchange ion capacity of IRC718 resin at initial mercury concentration 118.5 µg/l at pH 2 and flow rate 220 ml/hour.

Resin IRC 718		$Hg_{exchaged}$ (µg)		Exchange Capacity (µg Hg per g resin)		
Volume (mL)	Mass (g)	Total	Breakthrough	Total	Breakthrough	%Total
880	591.36	436.93	273.21	0.74	0.46	62.2
440	295.68	269.16	145.35	0.91	0.49	54.0

Remark : Density of IRC718 resin = 0.672 g/ml

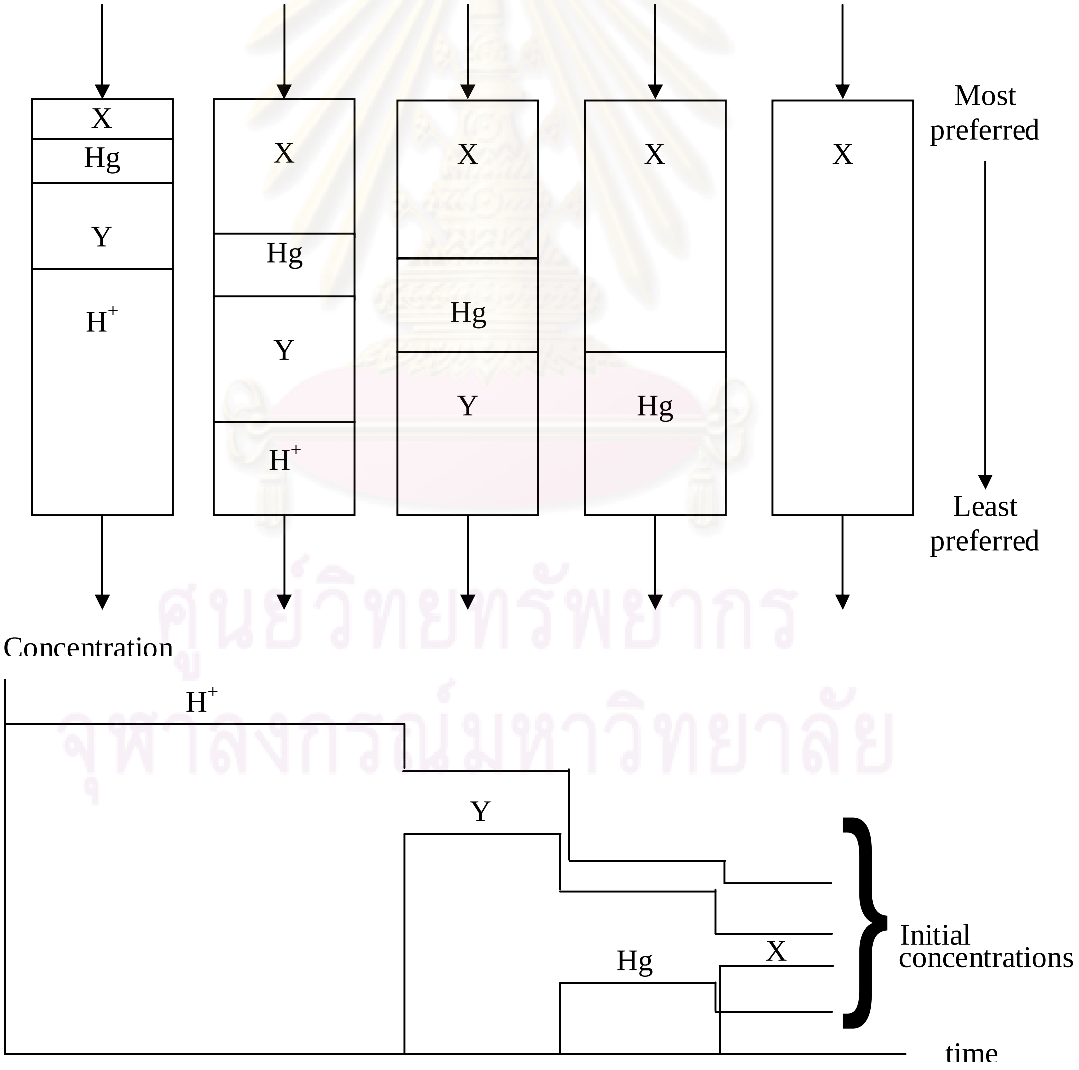


Figure 4.24 Profile of concentration in column and breakthrough curve.

Table 4.4 Regeneration of IRC718 resin volume of resin 50 ml by 10% HCl

Condition for regeneration	**Mercury concentration in regenerant (μg/l)**	**Mass of mercury in regenerant (μg)**
Acid 50 ml in the first period	65.5	3.27
Acid 50 ml in the second period	49.2	2.46
Acid 50 ml in the third period	41.3	2.07
Acid 50 ml in the fourth period	39.7	1.98
Water 50 ml in the first period	37.3	1.86
Water 500 ml	32.7	16.33
Water 450 ml in the last period	30.6	13.79
Total mass of mercury in regenerant		41.76

Table 4.5 Regeneration of IRC718 resin volume of resin 50 ml by 15% HCl

Condition for regeneration	**Mercury concentration in regenerant (μg/l)**	**Mass of mercury in regenerant (μg)**
Acid 50 ml in the first period	239.7	11.99
Acid 50 ml in the second period	233.5	11.67
Acid 50 ml in the third period	228.4	11.42
Acid 50 ml in the fourth period	191.8	9.59
Acid 50 ml in the fifth period	137.5	6.87
Acid 50 ml in the sixth period	128.8	6.44
Acid 50 ml in the seventh period	89.4	4.47
Acid 50 ml in the eighth period	81.8	4.09
Acid 50 ml in the ninth period	35.2	1.76
Acid 50 ml in the tenth period	18.7	0.93
Acid 50 ml in the eleventh period	15.1	0.75
Acid 50 ml in the twelfth period	8.3	0.41
Water 50 ml in the first period	2.5	0.12
Water 500 ml	1.2	0.58
Water 450 ml in the last period	1.0	0.43
Total mass of mercury in regenerant		71.52

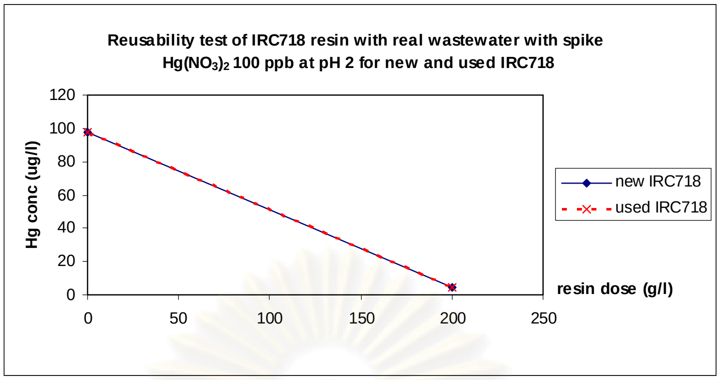


Figure 4.25 Reusability test of IRC718 resin with real wastewater with spike 100 ppb $Hg(NO_3)_2$ at pH 2 and equilibrium time.

