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นางสาวสุชาดา อำพินธุ์

ADSORPTION OF MERCURIC CHLORIDE AND PHENYLMERCURIC ACETATE FROM AQUEOUS SOLUTION USING CHITOSAN BEADS

Miss Suchada Ampin

Thesis Title   Adsorption of Mercuric Chloride and Phenylmercuric Acetate from Aqueous Solution Using Chitosan Beads

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Field of Study   Chemical Engineering

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ละลายน้ำโดยใช้ไคโตซานแบบเม็ด (ADSORPTION OF MERCURIC CHLORIDE AND
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การวิจัยครั้งนี้เป็นการศึกษาการกำจัดสารประกอบปรอทจากสารละลายน้ำโดยการดูดซับ
ตัวดูดซับที่ใช้ในการวิจัยนี้คือไคโตซานชนิดเม็ด ไคโตซานชนิดเม็ดที่เตรียมขึ้นใช้สำหรับการดูดซับ
มี 2 ชนิด คือไคโตซานชนิดเม็ดวุ้นและชนิดเม็ดแห้ง แต่ละชนิดมีความเข้มข้นของสารละลายไคโต
ซานร้อยละ 2 3 และ 4 การทดลองทำที่ความดันบรรยากาศ อุณหภูมิ 30 40 และ 50 องศา
เซลเซียส ค่าพีเอชเริ่มต้นของสารละลายคือ 5 7 และ 9 โดยใช้เมอร์คิวริกคลอไรด์เป็นตัวแทนสาร
ประกอบปรอทในรูปของโลหะอนินทรีย์ และฟีนิลเมอร์คิวริกอะซิเตตเป็นตัวแทนของสารประกอบ
ปรอทในรูปของโลหะอินทรีย์ สารละลายปรอทแต่ละชนิดละลายโดยน้ำกลั่น เพื่อใช้เป็นสารตั้งต้น
ที่มีความเข้มข้นของปรอท 10 ส่วนในล้านส่วน

จากการทดลองพบว่าตัวดูดซับไคโตซานทั้งแบบเม็ดวุ้นและเม็ดแห้งสามารถดูดซับสาร
ประกอบปรอททั้งสองชนิดได้ ความสามารถในการดูดซับขึ้นกับชนิดของสารประกอบปรอท พีเอช
เริ่มต้น อุณหภูมิ ความเข้มข้นของไคโตซาน และชนิดของเม็ดไคโตซาน โดยที่ความสามารถในการ
ดูดซับสารประกอบปรอททั้งสองชนิดของไคโตซานเม็ดลดลงเมื่อค่าพีเอชเริ่มต้นของสารละลาย
เพิ่มขึ้น สำหรับผลของอุณหภูมิ ความสามารถในการดูดซับเมอร์คิวริกคลอไรด์เพิ่มขึ้นเมื่ออุณหภูมิ
สูงขึ้น ในขณะที่ความสามารถในการดูดซับฟีนิลเมอร์คิวริกอะซิเตตมีค่าลดลง และพบว่าไคโตซาน
ชนิดเม็ดวุ้นสามารถดูดซับสารปรอททั้งสองชนิดได้ดีกว่าไคโตซานชนิดเม็ดแห้ง โดยที่ความ
สามารถในการดูดซับของไคโตซานชนิดเม็ดวุ้นที่แต่ละความเข้มข้นมีค่าไม่ต่างกันมากนัก แต่
สำหรับไคโตซานชนิดเม็ดแห้งความสามารถในการดูดซับขึ้นกับค่าความเข้มข้นของไคโตซาน โดย
ที่ความสามารถในการดูดซับมีค่าลดลงเมื่อความเข้มข้นของไคโตซานมีค่ามากขึ้น

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Removal of mercury compounds from aqueous solution by adsorption was investigated in this study. Chitosan gel and dry beads are used as adsorbents. Both types of beads were prepared using chitosan solution having 2, 3, and 4 percent by weight of chitosan in 1 M acetic acid solution. The experiments were conducted at atmospheric pressure and at temperatures of 30 ^{o}C, 40 ^{o}C, and 50°C. Initial pH of solutions were 5, 7, and 9. Mercuric chloride and phenylmercuric acetate were selected as model mercury compounds to represent inorganic and organic forms. Mercury compounds were dissolved in demineralized water to obtain feedstock solutions containing 10 ppm of mercury.

The results showed that chitosan beads adsorbents can be used effectively in the removal of mercury compounds in aqueous solution. Removal of mercury compounds depended on type of mercury compounds, initial pH of solution, temperature, concentration of chitosan solution, and type of chitosan. Adsorption ability of chitosan beads on mercuric chloride and phenylmercuric acetate decreased with increasing initial pH of solution. Mercuric chloride can be adsorbed better with increasing operating temperature but phenylmercuric acetate showed an opposite result. It is also found that chitosan gel beads can be used to remove mercury compounds more effectively than chitosan dry beads. Concentration of chitosan solution does not affect adsorption ability of mercury compounds but adsorption ability of chitosan dry beads decreased with increasing concentration of chitosan solution.

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CHAPTER I

INTRODUCTION

Mercury is one of the most useful heavy metals indispensable for industries. It has many applications in industry because of its unique properties, such as fluidity, uniform volume expansion over the entire liquid temperature range, etc. The largest commercial use of mercury is the electrolytic production of chlorine and caustic soda in mercury cell. The second largest user is the electrical and electronics industries. Other users of various mercury forms include explosives manufacturing, the photographic industry, paint industry, dental equipment, and electric lighting. The processing in industry used water for both production and cleaning. Therefore wastewater from these industries contain high levels of mercury.

Mercury and mercury compounds are important pollution in wastewater because they are extremely toxic and harmful to human, animal, and environment. Therefore it is very important to develop techniques to recover mercury from various kinds of wastes. Several methods have been proposed for removal of mercury from wastewater. It can be classified into three groups, Physical Treatment, chemical treatment and adsorption (Details of each method is shown in Chapter II). Physical treatment is the method that is uses physical process such as precipitation, sedimentation, and filtration. Chemical treatment is the method that is uses chemicals to convert mercury into form that is easy to remove such as reduction. Adsorption technique is the method about the accumulation at the interface between two phases, such as liquid and a solid or a gas and a solid. The molecule that accumulates, or adsorbs, at the interface is called adsorbate and the solid on which adsorption occurs is the adsorbent. Adsorbents of interest in water treatment include activated carbon (either granulated or powdered), ion exchange resins, adsorbent resins, metal oxides, activated alumina, and etc. Many types of adsorbents are proposed for removal of mercury from aqueous phase such as activated carbon, zeolites, and resin.

A number of chelating resin has been widely used to remove mercury from industrial wastewater. Kawamura, 1998 described that the adsorption of mercury on chelate resin is very strong and mercury is usually recovered by distilling the

Hg-form chelate resin. Since the resin particles can not be used again in this process, it is then necessary to develop a more economical process. The separation techniques using chelate resin are considered to be the most effective and energy-saving separation techniques. Hence, the development of the selective adsorbent for the recovery of mercury using chitosan was planned from the viewpoints of both environmental protection and the utilization of biomass.

