ประสิทธิภาพการกำจัดปรอทจากน้ำเสียอมัลกัมทางทันตกรรมโดยการดูดซับด้วยแร่ดินเบา

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MERCURY REMOVAL EFFICIENCY FROM DENTAL AMALGAM WASTEWATER BY ADSORPTION WITH DIATOMITE
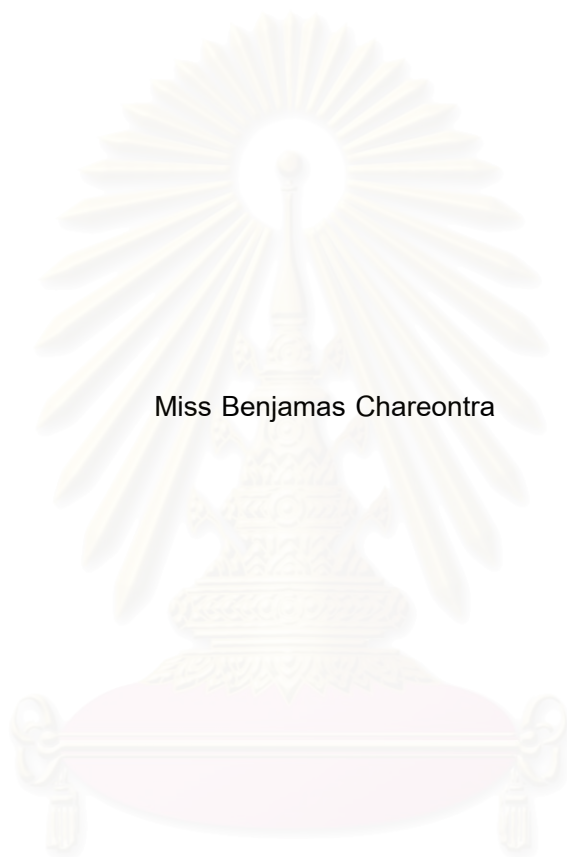
Miss Benjamas Chareontra

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By   Miss. Benjamas Chareontra

Program in   Environmental Science

Thesis Advisor   Associate Professor Supawan Tantayanon, Ph.D.

Thesis Co - advisor   Paramee Pengprecha, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirement for Master's Degree.

………………………………… Dean of Graduate School

(Professor Suchada Kiranandana, Ph.D.)

Thesis Committee

…………………………………Chairman

(Art – ong Pradatsundarasar, Ph.D.)

…………………………………Thesis Advisor

(Associate Professor Supawan Tantayanon, Ph.D)

……………………………..Thesis Co - Advisor

(Paramee Pengprecha, Ph.D)

…………………………………..member

(Associate Professor Gullaya Wattayakorn, Ph.D)

…………………………………..member

(Apichat Imyim, Ph.D)

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ทางทันตกรรม วัดความเข้มข้นของปรอทในน้ำเสียจากคลินิคบริการทันตกรรม คณะทันตแพทยศาสตร์
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ศึกษาประสิทธิภาพการกำจัดปรอทในน้ำเสียสังเคราะห์ด้วยแร่ดินเบา โดยแปรผัน ระยะเวลา
ในการสัมผัส พีเอชของสารละลาย และปริมาณของแร่ดินเบา ผลการทดลองพบว่า แร่ดินเบา 1 กรัม มี
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และ ไคโตซาน แต่มีประสิทธิภาพสูงกว่าถ่านกัมมันต์

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สหสาขาวิชา   วิทยาศาสตร์สิ่งแวดล้อม   ลายมือชื่อนิสิต.......................................

สาขาวิชา   วิทยาศาสตร์สิ่งแวดล้อม   ลายมือชื่ออาจารย์ที่ปรึกษา.........................

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This research was aimed to study the efficiency of mercury removal from dental amalgam wastewater. The mercury concentration in wastewater from dental clinics, Faculty of Dentistry, Chulalongkorn University was determined. It was found that the concentration of mercury was in the range of 4.69 – 19.26 ppb. and not directly correlated with the number of patients.

The adsorption efficiency of mercury in synthetic wastewater by diatomite was studied by varying the contact time, the pH and the amount of diatomite. The result was shown that adsorption efficiency of mercury was > 95 % by using 1.0 gram of diatomite at pH 3 - 9 for 120 minutes. The adsorption efficiency and adsorption capacity of diatomite is equal to polymer (Lewatit TP 214) and chitosan but higher than activated carbon.

It was found that 0.05 gram of diatomite can reduce the concentration of mercury from 20.42 ppb. to < 5 ppb. which meets the Ministry of Industry requirement of discharged wastewater .

Department   Inter-department of Environmental   Science Student's signature……………………………..

Filed of study   Environmental Science   Advisor's signature……………… ……………………

Academic year _____2003_____   Co-advisor's signature…………………………………

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CHAPTER I

INTRODUCTION

The mercury content of dental – unit wastewater has been issue of increasing importance to the environment. The regulations governing mercury discharge into environment are becoming more stringent. Mercury has been among the top 3 hazardous substances listed on the Agency for Toxic Substance and Disease Registry (ATSDR) / Environmental Protection Agency (EPA) priority list, from 1997 – 2003.

Around 10,000 ton of mercury is yearly produced for anthropogenic use. It has been estimated that approximately 3 % are used in dentistry for dental amalgam restoration. [1] When placing new amalgam filling, freshly trituration amalgam is inserted into the newly prepared tooth cavity. Primary surplus of trituration amalgam and major amalgam particles generated during the filling and contouring procedures are generally routinely collected in coarse filters and sold for refinement. Minor amalgam particles are released by production of new fillings or by the removal of old restorations are partly sedimented in wastewater tubes and drains.[2]

There are several methods to treat the metal contaminated effluent such as precipitation, ion – exchange and adsorption, etc., but the selection of the wastewater treatment methods are based on the concentration of waste and the cost of treatment. Adsorption is one of the most popular techniques for the removal of heavy metals from the wastewater. Adsorption is a complex process involving physical, chemical and electrical interactions at sorbent surfaces, which can be exceedingly more complicated than reaction in the bulk solution.

Mercury in natural aquatic systems is largely controlled by adsorption with fixed or mobile adsorbents. In addition to affecting the physical transport of dissolved species, adsorption can lead to changes in chemical activity and biological activity. The clay minerals are considered very importance adsorbent in natural water systems because of

their high specific surface area combined with the structural molecules and pH dependent charge developed on their surfaces. Diatomite is very common clay mineral in weathered feldspathic aquifers due to cheap cost and easy procuring. The understanding of Hg (II) adsorption on diatomite is therefore important in determining the ultimate fate of this element in such environments.

1.1 Study objective

1. To determine the optimum condition for the Hg (II) removal from dental amalgam wastewater using diatomite.
2. To compare the Hg (II) removal efficiency between diatomite and other adsorbents ; activated carbon, chitosan and polymer containing thiocarbamide group (Lewatit TP 214) .

1.2 Scope of study

1. To determine the optimum condition for Hg (II) removal from synthetic wastewater using diatomite by varying the following parameters ; pH, the contact time and the amount of adsorbent (diatomite).
2. To remove Hg (II) from synthetic wastewater using other adsorbents ; activated carbon, chitosan and polymer containing thiocarbamide group (Lewatit TP 214) at the individual optimum condition reported .
3. To determine and compare the efficiency of Hg (II) removal of adsorbents ; diatomite, activated carbon, chitosan and polymer containing thiocarbamide group (Lewatit TP 214).
4. To utilize the diatomite for Hg (II) removal from dental amalgam wastewater.

1.3 Benefits

1. The optimum condition of removal efficiency of mercury by diatomite.

2. Comparison on the removal of mercury by diatomite and other adsorbents ; activated carbon, chitosan and polymer (Lewatit TP 214).

3. The possibility to substitute diatomite abundant natural resource in Thailand for imported adsorbents.

4. The increase valuable property of abundant natural occurred clay in Thailand.

5. Guidance applied method of removal mercury in dental amalgam wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEW

This chapter gathers the information of the removal of mercury. The literatures are divided into six sections. The occurring of mercury as well as the existing species, which effect the living organisms are explained in this chapter. The cycle of mercury in the environment related to the dental procedure is discussed. The composition of dental amalgam is included. The adsorbents used for wastewater treatment are also given for example. Furthermore this chapter contains the literature review.

2.1 Mercury in the environment

Mercury commonly occurs in nature as sulfides and in a number of minerals. From these deposits, mercury is circulated naturally in the biosphere, primarily by degassing from the earth is crust and oceans. Natural emission of mercury amounts to around 150,000 tons a year. Globally, approximately 10,000 tons of mercury produced yearly for anthropogenic use, with an estimate 3 – 4 % used in dentistry. [3] Between 20,000 – 30,000 tons of mercury are discharge annually into the environment each year as a result of human activities. Including processing of minerals and ores and fossil fuel combustion. [4]

The possible toxic effects of mercury are strongly dependent on its chemical form. In dentistry, only the metallic form is used, while inorganic and organic compounds of mercury are also present in the wastewater from the dental clinics. The metallic form is mainly absorbed in the human body through skin, while mercury vapor absorption is through the lungs. The absorbed mercury passes into the circulation and is disseminated throughout the body. After cellular absorption, metallic mercury is converted into mercuric ions, which can produce toxic effects.

Mercury is accumulated in both aquatic and terrestrial food chains, with higher levels occurring in predators. [4] In polluted waters mercury can change form to

methylmercury. The levels of methylmercury in living organisms such as fish will increase, with higher levels with increasing size and age of fish.

Elementary mercury entering the waterways is converted to methylmercury, mediated by methyl – cabalamin or by sediment micro – organisms, including bacteria and fungi. The subsequent uptake of methylmercury occurs via two mechanisms either directly from the water or through the food chain. Direct extraction of mercury from water occurs as a result of mercury is high affinity for sulfur and sulfalhydryl groups. The food chain facilitates the biomagnification of mercury levels when organisms higher in the food chain ingest other organisms contaminated with methylmercury. Plankton and algae that are take up methylmercury and consumed by small fish. There are in turn consumed by larger fish and other predators, thus allowing the accumulation of mercury through the food chain [5]

The toxicokinetics of mercury compounds varies considerably in different species. Due to the basic chemicalproperties of mercury, several basic biological mechanisms are affected in living organisms in general.   A major factor underlying the biochemical properties of mercury and mercury compounds are the fact that mercury possesses a strong affinity for sulfur and sulfalhydryl groups and thereby may interfere with importance basal biological functions in living organisms, i.e. membrane and enzyme functions. [4]

$$Hg^{2+} + 2RSH \text{ (protein)} \longrightarrow R\text{- S- Hg –SR}$$
$$CH_3HgCl + RSH \text{ (protein)} \longrightarrow R\text{ -S- Hg – }CH_3 + HCl \qquad \text{……………(2.1)}$$
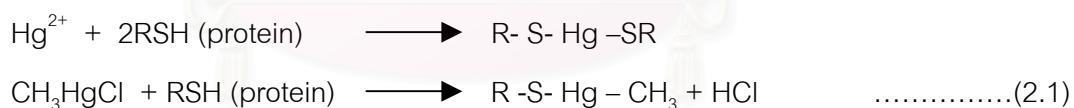
2.2 Mercury cycle in dentistry [3]

Large amalgam particles (around 15%), surplus in trituration capsules and carved surplus are expected to be collected for recycling. Small amalgam particles produced during carving, burnishing and polishing procedures will be sucked up and transported by the vacuum system. Some will sediment in tubes and some will drain in the clinic drainage. Depending on the presence or absence of an amalgam separator unit in the clinic. Amalgam - contaminated sludge will be discharged into the sewage. Lost or extracted teeth with amalgam filling and amalgam - contaminated waste as trituration

capsules and cotton rolls will be discharged with the solid waste and in most instances. Later these will be subjected to combustion. Furthermore corpses with or without amalgam fillings are cremated or buried. During cremation, mercury bound in amalgam fillings will be released as mercury vapor. Estimates of the mean amount of mercury emitted during cremation have ranged between 3.8 - 1.8 g. mercury per cremation [6]. The released of mercury from dentistry into the environment is shown in Figure 2.1
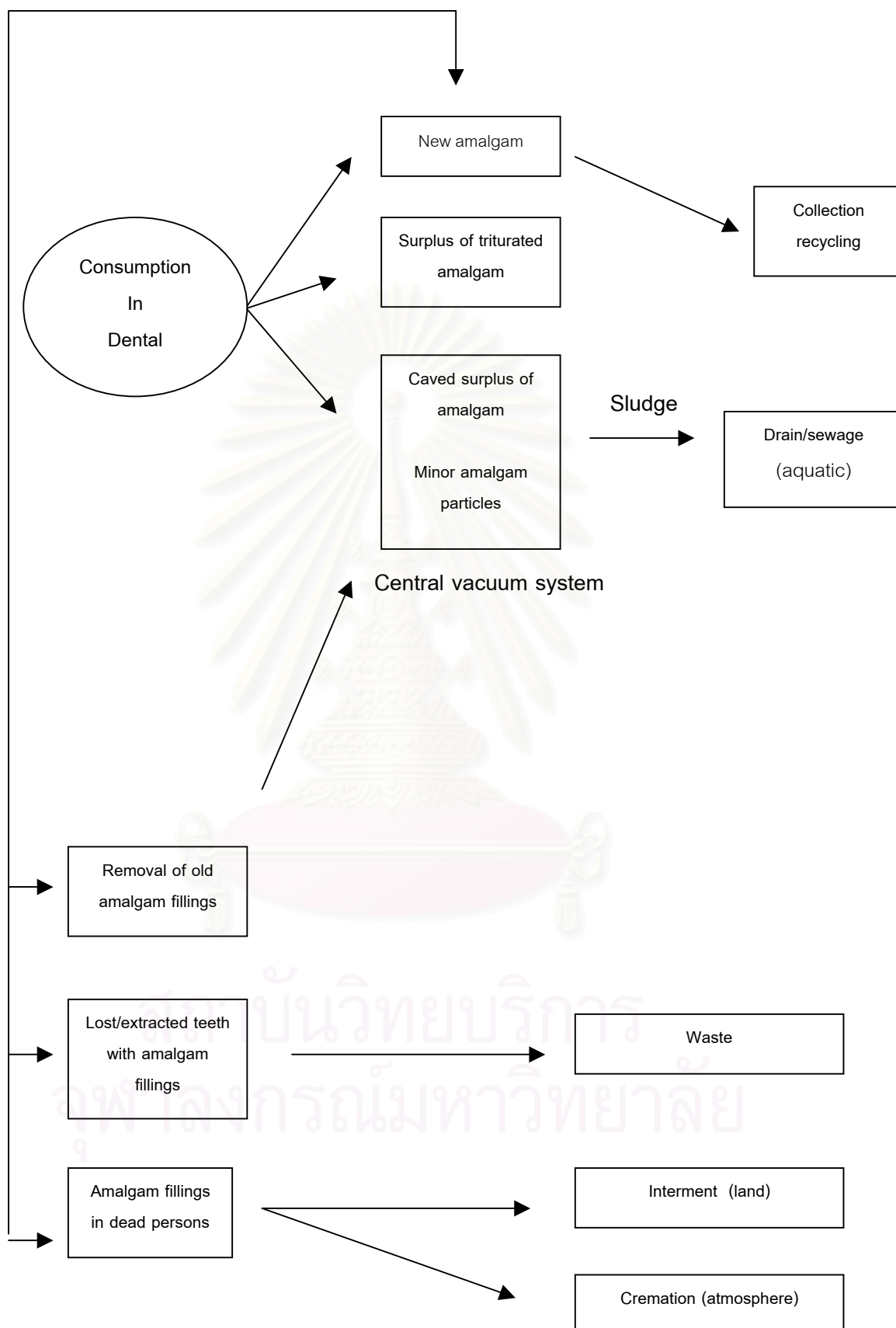
Figure 2.1 The released of mercury from dentistry into the environment [7]

Mercury exposure from dental procedures

In the dental practice using amalgam can be exposed to mercury either in the form of vapor or particulate amalgam dust. It can also result from dental procedures such as preparation of amalgam, placement, removal and polishing of amalgam restorations.