4.9 The comparison of efficiency in removal of mercury in wastewater by ion exchange resin and adsorption by activated carbon.

From the batch study in pH 2 and 5, the efficiency of two resins C433, IRC718, activated carbon (Mersorb LW, NORIT 1240 and CGC-12 from Lortpenpien, 2010) were compared. The results of five adsorbent in pH 2 showed that IRC718 had the best performance in mercury removal, then CGC-12, NORIT 1240, C433 and MERSORB-LW as shown in Figure 4.26

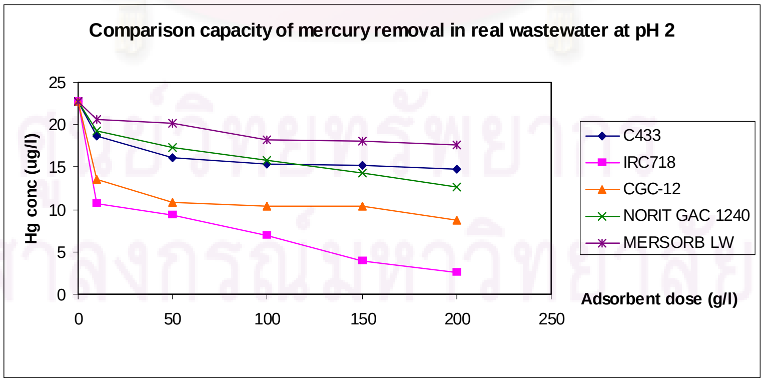


Figure 4.26 Comparison capacity in mercury removal of real wastewater at pH 2 between C433, IRC718, CGC-12, NORIT GAC 1240 and MERSORB LW (Activated carbon adsorptions are from Lortpenpien, 2010)

In the case of pH 5, the results showed that activated carbons such as NORIT 1240 and MERSORB LW had the efficiency in mercury removal in the same level. Then, IRC718 resin, CGC-12 and the last was C433 resin as shown in Figure 4.27

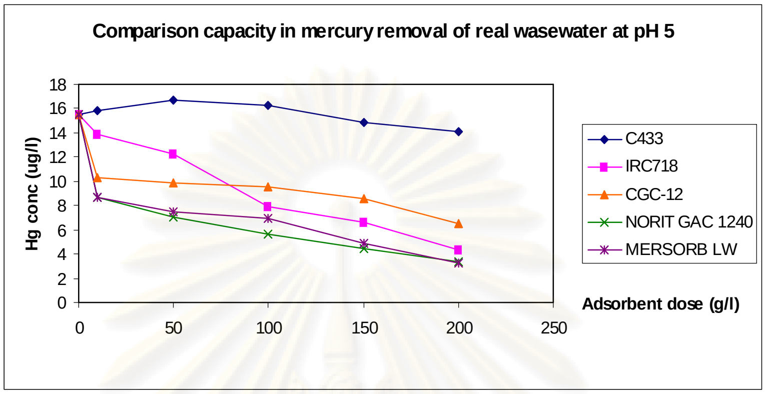


Figure 4.27 Comparison capacity in mercury removal of real wastewater at pH 5 between C433, IRC718, CGC-12, NORIT GAC 1240 and MERSORB LW (Activated carbon adsorptions are from Lortpenpien, 2010)

In the mercury concentration in the experiment similar to the real operation (100 µg/l), the results showed that NORIT 1240 activated carbon had the best efficiency, so the comparison efficiency by isotherm graph between NORIT 1240 and IRC718 were performed at pH 2. The isotherm graph presented that NORIT 1240 had better efficiency than IRC718 resin as shown in Figure 4.27. These results were correlated to the continuous study that NORIT 1240 was the best adsorbent for treatment of mercury from petrochemical wastewater.

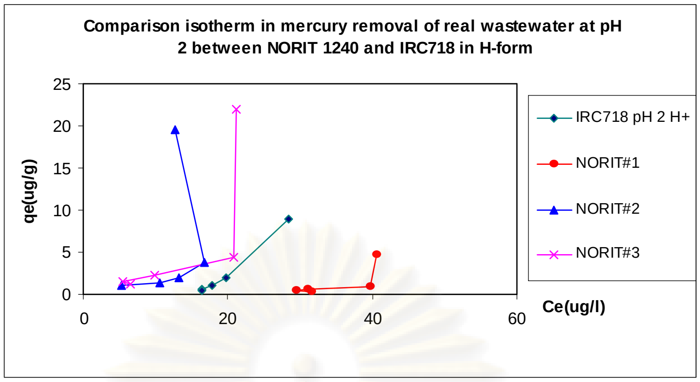


Figure 4.28 Isotherm graph of mercury removal of real wastewater at pH 2 between NORIT GAC 1240 three times and IRC718 in H^+ form

4.10 The economic consideration for treatment mercury in wastewater from petrochemical industry by IRC718 resin

The results from column test can be applied to design the real ion exchange 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, 1995). 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 Hg was considering as a trace substance in this wastewater (in µg/L scale) as compared to other adsorbate species (in mg/L scale); hence, the adsorption behavior of Hg 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 EBCT of the tested column was similar to those of the existing columns of the studied factory.

$$\frac{C}{C_0} \cong \frac{1}{1+e^{\frac{k_1}{Q}(q_0 M - C_0 V)}} \qquad \text{Eq. (4.1)}$$

$$\ln\left(\frac{C_0}{C}-1\right) = \frac{k_1 q_0 M}{Q} - \frac{k_1 C_0 V}{Q} \qquad \text{Eq. (4.2)}$$

From the results of continuous test, the ratio between breakthrough volume and resin volume were 2.84 and 2.67. The flow rate in real operation of the studied factory equaled to 8 m^3/day. It needed resin 2.9 m^3. The cost of IRC718 resin was 850 baht/liter. The capital cost equaled to 2,465,000 baht. The volume of resin calculated based on regeneration 1 time/day. The IRC718 resin was not valuated to apply in this petrochemical industry.

The total treatment cost of wastewater from petrochemical industry by IRC718 resin.