Chitin is produced from shells of crabs, shrimps, insect, fungal cell wall, and etc. Chitin is virtually insoluble with water and organic solvents, so it has been considered to be an abundant biomass. Chitosan, poly(D-glucosamine) is obtained by deacetylation of chitin. Chitosan is soluble in organic acid solution, and it contains a reactive amino group, which is useful for chemical modifications. It has many useful features, for example, hydrophilicity, biocompatibility, biodegradability, antibacterial property, and remarkable affinity for many proteins. As it is harmless to humans and abundantly available, ion exchangers or adsorbents made from chitosan may also have potential as separators in food and pharmacy processes, medical and agricultural drugs, wastewater treatment, and other industrial applications. Chitosan has been widely used as adsorbent for metal ions because the amino and hydroxy groups on chitosan chains can serve as the coordination and reaction sites. Kawamura et al.(1993) reported that chitosan could be adsorb metal ions such as $Hg(II)$, $UO_2,(II)$, $Cd(II)$, $Zn(II)$, $Cu(II)$, and $Ni(II)$.

Vichit (2001) studied the adsorption of mercury compounds in aqueous solution using chitosan flakes and the result showed that chitosan flakes could adsorb mercuric chloride and phenylmercuric acetate. However, when chitosan is used as a separator in an industrial scale column, flake chitosan may cause a pressure drop and it does not give high efficiency (Kawamura et al.,1993). In order to reduce this problem, the objective of this experiment is to synthesize chitosan beads that has a higher surface area and efficiency than the chitosan flakes. In addition, this research is also studies the effective of type of chitosan bead (Gel and Dry), chitosan concentration, initial pH of feed solution, and operating temperature. Mercuric chloride and phenylmercuric acetate are selected as mercury compounds to represent of inorganic and organic mercury, respectively.

CHAPTER II

LITERATURE REVIEWS

2.1 Mercury Compounds

Mercury is a naturally occurring element that is usually found as mercuric sulfide, an insoluble, stable compound. It occurs in the earth's crust at concentration levels averaging 0.5 ppm but the actual concentration varies considerably depending on location.

Mercury has many applications in industry due to its unique properties, such as its fluidity, its uniform volume expansion over the entire liquid temperature range, the high surface tension, and its ability to alloy with other metals. The largest commercial use of mercury in the United States was for electrolytic production of chlorine and caustic soda in mercury cell, accounting for 35% of domestic consumption. Manufacturing of wiring devices and switches account for 19%, measuring and control instruments for 9%, dental equipment and supplies used 7%, electric lighting used 7%, and other uses used 21%. Due to the high toxicity of mercury in most of its forms, many applications have been canceled as a result of attempts to limit the amount of exposure to mercury waste (U.S. Department of Health and Human Services,1999).

2.1.1 Chemistry

Mercury is one of two metallic elements that are liquid at room temperature. It is in the fifth period and the third member of the IIB groups of periodic table. All of the elements in IIB group lose two electrons to form ions. The oxidation state of mercury is 80 while atomic weight is 200.59. Mercury metal has a high vapor pressure at ordinary temperature.

2.1.2 Mercury compounds in wastewater

Mercury and mercury compounds are important pollution in wastewater because they are extremely toxic and harmful to human, animal, and environment.

Mercuric Chloride

Mercuric chloride or mercury(II) chloride is a white powder of colorless rhombohedral crystals and soluble in water. It is also called bichloride of mercury or corrosive sublimate. It is inorganic mercury compound and extremely poisonous. Domestic garbage contains a large amount of mercury, which originates from disposed thermometers, fluorescent lamp, mercury batteries, and other sources. When the garbage is burned in a refuse incinerator, mercury vaporizes into the flue gas. The flue gas is cleaned using an electric dust collector, bag filter, and then washing with HCl aqueous solution using scrubber. As the effluent solution is neutralized with NaOH aqueous solution, it contains $HgCl_2$ and HCl(Kawamura et al.,1998). In the study of mercury removal, mercuric chloride is the mercury compound that is representative of inorganic mercury.

Phenylmercuric Acetate

Phenylmercuric acetate is an important example of twenty or more organic mercury compounds. It is sparingly soluble in water but soluble in many organic solvents. It has been used in aqueous preparations such as inks, adhesives, and caulking compound, as a catalyst for the manufacture of certain polyurethanes, and as a fungicide in seed dressings and interior and exterior paints. In medical application, phenylmercuric acetate used in contraceptive gels and foams and as a disinfectant (U.S. Department of Health and Human Services,1999). In agricultural, phenylmercuric acetate used as a foliage fungicide and herbicide. It is extremely toxic and a powerful vesicant agent; painful blistering of the skin will results about 8 hours after contact.

2.2 Study of Mercury Removal in Wastewater (Patterson, 1985)

Many types of mercury treatment technology have been reported. The effectiveness, and economics, of treatment by each type of technology depends upon the chemical nature and initial concentration of mercury. Common types of treatment are sulfide precipitation, ion exchange, adsorption and coagulation, and reduction of ionic mercury to elemental form with removal by filtration.

2.2.1 Physical Treatment

Precipitation

Sulfide addition, in order to precipitate highly insoluble mercury sulfide, is the most common precipitation treatment reported. Precipitation may be combined with flocculation and separation by gravity setting, filtration, or dissolved air flotation. For high initial mercury levels, sulfide precipitation will achieve 99.9 % removal, but even with filtration or activated carbon-polishing treatment, minimum effluent mercury achievable appears to be 10-20 μg/l. Most effective precipitation, with regard to minimizing sulfide dosage, appears to occur in the near – neutral pH range. Precipitation efficiency declines significantly at pH above 9. In addition to lack of capability to reduce mercury below 10 μg/l, other drawbacks of this method include the formation of soluble mercury sulfide complexes at high levels of excess sulfide, the difficulty of monitoring excess sulfide levels, and the problem of toxic sulfide residual in the treat effluent.

2.2.2 Chemical Treatment

Ion Exchange

Most ion exchange treatment of inorganic mercury involves formation of a negatively charged mercuric chloride complex by addition of chlorine or hypochlorite (to oxidize metallic mercury), or chloride salts, and removal of the mercuric chloride complex on an anion exchange resin. Most experience with ion exchange treatment has been with chlor-alkali plant wastes, which contain high background chloride level. Ion exchange has also been suggested as a polishing step after precipitation. In wastes where chloride is not high, cation exchange resin are effective. Although information. Regardless of whether anionic resins are used for mercuric chloride complex removal, or cationic resins for mercuric ion removal, the best ion exchange treatment for inorganic mercury appear to yield an effluent of 1-5 μg/l. Most effective treatment result from two-stage treatment, at neutral slightly acidic pH.

Coagulation Treatment

Removal of mercury by coagulation has been reported for a variety of mercury containing wastewater. Coagulants employed include aluminum sulfate (alum), iron salts and lime. The process has been applied with some success to both organic and inorganic mercury. In studies on coagulation treatment for removal of inorganic mercury dosed to domestic sewage, both iron and alum coagulation, followed by filtration, reduced initial mercury levels of 50-60 μg/l by 94-98%. Lime coagulation treatment, applied at a higher mercury level of 500 μg/l, provided 70% removal with filtration.

2.2.3 Adsorption

Sorption Kinetics (M. Ruiz et al.,2002)

The sorption of solutes on solid particles has been extensively studied. The overall mechanism can be described as succession of various steps:

(1) Solute transfer from the bulk solution to the boundary film.
(2) Solute transport from the boundary film to surface of the sorbent (external diffusion).
(3) Transfer of solute from surface of the sorbent to the intraparticle active sites (intraparticle diffusion).
(4) Adsorption of the solute onto the active sites.

The first and fourth steps are considered as non limit as agitation provided is sufficient to avoid a concentration gradient in the solution, whereas the sorption is seen as a quasi instantaneous mechanism. So, external mass transfer resistance and intraparticle mass transfer resistance are the major controlling stages.

Activated carbon

The effectiveness of carbon treatment is dependent upon several factors, including initial form and concentration of mercury, dosage and type of activated carbon, treatment pH, and contact period between the carbon and mercury containing wastewater. Increasing carbon dosages and increasing contact times improve removal

of both inorganic and organic mercury. Organic mercury is more effectively removed than is inorganic mercury.