The amount of mercury released from all these procedures, has been quantified as follow : [8]

Trituration	1 - 2 μg
Placement of amalgam restoration	6 – 8 μg
Dry polishing	44 μg
Wet polishing	2 – 4 μg
Removal of amalgam restorations	15 – 20 μg
(Under water spray and high volume)	

2.3 Dental amalgam composition [9]

Modern dental amalgams are prepared from two types of alloy. Conventional silver tin amalgam is prepared from a silver tin alloy containing small amounts of copper and zinc. High copper amalgams are prepared from either a mixture of silver-tin and silver-copper alloys (admixed alloys) or from a ternary silver-copper-tin alloy (single composition alloys). High copper amalgams have superior clinical properties with a higher resistance to corrosion and marginal breakdown.

Conventional amalgam

The alloy must contain a minimum of 65% silver and a maximum of 29% tin with approximately 3% copper and less than 1% zinc. The main constituent of the alloy is the gamma phase (Ag_3Sn). Trituration of alloy powder with mercury produces a plastic mass,

which sets by the formation of new inter-matallic compounds. The setting mechanism can be summarised as :

$$Ag_3Sn + Hg \quad = \quad Ag_3Sn \quad + \quad Ag_2Hg_3 \quad + \quad Sn_{7-8}Hg \quad ....(2.2)$$

$$(\gamma_1\text{phase}) \qquad\qquad (\gamma\text{ phase}) \quad (\gamma_1\text{phase}) \quad (\gamma_2\text{ phase})$$
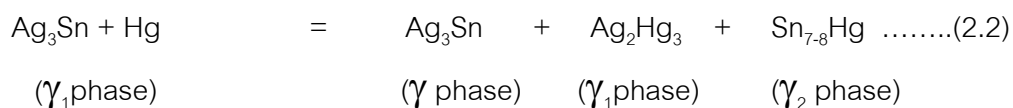
The unreacted γ phase particles are embedded in a matrix of γ_1 phase and γ_2 phase in set amalgam.

High copper amalgam

These are prepared from either admixed or single composition alloys containing 13 – 20 % copper.

Admixed alloys : these react as follows.

$$\gamma \text{ phase + silver – copper eutectic + Hg } = \gamma_1 \text{ phase + } \eta \text{ phase } (Cu_6Sn_5) \text{ + unreacted}$$
$$\text{particles of both types.} \qquad ....(2.3)$$
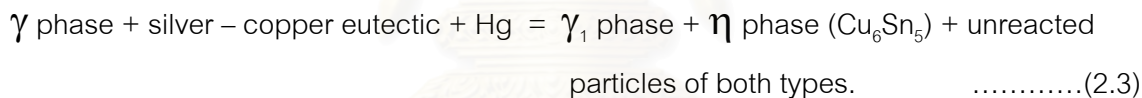
Single composition alloys : these react with mercury as follows.

$$Ag – Sn – Cu + Hg = \gamma_1 \text{ phase + } \eta \text{ phase plus unconsumed alloy.} \qquad ....(2.4)$$
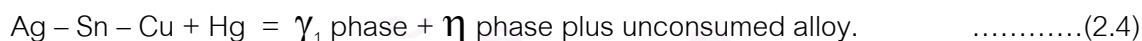
Neither type of high copper amalgam contains the γ_2 phase.

2.4 Adsorption

Adsorption is a surface phenomenon that is defined as the increase in concentration of particular compound at the surface or interface between solid or liquid phase. In discussing the fundaments of adsorption. It is useful to distinguish between physical adsorption, involving only relatively weak intermolecular force and chemisorption, which involves essentially the formation a chemical bond between the sorbate molecule and the surface adsorbent [10]. Physical adsorption can be distinguished from chemisorption according to one or more the following criteria [11]:

- Physical adsorption does not involve the sharing or transfer of electrons and thus always maintains the individuality of interacting species. The interactions are fully reversible, enabling desorption to occur at the same temperature, although the process may be slow because of diffusion effects. Chemisorption involves chemical bonding and is irreversible.

- Physical adsorption is not site specific; the adsorbed molecules are free to cover the entire surface. In contrast, chemisorption is site specific ; chemisorbed molecules fixed at specific sites.

- The heat of physical adsorption is low compare to that of chemisorption. The upper limit for physical adsorption may be higher than 20 kcal/mol. for adsorption on adsorbent with very narrow pores. The heat of chemisorption range between 20 – 100 kcal/mol.

The following adsorbents are widely used in industries :

-    **Diatomite or diatomaceous earth [12]**

Diatomite knows as kieselguhr, tripolite, fossil flour, etc. It consists of the siliceous that remains of microscopic aquatic organisms know as diatoms.   Individual diatoms size may be vary in length from 0.005 to 0.4 mm. The chemical composition of diatomite is illustrated in Table 2.1.

General description

Diatomite has light – colored, light - weight, finely granular porous aggregate varying in texture from loosely coherent to compact. It is composed of the siliceous remains of exceedingly minute aquatic organisms, know as diatoms, radiolaria, etc.   These organisms are exceedingly minute and are usually so small, that they can be distinguished only by the aid of a high – power microscope. Diatomite is used as [13]

1.   The filtering agent in the clarification of sugar, fruit juices and oils.
2.   The insulation for heat and sound, in the form of bricks or loose powder.
3.   The extender and fiatting the agent in certain paints.
4.   The dusting agent to prevent the caking of fertilizers containing ammonium nitrate.
5.   The filter in light – weight concrete, rubber goods and paper.

Table 2.1 The compositions type of diatomite. [10]

Composition(%)	Celite	Dicalite	Clarcel	From German
SiO_2	89.6	88.92	71.0	95.48
Al_2O_3	4.0	3.12	16.0	1.15
Fe_2O_3	1.5	1.61	1.0	1.45
TiO_2	0.2	0.16	ND	0.14
CaO	0.5	0.4	1.5	0.14
MgO	0.6	0.78	ND	Trace
Na_2O	3.3	4.91	9.0	0.49
K_2O	ND	ND	ND	0.88
Water soluble matter	0.15	ND	ND	ND
Moisture	0.1	ND	2.0	0.21
Loss on ignition	0.2	ND	1.0	0.6

Celite   : Product of diatomite from Johns – Manville Company.

Dicalite : Trade mark of Great Lakes Carbon Corporation.

Clarcel : Trade mark of product from France and North Africa.

- Activated carbon

Adsorption on granular activated carbon is one of the best commercially proven methods for removing mercury from wastewater. The effectiveness of activated carbon is dependent upon initial form and concentration of mercury, dosage and type of activated carbon, treatment pH, and contact period between activated carbon and mercury containing wastewater. Increasing carbon dosages and increasing contact times improve removal of both inorganic and organic mercury.

- Chitosan
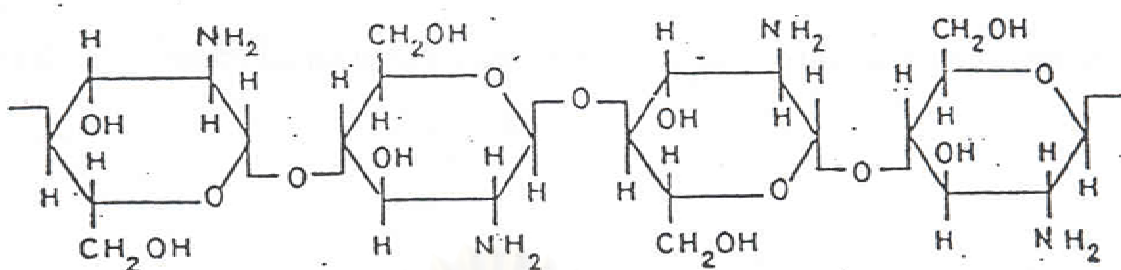
Figure 2.2 Structure of chitosan

Chitosan (poly - β - (1,4) – 2 – amino – 2 - deoxy – D- glucose) is a crystalline, structural polysaccharide generally obtained after deacetylation by alkaline treatment. Chitin (poly - β(1,4) – 2 – acetamino – 2 – deoxy – D – glucose), a cellulose – like biopolymer, is the second most abundant natural biopolymer in the world. Chitin is produced in shells of crabs, shrimps, insects, cell wall of fungi and yeast, etc. Advantages of chitosan include availability, low cost, high biocompatibility, biodegradation; ease of chemical modification and it is also nontoxic. [14]

2.5 Literature review

In 1994, the wastewater from dental clinic with and without amalgam separator in Denmark were collected and investigated the amount of mercury. It was found that with amalgam separator, the amount of mercury was in range 12 – 99 mgHg/dentist/day, meanwhile the range 65 – 842 mgHg/dentist/day was found in dental wastewater without amalgam separator [15]. The similar work also had been in Thailand in 1993 and the amount of mercury in dental wastewater was higher than 5 ppb. in the most dental clinic. [16]

The effort removal of mercury have been done most in industrial wastewater. The adsorption of mercury by using many types of adsorbent are popular. Acitivated carbon has also been used by Lean, L., et al. in 1976 [17] , they revealed that the removal mercury efficiency is depended on pH. The efficiency was increased, when adding tannic acid and

EDTA. Further Gordon, M., et al. (1988) [18], used biopolymer adsorbent known as chitosan remove metal (II) cations, including Hg^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}. They reported the monolayer sorption capacity is 815, 222, 164 and 75 mg/g chitosan respectively. The similar work also had been done by Kasem (2000) [19]. He studied the removal efficiency of chitosan on Hg (II) from Thai Asahi Chemical CO., LTD wastewater. The chitosan can remove up to 97.8 % at optimum pH 5.0 with 24 hr setting time and removal efficiencies were   2.2 g/400 ml wastewater. The development of adsorbent has been done by Bauman, T.F., et al.(1999) [20]. He used a synthetic polymer (N,N – (4 – 4 vinylbenly benzyl methyl) – 2 – aminomethyl – 1,4,8,8,11,14 – pentathiacycloheptadecane and DVB (80% divinylbenzene), which can remove up to 95% of mercury and the advantage of this synthetic polymer is that the wide range of pH can be used. In 1994 Pederson,E.D. [21], used Aluminum hydroxy and Polyquarternary amine to treat dental - operatory wastewater. Used separately, each polymer removed Hg from dental wastewater supernatant from 74.9 % to 88.4 %. Meanwhile, the polymers used in combination within the recommended pH range, removed up to 99.9 % of the total Hg from dental - wastewater supernatant.

Mercury compounds are adsorbed and remained in the adsorbent. There are many studies about the adsorption of mercury by activated carbon, chitosan and polymer. However there is no study the adsorption of mercury by diatomite which is abundant in Thailand.

The desired experiment in order to use diatomite as an adsorbent for mercury removal from dental clinic wastewater is in the following chapter.

CHAPTER III

EXPERIMENTAL

The experiment and analysis techniques are described in this chapter. It is divided into four sections. The first section describes the research procedures. The second section describes the experimental apparatus and chemical reagents. The third section describes the experimental procedures and the fourth section describes the experimental preparation.

3.1 The research procedures.

3.1.1 Validate the method of the determination of Hg (II) following The Guide Book of Flow Injection Mercury/Hydride Analysis Atomic Absorption Spectroscopy.

3.1.2 Determination the Hg (II) concentration of dental amalgam wastewater from the dental clinic (Faculty of Dentistry, Chulalongkorn University).

3.1.3 Investigate the optimum condition of Hg (II) removal from synthetic wastewater using diatomite by vary pH, the contact time and the amount of adsorbent.

3.1.4 Compare the Hg (II) removal efficiency of diatomite, activated carbon, chitosan and polymer containing thiocarbamide group (Lewatit TP 214) from synthetic wastewater.

3.1.5 Removal efficiency of diatomite at optimum condition in dental amalgam wastewater from dental clinic (Faculty of Dentistry, Chulalongkorn University).

3.2 Chemical reagents and apparatus.

      3.2.1   Chemical reagents.

Adsorbents :

-    Diatomite from Amphur Maetha,Lumphang.

-    Activated carbon Biosis[TM](Polychem Marketing CO.,LTD.)

-    Chitosan (T.C.UNION FOOD CO.,LTD.)

-    Polymer Lewatit TP 214 (Bayer Chemical AG.)

The properties of the adsorbents are presented below :

Parameter	Diatomite
Mesh size (mesh)	100
Surface area (m/g)	38.28
Pore volume(cm^3/g)	0.07
Pore size(A°)	71.66
Moisture constant	<10%
pH	8-9

Parameter	Activated carbon (GAC)
Mesh size (mesh)	12 x 40
ID. Number(mg/g min)	1000
Ash (%)	12 (max)
Moisture constant (%)	5 (max)
Bulk density(g/cc)	460 $\pm$30
Hardness (%min)	90
pH	7-9

Parameter	Chitosan
Particle size	80% pass through 60 mesh
Degree of acetylation (%)	94.59
Moisture content (%)	5.68
Viscosity (CPS)	53.00
Ash content (%)	0.4

Parameter	Polymer (Lewatit TP 214)
Bead size (mesh)	12-38
Bulk weight (ibs/ft)	43.6
Density (appr)	69.8
Stability at temperature($^{\circ}$F)	-4 – 175
Stability pH range	0-14

Reagents :

Number	Reagent	Reagent Type
1	Nitric acid 65% (HNO_3)	Analytical Reagent Grade
2	Hydrochloric acid 37% (HCl)	Analytical Reagent Grade
3	Mercury chloride ($HgCl_2$)	Analytical Reagent Grade
4	Sodium hydroxide (NaOH)	Analytical Reagent Grade
5	Sodium borohydride ($NaBH_4$)	Analytical Reagent Grade

The preparation of above reagent chemical solutions are detailed in appendix A.

3.2.2   Apparatus.

Number	Apparatus	Brand : Series
1	Weigh Balance	Sartorius : BP 211D
2	Shaker	GFL : 3016
3	pH meter	EDT instruments : BA350
4	Flameless Atomic Absorption Spectrometer	Perkin Elmer : FI – MH –AAS
5	Fiter Paper No.40 and 42	Whatman
6	Glassware	

3.3 Experimental procedure.

The parameters ; pH, the contact time and the amount of diatomite were studied by varying range as described in Table 3.1, then Hg (II) in the synthetic wastewater will be analyzed in order to find out removal efficiency of $HgCl_2$.

This experiment can use as a guidance application for removal trace mercuric ion in wastewater.

Table 3.1 Parameter in removal mercury with diatomite. (Hg (II) = 1ppm)

Number	Parameter	Range
1	p H	3,4,5,6,7,8 and 9
2	Contact Time	5,10,20,30,40,50,60,80,120,150 and180 minutes
3	Amount of Diatomite	0.05,0.1,0.2,0.5,1.0 and 2.0 g

3.4 Experiment preparation.

3.4.1 Dental amalgam wastewater collection.

The collection of wastewater samples had been carried at the final drainage of the dental clinic building (Faculty of Dentistry, Chulalongkorn University) for 5 days from 9.00 a.m. – 6.00 p.m. in every 1.5 hr. About 500 mL of sample was collected in polypropylene (PP) bottle. The original pH was recorded then the wastewater was preserved by adding HNO_3 to maintain at pH < 2 and the sample was stored at 4°C.