1. Adsorbent cost

Used resin	880 ml or 0.88 L
IRC718 price	850 baht/liter*
Resin 1 liter could treat wastewater	2.35 L
Resin could use	20 times
Adsorbent cost	$= \frac{0.88x850}{2.35x20}x1000$
	= 15,915 baht/m^3

2. Regeneration process cost

Operation 20 times use resin	880 ml
Use acid as regenerant	400 ml, 0.4 L
HCl price	20 baht/liter**
Resin 1 liter could treat wastewater	2.35 L
Regeneration cost	$= \frac{0.4x20}{2.35}x1000$
	= 3,404 baht/m^3

Total treatment cost = 15,914 + 3,404

= 19,318 baht/m^3

Remark: * Price at May 2010

** Price at April 2011

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

Ion exchange was the feasible technique to remove mercury from petrochemical industry and could reduce mercury to meet the 5 ppb standard of drainage wastewater from industrial sector of Thailand.

The Conclusions can be drawn as follows.

5.1.1 The wastewater from petrochemical industry had high concentrations of TDS, COD and TOC. With an acidic pH of around 4. Mercury concentrations were found to be different among samples abtained at three different sampling time, such as 459, 85 and 73 µg/l for mercury in total form and 125, 18 and 1.3 µg/l for mercury in filtrate. Most of mercury was attached with organic carbon in wastewater, which could be pretreated by filtration. Arsenic concentration was significantly high but it did not interfere with ion exchange process. This is because it stayed in anion species, such as arsenate (AsO_4^{3-}) and arsenite (AsO_2^-). Chloride ion, on the other hand, interfered with the ion exchange process because it formed chlorocomplex with Hg^{2+} and became $HgCl_2$.

Concentrations of organic carbon and inorganic carbon were fond to be much greater than that of mercury, so they interfered the ion exchange process and obstructed the treatment of mercury to meet the mercury effluent standard.

5.1.2 When pH was raised, solubility of mercury ion slightly increased. Due to it was not significantly different between each pH, so the comparison between each pH could perform by less error.

5.1.3 The suitable resin for mercury treatment was Amberlite IRC718 because of its functional groups containing iminodiacetic acid and its high selectivity for mercury ions at pH 2. (Rengan, 1997 cited in Dą browski et al., 2004)

5.1.4 The equilibrium time was 3 hours, while activated carbon took time 12 hours because activated carbon needed time for pollutant diffused to meso-porous, micro-porous and adsorptive site by Brownian motion, but ion exchange process was the reaction occurred at surface of adsorbent.

5.1.5 The efficiency in removal mercury was 88.98% at pH 2 and 71.84% at pH 5. The results pointed that the optimum pH for treatment of mercury was pH 2. The reason was IRC718 which was the mercury selective cation exchange resin had the selectivity to mercury 43,000 times based on calcium ion and IRC718 could form cheated with the mercury ion which enhances resin binding and heavy metal stability at pH 2 (Agrawal and Sahu, 2006). While C433 was non selective to mercury ion.

5.1.6 The suitable exchange ion for treatment mercury was proton (H^+) better than sodium ion (Na^+) because the degree of exchange depended on size and charge of ion which small ion had the degree and selectivity in exchange better than large ion. (Eckenfelder and Wesley, 2000; Clifford, 1986)

5.1.7 Freundlich isotherm could interpret the ion exchange behavior. From the graph, ion exchange process occurred in non-favorable, which mercury ion tended to stayed in wastewater more than exchange ion with IRC718 resin. The reason was that the real wastewater contained high concentrations of organic carbon compounds. They might have positive charges that could compete for exchange sites on IRC718 resin, or competition between cation from organic compound and mercury ion could occur, so it needed to use resin more than usual From this problem, it affected K (sorption capacity) and n (sorption intensity) were very low, some were minus. Though, Freundlich isotherm could describe ion exchange behavior, but it did not the best because R^2 value pointed that it did not linear trend or low R^2. The treatment of wastewater by IRC718 needed the very high amount of resins.

5.1.8 The continuous test showed that IRC718 resin could treat mercury downed to meet the 5 ppb standard for volume resin 440 ml and 880 ml with flow rate 200 ml/hour and real wastewater pH 2. The average ratio of throughput volume and volume of resin equaled to 2.76. This showed that mass transfer zone was short and resin was used full capacity.

The pH was 1.79 and 2.07 for HRT 2 and 4 hours respectively. They were less than 2. It supported the optimal condition for continuous test. The temperature was 28.8 °C and 27.6 °C for HRT 2 and 4 hours respectively, so it could apply to use in real operation. The maximum exchange ion capacity of IRC718 resin in H^+ form should be 0.74-0.91 µg Hg per gram of resin. While, the exchange ion capacity of IRC718 resin in H^+ form at breakthrough were same at 0.49 and 0.46 µg Hg per gram of resin for HRT 2 and 4 hours respectively. Even though the resin bed depth was increased by two times, the exchange capacity at breakthrough were similar. Apparently, the mass transfer zone was short. The reason why the continuous test showed lower capacity than the batch test was because most preferred ions could replace mercury ion, which had lower selectivity.

5.1.9 The optimal condition for resin regeneration was 400 ml of 15% HCl, 2 hours with flow rate 200 ml/hours. The reusability of used IRC718 and new IRC718 resin were not markedly differnt because they were able to reduce mercury concentrations from 97.451 µg/l down to 4.745 and 4.276 µg/l respectively. The percentage of recovery for used IRC718 resin was 85%.

The IRC718 resin had the potential to treat mercury and the optimal condition for mercury treatment by IRC718 resin was pH 2, equilibrium time 3 hours, exchange ion in proton form and resin dose was 200 g/l for batch study and using IRC718 resin at pH 2, flow rate 200 ml/hour and volume of resin 440 ml or 880 ml for continuous study.

5.1.10 The comparison of mercury removal efficiency in wastewater between ion exchange resin and adsorption by activated carbon. The experiments showed that IRC718 had the best efficiency in removal mercury at pH 2. Then CGC-12, NORIT 1240, C433 and MERSORB-LW. The NORIT 1240 and MERSORB LW had the efficiency in mercury removal at the same level. Then, IRC718 resin, CGC-12 and the last was C433 at pH 5.

In the mercury concentration in real wastewater similar to the mercury concentration in real operation, NORIT 1240 activated carbon had the best efficiency for mercury removal in real wastewater similar to the mercury concentration in real operation.

5.1.11 The economic aspect of ion exchange resin to application in real operation. Assuming a flow rate in real operation of 8 m^3/day, a treatment unit would require 2.9 m^3 of resin. With the unit price of 850 baht/liter, the cost for IRC718 resin alone would amount to 2,465,000 Baht. The resin would also require daily regeneration. Due to these shortcomings, it is quite obvious that IRC718 resin does not fit to apply in the petrochemical industry.

5.2 Suggestions

Due to the IRC718 resin could treat mercury from petrochemical industry, but it did not satisfy results, so the suggestion as follow might be help for further study.