Chitosan

Chitosan is the name used for low acetyl substituted forms of chitin and is composed primarily of glucosamine, 2-amino-2-deoxy-β-D-glucose, know as (1→ 4)-2-amino-2-deoxy-(D-glucose)(Fig.1). Chitosan has three types of reactive functional groups, an amino group as well as both primary and secondary hydroxyl groups at the C-2, C-3 and C-6 positions, respectively. Chemical modifications of these groups have provided numerous useful materials in different fields of application. Chitin is the major structural component of the exoskeleton of invertebrates and the cell walls of fungi. Since the biodegradation of chitin is very slow in crustacean shell waste, accumulation of large quantities of discards from processing of crustaceans has become a major concern in the seafood processing industry.
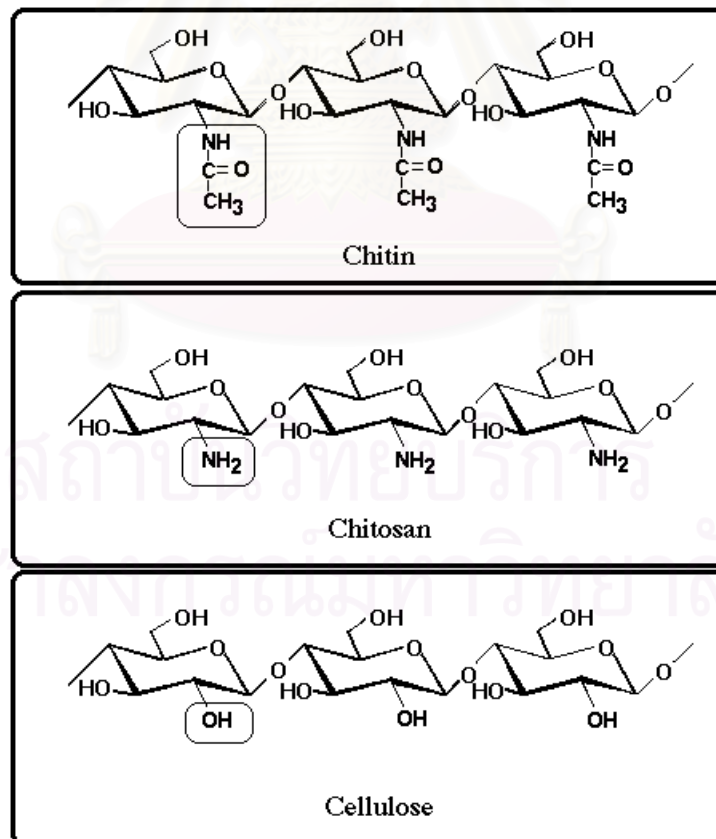
Figure 2.1 Structure of Chitin Chitosan and Cellulose

Preparation of chitosan (M. Ruiz et al.,2002)

Purification of chitin

The main sources of material for laboratory preparation of chitin are the exoskeletons of various crustacea, principally crab and shimp. In these, chitin is closely associated with proteins, inorganic material which is mainly $CaCO_3$ pigments and lipids. Various procedures have been adopted to remove these impurities. Demineralisation is most frequency carried out by treatment with HCl and deproteinisation by treatment with NaOH, but other methods may be used and the order in which these two steps are carried out has varied with different workers, although in most instances deproteinisation has been carried out prior to demineralisation.

The exoskeletons of crustacea contain coloring matter, principally carotenoids, which do not appear to be complex with either inorganic material or protein, since treatment which remove these components do not remove the carotenoids. However, they may be removed by extracting the shell with ethanol or acetone after demineralisation. Alternatively, the coloring matter may be destroyed by bleaching using $KMnO_4$ or H_2O_2.

Deacetylation of chitin

One of the main reactions carried out on chitin is deacetylation, most commonly by using aqueous alkali. The most frequently used alkali is NaOH. The extent of deacetylation is governed by the alkali concentration, temperature, time of reaction, particle size, and density. While treatment with 50 wt % NaOH at 100 ^{o}C for 1 hour gave a product having 82 % deacetylation, extending the reaction time to 48 hours enabled almost 100 % deacetylation to be achieved. However this was at the expense of a considerable decrease in solution viscosity, indicating chain degradation.

Other variations on the standard aqueous alkali treatment to avoid chain degradation have been directed towards reducing the quantity of alkali required in the treatment. Batista and Roberts (1990) suggested the use of water miscible solvents such as 2- propanol or acetone as a diluent to ensure ease of stirring, and as a transfer medium to ensure uniform distribution of the aqueous alkali throughout the chitin mass. These solvents decrease the depolymerisation of chitosan.

Physicochemical Characteristics of Chitosan

Degree of N- Acetylation

Chitosan is characterised by either the degree of acetylation (DA), which corresponds to the N-acetylamine groups, or the degree of deacetylation DDA (DDA = 100 - DA), D-glucosamine groups.

The degree of acetylation has an influence on all the physicochemical properties, (molecular weight, viscosity, solubility, etc,…) so, it is one of the most important parameters. Many techniques have been tried in order to determine the degree of acetylation more precisely. The most appropriate technique for rapid characterisation seems to be the IR spectroscopy.

Molecular Weight

The definition of average molecular weight of polysaccharides and the understanding of its consequences on their physicochemical behavior have presented a real challenge to chemists for a number of years. In the case of chitin and its derivatives, knowledge of such data is very important for industrial uses and for advanced research in numerous fields. Although the primary structure of chitosan is a blackbone of $(1 \rightarrow 4)$-β-D-glucosamine residues randomly acetylated to various extents, the name chitosan is in fact a collective term for deacetylated chitins differing in terms of crystallinity, optical characteristics, degree of acetylation, impurity content, and average molecular weights.

Solubility

Chitosan in the form of free amine is insoluble in water to pH near neutrality, in concentrated acids with the exception of sulfuric acid, the bases and organic solvents. Their acid base properties allow easy dissolution. Therefore, chitosan is soluble in dilute HCl, HBr, HI, HNO_3, and $HClO_4$. Chitosan is also slightly soluble in dilute H_3PO_4 but is insoluble in dilute H_2SO_4 at room temperature, although chitosan sulfate dissolves in water on heating and reforms on cooling.

In fact, chitosan is soluble in diluted acids on account of a protonation of free amine groups. The dissociation constant K_b, of an amine group is obtained from the equilibrium

$$R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + OH^- \qquad \ldots\ldots\ldots\ldots(2.1)$$
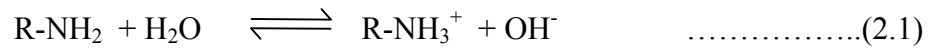
$$k_b = \frac{[R - NH_3^+][OH^-]}{R - NH_2} \quad \text{and } pK_b = - \log K_b$$

While the dissociation constant of conjugated acid is obtained from the equilibrium

$$R\text{-}NH_3^+ + H_2O \rightleftharpoons R\text{-}NH_2 + H_3O^+ \qquad \ldots\ldots\ldots\ldots(2.2)$$
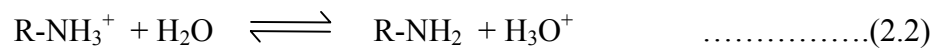
$$k_a = \frac{[R - NH_2][H_3O^+]}{R - NH_3^+} \quad \text{and } pK_a = - \log K_a$$

As in all polyelectrolytes, the dissociation constant of chitosan is not, in fact, constant but depends on the degree of dissociation at which it is determined. The variation of the pK_a value can be calculated using Katchalsky's equation

$$pKa = pH + \log((1 - \alpha)/\alpha) = pK_0 - \varepsilon \, \Delta\psi(\alpha)/k_T$$

where $\Delta\Psi$ is the difference in electrostatic potential between the surface of the polyion and the reference, α is the degree of dissociation, k_T is boltzman's constant and ε is the electron charge. Extrapolation of the pK_a values to $\alpha = 1$, where the polymer becomes uncharged and hence the electrostatic potential becomes zero, enables the value of the intrinsic dissociation constant of the ionisable groups, pK_0, to be estimated. The value obtained, ~ 6.5, is dependent of the degree of N-acetylation, whereas the pK_a value is highly dependent on this factor. The pK_0 is called the intrinsic pK_a of the chitosan. Therefore, the solubility of chitosan depending on its degree of dissociation and the method of deacetylation used.