3.4.2 The preparation of synthetic wastewater. (Hg (II) = 1 ppm.)

A 1.00 mL of analytical reagent grade mercuric chloride ($HgCl_2$) 1000 mg/L was pipetted into a mixture of 500 mL of water add 2 mL of HNO_3 (Conc.) and diluted to 1000 mL with water. The solution was freshly prepared.

3.4.3 The determination of Hg (II) concentration from dental amalgam wastewater.

The analytical for total mercury in the wastewater followed The Guide Book of Flow Injection Mercury/Hydride Analysis Atomic Absorption Spectroscopy [22] and use standard practices for digestion of sample for determination of metal by Atomic Absorption or Plasma Emission Spectrometer (ASTM D-1971) [23]. The measurement of mercury was success by Flameless Atomic Absorption Spectrometer.

3.4.4 The investigation of the optimum condition of Hg (II) removal from synthetic wastewater using diatomite.

3.4.4.1 Contact time of adsorption.

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask. The 2.00 g of diatomite was added, the mixture solution was shaken at 150 rpm the contact time was varied from 5, 10, 20, 30, 40, 50, 60, 80, 100, 120, 150 and 180 minutes, each experiment was repeated 3 times. The solution was immediately filtered

through filter paper (Whatman No.42). The filtrate was determined in Hg (II) by Flameless Atomic Absorption spectrometer. The optimum contact time was used in following measurement.

3.4.4.2 pH of adsorption.

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask and adjust pH of solution to 3, 4, 5, 6, 7, 8 and 9.The 2.00 g of diatomite was added. The mixture solution was shaken at 150 rpm using the optimum in 3.4.4.1, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtrate was determined Hg (II) by Flameless Atomic Absorption Spectrometer.

3.4.4.3 Amount of adsorbent.

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask. Using the optimum pH in 3.4.4.2. by adding 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00 g. of diatomite. The mixture of solution was shaken at 150 rpm, using the optimum time in 3.4.4.1, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtrate was determined Hg (II) by Flameless Atomic Absorption Spectrometer.

3.4.5 Compare the Hg(II) removal efficiency of diatomite, activated carbon, chitosan and polymer. (Lewatit TP 214)

3.4.5.1 Compare the Hg (II) removal efficiency between diatomite and activated carbon.

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask. Adjust pH of solution to 7 and adding activated carbon for 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00 g. The mixture solution was shaken at 150 rpm for 120 minutes, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtrate determined Hg (II) by Flameless Atomic Absorption Spectrometer.

3.4.5.2 Compare the Hg (II) removal efficiency between diatomite and chitosan.

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask. Adjust pH of solution to 6 and adding chitosan for 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00 g. The mixture solution was shaken 150 rpm for 120 minutes, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtrate determined Hg (II) by Flameless Atomic Absorption Spectrometer.

3.4.5.3 Compare the Hg (II) removal efficiency between diatomite and polymer. (Lewatit TP 214)

A 100 mL synthetic wastewater (Hg (II) = 1ppm.) was taken into a 250 mL Erlenmeyer flask. Adjust pH of solution to 7 and adding polymer (Lewatit TP 214) for 0.05, 0.10, 0.20, 0.50, 1.00m and 2.00 g. The mixture solution was shaken 150 rpm for 60 minutes, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtrate determined Hg (II) by Flameless Atomic Absorption Spectrometer.

Therefore the results of adsorption experiments in this chapter are reported in term of percentage removal of mercury, which is calculated from equation (3.1) and adsorption capacity of adsorbent (q) is calculated from equation (3.2)

$$\text{Percentage removal of mercury (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \text{.......(3.1)}$$

C_0 = The concentration of initial mercury (ppm)

C_e = The concentration of remaining mercury (ppm)

$$\text{Adsorption capacity of adsorbent (q)} = \frac{(C_0 - C_e) \times V}{M} \qquad .....(3.2)$$

C_0 = The concentration of initial mercury (ppm)

C_e = The concentration of remaining mercury (ppm)

V = Volume of solution (L)

M = Weight of adsorbent (g)

3.4.6 Removal efficiency of diatomite at optimum condition in dental amalgam wastewater from dental clinic (Faculty of Dentistry, Chulalongkorn University)

A 100 mL dental amalgam wastewater (unfixed pH) was taken into a 250 mL Erlenmeyer flask and adding 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00 g of diatomite. The mixture of solution was shaken at 150 rpm for 120 minutes, each experiment was repeated 3 times. The solution was immediately filtered through filter paper (Whatman No.42). The filtered was determined Hg (II) by Flameless Atomic Absorption Spectrometer.

The amount of Hg (II) in dental amalgam wastewater from dental clinic is reported after the validation method. The achievement of optimizing the Hg (II) removal condition by diatomite leads to the comparison between diatomite and other adsorbents. All these are disclosed and discussed in chapter IV.

CHAPTER IV

RESULTS AND DISCUSSIONS

The results the chapter III will be discussed in this chapter. The section is divided into five parts. The first part presents the validated method of determination of Hg (II) in synthetic wastewater. The second part involves the determination of mercury concentration from dental amalgam wastewater. The third part is seek the best condition for the removal of the Hg (II) from the synthetic wastewater using diatomite. The fourth part is the comparison of the Hg (II) removal efficiency of diatomite with other adsorbent. The last part treats the dental amalgam wastewater by diatomite.

4.1 Validate the method of determination of Hg. (II)

The analytical procedure for determination for total mercury following Guide Book of Flow Injection Mercury/Hydride Analysis Atomic Absorption Spectroscopy [22] is applicable to fresh water, industrial wastewater and sewage effluents. The standard concentration of Hg (II) ranged from 1.0 – 20.0 μg Hg/L. The standard curve are plotted in Figure 4.1
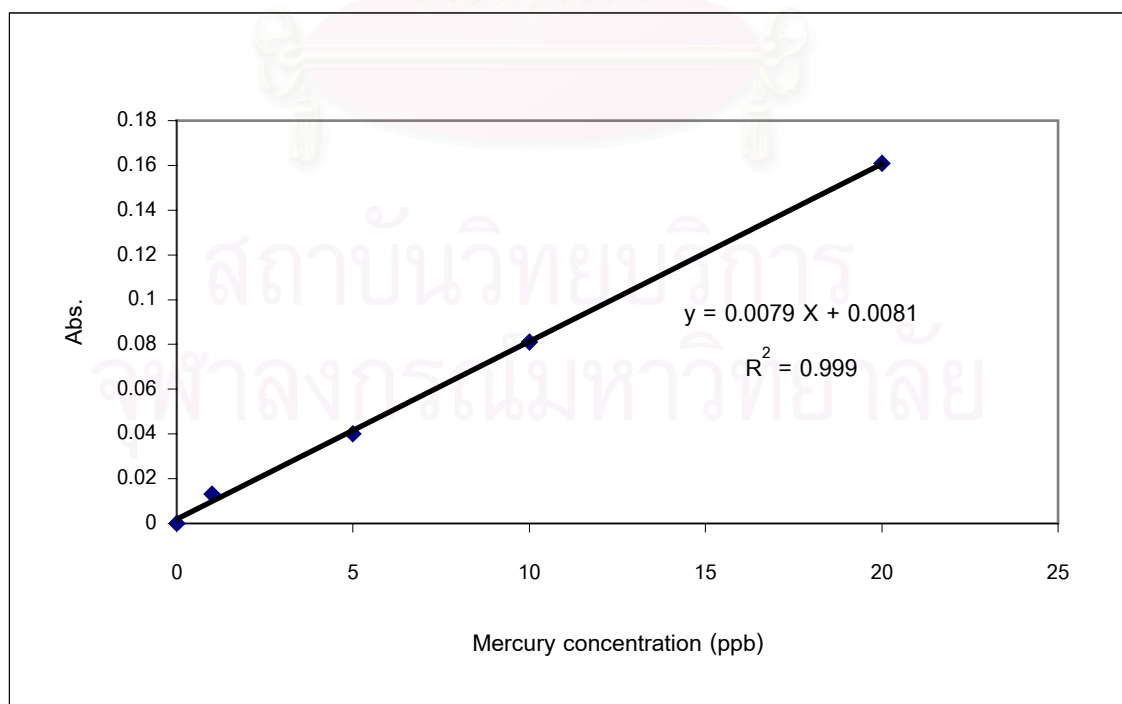
Figure 4.1 Standard curve for evaluation of mercury concentration.

The accuracy of the method was investigated by using 10 ppb standard Hg (II) and following ASTM –D-1971. The percent recover as shown in Table 4.1

Table 4.1 Percentage of recovery for digest Hg (II) synthetic wastewater (n=5)

Number	Initial Hg conc. (ppb)	Remaining Hg conc. (ppb)	% recovery
1	10.37	9.75	94.02
2	10.37	9.88	94.27
3	10.37	9.26	89.30
4	10.37	9.75	94.02
5	10.37	8.77	84.57
Average		9.48	91.43
SD		0.47	4.49
RSD		4.91	4.91

- Hg (Blank) = 0.01 ppb.

- LOQ = 1 ppb. (Limit of Quantitation, the lowest concentration that can be reported with accuracy and confidence.)

- LOD = 0.15 ppb. (Limit of detection,calculated from 3 SD+Blank) is the signal from blank solution.

$$\% \text{ recovery} \quad = \quad (C_e / C_o) \times 100$$

C_o = The concentration of initial mercury (ppb.)

C_e = The concentration of remaining mercury (ppb.)

From the experimental result of 5 replicates, the average percentage recovery is 91.43 $\pm$4.49 %. It can be considered as the reliable method for digesting Hg (II) dental amalgam wastewater. [24]

4.2 Determination the Hg (II) concentration of dental amalgam wastewater.

The samples were taken from drainage of the central building of Faculty of Dentistry, Chulalongkorn University. They were collected before going to the main sewage system(after passage of sedimentation or filtration equipment). Samples had been collected in 5 consecutive days from 28 April 2003 till 2 May 2003. The measurement of total mercury was carried out by Flameless Atomic Absorption Spectrometer follow Guide Book of Flow Injection Mercury/Hydride Analyses [22] and use standard practices for digestion of sample for determination of metal (ASTM–D-1971) [23].

The concentration of Hg (II) in dental amalgam wastewater samples from a dental clinic is shown in Table 4.2

Table 4.2 Mercury content in dental amalgam wastewater from dental clinic. (Faculty of Dentristry, Chulalongkorn University)

Time(hr) Sampling(Patients)	Mercury concentration. (ppb.) / pH				
	9.00	10.30	13.30	15.00	18.00
1(488)	9.01/7	14.69/7	17.16/7	11.23/6	14.44/7
2(428)	19.14/7	9.14/6	9.63/6	7.65/6	4.69/6
3(460)	11.23/7	6.05/6	12.96/6	13.70/6	10.86/6
4(391)	19.26/6	11.48/7	8.88/7	7.41/7	16.17/7
5(333)	10.25/6	6.05/6	7.04/7	9.88/7	9.63/6
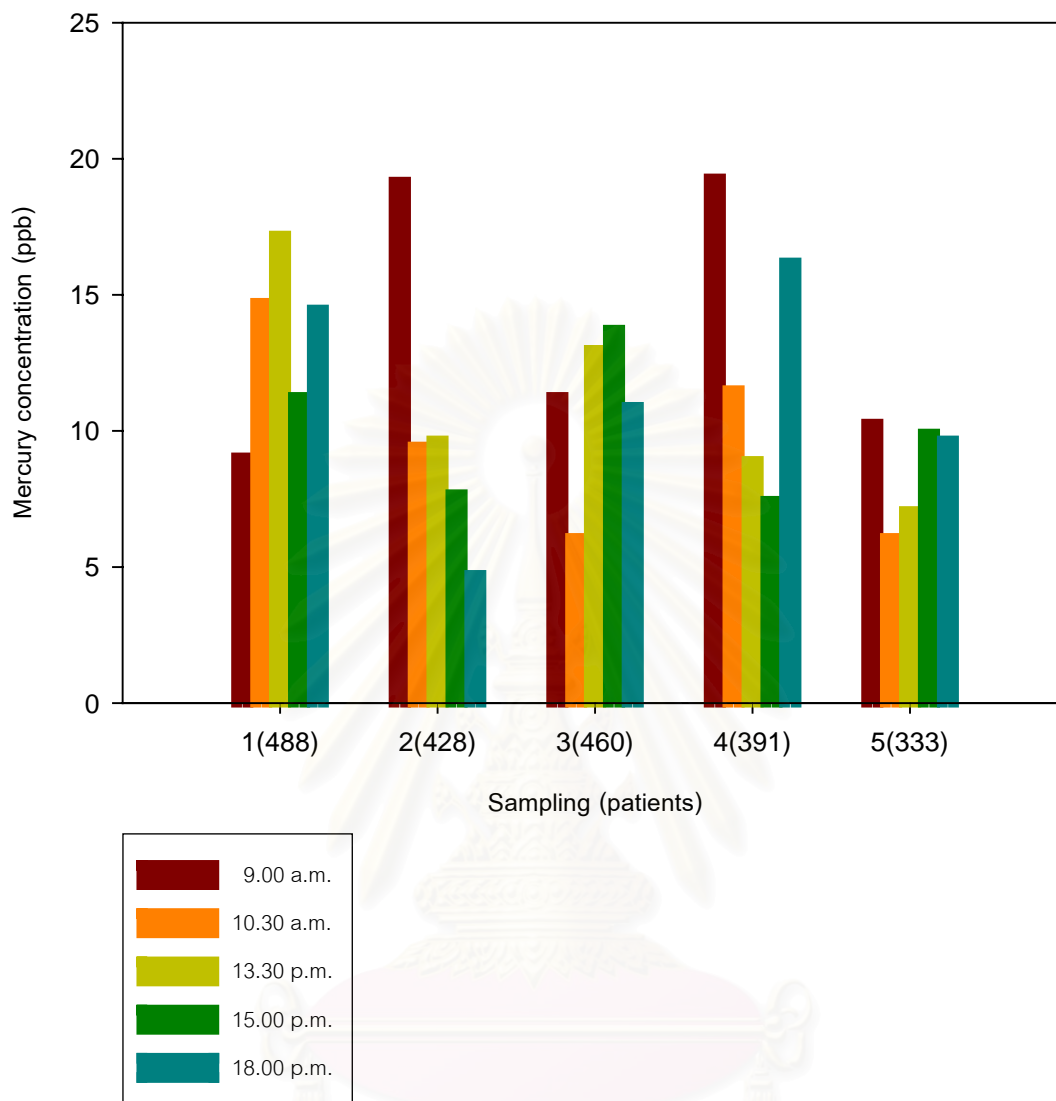
Figure 4.2 Mercury content found in dental amalgam wastewater for 5 days.

The highest value obtained was 19.26 ppb. The lowest value obtained was 4.69 ppb. and pH was between 6 and 7 for five consecutive days. The concentration of Hg (II) in the dental amalgam wastewater from dental clinic was found no direct correlation between the patients and the amount of Hg (II) concentration levels in dental wastewater. These observations are in accordance with the data by Senkpile,et.al [24], he determined the amount of mercury in the wastewater from one clinic on six consecutive days and found no direct correlation between the number of surface removed or produced and the amount of mercury determined in the wastewater. There is a research in Thailand reporting that the

effluent from university dental center and hospital had shown mercury concentration level 8.35 – 2,210.8 ppb. [16]. It is possible that amalgam particle previously setting in tubes and drains are continuously released from the drainage system result hight amount of mercury in wastewater. It is found that, mercury concentrations of dental amalgam wastewater from dental clinic almost are higher than standard value of the Ministry of Industry (5 ppb.).