5.2.1 The pretreatment of real wastewater such as filtration was needed in order to remove organic carbon compound and mercury in total form. After that, it might be treat by adsorption with activated carbon or ion exchange resin. The pretreatment might reduce the competitive in ion exchange reaction and made the favorable behavior was presented, so ion exchange resin should be polishing step to meet standard Hg 5 ppb.

The pretreatment by coagulation and precipitation were interested in order to reduce TDS and then used ion exchange at pH 2 to reduce mercury concentration to meet 5 ppb standard.

5.2.2 Another commercial mercury selective ion exchange resin which was more specific to Hg should be try to study because some resin might be well performance in treatment mercury more than Amberlite IRC718.

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APPENDICES

APPENDIX A

Table A.1 The selectivity of IRC718 resin at pH 2. (Technical data sheet of Rohm and Haas company, USA)

Metal ion	$\mathbf{K^{M}{}_{Ca}}$
Fe^{3+}	325,000
Cu^{2+}	130,000
Hg^{2+}	> 43,000
Au^{3+}	> 8,100
Ag^{+}	4,600
Ni^{2+}	3,200
Cd^{2+}	620
Fe^{2+}	190
Mn^{2+}	120
Zn^{2+}	120
Al^{3+}	50
Mg^{2+}	20
Ca^{2+}	1.0

Table A.2 The selectivity of IRC718 resin at pH 4. (Technical data sheet of Rohm and Haas company, USA)

Metal ion	$\mathbf{K^{M}{}_{Ca}}$
Hg^{2+}	2,800
Cu^{2+}	2,300
Pb^{2+}	1,200
Ni^{2+}	57
Zn^{2+}	17
Cd^{2+}	15
Co^{2+}	6.7
Fe^{2+}	4.0
Mn^{2+}	1.2
Ca^{2+}	1.0

Table A.3 The selectivity of IRC718 resin at pH 9. (Technical data sheet of Rohm and Haas company, USA)

Metal ion	$\mathbf{K^{M}{}_{Ca}}$
Ni^{2+}	30
Cd^{2+}	14
Cu^{2+}	10
Zn^{2+}	3.0
Ca^{2+}	1.0

Calculation of percentage of recovery

From the table 4.4 mass of mercury come from

Mass of mercury in regenerant (µg/l) = mercury concentration (µg/l) x volume (L)

Example : Mass of mercury in regenerant for first period

1) Mass of mercury in regenerant = 65.5 µg/l x 0.05 L = 3.27 µg

2) Then, calculation will perform in every period and summation in every period as total mass of mercury in regenerant = 41.76 µg

3) Mercury in regenerant

$$= \frac{\text{total mass mercury in regenerant}}{\text{Volume of resin}}$$

$$= \frac{41.76}{50} = 0.835 \ \mu\text{g Hg/ml resin}$$

4) Mercury in exhausted resin

$$= \frac{\text{total mass adsorb in resin}}{\text{Volume of resin}}$$

$$= \frac{528.568}{440} = 1.19 \ \mu\text{g Hg/ml resin}$$

5) Percentage of recovery

$$= \frac{\text{Mercury in regenerant}}{\text{Mercury in exhausted resin}} \times 100$$

$$= \frac{0.835}{1.19} x100 = 70\%$$

APPENDIX B

Experimental result for CHAPTER IV

Table B.1 Effect of pH to the solubility of mercury ion. (Figure 4.2)

Raw wastewater mercury concentration = 77.3 µg/l.

pH of wastewater	**Hg concentration (µg/l)**	
	Total form	**Soluble form**
2	510.30	64.30
3	585.40	61.40
4	542.30	81.15
5	531.20	97.80
6	513.60	94.70
7	503.80	120.80
8	499.35	124.70
9	488.60	135.90

Equilibrium time

Table B.2 Adsorption of mercury by C433 and IRC718 in Na^+ form at 10g/l between 0-180 minutes. (Figure 4.3)

Time (min)	**Hg Concentration (µg/l)**	
	C433	**IRC718**
0	157.40	141.70
5	157.50	135.90
10	149.80	137.50
15	156.40	126.30
30	157.10	130.50
45	130.10	128.30
60	129.10	129.70
90	125.00	126.60
120	125.00	128.30
180	129.20	125.10

Effect of pH to ion exchange reaction

Table B.3 Concentration of mercury in real wastewater at equilibrium and resin dose in Na^+ form at pH 2. (Figure 4.4)

Resin dose (g/L)	**Hg Concentration (μg/l)**						**pH**	
	C433			**IRC718**			**C433**	**IRC 718**
	conc1	**conc 2**	**avg**	**conc1**	**conc 2**	**avg**		
0	22.640	22.900	22.770	22.640	22.900	22.770	2.00	2.00
10	19.132	18.164	18.648	11.164	10.204	10.684	2.10	2.08
50	15.360	16.819	16.090	8.822	9.917	9.370	2.17	2.15
100	15.660	15.121	15.391	6.912	6.937	6.925	2.20	2.27
150	14.549	15.730	15.140	3.604	4.276	3.940	2.29	2.35
200	14.880	14.647	14.764	2.500	2.504	2.502	2.31	2.40

Calculation of mercury concentration from AAS

Example from table B.3

1) Value from AAS = 1.200 ppb and filtered sample = 96 ml for first duplicate

Sample volume	1000 ml	has Hg	1.200	μg
Sample volume	100 ml	has Hg	$\frac{1.200x100}{1000}$	μg
Due to take sample	50 ml	so	$\frac{1.200x100}{1000}$	μg
Adjust sample volume to	100 ml	so	$\frac{1.200x100x100}{1000x50}$	μg
Filtered sample	96 ml	so	$\frac{1.200x100x100}{1000x50}$	μg
If sample	1000 ml	so	$\frac{1.200x100x100x1000}{1000x50x96}$	μg
			= 2.500	μg

So, the sample has the mercury concentration equal to 2.500 μg for first duplicate.

2) Value from AAS = 1.202 ppb and filtered sample = 96 ml for second duplicate

Sample volume	1000 ml	has Hg	1.200	µg
Sample volume	100 ml	has Hg	$\frac{1.202x100}{1000}$	µg
Due to take sample	50 ml	so	$\frac{1.202x100}{1000}$	µg
Adjust sample volume to	100 ml	so	$\frac{1.202x100x100}{1000x50}$	µg
Filtered sample	96 ml	so	$\frac{1.202x100x100}{1000x50}$	µg
If sample	1000 ml	so	$\frac{1.202x100x100x1000}{1000x50x96}$	µg
			= 2.504	µg

So, the sample has the mercury concentration equal to 2.504 µg for second duplicate.