2.3 Study of Metal Ions Removal Using Chitosan and Chitosan Derivative as Adsorbent

Coughlin (1991) studied the removal of nickel and copper in aqueous solution using chitosan. The initial concentration of feed was 1000 ppm. The results indicated that the higher degree of deacetylation had efficiency in percent removal of heavy metal more than lower degree of deacetylation.

Matani (1992) studied the removal of heavy metal by chitosan gel beads. The solution containing 10 and 100 mg/liter of heavy metal. One gram of beads and 19 grams of solution were adsorbed at 30 °C for 48 hours. The results showed that the selectivity of adsorption was Cu > Ni > Zn > Co > Mn.

Kawamura et al. (1993) studied the adsorption of heavy metal in aqueous solution using highly porous chitosan resin. The selectivity for adsorption of metal ions was determined by single-solute conditions. The pH and concentration of each solution were adjusted to pH = 7 and 100 ppm respectively. One milliliter of wet resin was stirred in 80 ml of metal solutions at 25 °C for 72 hours. The result indicated that chitosan resin adsorbed Hg(II) completely and very high selectivity. The selectivity was Hg(II) > UO_2(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II). Mg(II), Ca(II), Ga(III), As(III), and Sr(II) were not adsorbed on the resin at all.

Rorrer (1993) studied the removal of cadmium ions from wastewater using porous magnetic chitosan beads. Chitosan beads were prepared by dropwise of an acidic chitosan solution into sodium hydroxide. The gelled chitosan beads were cross-linked with glutaraldehyde and then freeze dried. Adsorption at 25 °C and pH 6.5 over the concentration rang 1-1690 mg Cd^{2+}/L. The volume of solution used in the experiments was 200 cm^3 and the beads solution ratio was 1 mg/cm^3 solution. The results showed that the maximum adsorption capacities for the 1 mm and 3 mm beads were 518 and 188 mg of Cd/g of beads, respectively.

Juang et al.(1997) studied the effect of pH of feed in the removal copper using polyaminated chitosan beads. The results show that the percent removal of copper compound increased with pH of feed increasing between 3-6, but at pH < 3 or pH >6 the percent removal was decreased with pH of feed increasing.

Guible et al. (1999) studied the influence of polymer structural parameters and experimental conditions on arsenic adsorption. The chitosan gel beads were prepared from dissolved chitosan flakes in 4 % w/w acetic acid. The final weight percentage of chitosan was 4 % w/w. The viscous solution were dropped into sodium hydroxide solution and cross-linked with glutaraldehyde. The experiments were adsorbed in the fixed bed column systems. The results showed that the maximum

adsorption capacity depends on the crystallinity and degree of deacetylation. Chitosan gel beads can be used instead of flakes to decrease crystallinity.

Wu et al. (2000) studied and compared the adsorption of metal and dye on flakes and beads type of chitosan. The chitosan flakes were prepared from fishery waste (shrimp, lobster and crab shells). The chitosan beads were prepared from dissolved the chitosan flakes in 1 mol/dm^3 acetic acid solution and pored into sodium hydroxide solution. The solutions were settled for 24 hours and dried at 50 °C in vacuum for 12 hours. The adsorption capacity of Cu(II) on flakes and beads type of chitosan appeared to be comparable, but the adsorption capacity of dye (RR 222) on beads type was much larger than that on flakes type by factor 2.0-3.8.

Bassi et al.(2000) studied the removal of zinc, copper, cadmium and lead using chitosan flake. The results show that percent removal of zinc, copper, cadmium and lead increased with amount of chitosan increasing but decreased when amount of chitosan over 0.24g/25 ml. of solution. Stir cloud not effect to removal of these metals and the maximum result in percent removal of zinc, copper, cadmium and lead was at pH 7.

2.4 Study of Mercury Removal Using Chitosan and Chitosan Derivatives as Adsorbent

Baba et al.(1998) studied the selective adsorption of mercury(II) on chitosan derivatives from hydrochloric acid. They were newly synthesized chitosan derivatives as the adsorbents of metal ions, copper, cadmium, nickel cobalt, zinc, iron, and mercury. The solution contained 1 mmol/dm^3 of metal ions and 0.01-6 mol/dm^3 of HCl. The operating temperature was 30 °C in a batch system. The results shown that the high selectivity of mercury over copper, cadmium, and nickel but iron, cobalt, and zinc were not adsorbed in the concentration range of HCl. For adsorption of mercury, the results indicated that the decrease in the amount of adsorbed mercury (II) with an increase in the HCl concentration was attributable to not the hydrogen ion but the chloride ion.

Kawamura et al.(1998) studied the removal of $HgCl_2$ using polyaminated highly porous chitosan beads. The solution containing 1000-14000 ppm of mercury were passed in upflow direction through chitosan beads column at room temperature (25 °C). This experiment studied the effect of salt and acid using NaCl and HCl, respectively. The results shown that when HCl existed in Hg(II) solution, the saturation capacity and equilibrium constant for adsorption of Hg(II) on chitosan decreased with increasing concentration of HCl. When NaCl existed in Hg(II) solution, the equilibrium constant was constant but the saturation capacity decreased with an increased on the concentration of NaCl.

Yunhua et al.(2000) studied the adsorption behavior of metal ions on cross-linked chitosan column. Chitosan were cross-linked with glutaraldehyde. The experiment used 60 elements of metal ions. The pH of this experiment were adjusted to 1-9 at 25 °C. The results indicated that most of metal ions adsorbed on chitosan at pH < 5 but mercury (II) adsorbed on the cross-linked chitosan at pH from 3 to 6.

Oshita et al.,(2002) studied the adsorption behavior of mercury and precious metals on cross-linked chitosan. Chitosan was cross linked with ethylene glycol diglycidyl ether. This study was applied to the removal of mercury in hydrochloric acid by a column treatment with cross-linked chitosan. The initial concentration of metal ions was prepared by diluting the standard solution to 10 ppb. The cross-linked resin were packed in small-sized polypropylene columns (5.0-5.5 mm-i.d.). The results showed that more than 97 percent of mercury was removed. Mercury adsorbed on the cross-linked chitosan could be easily desorbed with an eluent containing 1 M hydrochloric acid nad 0.05 M thiourea. The refreshed cross-linked chitosan could be repeatedly used for the removal of mercury in hydrochloric acid.

Different Forms of Chitosan for Treatments

Gel

Chitosan- based gels may be broadly divided into thermally non-reversible gels and the far smaller group of thermally reversible gels. Within the first group a further subdivision into those formed by N-acylation and those produced by Schiff's base (aldimine) formation is useful, and this division of the topic is used here.