The released Hg (II) is probably by dental amalgam work procedures. However major amalgam particles (around 15 %), surplus in trituration capsules and carved surplus are expected to be collected for recycling. Minor amalgam particles produced during carving, burnishing and polishing procedures will be sucked up and transported by the vacuum system. A part of the generated amalgam contamination sludge will be discharged with the sewage.

Regarding the highest Hg (II) concentration of ≈ 20 ppb, therefore the concentration of 1 ppm. Was prepared as a model solution. Because the requirement of the project is to use diatomite as the adsorbent in dental clinic drainage system which receives load of waste from dental procedure each day. So that the concentration of Hg (II) of 50 times higher is reasonable. Further Flameless Atomic Absorption Spectrometer have good detection limit of low concentration of Hg (II) (in expectation that 95 % of Hg (II) concentration is removed after treating with adsorbent and the remained would be the concentration of ppb. unit)

4.3 Investigate the optimum condition of Hg (II) removal from synthetic wastewater using diatomite by vary the pH, the contact time and the amount of adsorbent.

4.3.1 Contact time.

The results as shown in Table 4.3 and percentage removal mercury are plotted in Figure 4.3 (initial synthetic wastewater. (Hg (II) =1 ppm.)

Table 4.3 Concentration of Hg (II) after adsorb by diatomite at different contact time. (n=3)

Time (minute)	Remained Hg conc. (ppb.)	Percentage removal (%)
5	35.20	96.50
10	33.96	96.64
20	25.85	97.42
30	23.17	97.68
40	22.10	97.79
50	19.27	98.07
60	16.70	98.32
80	16.67	98.33
100	15.48	98.45
120	12.85	98.72
150	14.08	98.60
180	13.84	98.61
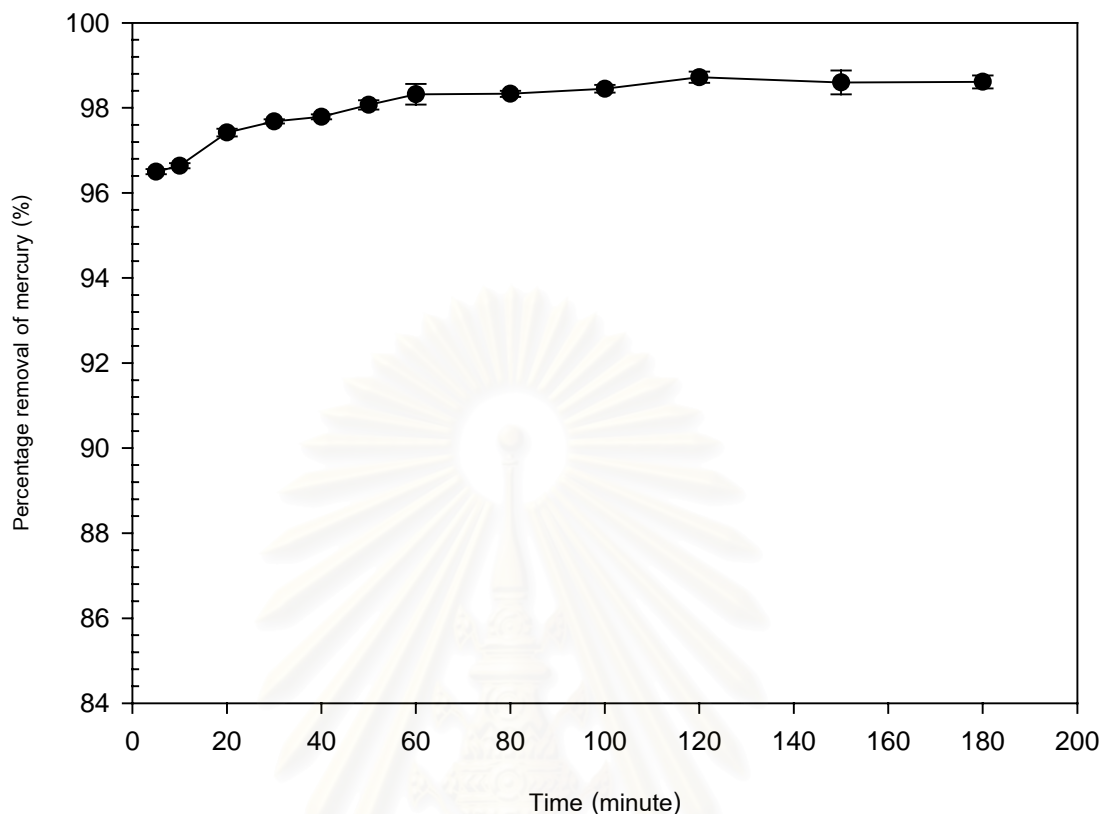
Figure 4.3 Percentage removal of Hg (II) by diatomite at different contact time.

From the experiment, the first 5 minutes of the contact time the percentage removal of mercury slightly increases from 96.50 – 98.72 % and remains at 98.07 – 98.61 % for 180 minutes. It is found that the contact time hardly effects the percentage removal of Hg (II). However the highest percentage removal of 98.72 % is at 120 minutes.

Due to diatomite consist of many Hydro silica and inorganic substance such as alumina, ferric and alkaline metal and the structure of diatomite is high complicated porous. So it is concluded that diatomite is appropriate to be adsorbent because of Hg (II) ion can adsorb into complicated porous and react with hydro silica group on the surface of diatomite.

4.3.2 pH of adsorption.

The results are shown in Table 4.4 and percentage removal Hg (II) are plotted in Figure 4.4 (initial synthetic wastewater. (Hg (II) =1 ppm, contact time 120 minutes)

Table 4.4 Concentration of Hg (II) after adsorption by diatomite at different pH. (n=3)

pH (of the solution)	pH (after)	Remained Hg conc. (ppb.)	Percentage removal (%)
3	8.03	21.08	97.89
4	8.02	18.82	98.12
5	8.03	18.37	98.16
6	8.05	18.53	98.14
7	8.25	22.85	97.70
8	8.26	22.15	97.79
9	9.25	22.36	97.76
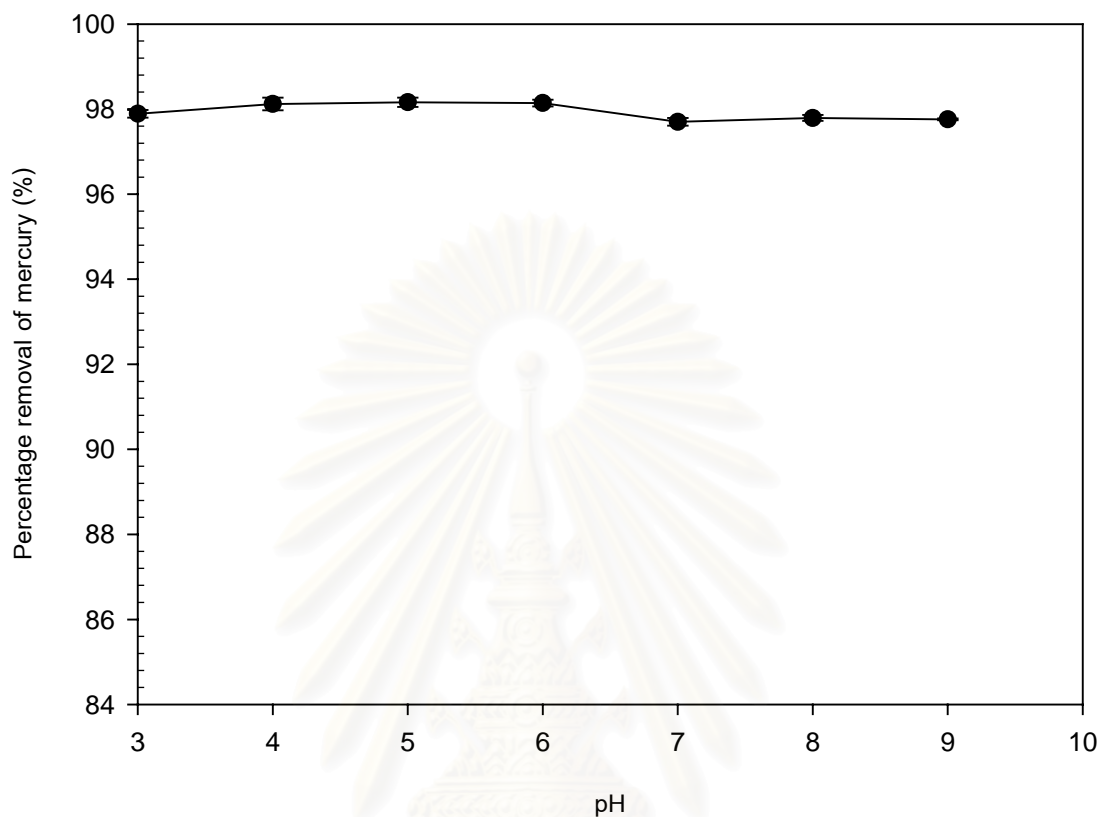
Figure 4.4 Percentage removal of Hg (II) by diatomite at different pH.

From the experiment, the pH vary of solution was varied in the range of 3-9, the percentage removal of Hg (II) slightly increase from 97.89%, 98.12%, 98.16% and 98.14% respectively at pH 3-9.

From the result, diatomite can adsorb Hg (II) at wide pH range. Whenever the pH starts increasing, the percentage removal of mercury will decrease. This declining will be at minimal level, as the percentage removal of mercury still maintains high at 97%. This shows that variation of pH will hardly effect to the efficiency of Hg (II) removal. The maximum pH for adsorbing Hg (II) is at pH 5.

Since diatomite contents of amorphous silica with mainly hydro silinol group (SiOH). This group will adsorb Hg (II) ion in the wastewater, then the decrease in adsorption may be explained by the loss of exchangeable ligands (H_2O or OH^-) from the surface. The concentration of the protonated surface functional groups will decrease with increasing pH, with a concomitant increase in the deprotonated groups [26]. The Hg (II) ion adsorption process can be illustrated by the reaction (as shows in equation 4.1)

$$Hg^{2+} \quad + \quad H_2O \quad \longrightarrow \quad HgOH^+ \quad + \quad H^+ \quad ....(4.1)$$
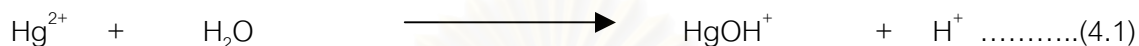
The diatomite surface may be negatively charge providing adsorption site for mercury ions : (as shown in equation 4.2 and 4.3) [26]

$$Si-O^- \quad + \quad HgOH^+ \quad \longrightarrow \quad SiOHgOH \quad ....(4.2)$$

$$Si-O^- \quad + \quad HgOH^+ + H_2O \longrightarrow \quad SiOHg(OH)_2 \quad .... (4.3)$$
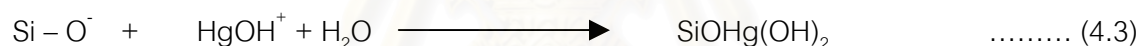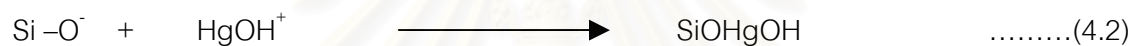
The increased concentration of the OH^- ion in solution with increasing pH may also contribute to reduce Hg (II) ion retention, particularly if both ligands are competing for the same surface functional groups.

4.3.3 Amount of adsorbent.

The results are shown in Table 4.5 and percentage removal Hg (II) are plotted in Figure 4.5 (initial synthetic wastewater (Hg (II) = 1 ppm, pH 5 and contact time 120 minutes)

Table 4.5 Concentration of Hg (II) after adsorb by diatomite at different amount. (n = 3)

| Amount of diatomite(g)	pH (after)	Remained Hg conc. (ppb.)	Percentage removal (%)
0.05	7.60	145.77	86.27
0.10	7.80	141.08	86.61
0.20	7.93	130.92	87.40
0.50	7.95	82.02	91.80
1.00	7.96	42.52	95.75
2.00	8.21	17.58	98.24
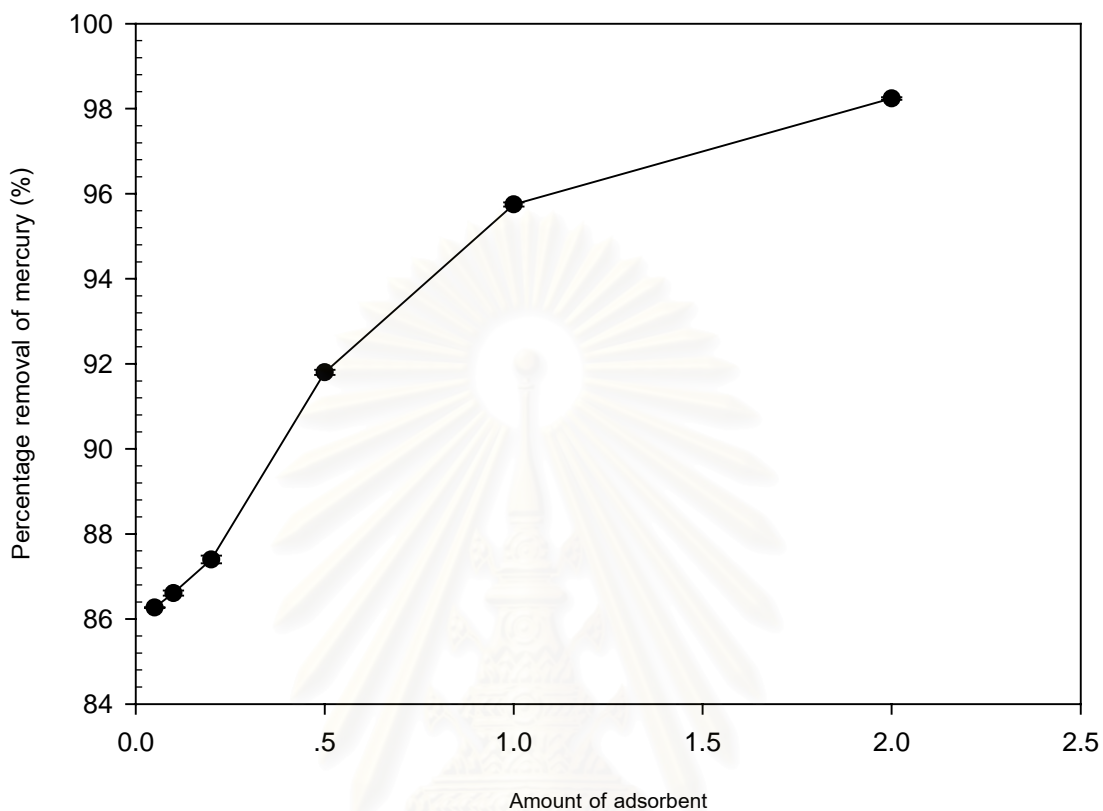
Figure 4.5 Percentage removal of Hg (II) by diatomite at different amount of diatomite.