Then, Value from two duplicates would bring to find the average, so

$$\frac{2.500+2.504}{2} = 2.502 \quad \mu g$$

This sample had the mercury concentration equaled to 2.502 µg

Table B.4 Concentration of mercury in real wastewater at equilibrium and resin dose in Na^+ form at pH 5. (Figure 4.4)

Resin dose (g/L)	Hg Concentration (µg/l)						pH	
	C433			IRC718			C433	IRC 718
	conc1	conc 2	avg	conc1	conc 2	avg		
0	15.684	15.302	15.493	15.684	15.302	15.493	5.00	5.00
10	18.699	19.155	18.927	14.269	13.406	13.838	5.08	5.05
50	16.754	16.704	16.729	12.623	11.779	12.201	5.15	5.13
100	15.998	16.464	16.231	7.454	8.274	7.864	5.23	5.20
150	14.672	14.995	14.834	6.325	6.825	6.575	5.29	5.24
200	14.894	13.294	14.094	3.914	4.811	4.363	5.45	5.30

Table B.5 Concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose in Na^+ form at pH 2. (Figure 4.5)

Resin dose (g/L)	Hg Concentration (µg/l)						pH	
	C433			IRC718			C433	IRC 718
	conc1	conc 2	avg	conc1	conc 2	avg		
0	88.220	87.940	88.080	88.220	87.940	88.080	2.00	2.00
10	80.788	78.323	79.556	54.478	56.783	55.631	2.01	2.01
50	79.122	77.429	78.276	42.640	42.274	42.457	1.98	2.21
100	74.400	76.758	75.579	41.172	42.161	41.667	1.98	2.35
150	73.626	72.321	72.974	35.898	36.959	36.429	1.95	2.39
200	71.636	71.250	71.443	18.887	20.639	19.763	1.93	2.45

Table B.6 Concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose in Na^+ form at pH 5. (Figure 4.5)

Resin dose (g/L)	**Hg Concentration (µg/l)**						**pH**	
	C433			**IRC718**			**C433**	**IRC 718**
	conc1	**conc 2**	**avg**	**conc1**	**conc 2**	**avg**		
0	172.380	162.120	167.250	172.380	162.120	167.250	5.00	5.00
10	128.569	130.213	129.391	103.021	102.250	102.636	5.01	5.07
50	121.574	121.000	121.287	100.495	101.828	101.162	4.94	5.17
100	115.088	116.373	115.731	87.556	86.990	87.273	4.92	5.28
150	112.630	112.935	112.783	85.939	84.694	85.317	4.90	5.31
200	113.647	110.894	112.271	78.516	76.753	77.635	4.88	5.45

Table B.7 Concentration of mercury in real wastewater at equilibrium and resin dose in Na^+ form at pH 2 and isotherm

pH2 C433 of Figure 4.6

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,,µg/l)**	**$q_e = x/m$**
10	22.770	18.648	0.412
50	22.770	16.090	0.134
100	22.770	15.391	0.074
150	22.770	15.140	0.051
200	22.770	14.764	0.040

pH2 IRC718 of Figure 4.6

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**$q_e = x/m$**
10	22.770	10.684	1.209
50	22.770	9.370	0.268
100	22.770	6.925	0.158
150	22.770	3.940	0.126
200	22.770	2.502	0.101

Table B.8 Concentration of mercury in real wastewater at equilibrium and resin dose in Na^+ form at pH 5 and isotherm

pH5 C433 of Figure 4.6

Resin dose(g/L)	Initial concentration (C_0,µg/l)	Equilibrium concentration (C_e,µg/l)	$q_e = x/m$
10	15.493	18.927	-0.343
50	15.493	16.729	-0.025
100	15.493	16.231	-0.007
150	15.493	14.834	0.004
200	15.493	14.094	0.007

pH5 IRC718 of Figure 4.6

Resin dose(g/L)	Initial concentration (C_0,µg/l)	Equilibrium concentration (C_e,µg/l)	$q_e = x/m$
10	15.493	13.838	0.166
50	15.493	12.201	0.066
100	15.493	7.864	0.076
150	15.493	6.575	0.059
200	15.493	4.363	0.056

Table B.9 Concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose in Na^+ form at pH 2 and isotherm

pH2 C433 of Figure 4.7

Resin dose(g/L)	Initial concentration (C_0,µg/l)	Equilibrium concentration (C_e,µg/l)	$q_e = x/m$
10	88.080	79.556	0.852
50	88.080	78.276	0.196
100	88.080	75.579	0.125
150	88.080	72.974	0.101
200	88.080	71.443	0.083

pH2 IRC718 of Figure 4.7

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	88.080	55.631	3.245
50	88.080	42.457	0.912
100	88.080	41.667	0.464
150	88.080	36.429	0.344
200	88.080	19.763	0.342

Table B.10 Concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose in Na^+ form at pH 5 and isotherm

pH5 C433 of Figure 4.7

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	167.250	129.391	3.786
50	167.250	121.287	0.919
100	167.250	115.731	0.515
150	167.250	112.783	0.363
200	167.250	112.271	0.275

pH5 IRC718 of Figure 4.7

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	167.250	102.636	6.461
50	167.250	101.162	1.322
100	167.250	87.273	0.800
150	167.250	85.317	0.546
200	167.250	77.635	0.448

Effect of type of exchange ion

Table B.11 Effect of exchange ion between H^+ and Na^+ to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose at pH 2. (Figure 4.8)

Resin dose (g/L)	**Hg Concentration (μg/l)**		**pH**		**Hg Concentration (μg/l)**		**pH**	
	C433 Na^+	**IRC 718 Na^+**	**C433 Na^+**	**IRC 718 Na^+**	**C433 H^+**	**IRC718 H^+**	**C433 H^+**	**IRC 718 H^+**
0	88.080	88.080	2.00	2.00	118.450	118.450	2.00	2.00
10	79.556	55.631	2.01	2.01	110.416	28.372	1.93	2.05
50	78.276	42.457	1.98	2.21	107.556	19.796	1.81	1.94
100	75.579	41.667	1.98	2.35	108.245	17.781	1.74	1.89
150	72.974	36.429	1.95	2.39	106.623	16.428	1.67	1.83
200	71.443	19.763	1.93	2.45	103.118	16.395	1.57	1.79

Table B.12 Effect of exchange ion between H^+ and Na^+ to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose at pH 2 and isotherm.