N-Acylchitosan are prepared treating chitosan in solution acetic acid 10%, or in 5% water-methanol acetic acid and range of acyl anhydrides including dodecanoic anhydride and also benzoic anhydride . The effects of variation in the acetic anhydride : -NH$_2$ group mole ratio has been investigated by Hirano and Yamaguchi(1976). This study showed that the presence of anhydrous acids increases the rate of N-acylation in the polymer, reducing solubility and allowing gelation to occur. The rate of gelation was found to increase with a corresponding increase in the chitosan concentration, acyl anhydride concentration and temperature, and when the molecular weight of the acyl anhydride decreased.

The most widely studied gel system involving Schiff's base formation is that using glutaraldehyde, which involves covalent cross-linking formation between the chains. Using viscosity measurements to determinate the rate of gelation, Roberts and Taylor (1989) found it to be proportional to the chitosan and the glutaraldehyde concentrations and to the temperature, while it is inversely proportional to the acetic acid concentration.

Hirano et al. (1990) reported chitosan – based thermally reversible gels. They prepared these gels by mixing a chitosan solution with a concentration below 2 % with a 3 % oxalic acid solution. The gels formed melted on heating and gelled on cooling. The melting points were reasonably high, being 88 ^{o}C and 92 ^{o}C, and increased when the chitosan concentration was increased. These authors proposed that the mechanism of the formation of the junction points is one of salt formation, similar to that for formation of alginate gels is presence of Ca^{2+}. In a study of partial N-succinylation of chitosan, the same authors noted that the product which contained 35 % of the amine acylated groups produced a thermoreversible gel, through no details this were provided.

Solution

By completely mixing chitosan with acetic or formic acids, a viscous biopolymer solution can be obtained. This type of chitosan displays a particular type of rheological behavior: the viscosity increases when the chitosan concentration is increased and the temperature is reduced. It is therefore possible to produce 1 to 4 % solutions in large quantities, while 20 % solutions may be produced in large quantities by using chitosans with a low molecular weight. Once the chitosan solution has been

obtained, a simple final preparation or coagulation reaction will allow the resulting chitosan to be treated in various ways – for example, for the formation of chitosan membranes and beads.

Membrane

Owing to its solubility in formic or acetic acid, chitosan is suitable for the preparation of membrane. There is interest in making chelating membranes available for preconcentration of trace element, for selective isolation of certain elements from saline solutions, or for special sample preparations in nuclear chemistry or in electrochemistry. A chelating membrane is expected to exhibit superior characteristics as it would be selective, would not release ions to solution, and would bind transition metals by dative bonds instead of ionic bonds.

The chitosan membranes were described and characterized for the first time by Muzzarelli and co-workers (1974). Chitosan membranes were produced from a solution of chitosan in formic acid. This solution was poured on a glass plate and kept perfectly horizontal upon a water bath. When formic acid was completely evaporated, the glass plate was exposed to cold air so that the membrane could easily be removed from the glass surface. These water soluble chitosan formate membranes were dipped into 1 M NaOH. The membrane was then washed with distilled water to neutrality and then placed on a clean glass plate and kept at 60 $^{\circ}$C until dry.

Chitosan membranes generally show lower capacity than chitosan powder, due to the reduced contact surface; however, collection is good, especially for molybdenum, chromate and mercury.

The chitosan membranes are resistant to both alkaline solutions and many organic solvents. Uragami et al.(1994) have analyzed the structure of chitosan membranes which were chemically modified with aldehydes, such as glutaraldehyde and n- butyl aldehyde and their characteristics in terms of permeation and the separation of aqueous ethanol solutions.

Kaminski and Modrzejewska (1997) present and application of chitosan membranes for the removal of heavy metal ions. In this study, the metal ions Cu (II), Cd (II), Co (II), Zn (II), and Ni (II) are almost entirely separated by the membranes. In the case of Cr (VI) and Mn (II) ions, the separation depends on pH and process conditions.

Beads

For the fabrication of gel beads, the concentration of the chitosan solution can be freely selected according to the molecular weight of chitosan from a point at which it flows easily and can be handled without difficulty. The preferred concentration for the solution is in the range of 2 % to 20 %. A viscosity regulator such as urea may also be added to the acidic aqueous solution.

The aqueous acidic solution of chitosan is prepared and a predetermined quantity is poured into a coagulating bath through a discharge hole. The pore diameter of the discharge port, pressure, etc. can of course be selected optionally according to the desired particle size. For the coagulating bath, a basic solution may be used. Basic usable material can include alkali material such ac sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, ammonia and ethylene diamine. The basic solution used is prepared by adding the above – mentioned basic material to water or alcohol with a polarity such as methanol and ethanol, or a mixture of water and alcohol. Since the alcohol reduces surface tension of coagulating bath, it can moderate the shocks during pouring and therefore control the specific surface area. The concentration of the basic solution can optionally be selected according to the concentration of the aqueous acidic solution of chitosan used, or the characteristics of the desires granular porous chitosan.

For metal ion sorption applications, the high internal surface area of the porous beads can improve the metal binding capacity and also increase the transport rate of metal ion into the particle. But when chitosan is used as a separator in an industrial scale column, flake and gel chitosan may cause a pressure drop, and they do not offer a high efficiency. In order to reduce this problem, several authors have proposed reticulation.

2.5 Study of Mercury Removal Using Other Adsorbents

Canstein et al.(1999) studied the removal of mercury from chloralkali electrolysis wastewater using a mercury-resistant bacterial strain. A mercury-resistant bacterial strain was isolated from polluted river sediments. It was grown on porous carrier material in laboratory column bioreactors. The bioreactors were continuous fed. It was found that mercury concentration up to 7 mg/liter could be treated with the bacterial biofilm with no loss of activity.

2.6 Literature Summary

1. Mercury and mercury compounds are extremely toxic, exist in wastewater in elemental, organic and inorganic mercury.

2. Several methods have been proposed for removal mercury from wastewater. It can be classified into three groups, Physical Treatment, chemical treatment and adsorption.

3. Chitosan, an N-deacetylation product of chitin, is one of the useful chelating polymers. Chitosan could also adsorb metal ions such as Hg(II), Cu(II), Cr(III), Pb (II), Cd(II), UO_2^{2+},etc.

4. The mercury that used to study removal of inorganic mercury was mercuric chloride.

5. The study of factors that have effective to adsorption by chitosan was pH, temperature, pore structure, specific functional group, degree of deacetylation, and crystallinity of polymer structure.

6. Chitosan are used as adsorbent in various forms such as gel, solution, membrane, beads.

7. Chitosan beads can be used instead of flakes to decrease crystallinity because the maximum adsorption capacity depends on the crystallinity.

8. When chitosan are used as a separator in an industrial scale column, flake may cause a pressure drop and do not give a high efficiency.

CHAPTER III

EXPERIMENTAL PROCEDURE AND ANALYSIS TECHNIQUES

This Chapter covers all of the experiments, analysis techniques, and experimental error in this study. It is divided into four sections. The first section concerns with the adsorbent preparation. Bead preparation is described in this section. The second section describes the experimental apparatus and adsorption procedures. The third section refers to analysis techniques. The fourth section described the experimental error.

3.1 Adsorbent Preparation

3.1.1 Preparation of Chitosan Gel Beads

Chitosan flakes are used in this experiment, the degree of deacetylated N-acetyl is 95 percent. It is a commercial grade and produced by Seafresh Chitosan (Lab) Co.,Ltd. The specification of chitosan flakes shows in Appendix B. Chitosan are dissolved in 1 M acetic acid solution with approximately 2, 3, and 4 wt % chitosan, respectively. Dissolved chitosan are a viscous solution. The resulting viscous solutions are gradually dropped into 1 M sodium hydroxide solution through a 0.8-mm i.d. needle. Chitosan droplets turn to gel beads. The gel beads are left in sodium hydroxide solution for 24 hours to allow the chitosan form to gel beads all of spherical particles. The gel beads are separated from sodium hydroxide solution and then washed and rinsed gel beads with demineralized water until the pH of rinsed water is equal to the pH of demineralized water. Chitosan gel beads are obtained and kept it in demineralized water. The experimental apparatus show in Figures 3.1 to 3.3.