From experiment, it found that using the amount of diatomite 0.05 g. can remove of mercury as high as 86.27%. When increasing of diatomite to 0.10, 0.20, 0.50, 1.00 and 2.00 g. the percentage removal of mercury will be 86.61%, 87.40%, 91.80%, 95.75%, 98.24%, respectively. This is due to increasing amount of diatomite that it has increased the porous surface and hydro silinol group [27] . The adsorption capacity of adsorbent is 0.096 mgHg / 1 g of diatomite. (Calculated at 1 g adsorbent used as shown in equation 4.4)

Adsorption capacity of adsorbent (q) $\quad = \quad \dfrac{(C_o - C_e) \times V}{M}$ ………(4.4)

C_0 = The concentration of initial mercury (ppm)

C_e = The concentration of remaining mercury (ppm)

V = Volume of solution (L)

M = Weight of adsorbent (g)

Adsorption capacity of adsorbent (q) $\quad = \quad \dfrac{(1 - 0.0425) \times (0.1)}{1}$

$\qquad\qquad\qquad\qquad\qquad\qquad = \quad$ 0.096 mgHg / g of diatomite.

Furthermore, Freudlich adsorption equation is used to explain mathematical description of adsorption in aqueous system. The Freudlich is expressed as :

$$X/M \quad = \quad KC_e^{1/n}$$ …………(4.5)

X   = The amount of solute adsorbed (mg)

M   = The weight of adsorbent (g)

C_e = The solute equilibrium concentration (ppm)

K   = Constant characteristic of system

1/n = Constant characteristic of system

For linearization of data, the Freudlich equation is written in logarithmic from :

$$\log X/M \quad = \quad \log K + 1/n \log C_e$$ ……………(4.6)

Study the characteristic on the amount of diatomite by isotherm of Freudlich adsorption method is as shown in Figure 4.6
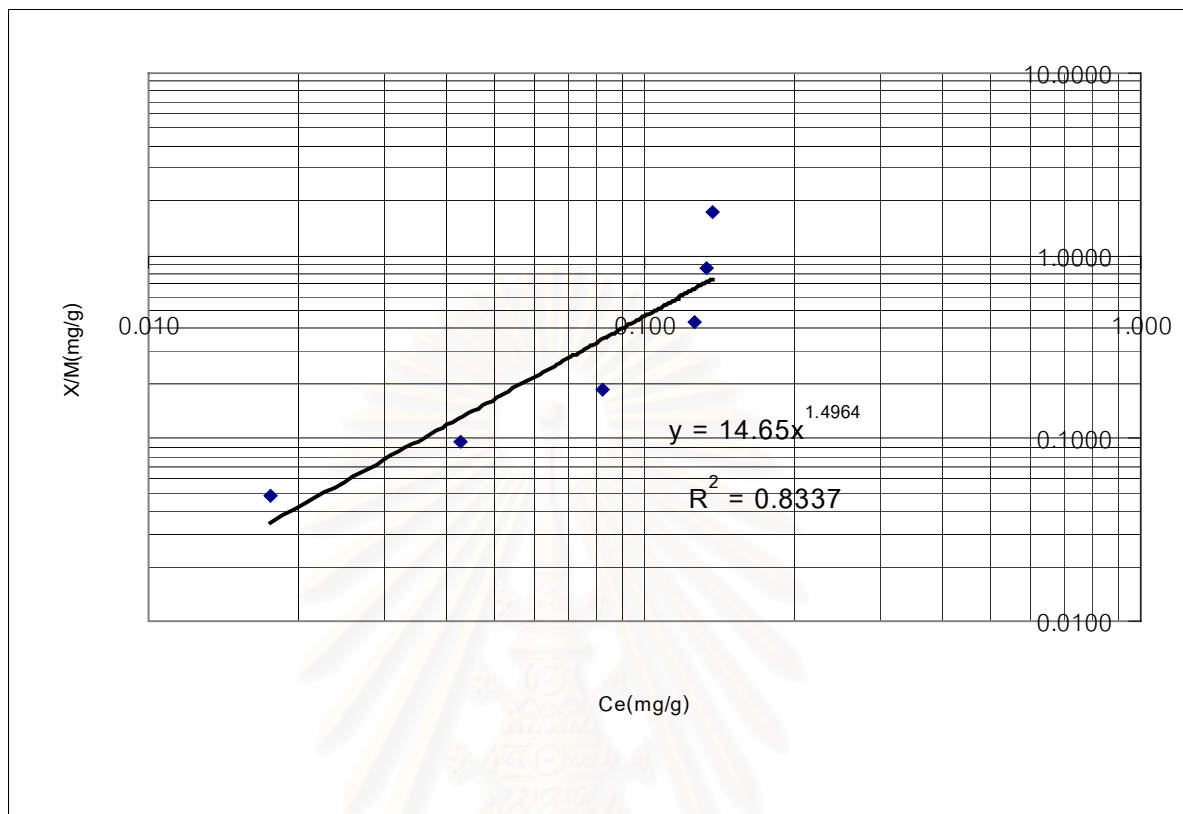
Figure 4.6 Adsorption isotherm of Hg (II) using diatomite. (at Hg (II) = 1 ppm, the contact time 120 minutes and pH 5)

K and 1/n factions from Freudlich equation can evaluate adsorption efficiency of diatomite as log K is the intercept of Y axis and 1/n is slope of straight line. It is shown in Table 4.6

Table 4.6 Equation and constant value of removal Hg (II) by diatomite from isotherm Freudlich. (Hg (II) = 1 ppm)

Equation	$Y = 14.65 \, X^{1.4964}$
K	14.65
1/n	1.4964

The value of 1/n is higher than 1, it means that diatomite showing good adsorption at high concentration of Hg (II) If the adsorption isotherm line is high slope will have higher efficiency in adsorption. While K value is the adsorption ability as here in K value is high of 14.65 that it indicates high absorbency to Hg (II) by diatomite.

4.4 Compare the Hg (II) removal efficiency of diatomite, activated carbon, chitosan and polymer. (Lewatit TP 214)

4.4.1 Compare the Hg (II) removal efficiency between diatomite and activated carbon.

Activated carbon can be made from any carbon containing raw material, e.g. coal, wood, nutshells or petroleum residues. Activated derived from bituminous coal is preferred for wastewater treatment. The result of comparison Hg (II) removal efficiency between diatomite and activated carbon is shown in Table 4.7 and Figure 4.7

Table 4.7 Comparison percentage removal of Hg (II) between diatomite and activated carbon at different amounts (n=3,each)

Amount of adsorbent (g)	Percentage removal (%)	
	Diatomite	Activated carbon
0.05	86.27	85.42
0.10	86.61	85.89
0.20	87.40	86.91
0.50	91.80	87.88
1.00	95.75	92.39
2.00	98.24	97.59

Figure 4.7 Comparison percentage removal of Hg (II) between different amount of diatomite and activated carbon

From the experiment, we found that using the amount of diatomite and activated carbon between 0.05-2.00 g. has percentage removal of Hg (II) between 85 - 97 %. The percentage removal of Hg (II) rapidly increases from 87.40 to 91.80, when using diatomite from 0.20 to 0.50 g. The percentage removal of Hg (II) rapidly increases from 86.91% to 92.39%, when using activated carbon from 0.20 to 1.00 g because activated carbon has many free pores sites for Hg (II) ion to be adsorbed. So that the removal efficiency of Hg (II) by diatomite is higher than activated carbon due to higher complicated porous of diatomite. It can be seen from SEM of diatomite and activated carbon (SEM of

diatomite is shown in Figure 4.8 and activated carbon is shown in Figure 4.9) and particle size of diatomite is smaller than of activated carbon (as shown in appendix E). Diatomite is a muti – component oxide system containing hydro silinol (SiOH) function group on the surface and has many complicated porous. The orders to adsorption rates are dependent upon the substitution of hydrogen in hydroxyl groups of diatomite. In aqueous $HgOH^+$ is formed and adsorption process is rapidly completed by interaction with negative charge on diatomite, but also diatomite absorbs metal ions by its outer sheet of hygroxyl groups. [27]
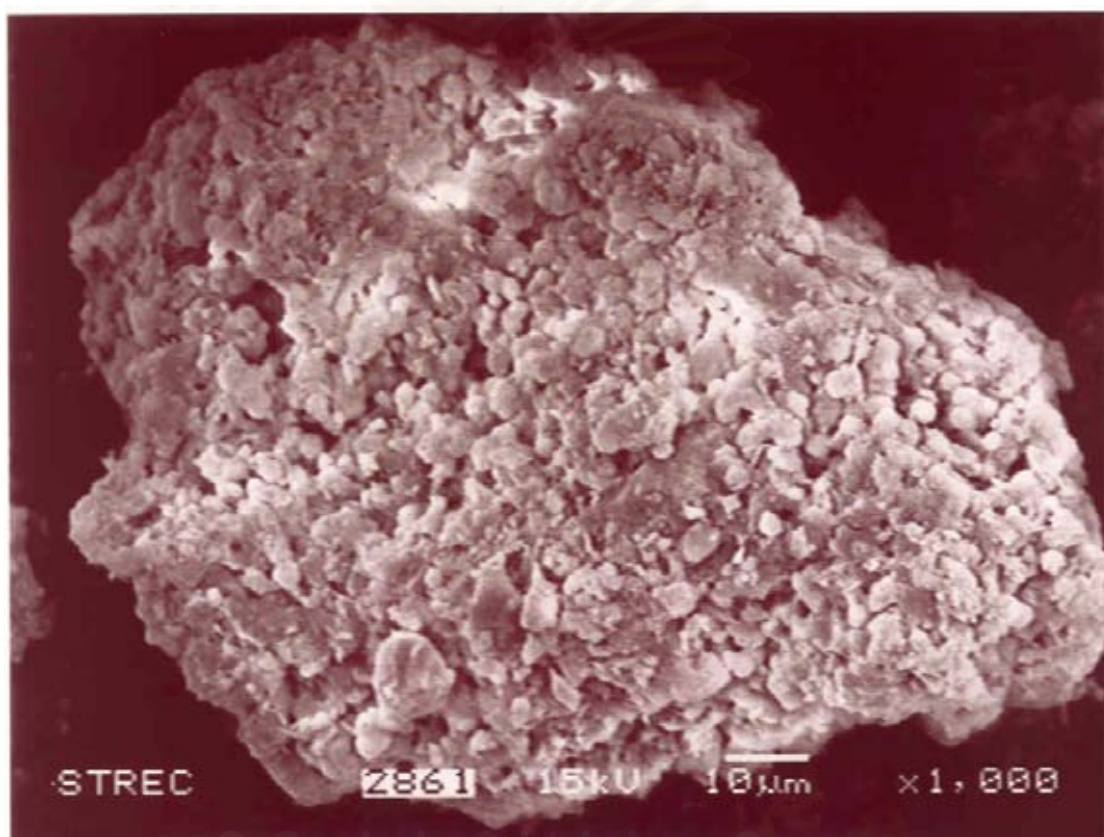
Figure 4.8 SEM of diatomite.
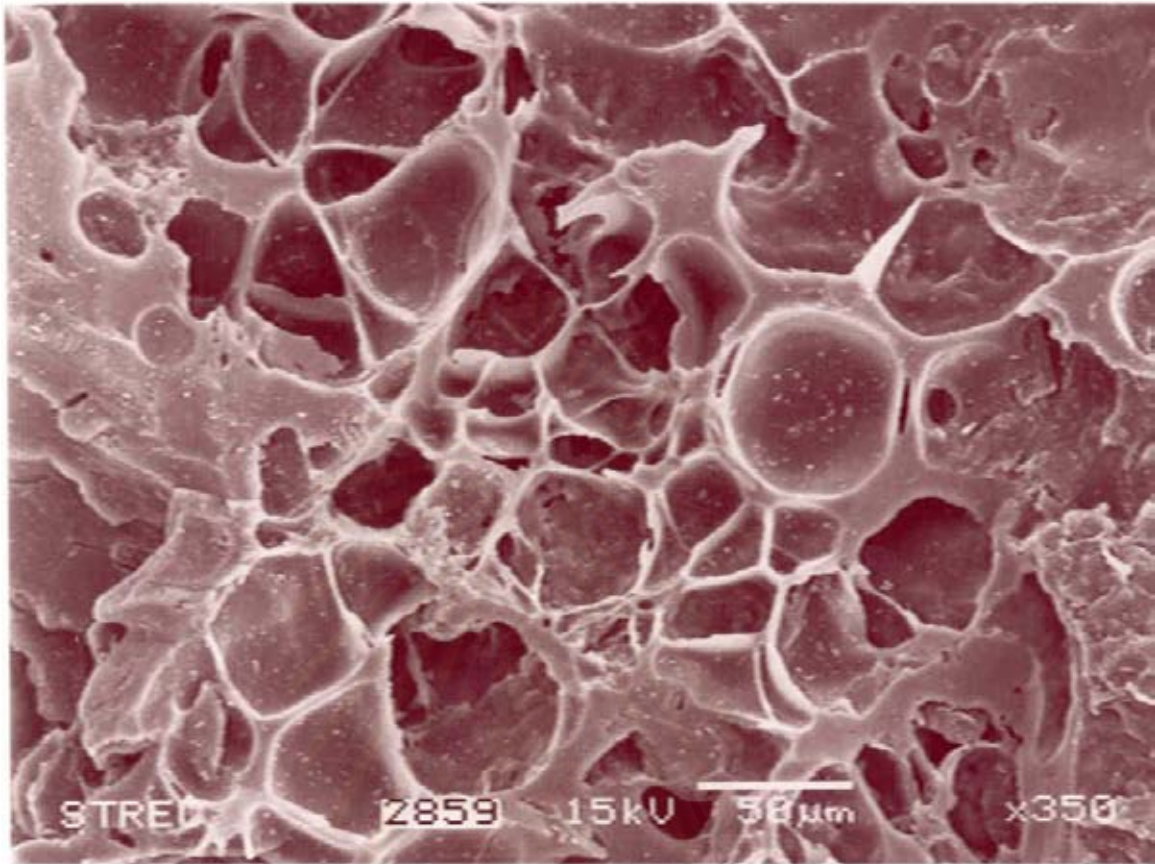
Figure 4.9 SEM of activated carbon.

The adsorption mechanism of Hg (II) in activated carbon happens in pore sites, molecules in the bulk of the solution must migrate to the carbon particle. Then they must migrate across a liquid film surrounding the particles, and thus into a pore. Thereafter they must migrate through the pore to finally come to rest on the ultimate adsorption site. When all of the available sites have been used up, the carbon particle is in equilibrium with the surrounding solution; and it has capacity for further adsorption is exhausted.

.