pH2 C433 of Figure 4.9

Resin dose(g/L)	**Initial concentration (C_0,μg/l)**	**Equilibrium concentration (C_e,μg/l)**	**$q_e = x/m$**
10	88.080	79.556	0.852
50	88.080	78.276	0.196
100	88.080	75.579	0.125
150	88.080	72.974	0.101
200	88.080	71.443	0.083

pH2 IRC718 of Figure 4.9

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	88.080	55.631	3.245
50	88.080	42.457	0.912
100	88.080	41.667	0.464
150	88.080	36.429	0.344
200	88.080	19.763	0.342

pH2 C433 of Figure 4.9

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	118.450	110.416	0.803
50	118.450	107.556	0.218
100	118.450	108.245	0.102
150	118.450	106.623	0.079
200	118.450	103.118	0.077

pH2 IRC718 of Figure 4.9

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	118.450	28.372	9.008
50	118.450	19.796	1.973
100	118.450	17.781	1.007
150	118.450	16.428	0.680
200	118.450	16.395	0.510

Table B.13 Effect of exchange ion in H^+ form to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose at pH 2 (First time) (Figure 4.10)

Resin dose (g/L)	**Hg Concentration (µg/l)**						**pH**	
	C433			**IRC718**			**C433**	**IRC 718**
	conc1	**conc 2**	**avg**	**conc1**	**conc 2**	**avg**		
0	118.320	118.580	118.450	118.320	118.580	118.450	2.00	2.00
10	111.411	109.421	110.416	27.920	28.824	28.372	1.93	2.05
50	108.828	106.283	107.556	20.423	19.169	19.796	1.81	1.94
100	109.469	107.020	108.245	17.752	17.810	17.781	1.74	1.89
150	107.035	106.211	106.623	16.581	16.274	16.428	1.67	1.83
200	102.256	103.979	103.118	16.247	16.543	16.395	1.57	1.79

Table B.14 Effect of exchange ion in H^+ form to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose at pH 2 and isotherm (First time)

pH2 C433 of Figure 4.11

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	118.450	110.416	0.803
50	118.450	107.556	0.218
100	118.450	108.245	0.102
150	118.450	106.623	0.079
200	118.450	103.118	0.077

pH2 IRC718 of Figure 4.11

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	118.450	28.372	9.008
50	118.450	19.796	1.973
100	118.450	17.781	1.007
150	118.450	16.428	0.680
200	118.450	16.395	0.510

Table B.15 Effect of exchange ion in H^+ form to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose at pH 2 (Second time) (Figure 4.12)

Resin dose(g/L)	**Hg Concentration (μg/l)**		**pH**	
	C433	**IRC718**	**C433**	**IRC718**
0	214.000	214.000	2.00	2.00
10	198.995	30.224	1.97	1.95
50	188.061	23.959	1.96	1.90
100	184.122	21.542	1.93	1.80
150	183.653	16.863	1.90	1.78
200	181.155	15.794	1.84	1.74

Calculation

Example from table B.15

Value from AAS = 7.660 ppb and filtered sample = 97 ml

Sample volume	1000 ml	has Hg	7.660	µg
Sample volume	100 ml	has Hg	$\frac{7.660x100}{1000}$	µg
Due to take sample	50 ml	so	$\frac{7.660x100}{1000}$	µg
Adjust sample volume to	100 ml	so	$\frac{7.660x100x100}{1000x50}$	µg
Filtered sample	97 ml	so	$\frac{7.660x100x100}{1000x50}$	µg
If sample	1000 ml	so	$\frac{7.660x100x100x1000}{1000x50x97}$	µg
			= 15.794	µg

So, the sample has the mercury concentration equal to 15.794 µg.

Table B.16 Effect of exchange ion in H^+ form to the concentration of mercury in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium and resin dose and isotherm (Second time)

pH2 C433 of Figure 4.13

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**$q_e = x/m$**
10	214.400	198.995	1.541
50	214.400	188.061	0.527
100	214.400	184.122	0.303
150	214.400	183.653	0.205
200	214.400	181.155	0.166

pH2 IRC718 of Figure 4.13

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**$q_e = x/m$**
10	214.400	30.224	18.418
50	214.400	23.959	3.809
100	214.400	21.542	1.929
150	214.400	16.863	1.317
200	214.400	15.794	0.993

Table B.17 Fruendlich constant of mercury concentration in real wastewater and resin in Na^+ form.

From C_e and q_e of pH2 C433 of Figure 4.14

Condition	**Equilibrium concentration (C_e,,µg/l)**	**$q_e = x/m$ (µg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH2 C433	18.648	0.412	1×10^{-13}	9.8849	0.9706
	16.090	0.134			
	15.391	0.074			
	15.140	0.051			
	14.764	0.040			

From C_e and q_e of pH2 IRC718 of Figure 4.14

Condition	**Equilibrium concentration (**C_e**,,µg/l)**	q_e **= x/m (µg/g)**	**K**	$\frac{1}{n}$	R^2
pH2 IRC718	10.684	1.209	0.0271	1.3041	0.6413
	9.370	0.268			
	6.925	0.158			
	3.940	0.126			
	2.502	0.101			

From C_e and q_e of pH5 C433 of Figure 4.14

Condition	**Equilibrium concentration (**C_e**,,µg/l)**	q_e **= x/m (µg/g)**	**K**	$\frac{1}{n}$	R^2
pH5 C433	18.927	-0.343	2×10^{-8}	-9.08	1.000
	16.729	-0.025			
	16.231	-0.007			
	14.834	0.004			
	14.094	0.007			

From C_e and q_e of pH5 IRC718 of Figure 4.14

Condition	**Equilibrium concentration (**C_e**,,µg/l)**	q_e **= x/m (µg/g)**	**K**	$\frac{1}{n}$	R^2
pH5 IRC718	13.838	0.166	0.0183	0.6823	0.5235
	12.201	0.066			
	7.864	0.076			
	6.575	0.059			
	4.363	0.056			

Table B.18 Fruendlich constant of mercury concentration in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium time resin in Na^+ form

From C_e and q_e of pH2 C433 of Figure 4.15

Condition	**Equilibrium concentration (C_e,,μg/l)**	**q_e = x/m (μg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH2 C433	79.556	0.852	8×10^{-35}	17.753	0.7450
	78.276	0.196			
	75.579	0.125			
	72.974	0.101			
	71.443	0.083			

From C_e and q_e of pH2 IRC718 of Figure 4.15

Condition	**Equilibrium concentration (C_e,,μg/l)**	**q_e = x/m (μg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH2 IRC718	55.631	3.245	0.0010	1.8124	0.5394
	42.457	0.912			
	41.667	0.464			
	36.429	0.344			
	19.763	0.342			

From C_e and q_e of pH5 C433 of Figure 4.15

Condition	**Equilibrium concentration (C_e,,μg/l)**	**q_e = x/m (μg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH5 C433	129.391	3.786	8×10^{-37}	17.334	0.9834
	121.287	0.919			
	115.731	0.515			
	112.783	0.363			
	112.271	0.275			

From C_e and q_e of pH5 IRC718 of Figure 4.15

Condition	Equilibrium concentration (C_e,µg/l)	q_e = x/m (µg/g)	K	$\frac{1}{n}$	R^2
pH5 IRC718	102.636	6.461	1×10^{-15}	7.6770	0.7295
	101.162	1.322			
	87.273	0.800			
	85.317	0.546			
	77.635	0.448			

Table B.19 Fruendlich constant of mercury concentration in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium time resin in H^+ form, First time.