Figure 3.1 Chitosan beads preparation apparatus.

Figure 3.2 Chitosan form to gel beads in NaOH solution.

Figure 3.3 Chitosan gel beads.

3.1.2 Preparation of Chitosan Freeze Dry Beads

Chitosan dry beads are prepared by freeze drying chitosan gel beads at – 40 °C in vacuum until the chitosan gel beads is dried, about 2 days. Chitosan dry beads are obtained and kept it in dry place.

Figure 3.4 Chitosan dry beads.

3.2 Experimental Apparatus and Adsorption Procedure

3.2.1 Experimental Apparatus

Figure 3.5 shows apparatus of adsorption experiment. The apparatus consist of a 250-ml. flask, connected to a propeller and a motor. The experiments are

carried out at atmospheric pressure. The temperature of the oil bath is controlled with the temperature controller for constant temperature at 30, 40, and 50°C.
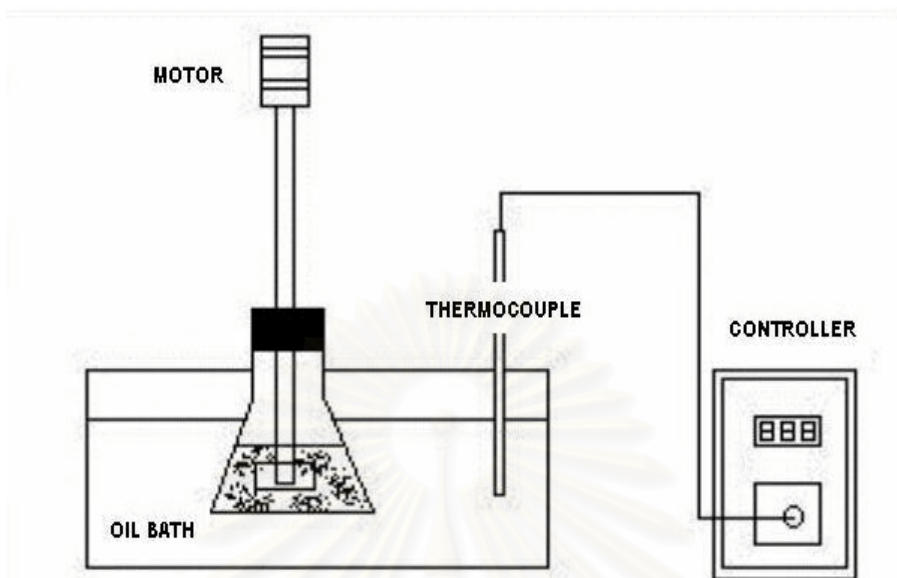
Figure 3.5 Schematic diagram of the experimental apparatus.

Table 3.1 shows variables of this experiment. The adsorption procedures are described below.

Table 3.1 Variables of the adsorption experiment.

Compound	Mercuric chloride (HgCl₂) and Phenylmercuric acetate (PMA)
Type of Adsorbent (%wt)	Chitosan gel beads 2, 3, 4 Chitosan dry beads 2, 3, 4
Initial pH of solution	5, 7, 9
Temperature (°C)	30, 40, 50

3.2.2 Feed Preparation

In this study, mercuric chloride and phenylmercuric acetate are selected as representatives of inorganic and organic mercury compound respectively. The initial concentration of mercury compound in solutions is prepared at 10 ppm. Mercury compounds are weighed and put in 2-liter erlenmeyer flask. Magnetic stirrer is used to stir the solution at least 2 hours for mercuric chloride and 5 hours for phenylmercuric acetate. The solutions are used as feedstock and kept in a refrigerator.

3.2.3 Adsorption Procedures

1. Approximately 15 milligrams of adsorbent, basis with dry chitosan, is put into a 250-ml. erlenmeyer flask.

2. For chitosan dry beads, the flask is vacuumed by a vacuum pump. Approximately 0.5 ml. of demineralized water are dropped in the flask to fill pore of the adsorbent. Slowly shake the flask to mix demineralized water and the adsorbent.

3. Approximately 150 grams of feedstock are poured into the sample flask.

4. The sample flask is placed in a controlled temperature oil bath. It is stirred for 9 hours.

5. After each experiment, the products are filtered using Whatman No.1 filter papers to separate the spent adsorbents from the liquid product.

3.3 Analysis Techniques

3.3.1 Adsorbent Characterizations

Surface and Pore Volume

A Micrometrics model ASAP 2000 is an instrument to measure surface area, pore volume, and pore size distribution of the adsorbents. The instrument detects the volume of adsorbed nitrogen gas on surface at various relative pressures. There are two operating steps; the degassing step and analysis step. Firstly, the adsorbent is heated and placed under vacuum to remove the moisture and other contaminants. The condition of degassing is operated at 70 °C and vacuum until pressure to 10 μm.Hg. After that, The sample cell is transferred from a degas port to an analyze port.

At the analyze port, the sample is analyzed at various relative pressures and liquid nitrogen is used as coolant. Nitrogen gas is used as an analysis gas. The volume of adsorbed nitrogen on the sample will relate with the relative pressure (P/P_o). The volumes of adsorbed nitrogen gas and relative pressure are plotted on a graph. The Y-intercept and slope of the graph is calculated for BET surface area of thesample. The other results of the instrument are BJH cumulative pore volume and average pore diameter.

3.3.2 Standard Test Method for Total Mercury in Water

The determination of total mercury in water followed the standard test method ASTM 3223-91. The test method consists of a wet chemical oxidation and cold vapor atomic absorption analysis. Chemical oxidation converts all mercury to the mercuric ion and reduction of mercuric ion to metallic mercury, followed by a cold vapor atomic absorption analysis. Because total mercury in aqueous phase cannot be directly measured by an atomic absorption spectroscopy technique, chemical oxidation is the method that is using strong acids and high temperature to change all mercury species to mercury (II) ion (Hg^{2+}). Figure 3.6 shows the apparatus for converting all mercury to the mercuric ion. It is comprised of a round bottom flask that is connected with a condenser. The flask is immersed in the oil bath and heat at 95°C for 2 hours. The procedure of digestion is described below.
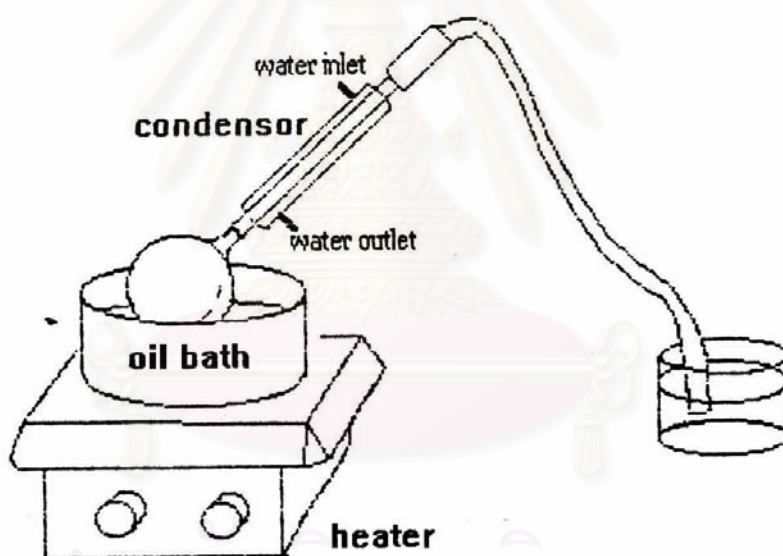
Figure 3.6 Schematic diagram of the digestion apparatus.