During the adsorption of metal ion in solution on porous adsorbents, there are essentially three consecutive stages involved : transport of the adsorbate to the external surface of the adsorbent, diffusion of the adsorbate into the pores of the adsorbent, and adsorption of the solute on the internal surface of the adsorbent. This last stage is, in general, relatively rapid, and if the stirring is made sufficiently high, the adsorption rate will be controlled by the rate of diffusion of the solute into the capillary pores of the adsorbent.[28]

4.4.2 Compare the Hg (II) removal efficiency between diatomite and chitosan

Chitosan, essentially poly-D-glucosamine, is a polymer obtained by extensive deacetylation of chitin. It is capable of adsorbing a number of metal ions including Hg^{2+}. chitosan can be considered as a microporous material. When an amorphous polymer is below its glass transition, the thermal movements of the chain segment are restricted in such a way that pores resulting from irregularities in molecular packing actually exist [28]. Because of the relatively bulky chitosan chains, pores are large enough to let small molecule and ions passing through. The result of comparison removal efficiency Hg (II) between diatomite and chitosan are shown in Table 4.8 and Figure 4.10

Table 4.8 Comparison percentage removal of mercury between diatomite and chitosan at different amount. (n=3,each)

Amount of adsorbent (g)	Percentage removal (%)	
	Diatomite	Chitosan
0.05	86.27	97.74
0.10	86.61	97.89
0.20	87.40	98.16
0.50	91.80	98.47
1.00	95.75	98.79
2.00	98.24	99.08

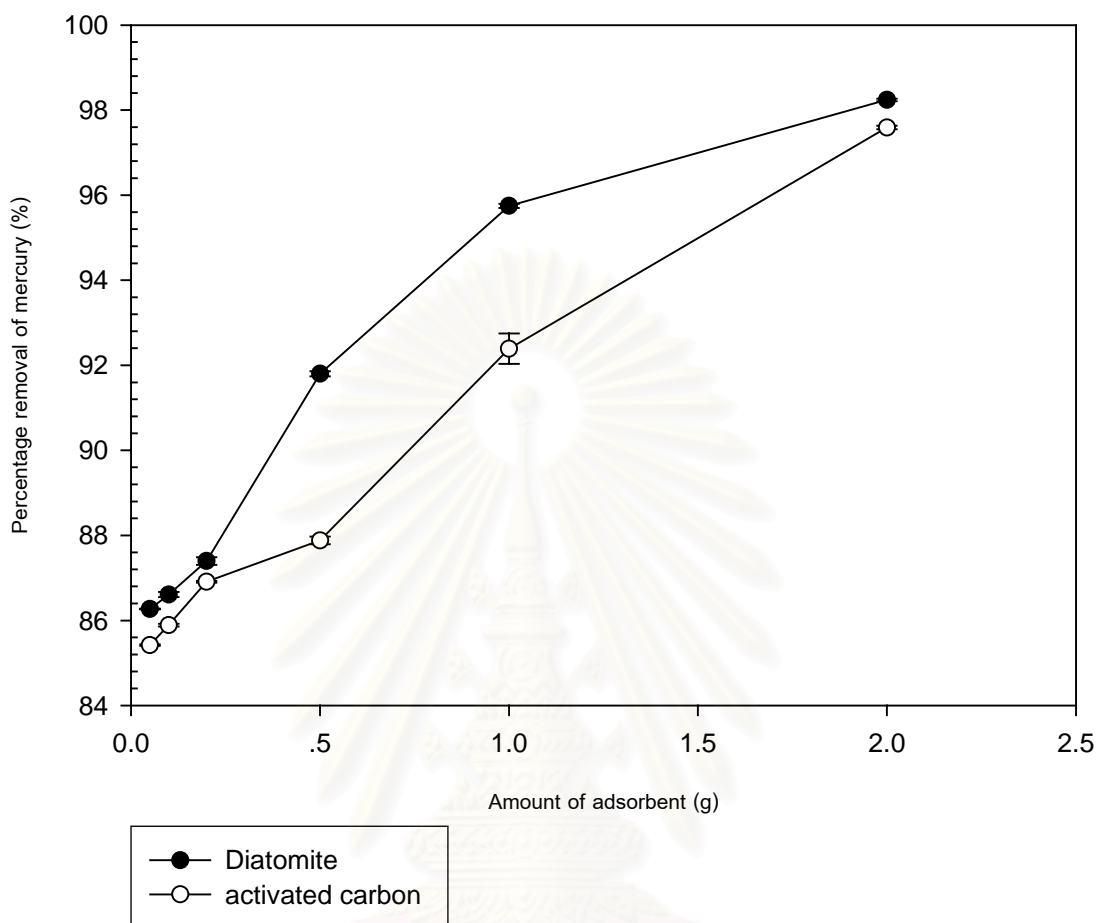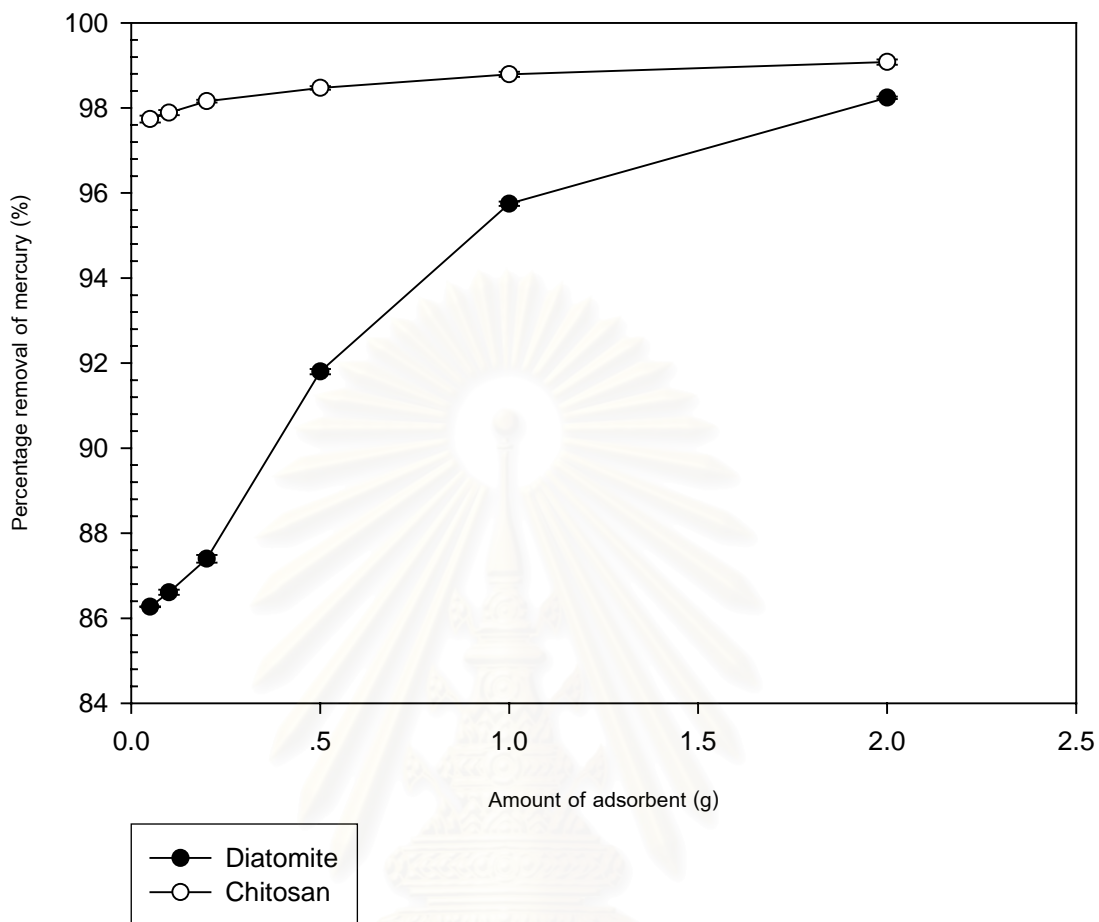**Figure 4.10** Comparison percentage removal of Hg (II) between different amount of diatomite and chitosan.

From the experiment, the percentage removal of Hg (II) is 97.74% at the amount of chitosan 0.05 g. While using as high of 2.00 g of diatomite can achieve of Hg (II) removal efficiency (98.24%) close to 0.05 g of chitosan. The advantage of chitosan over diatomite is due mainly to complexation of the Hg (II) with a number of the amino groups of long polysaccharide chain on chitosan.[28], with the constant efficiency rate. Meanwhile diatomite gradually increases with the amounts due to the increasing number of porous areas and hydro silinol groups of diatomite.

4.4.3 Compare the removal Hg (II) efficiency between diatomite and polymer. (Lewatit TP 214)

Lewatit TP 214 is a macroporous cations exchange resin with chelating thiocarbamide group. It is used for the removal of Hg (II) from the effluents of chloralkali electrolysis plants using mercury cell and from neutralized mixed effluents. So Lewatit TP 214 was choose to be the adsorbent in this experiment. The result are shown in Table 4.9 and Figure 4.11

Table 4.9 Comparison percentage removal of Hg (II) between diatomite and polymer (Lewatit TP214) at different amount. (n=3, each)

Amount of adsorbent (g)	Percentage removal (%)	
	Diatomite	Polymer (Lewatit TP 214)
0.05	86.27	85.72
0.10	86.61	90.77
0.20	87.40	97.63
0.50	91.80	99.15
1.00	95.75	99.32
2.00	98.24	99.46
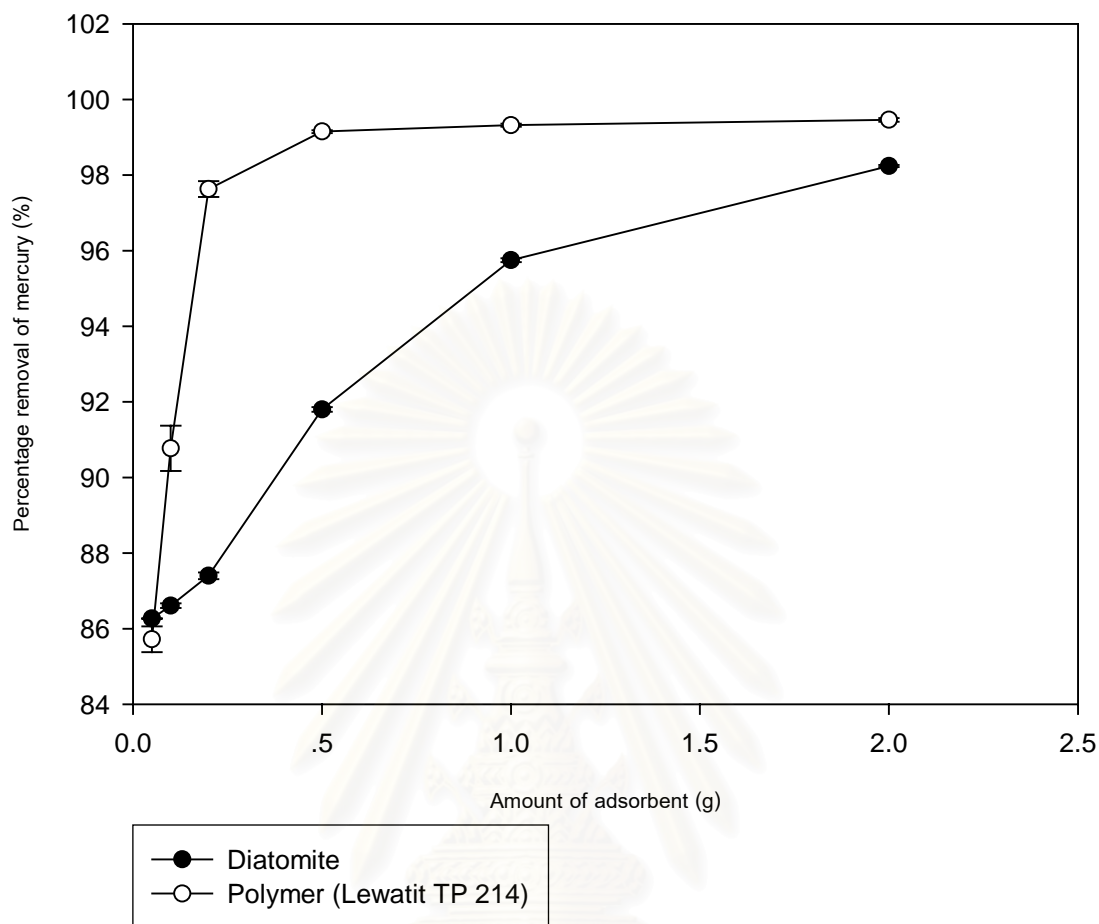
Figure 4.11 Comparison percentage removal of Hg (II) between different amount diatomite and polymer. (Lewatit TP 214)

From experiment, the percentage removal of Hg (II) is as high as 90.77% at the amount of polymer (Lewatit TP 214) 0.10 g. and increased rapidly to 99.15% by using polymer of 0.05 g. While the percentage removal of Hg (II) increases from 86.27% to 98.24% by using diatomite up to 2.00 g. The efficiency removal of Hg (II) by polymer (Lewatit TP 214) is higher than diatomite as by polymer (Lewatit TP 214) uses ion exchange between specific functional group on surface of polymer and Hg (II) ion solution and that performing faster is than diatomite.

Lewatit TP 214 has a cation exchange with chelating thiocarbamide group. Mechanism of ion exchange reactions have identified the possible rate controlling three Steps. (as shown in Figure 4.12)
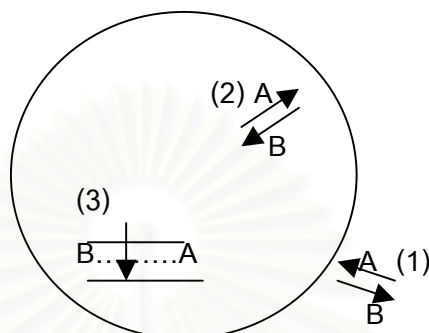
Figure 4.12 Rate determining steps in ion exchange.

Step 1 : Coupled Diffusion of Counter – Ion in the External Solution

Rate control by mass transfer in the "external" solution is interpreted as coupled mass transfer across the hypothetical film or nernst layer surrounding the polymer particle by mechanism of diffusion call film diffusion.

Step 2 : Coupled Diffusion of Counter –Ion in the polymer

Mass transfer in the film and polymer are sequential processes and either process may be rate controlling. Polymer phase diffusion coefficients are about one or two order of magnitude smaller than found for aqueous solution because of the steric resistance. The hindrance effect of thee hetergeneous in polymer structure on the ions diffused to the inside of polymer, offered by copolymer matrix.

Step 3 : Chemical Reaction Rate Control

The true chemical reaction at the sites of the functional groups is represented purely schematically in Figure 4.12 by an imaginary transition state complex between ions A, B and the Hg (II) groups. Such a concept involved the making and breaking of ionic, covalent bond. Reactions between simple, freely dissociated, aqueous ions are usually very fast and therefore not rate controlling, but some research papers suggest chemical reaction rate control for the exchange of transition metal ions or complex

ions capable of strong chelate, which occur by following the chelating step, the co – ordination complex formation between the heavy metal and electron pair donating ligands.

We are able to compare Hg (II) removal efficiency of diatomite, activated carbon, chitosan and polymer (Lewatit TP 214), in term of the adsorption capacity of adsorbent (q). They calculate used is from the equation of (3.2) The result is shown in Table 4.10 and is plotted in Figure 4.13

Table 4.10 Adsorption capacity of adsorbent.

Adsorbent	(Adsorption capacity : mgHg/g adsorbent)
Diatomite	0.096
Activated carbon	0.092
Chitosan	0.098
Polymer(Lewatit TP 214)	0.099

$$\text{Adsorption capacity of adsorbent (q)} \quad = \quad \frac{(C_o - C_e) \times V}{M}$$

C_0 = The concentration of initial mercury (ppm)

C_e = The concentration of remaining mercury (ppm)

V = Volume of solution (L)

M = Weight of adsorbent (g)

C_e of activated carbon is 0.076 ppm.

C_e of chitosan is 0.012 ppm.

C_e of polymer (Lewatit TP 214) is 0.0068 ppm.

Adsorption capacity of adsorbent (q)　　=　　$\dfrac{(1 - 0.076) \times (0.1)}{1}$

　　=　　0.092 mgHg / g of activated carbon.

Adsorption capacity of adsorbent (q)　　=　　$\dfrac{(1 - 0.012) \times (0.1)}{1}$

　　=　　0.098 mgHg / g of chitosan.