From C_e and q_e of pH2 C433 of Figure 4.16

Condition	Equilibrium concentration (C_e,µg/l)	q_e = x/m (µg/g)	K	$\frac{1}{n}$	R^2
pH2 C433	110.416	0.803	$2x10^{-63}$	30.522	0.5941
	107.556	0.218			
	108.245	0.102			
	106.623	0.079			
	103.118	0.077			

From C_e and q_e of pH2 IRC718 of Figure 4.16

Condition	Equilibrium concentration (C_e,µg/l)	q_e = x/m (µg/g)	K	$\frac{1}{n}$	R^2
pH2 IRC718	28.372	9.008	$6x10^{-7}$	4.9611	0.9811
	19.796	1.973			
	17.781	1.007			
	16.428	0.680			
	16.395	0.510			

Table B.20 Fruendlich constant of mercury concentration in real wastewater with spike $Hg(NO_3)_2$ 100 ppb at equilibrium time resin in H^+ form, Second time.

From C_e and q_e of pH2 C433 of Figure 4.17

Condition	**Equilibrium concentration (C_e,,µg/l)**	**q_e = x/m (µg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH2 C433	198.995	1.541	5×10^{-55}	23.719	0.9675
	188.061	0.527			
	184.122	0.303			
	183.653	0.205			
	181.155	0.166			

From C_e and q_e of pH2 IRC718 of Figure 4.17

Condition	**Equilibrium concentration (C_e,,µg/l)**	**q_e = x/m (µg/g)**	**K**	$\frac{1}{n}$	**R^2**
pH2 IRC718	30.224	18.418	8×10^{-6}	4.2083	0.9135
	23.959	3.809			
	21.542	1.929			
	16.863	1.317			
	15.794	0.993			

Column test

Table B.21 Concentration of mercury in each time at pH 2 by use IRC718 resin volume 440 ml flow rate 220 ml/hour, HRT = 2 hours of Figure 4.18, 4.19 and 4.20. Initial mercury concentration = 118.310 µg/l

time (mins)	**volume (L)**	**Hg Concentration (µg/l)**	**pH**	**Temperature**
0	0	0.000	1.43	30.00
15	0.055	1.546	1.63	29.40
30	0.110	3.091	1.07	29.30
45	0.165	4.637	1.05	29.20
60	0.220	4.716	1.04	29.20
75	0.275	5.160	0.99	29.00
90	0.330	6.270	1.04	28.90

time (mins)	volume (L)	Hg Concentration (µg/l)	pH	Temperature
105	0.385	6.065	1.08	28.90
120	0.440	6.026	1.10	28.80
135	0.495	6.414	1.26	28.50
150	0.551	5.750	1.15	28.30
165	0.606	5.707	1.69	28.10
180	0.661	5.727	1.66	29.10
195	0.716	4.416	1.69	28.90
210	0.771	4.603	1.75	28.40
225	0.826	4.722	1.84	28.90
240	0.881	3.343	1.85	27.90
255	0.936	3.102	1.88	28.50
270	0.991	2.645	1.86	28.40
285	1.046	1.188	1.86	28.30
300	1.101	1.299	1.86	28.40
315	1.156	1.139	1.85	28.40
330	1.211	3.804	1.85	28.60
345	1.266	7.431	1.86	28.20
360	1.321	20.434	1.84	28.50
375	1.376	19.695	1.86	28.90
390	1.431	19.737	1.86	28.70
405	1.486	30.490	1.87	30.20
420	1.541	30.165	1.74	29.70
435	1.596	33.750	1.87	28.30
450	1.652	33.584	1.88	28.60
465	1.707	33.534	1.89	29.00
480	1.762	33.363	1.89	29.50
495	1.817	33.625	1.89	30.00
510	1.872	33.594	1.88	32.10
525	1.927	33.398	1.89	33.20
540	1.982	33.718	1.90	28.60
555	2.037	33.681	1.87	29.90
570	2.092	33.632	1.92	29.80
585	2.147	48.617	1.95	28.90
600	2.202	48.747	1.94	28.60
615	2.257	48.485	1.92	28.70
630	2.312	49.748	1.91	28.70
645	2.367	49.006	1.90	29.00
660	2.422	48.752	1.93	29.30
675	2.477	48.615	1.94	29.00

time (mins)	**volume (L)**	**Hg Concentration (μg/l)**	**pH**	**Temperature**
690	2.532	48.701	1.94	29.10
705	2.587	56.185	1.93	29.10
720	2.642	56.404	1.94	28.90
735	2.697	56.252	1.98	28.80
750	2.753	63.563	1.94	28.90
765	2.808	74.908	1.95	29.20
780	2.863	108.313	1.97	28.70
795	2.918	115.698	1.95	28.60
810	2.973	115.551	1.96	28.00
825	3.028	115.853	1.96	27.80
840	3.083	116.832	1.96	27.80
855	3.138	117.710	1.97	27.70
870	3.193	117.942	1.97	27.60
885	3.248	118.173	1.96	27.60
900	3.303	118.146	1.96	27.10
915	3.358	118.119	1.97	26.90
930	3.413	117.519	1.94	26.50
945	3.468	116.920	1.96	27.20
960	3.523	118.185	1.94	27.60
975	3.578	119.450	1.95	28.20
990	3.633	118.923	1.95	28.40
1005	3.688	118.397	1.95	28.30
1020	3.743	119.448	1.95	28.80
1035	3.798	120.500	1.94	28.50
1050	3.854	119.522	1.94	28.70
1065	3.909	118.545	1.94	28.70
1080	3.964	118.861	1.94	28.40
1095	4.019	119.176	1.94	28.90