Mercury Digestion

1. Approximately 10 grams of sample is transferred to a 250-ml. flat bottom round flask.
2. 5 ml. of concentrated sulfuric acid, 5 ml. of concentrated nitric acid and 15 ml. of 5 % potassium permanganate solution are added to the sample.

3. The sample is stirred at 600 rpm for 15 minutes. After that, 8 ml. of 5 % potassium persulfate is added to the flask.

4. The flask at the top is equipped with a reflux condenser and heated in an oil bath at 95 °C for approximately 2 hours.

5. After that, the flask is removed from the oil bath and cooled to ambient temperature.

6. 6 ml. of sodium chloride-hydroxylamine hydrochloride is add to the sample to reduce the excess permanganate. Slowly shake for approximately 10 minutes. The sample is transferred into a polyethylene bottle

7. Finally, demineralized water is added and is shaken vigorously to make the total volume to 100 ml.

Cold Vapor Technique

In this study, the high sensitivity measurement of mercury content is the cold vapor technique or the hydride technique. The cold vapor technique involves the reaction of acidified aqueous samples with a reducing agent such as sodium borohydride. Mercury is the only element apart from the inert gas with appreciable vapor pressure at room temperature. The reaction is show in following equations

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H \qquad \text{………(3.1)}$$

$$Hg^{n+} + H(radical) \rightarrow Hg + H_2 \qquad \text{………(3.2)}$$

Equation 3.1 shows the reaction between sodium borohydride and hydrochloric acid to generate radical hydrogen in quartz cell. In quartz cell, radical hydrogen reacts with mercury (II) ion to gaseous mercury atoms as show in Equation 3.2. Mercury atoms can absorb 253.7 nanometers of wavelength. The content of mercury is interpreted from the intensity of light that absorbed by mercury atoms. The sensitivity of this technique is approximately 10^{-9} g.

3.4 Experimental Error

3.4.1 Experimental Error

In this section, experiments are conducted to verify repeatability, an average and standard deviation value of the experiment. Equation 3.3 and 3.4 define an average value and percent deviation.

$$\text{Average value} \quad \overline{X} \quad \rightarrow \quad \frac{\sum x}{n} \qquad \qquad \text{…………..3.3}$$

$$\text{Percent deviation from average value} = \frac{\sqrt{(X - \overline{X})^2}}{\overline{X}} \times 100 \qquad \text{…………..3.4}$$

In each experiment has the marker to study experimental error that might occur during each experiment. Markers are operated in the same condition in all experiments. The conditions of marker in this experiment are 2% chitosan dry beads adsorbent, mercuric chloride adsorbate, pH 7 at room temperature. The contact time of marker is 3 hours. After adsorption in each experiment, the liquid solutions are digested and analyzed for mercury contents by using atomic absorption spectroscopy techniques. The percent removal is defined to compare adsorptive ability of each experiment and calculated by Equation 3.5

$$\text{Percent removal (\%)} = \frac{C_f - C_r}{C_f} \times 100 \qquad \qquad \text{………….(3.5)}$$

C_f = The concentration of feedstock (ppm).

C_r = The concentration of remaining mercury (ppm)

Average percent mercury removal of marker and the maximum percent deviation value is calculated and shown in Table 3.2

Table 3.2 Average percent mercury removal of marker and maximum deviation of mercury compound in adsorption experiment.

Number of marker	Average Percent removal (%)	Maximum Deviation(%)
24	46.17	5.73

3.4.2 Digestion Error

The experiment is conducted to study the error from digestion. In this experiment feedstock is digested at the concentration of 10 ppm. The experiment is repeated at the same condition for 4 times. Average concentration and maximum deviation of these experiments are shown in Table 3.3

Table 3.3 Average concentration and maximum deviation of mercury compound in digestion error.

Compounds	1 (ppm)	2 (ppm)	3 (ppm)	4 (ppm)	Average conc. (ppm)	Maximum Deviation (%)
Mercuric chloride	10.22	10.13	10.54	10.23	10.28	2.56

3.4.3 Blank Test

The experiments in this section are conducted to study stability of mercury compounds at adsorption temperatures and to verify adsorption of mercury compounds on reactor wall. No adsorbent is used in this test. The adsorption temperature of this test are 30ºC, 40 ºC, and 50 ºC. The concentrations of mercury after completion of the experiments are shown in Table 3.3. Vichit (2001) who conducted the experiment using chitosan flake obtained similar results. It is found that mercuric (II) chloride and phenylmercuric acetate concentration in product and feed are almost identical. It indicates that mercuric (II) chloride and phenylmercuric acetate disappear by adsorption of the glassware.

Table 3.4 Percent of mercury compounds losses feed at various temperatures.

Compounds	Mercury losses from feed (%)		
	30 ^{o}C	40 ^{o}C	50 ^{o}C
Mercuric chloride	1.8	2.4	2.9
Phenylmercuric acetate	2.0	2.5	3.2

CHAPTER IV

RESULTS AND DISCUSSIONS

This Chapter presents experimental results and discussions on adsorption of mercury compounds in aqueous solution. Mercury removal experiments by adsorption were conducted in a batch system. Chitosan gel beads and dry beads are used as adsorbents. This Chapter are categorized into three parts:

Part 4.1 Experimental procedure and preliminary results. This part describes experiments on determination of suitable adsorption period, and the conditions used in other experiments.

Part 4.2 Adsorption behavior of mercury compounds on chitosan adsorbent. This part summarizes discussions on ionization and adsorption behavior of mercury compounds.

Part 4.3 Effects of initial pH of solution, temperature, concentration of chitosan solution and types of chitosan beads are discussed.

4.1 Experimental Procedure and Preliminary Results

The experiments are conducted in a 250-ml. erlenmeyer flask. Mercuric chloride and phenylmercuric acetate are used to represent inorganic and organic mercury compounds, respectively. The adsorbents are chitosan gel beads and dry beads prepared at various chitosan concentrations in acetic acid solution. Chitosan dry beads are analyzed using BET surface area technique, described in Chapter III. The BET results are shown in Table 4.1.

Table 4.1 Surface area and pore diameter of chitosan dry beads and chitosan flake, 95 % DD

Chitosan type	Dry Beads 2 %	Dry Beads 3 %	Dry Beads 4 %	Flake
Pore diameter [A^o]	141.7347	121.1835	115.3593	114.2807
Surface area [m^2/g]	9.0585	8.3560	7.0923	1.3818

It is shown that when chitosan flake is prepared to chitosan dry beads, pore diameter of bead particles are slightly increased and surface area increases at least 5 times of flakes.

In each experiment, 150 g. of solution containing 10 ppm of mercury compound is used as liquid feedstock. After completion of each experiment, liquid product and spent adsorbent are separated by filter paper (Whatman no.1). Mercury concentration in liquid phase is analyzed using digestion and cold vapor atomic adsorption technique, described in Chapter III.

Since the analysis showed that initial concentrations of mercury in the solutions were not always equal to 10 ppm, actual mercury concentrations analyzed each time the experiments were conducted were used for calculation of percent removal using Equation 3.5 presented in Chapter III. The percent removal is defined to compare adsorption ability of each adsorbent at specified operating conditions.