Adsorption capacity of adsorbent (q)　　=　　$\dfrac{(1 - 0.0068) \times (0.1)}{1}$

　　=　　0.099 mgHg / g of polymer. (Lewatit TP 214)

From Table 4.10 adsorption capacity of adsorbent (q) of diatomite, activated carbon, chitosan and polymer (Lewatit TP 214) is 0.096, 0.092, 0.098, 0.099 mgHg/g adsorbent respectively. The degree of adsorption capacity of adsorbent (q) are as follows polymer $\geq$ chitosan > diatomite > activated carbon.The adsorption capacity of adsorbent (q) and efficiency removal of Hg (II) by diatomite is quit similar to polymer and chitosan but higher than activated carbon.
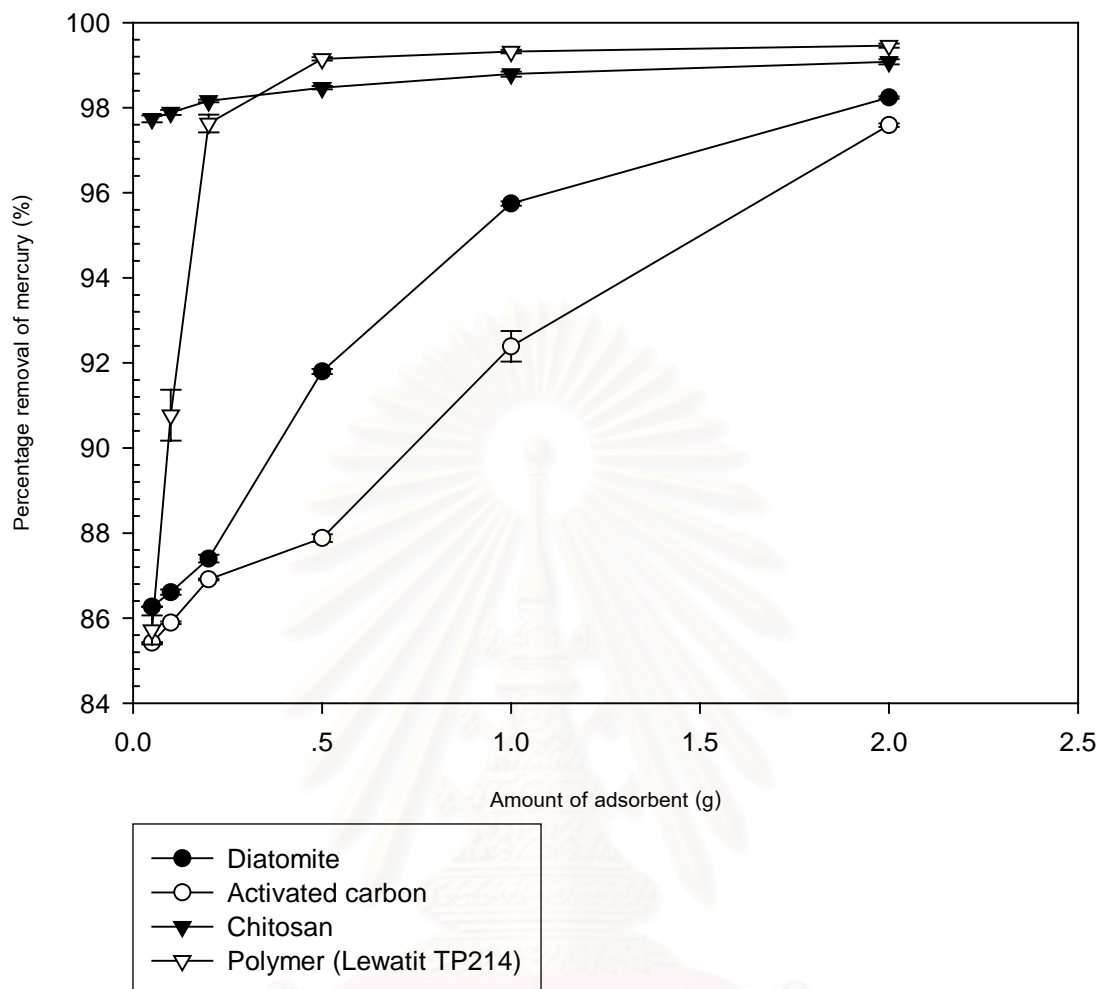
Figure 4.13 Comparison percentage removal of Hg (II) between diatomite and other adsorbents.

It can be noticed that chitosan is high efficiency to remove Hg (II) at any amount. Meanwhile polymer is more efficiency at the amount from 0.2 g. Polymer and chitosan have similar adsorption mechanism between Hg (II) ion and specific groups (amino group in chitosan and thiocarbamide in polymer) the percentage removal of Hg (II). Both of diatomite and activated carbon slightly increase because diatomite and activated carbon have adsorption mechanism at pore site in the initial state. In addition to the pore site, diatomite has the interaction of Hg (II) ion formed with hydro silinol groups.

However the research development is required in order to improve its application to suit the dentistry.

Apart from the adsorption capacity of four adsorbents, the cost of each adsorbent is compared (Table 4.11) . Chitosan is the most expensive as it has many production process. Polymer gives the best adsorption capacity and the price is reasonable (Baht 9.0 / kg) , however it has to be imported. Diatomite, commonly found in Thailand, gives a good adsorption capacity of 0.096 mgHg / g of diatomite and the cheapest price of Baht 2.00 / kg . Thus, diatomite can be considered as the appropriated adsorbent for removing Hg (II) due to cheap cost with high removal Hg (II) efficiency.

Table 4.11 Comparison of efficiency and cost of adsorbent.

Adsorbent	Adsorption capacity (mgHg / g of adsorbent)	Price (Baht / Kg)
Diatomite	0.096	2.0
Activated carbon	0.092	6.0
Chitosan	0.098	412.0
Polymer (Lewatit TP 214)	0.099	9.0

4.5 Removal efficiency of diatomite at optimum condition in dental amalgam wastewater from dental clinic. (Faculty of Dentistry, Chulalongkorn University)

The initial concentration of Hg (II) in dental amalgam wastewater collected (2 bottles) were 20.42 and 14.43 ppb. pH 6. After removal the Hg (II) with diatomite at different amount, it is found than 0.05 g. of diatomite can reduce the concentration of Hg (II) in the wastewater less than 5 ppb. The result is shown in Table 4.12 and is plotted in Figure 4.14

Table 4.12 Remain Hg (II) concentration after adsorb by diatomite.

Amount of diatomite	Remained Hg (II) conc. (ppb)			Percentage removal of dental wastewater (Average)
	1 (20.42 ppb.)*	2 (14.43 ppb.)*	3 (14.43 ppb.)*	
0.05	3.68	3.12	3.24	79.30
0.10	3.06	2.37	2.46	83.84
0.20	2.46	2.04	2.11	86.40
0.50	1.63	1.21	1.13	91.93
1.00	<1	<1	<1	>95
2.00	<1	<1	<1	>95

● Concentration of Hg (II) in dental amalgam wastewater. (ppb.) (before removal)

From experimental it found that in synthetic wastewater the adsorption capacity of diatomite is 0.096 mgHg/g (1 g. of diatomite can remove Hg (II) = 96 ppb.) If Hg (II) concentrations in dental amalgam wastewater are 20.42 and 14.43 ppb, it cans calculate that the weight of diatomite to use are 0.21 and 0.15 g ,respectively.

Calculate the weight of diatomite.

Mercury concentration   96   ppb. use diatomite to treat at   1   g

If mercury concentration 20.42 ppb use diatomite to treat at   (1 x 20.42) / 96   g

                                                         =   0.21 g

Mercury concentration   96   ppb. use diatomite to treat at   1   g

If mercury concentration 14.43 ppb use diatomite to treat at   (1 x 14.43) / 96   g

                                                         =   0.15 g

In the actual experimental of removal Hg (II) in dental amalgam wastewater if uses the amount of diatomite from calculation, it is unable to have fully achievement on removal Hg (II) in dental amalgam wastewater.
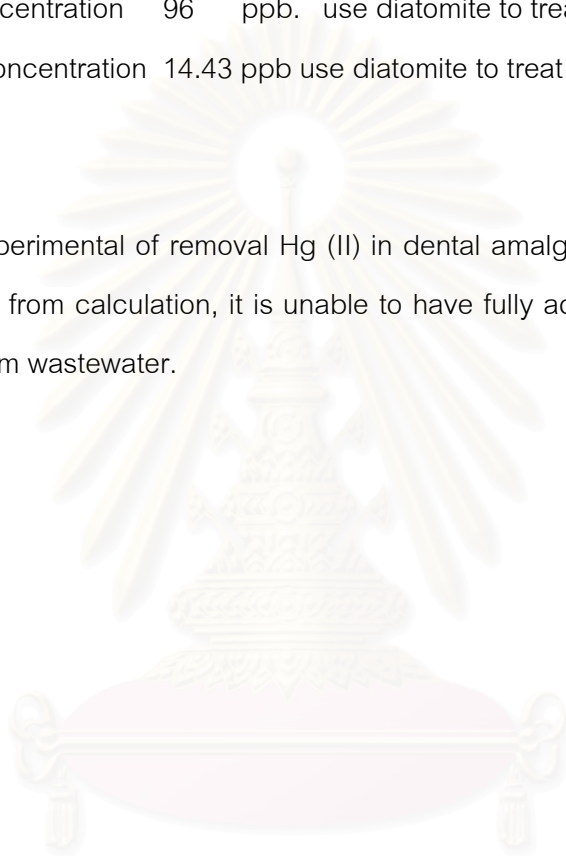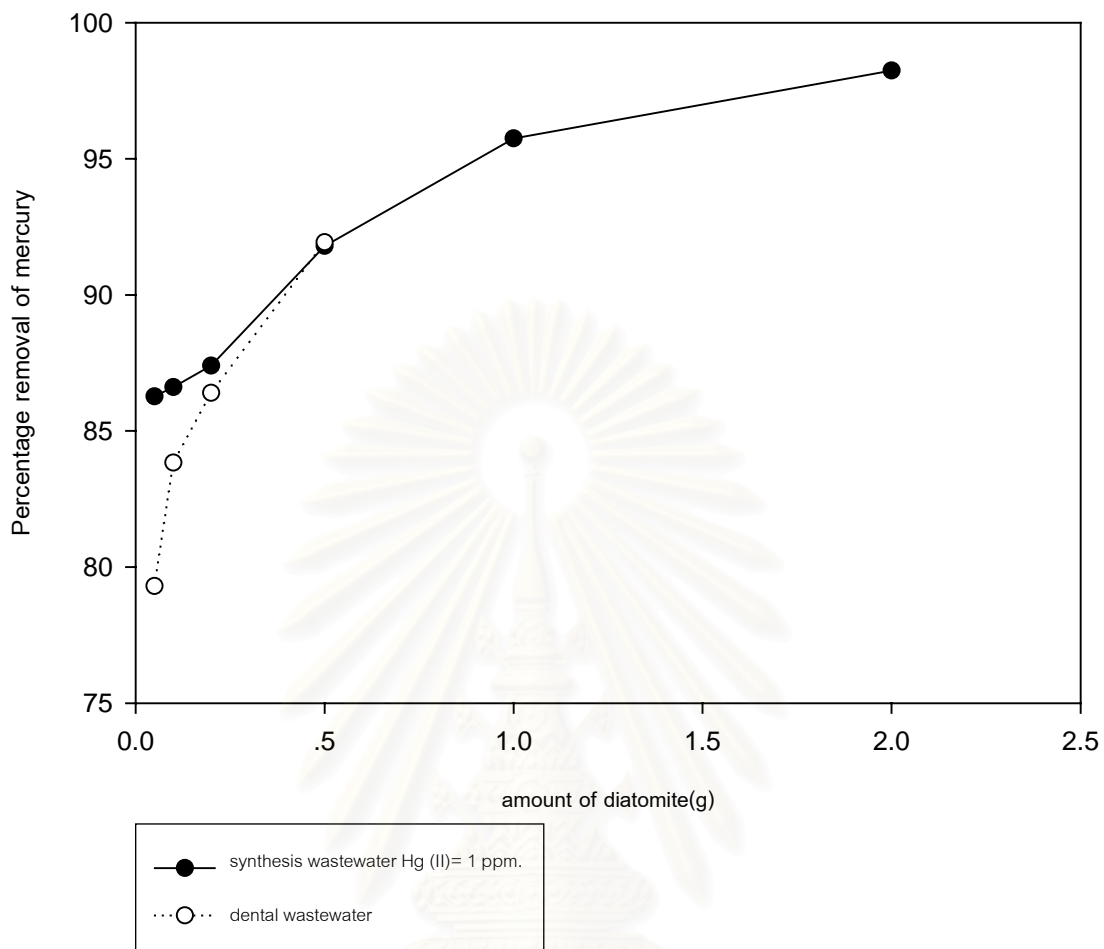
Figure 4.14 Comparison percentage removal of Hg (II) by diatomite between synthesis wastewater (Hg (II) =1ppm) and dental amalgam wastewater.

Using 0.05 g. of diatomite can remove Hg (II) from synthesis wastewater (Hg (II) = 1 ppm.) 86.27% whereas 79.30 % is obtained from dental wastewater. The percentage removal was slightly lower than synthesis wastewater Hg (II) because dental wastewater contains mercury ion, methylmercury and other metal ion which can compete the adsorption of Hg (II) by diatomite but the synthesis wastewater contains only Hg (II) ion.

If it is compare to work of Pederson [29] ,the removal of mercury from the dental – unit wastewater effluent by combination of two copolymers (N8186 and 93NP058 NALCO), shows a removal of 94.8% - 97.6% of the total (soluble and insoluble) mercury. Therefore

diatomite has good efficiency as polymer for the dental amalgam wastewater treatment. Thus, diatomite can be considered as an alternative material due to a good efficiency, low cost and availability from natural resources.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions are drawn from the study:

1. The highest Hg (II) concentration obtained from dental clinic (Faculty of Dentistry, Chulalongkorn University) was 19.26 ppb. And the lowest Hg (II) concentration obtained was 4.69 ppb.

2. The advantage of using diatomite adsorbent is wide range pH and short the contact time. The optimum conditions for use in this study is pH 5 at 120 minutes of the contact time. Adsorption capacity of adsorbent (q) is equal to 0.096 mg Hg / g diatomite.

3. Absorbency mechanism on diatomite probably involves two types of absorbency: porous type and complexity with hydro silinol group type.

4. The degree of adsorption capacity of adsorbent and efficiency removal of mercury are as follows polymer $\geq$ chitosan > diatomite > activated carbon.

5. Diatomite can be considered as an alternative material to removal mercury in dental amalgam wastewater due to high efficiency, low cost and availability from natural resources.

5.2 Suggestions.

1. The use of amalgam removal in drainage system for dental clinic should be considered in order to reduce the concentration of Hg (II) in dental wastewater in Thailand.

2. A similar study should be conducted in continuous process such as fixed bed in order to study capacity and lifetime of adsorbent.

3. This research has to be done for study in the effect of other metals that having in the dental amalgam wastewater influence to the absorbency.

4. Study the leaching ability of mercury wastewater from the applied diatomite.

5. Developing of diatomite for the highest efficiency for treating of mercury wastewater for industrial uses.

6. Study on applying of diatomite for absorbency of other heavy metals in the industrial fields such as lead, cadmium, arsenic, chromium and etc.,

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APPENDICES

APPENDIX A

Standard Practices for Digestion of Samples for Determination of metal by Flame Atomic Absorption or Plasma Emission Spectroscopy.