Table B.22 Concentration of mercury in each time at pH 2 by use IRC718 resin volume 880 ml flow rate 220 ml/hour, HRT = 4 hours of Figure 4.21, 4.22 and 4.23. Initial mercury concentration = 118.457 μg/l

time (mins)	volume (L)	Hg Concentration (μg/l)	pH	Temperature
0	0	0.000	2.05	28.20
30	0.1107	4.704	1.78	29.20
90	0.3321	5.394	1.80	28.20
150	0.5535	4.594	1.91	29.20
210	0.7749	2.708	1.95	28.00
270	0.9963	2.461	1.95	28.20
315	1.16235	2.835	1.93	28.00
330	1.2177	2.769	1.93	27.80
345	1.27305	2.653	1.93	27.50
360	1.3284	2.748	1.94	28.00
375	1.38375	2.697	1.93	28.00
390	1.4391	2.775	2.01	28.10
405	1.49445	2.451	1.97	28.90
420	1.5498	1.928	2.02	28.00
435	1.60515	2.447	2.02	27.60
450	1.6605	3.281	2.03	27.80
465	1.71585	3.383	2.03	27.60
480	1.7712	3.727	2.05	27.60
495	1.82655	3.390	2.05	27.40
510	1.8819	3.489	2.07	27.70
525	1.93725	3.496	2.10	27.40
540	1.9926	3.443	2.03	27.80
555	2.04795	3.776	2.11	27.40
570	2.1033	3.460	2.10	27.50
585	2.15865	3.787	2.11	27.30
600	2.214	5.716	2.14	27.40
615	2.26935	5.589	2.14	26.70
630	2.3247	6.081	2.10	27.00
645	2.38005	10.565	2.13	26.90
660	2.4354	14.306	2.14	27.20
675	2.49075	15.802	2.14	26.90
690	2.5461	17.122	2.09	27.30
705	2.60145	17.094	2.12	26.80
720	2.6568	16.833	2.12	27.80

time (mins)	volume (L)	Hg Concentration (µg/l)	pH	Temperature
735	2.71215	17.321	2.10	27.60
750	2.7675	17.548	2.12	27.60
765	2.82285	23.148	2.11	27.70
780	2.8782	22.969	2.12	27.60
795	2.93355	23.440	2.12	27.90
810	2.9889	23.430	2.09	27.50
825	3.04425	21.613	2.15	27.60
840	3.0996	26.223	2.13	27.40
855	3.15495	26.324	2.14	27.00
870	3.2103	24.155	2.16	27.40
885	3.26565	23.334	2.19	27.10
900	3.321	23.388	2.17	27.00
915	3.37635	22.797	2.19	27.40
930	3.4317	22.685	2.11	28.00
945	3.48705	23.001	2.08	27.60
960	3.5424	22.786	2.06	28.50
975	3.59775	22.736	2.06	28.60
990	3.6531	29.680	2.08	28.40
1005	3.70845	29.660	2.06	28.30
1020	3.7638	36.825	2.07	27.80
1035	3.81915	36.642	2.16	27.70
1050	3.8745	43.662	2.00	27.90
1065	3.92985	43.576	1.86	27.80
1080	3.9852	50.484	1.93	27.70
1095	4.04055	50.420	2.05	27.00
1110	4.0959	70.690	2.02	27.00
1125	4.15125	91.209	2.02	28.00
1140	4.2066	102.884	2.00	28.10
1155	4.26195	104.993	2.19	27.80
1170	4.3173	104.928	2.33	26.70
1185	4.37265	111.865	2.27	26.30
1200	4.428	111.395	2.22	25.90
1215	4.48335	111.527	2.20	25.80
1230	4.5387	116.268	2.16	26.00
1245	4.59405	120.353	2.15	27.10
1260	4.6494	119.835	2.14	27.00
1275	4.70475	120.005	2.15	28.00
1290	4.7601	122.865	2.10	27.60

Table B.23 Reusability test of IRC718 resin with real wastewater with spike 100 ppb $Hg(NO_3)_2$ at pH 2 and equilibrium time. (Figure 4.25)

Resin dose (g/l)	**Hg Concentration (µg/l)**		**pH**	
	New IRC718	**Used IRC718**	**New IRC718**	**Used IRC718**
0	97.451	97.451	2.00	2.00
200	4.276	4.745	1.92	1.95

Table B.24 The concentration of mercury removal of real wastewater at pH 2 between C433, IRC718, CGC-12, NORIT GAC 1240 and MERSORB LW. (Figure 4.26)

Type of adsorbents / **Resin dose (g/l)**	**Hg concentration (µg/l)**				
	C433	**IRC718**	**CGC-12**	**NORIT GAC 1240**	**MERSORB ®LW**
0	22.770	22.770	22.770	22.770	22.770
10	18.648	10.684	13.580	19.340	20.650
50	16.090	9.370	10.870	17.330	20.240
100	15.391	6.925	10.320	15.860	18.230
150	15.140	3.940	10.350	14.340	18.140
200	14.764	2.502	8.670	12.580	17.660

Table B.25 The concentration of mercury removal of real wastewater at pH 5 between C433, IRC718, CGC-12, NORIT GAC 1240 and MERSORB LW. (Figure 4.27)

Type of adsorbents / **Resin dose (g/l)**	**Hg concentration (µg/l)**				
	C433	**IRC718**	**CGC-12**	**NORIT GAC 1240**	**MERSORB ®LW**
0	15.493	15.493	15.490	15.490	15.490
10	18.927	13.838	10.320	8.700	8.710
50	16.729	12.201	9.920	7.030	7.490
100	16.231	7.864	9.580	5.640	6.930
150	14.834	6.575	8.520	4.470	4.850
200	14.094	4.363	6.540	3.400	3.280

Table B.26 The concentration of mercury removal of real wastewater at pH 2 between NORIT GAC 1240 three times and IRC718 in H^+ form and isotherm

pH2 IRC718 of Figure 4.28

Resin dose(g/L)	**Initial concentration (C_0,μg/l)**	**Equilibrium concentration (C_e,μg/l)**	**q_e = x/m**
10	118.450	28.372	9.008
50	118.450	19.796	1.973
100	118.450	17.781	1.007
150	118.450	16.428	0.680
200	118.450	16.395	0.510

pH2 NORIT# 1 of Figure 4.28

Resin dose(g/L)	**Initial concentration (C_0,μg/l)**	**Equilibrium concentration (C_e,μg/l)**	**q_e = x/m**
10	88.080	40.610	4.747
50	88.080	39.780	0.966
100	88.080	31.070	0.570
150	88.080	29.530	0.390
200	88.080	31.540	0.283

pH2 NORIT# 2 of Figure 4.28

Resin dose(g/L)	**Initial concentration (C_0,μg/l)**	**Equilibrium concentration (C_e,μg/l)**	**q_e = x/m**
10	208.200	12.750	19.545
50	208.200	16.710	3.830
100	208.200	13.240	1.950
150	208.200	10.580	1.317
200	208.200	5.300	1.015

pH2 NORIT# 3 of Figure 4.28

Resin dose(g/L)	**Initial concentration (C_0,µg/l)**	**Equilibrium concentration (C_e,µg/l)**	**q_e = x/m**
10	241.200	21.250	21.995
50	241.200	20.900	4.406
100	241.200	9.800	2.314
150	241.200	5.410	1.572
200	241.200	6.480	1.174

BIOGRAPHY

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