1. Summary of practice.

Samples are acidified with HNO_3 and HCl and heated on a hot plate or steam bath to reduce the volume to a defined level. After filtration, the samples are ready for analysis by atomic absorption spectrophotometry or plasma emission spectroscopy.

2. Apparatus.

Steam Bath or Hot Plate.

3. Reagents and materials.

3.1 Hydrochloric Acid (sp gr 1.19) – Concentrated hydrochloric acid (HCl)

3.2 Nitric Acid (sp. Gr. 1.42) – Concentrated nitric acid (HNO_3)

3.3 Filter paper – fine textured, acid washed, ashless, No. 19

4. procedure

4.1 Measure 100 ml of a well mixed sample into a 125 ml beaker or flask. Add 0.5 ml of HNO_3

4.2 Add 5 ml of HCl to the beaker or flask

4.3 Heat the samples on a stream bath or hot plate in a well – ventilated hood until the volume has been reduced to 100 ml to 20 ml, making certain that the sample does not boil. When analyzing samples containing appreciable amounts on solid matter, the   actual amount of reduction in volume is let to the discretion of the analyst.

4.4 Cool and remove solids. Quantitatively transfer sample to 100 ml volumetric flask. Adjust the volume.

4.5 Proceed with assay of digested sample by atomic absorption spectrophotometry or plasma emission spectroscopy.

APPENDIX B

Recommended Analytical Parameter for Mercury with NaBH$_4$

In order to become familiar with the feature and operation of the Flow injection Analysis – Mercury Hydride System (FI – MH –AAS), it strongly recommended that the analyst work through the example described in the FI – MH – AAS manual when operating the system for the first time.

With the FI – MH – AAS, system calibration and sample analysis are similar to the corresponding procedures for automated flame atomic absorption.

<u>Sample Handing and Preservation</u>

Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through small glass apparatus before the acid is added. For total mercury the filtration is omitted.

<u>Spectrometer</u>

Technique	AA
Integration Time (s)	20
Data Processing	Peak Height, Smoothing : 0.5 sec or 19 points
Lamp	HCl or EDL
Slit (nm)	0.7
Wavelength (nm)	253.7
Cell Temperature	100 $^{\circ}$C

<u>Reagent</u>

Carrier Solution :   3%(v/v) HCl

Reducing Agent :   0.2% $NaBH_4$ in 0.05%NaOH

Sample Solution : Hg^{2+} in slinghtly acidified solution

Mercury solution, Stock (1 ml = 1 mg/Hg) : Dissolve 0.1354 g of mercuric chloride ($HgCl_2$) in mixture of 75 ml of water and 10 ml of HNO_3 (sp gr 1.42) and dilute to 100 L with water.

Mercury Solution, Standard (1 ml = 10 μg Hg) : Pipet 10.0 ml of the stock mercury solution into a mixture of 500 ml of water and 2 ml of HNO_3 (sp gr 1.42) and dilute to 1 L with water. Prepare fresh daily.

<u>Sensitivity Check</u>

Relative or solution sensitivity (μg/L of analyte to produce a signal of 0.0044 A) for FI – NH – AAS is comparable with that obtained using other MHS techniques. Because FI – MH – AAS requires much smaller sample sizes, however the absolute sensitivity (nanograms of analyte to produce a signal of 0.0044A) attainable is significatly better than for most other MHS techniques.

The sensitivity of FI – MH – AAS determinations can, within liits, be adjusted to suit the concentration of the samples by varying the volume of the injection loop by changing the analytical wave – length.

Analysis of 500 μL of a 10 μg/L mercury solution should provide a signal of about 0.07 A.

<u>Replicates</u>

As FI – MH –AAS normally requires only 0.5 ml (500 μL) or less for each determination, the solution in one autosample vial can be used for a number of replicates. However, reproducibility for FI – MH – AAS is very good. As a result, the number of replicated determinations necessary to obtain required precision levels is usually small.

<u>Notes</u>

The flow of carrier should be increased to 70 – 100 ml/min to achieve quoted sensitivity.

Mercury sample and standard solutions should be stabilized by the addition of 1 – 2 drops of a 5% $KmnO_4$ solution.

The HCl acid concentration should be kept to a minimum to prevent the premature reduction of $KmnO_4$. Normally 1 ml conc. HCl for 100 ml of sample reference solution is sufficient. Low mercury concentration < 10 μg/L may be absorbed on the walls of the sample cups, this depends on the type of material used. The cups should be checked for their behavior.

APPENDIX C

Table C-1 Data of Hg (II) concentration at different contact time.(initial Hg (II)=1ppm,100mL)

Experiment	Number	Time (min)	Weight (g)	Initial pH	After pH	[Hg] ppb	% remove
1	1	5	2.0002	4.45	7.76	35.57	96.44
	2		2.0004		7.65	34.46	96.55
	3		2.0003		7.82	35.07	96.49
2	1	10	2.0004	4.45	7.67	33.22	96.68
	2		2.0007		7.54	33.35	96.67
	3		2.0001		7.52	34.33	96.57
3	1	20	2.0004	4.45	7.31	25.69	97.43
	2		2.0000		7.34	25.07	97.49
	3		2.0001		7.34	26.80	97.32
4	1	30	2.0004	4.45	7.15	23.10	97.69
	2		2.0001		7.11	22.73	97.73
	3		2.0003		7.18	23.72	97.93
5	1	40	2.0003	4.45	7.30	21.99	97.80
	2		2.0004		7.30	22.73	97.73
	3		2.0005		7.29	21.62	97.84
6	1	50	2.0005	4.45	7.22	20.38	97.96
	2		2.0004		7.18	18.28	98.17
	3		2.0005		6.92	19.15	98.09
7	1	60	2.0007	4.45	7.15	16.68	98.33
	2		2.0005		7.17	18.94	98.41
	3		2.0004		7.23	17.54	98.15
8	1	80	2.0003	4.45	7.29	17.42	98.16
	2		2.0004		7.46	16.68	98.33
	3		2.0008		7.60	15.94	98.41
9	1	100	2.0001	4.45	7.81	14.46	98.55
	2		2.0006		7.80	15.82	98.42
	3		2.0002		7.82	16.19	98.38

Table C-1 Data of Hg (II) concentration at different contact time. (continue)

Experiment	Number	Time (min)	Weight (g)	Initial pH	After pH	[Hg] ppb	% remove
10	1	120	2.0009	4.45	7.85	13.47	98.65
	2		2.0009		7.92	11.34	98.86
	3		2.0003		7.94	13.72	98.63
11	1	150	2.0004	4.45	8.00	16.68	98.33
	2		2.0007		8.12	11.12	98.89
	3		2.0001		8.24	14.46	98.55
12	1	180	2.0004	4.45	7.45	14.58	98.54
	2		2.0003		7.65	14.83	98.52
	3		2.0006		7.48	12.11	98.79

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Table C-2 Data of Hg (II) concentration at different pH. (initial Hg (II) = 1ppm,100 mL,
shaking 120 minutes)

Experiment	number	Weight (g)	Initial pH	After pH	[Hg] ppb	%remove
1	1	2.0004		8.03	20.11	97.79
	2	2.0001	3.00	8.03	20.39	97.96
	3	2.0006		8.05	20.75	97.93
2	1	2.0008		8.02	17.05	98.30
	2	2.0004	4.00	8.02	19.64	98.04
	3	2.0003		8.01	19.76	98.02
3	1	2.0005		8.01	19.64	98.04
	2	2.0005	5.00	8.02	17.67	98.23
	3	2.0003		8.05	17.79	98.22
4	1	2.0006		8.02	19.15	98.09
	2	2.0003	6.00	8.05	18.78	98.12
	3	2.0008		8.08	17.67	98.23
5	1	2.0007		8.21	23.84	97.62
	2	2.0006	7.00	8.21	21.99	97.80
	3	2.0008		8.34	23.22	97.68
6	1	2.0003		8.29	21.49	97.85
	2	2.0003	8.00	8.22	22.11	97.79
	3	2.0005		8.25	22.85	97.75
7	1	2.0003		9.25	22.61	97.74
	2	2.0008	9.00	9.27	22.36	97.76
	3	2.0001		9.22	22.11	97.79

Table C-3 Data of Hg (II) concentration at different amount of diatomite.

(initial Hg (II) = 1ppm, 100 mL, pH 5 and shaking 120 minutes)

Experiment	Number	Weight (g)	Initial PH	After pH	[Hg] ppb	% remove
1	1	0.0506		7.30	137.30	86.27
	2	0.0505	5.04	7.69	137.17	86.28
	3	0.0508		7.80	134.42	86.26
2	1	0.1004		7.76	133.34	86.67
	2	0.1006	5.04	7.81	134.46	86.55
	3	0.1007		7.85	133.96	86.60
3	1	0.2006		7.95	126.80	87.32
	2	0.2006	5.04	7.93	125.07	87.49
	3	0.2002		7.93	126.06	87.40
4	1	0.5008		7.95	82.60	91.74
	2	0.5009	5.04	7.95	81.49	91.85
	3	0.5005		7.95	81.99	91.80
5	1	1.0001		7.94	42.98	95.70
	2	1.0003	5.04	7.98	41.99	95.80
	3	1.0005		7.98	42.60	98.74
6	1	2.0001		8.12	17.91	98.21
	2	2.0002	5.04	8.23	17.54	98.25
	3	2.0003		8.25	17.29	98.27

<u>Table C-4</u> Data of Hg (II) concentration at different amount of activated carbon.

(initial Hg (II) = 1ppm, 100 mL, pH 7 and shaking 120 minutes)

Experiment	Number	Weight (g)	Initial pH	After pH	[Hg] ppb	% remove
1	1	0.0506		8.16	145.81	85.42
	2	0.0503	7.04	8.02	145.57	85.44
	3	0.0501		7.94	145.94	85.41
2	1	0.1001		8.01	140.63	85.94
	2	0.1002	7.04	7.96	141.62	85.84
	3	0.1005		8.26	141.00	85.90
3	1	0.2001		8.05	130.75	86.92
	2	0.2005	7.04	8.22	130.88	86.91
	3	0.2002		8.18	131.12	86.89
4	1	0.5005		9.36	121.62	87.84
	2	0.5004	7.04	9.46	120.26	87.97
	3	0.5009		9.20	121.86	87.81
5	1	1.0007		9.56	79.40	92.06
	2	1.0009	7.04	9.59	72.23	92.78
	3	1.0004		9.59	76.68	92.33
6	1	2.0009		9.78	24.46	97.55
	2	2.0003	7.04	9.75	23.72	97.63
	3	2.0001		9.79	24.09	97.59

Table C-5 Data of Hg (II) concentration at different amount of chitosan
(initial Hg (II) = 1ppm, 100 mL, pH 6 and shaking 120 minutes)

Experiment	Number	Weight (g)	Initial pH	After pH	[Hg] ppb	% remove
1	1	0.0503	6.04	7.24	21.99	97.80
	2	0.0502		7.28	23.22	97.68
	3	0.0502		7.31	22.60	97.74
2	1	0.1002	6.04	7.44	20.51	97.95
	2	0.1005		7.48	21.62	97.84
	3	0.1004		7.51	21.25	97.88
3	1	0.2005	6.04	7.54	18.16	98.18
	2	0.2001		7.48	18.28	98.17
	3	0.2007		7.47	18.78	98.12
4	1	0.5001	6.04	7.61	15.32	98.47
	2	0.5006		7.61	14.95	98.50
	3	0.5005		7.61	15.69	98.43
5	1	1.0009	6.04	7.70	11.86	98.81
	2	1.0003		7.77	11.62	98.84
	3	1.0006		7.74	12.72	98.73
6	1	2.0002	6.04	7.89	9.15	99.09
	2	2.0005		7.89	9.77	99.02
	3	2.0002		7.90	8.65	99.13

Table C-6 Data of Hg (II) concentration at different amount of polymer. (Lewatit TP 214)
(initial Hg (II) = 1ppm, 100 mL, pH 7 and shaking 60 minutes)

Experiment	Number	Weight (g)	Initial pH	After pH	[Hg] ppb	% remove
1	1	0.0502		6.61	146.43	85.36
	2	0.0501	7.02	6.62	139.77	86.02
	3	0.0505		6.60	142.24	85.78
2	1	0.1005		6.041	88.53	91.15
	2	0.1004	7.02	6.49	89.15	91.09
	3	0.1002		6.50	89.15	91.09
3	1	0.2005		6.20	26.19	97.38
	2	0.2007	7.02	6.19	22.36	97.76
	3	0.2007		6.18	22.61	97.74
4	1	0.5005		5.73	8.04	99.20
	2	0.5008	7.02	5.65	8.53	99.15
	3	0.5005		5.61	8.90	99.11
5	1	1.0004		5.03	6.56	99.34
	2	1.0005	7.02	4.95	7.30	99.27
	3	1.0006		5.00	6.68	99.33
6	1	2.0001		4.47	5.57	99.44
	2	2.0002	7.02	4.45	5.82	99.42
	3	2.0005		4.48	4.83	99.52

APPENDIX D

Product description (Lewatit TP 214)

Lewatit TP 214 is a macroporous cation exchange resin with chelating thiocarbamide groups. It is used for the removal of mercury from the effluents of chloralkali electrolysis plants using mercury cells and removal of mercury from neutralized mixted effluents.

The regeneration of LewatitTP 214 exhaused with mercury is not possible with normal regenerant solutions.Only 2 molar sodium sulfide solution desorbs mercury. Therefore, exhausted resins can only be disposed of in accordance with the regulations governing their disposal.

Product Data

Title	Subtitle	Value	Unit
Bead size	>90 %	12 – 38	Mesh
Effective size		15 –30	Mesh
Uniformity coefficient		1.8	Max
Bulk weight	(±5%)	43,6	lbs/ft
Density		69,8	Appr
Water retention		43 –48	%
Total capacity		56,6	Min
Volume change	Exhaustion	+5	Max
Stability	At temperature	-4 –175	°F
	In pH range	0 –14	
	Of the product	2	Min
	At temperature	-4 -100	°F

<u>Recommended operating conditions</u>

Title	Subtitle	Value	Unit
Operating temperature		175	Max. $^\circ$F
Operating pH range		0 – 10	
Bed depth		39,5	Min.inche
Specific pressure loss	(15°C) approx	0,12	Psi*ft / gpm
Pressure loss		36	Psi
Linear velocity	Exhaustion	8.2	Max.gpm
Linear velocity	Backwash (20°C)	3.3	Appr.gpm
Bed expansion	(20°C,per m/h)	7	Approx.%
Freeboard	as% of resin volume	80	%
Regenerant		$Na_2S * 9H_2O$	For Hg only
Co – current regeneration	Amount	30	Appr. Lbs/ft
Co – current regeneration	Concentration	2	Ca.Mol/l
Linear velocity	Regeneration	2	Appr.gpm
Linear velocity	rinsing	2	Appr.gpm
Rinse water requirement		30	Appr.gal/ft

APPENDIX E

Figure E-1 Diatomite

Figure E-2 activated carbon

Figure E-3 Chitosan

Figure E-4 polymer (Lewatit TP 214)

BIOGRAPHY

Miss Benjamas Chareontra was born on April 27, 1978 in Bangkok, Thailand. She received her Bachelor of Science Degree in Chemistry Science from Srinakharinwirot University, Bangkok, Thailand in 2001. After graduation, she has continued her Master Degree in Interdisciplinary Program in Environmental Science, Graduate School, Chulalongkorn University