4.1.1 Determination of Adsorption Period

A set of experiments was conducted to determine suitable adsorption period for other experiments in subsequent studies. The adsorption period is evaluated by conducting experiments with variation of time at 3, 6, 9, and 12 hours. Adsorbents used in the study are chitosan gel beads and chitosan dry beads, prepared using 2 percent by weight of chitosan in acetic acid solution. Adsorbent weight is 15 mg.(basis with dry chitosan). The adsorbates are mercuric chloride and phenylmercuric acetate. Initial pH of mercury compound solutions are 5, 7, and 9. The experiments are conducted at ambient temperature (30 ºC) and a pressure of 1 atm. Experimental results are summarized in Appendix A. The results were calculated to determine amount of mercury compounds adsorbed on chitosan and presented as percent removal. Table 4.2 shows the results of adsorption of mercury compounds at various contact times and is plotted as a function of time in Figures 4.1 to 4.4.

Table 4.2 The results of adsorption of mercury compounds at various contact time

Mercury Compounds/ Beads type	Contact time [Hrs]	Removal of mercury Compounds [%]		
		pH 5	pH 7	pH 9
$HgCl_2$ / Gel	3	43.36	31.21	28.30
	6	50.61	38.37	31.95
	9	56.56	39.38	35.95
	12	57.25	40.13	36.88
PMA/Gel	3	32.45	30.26	28.89
	6	34.03	34.54	32.51
	9	37.20	35.98	34.79
	12	37.80	36.30	35.80
$HgCl_2$ /Dry	3	34.35	22.72	13.42
	6	45.76	36.27	28.61
	9	51.50	45.53	36.54
	12	53.19	45.61	37.67
PMA/Dry	3	43.36	32.21	30.50
	6	46.61	40.37	37.95
	9	50.05	43.10	40.99
	12	51.21	43.51	41.13
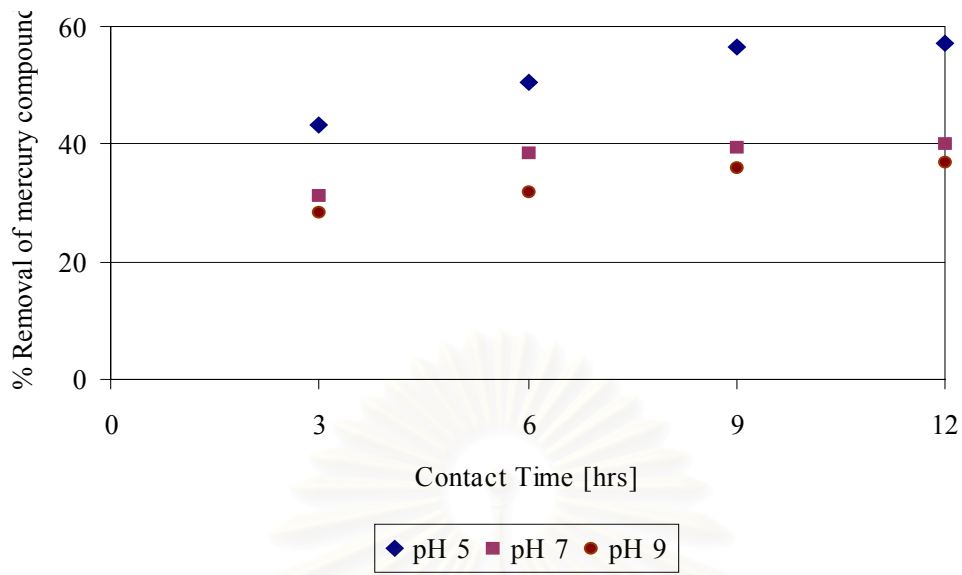
Figure 4.1 Effect of contact time on adsorption of mercuric chloride using chitosan
gel beads
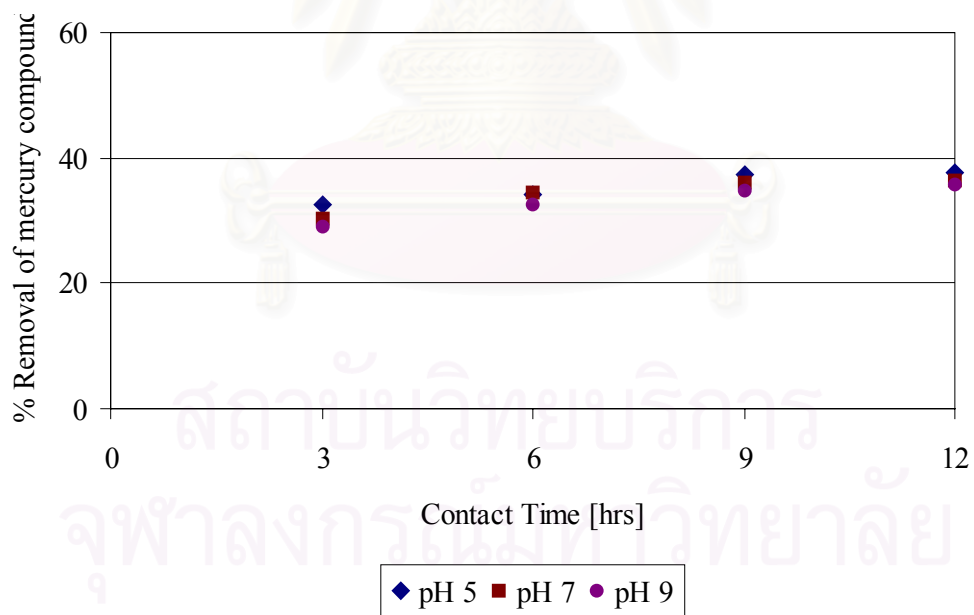
Figure 4.2 Effect of contact time on adsorption of phenylmercuric acetate using

chitosan gel beads
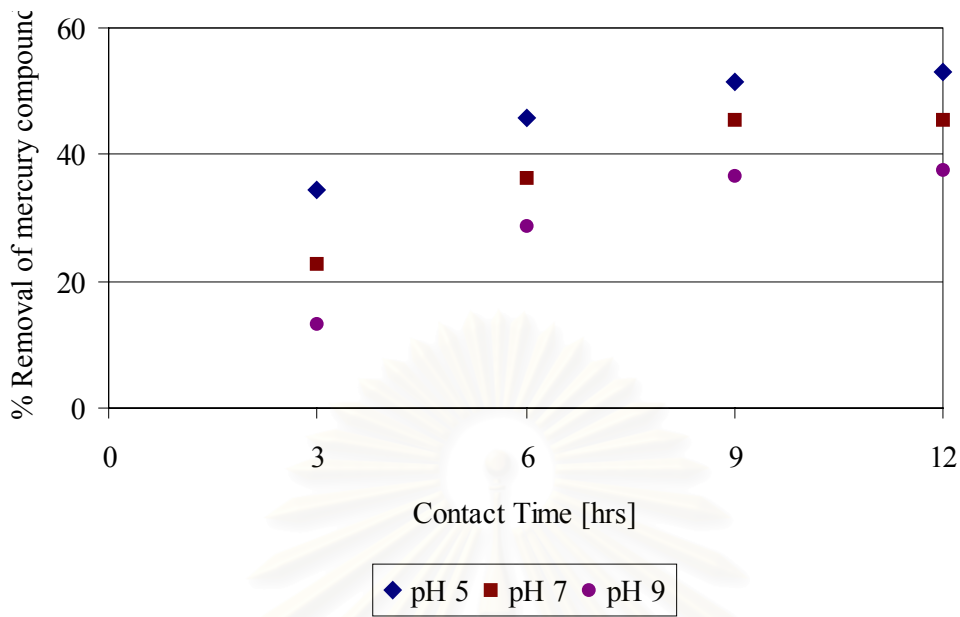
Figure 4.3 Effect of contact time on adsorption of mercuric chloride using
chitosan gel beads
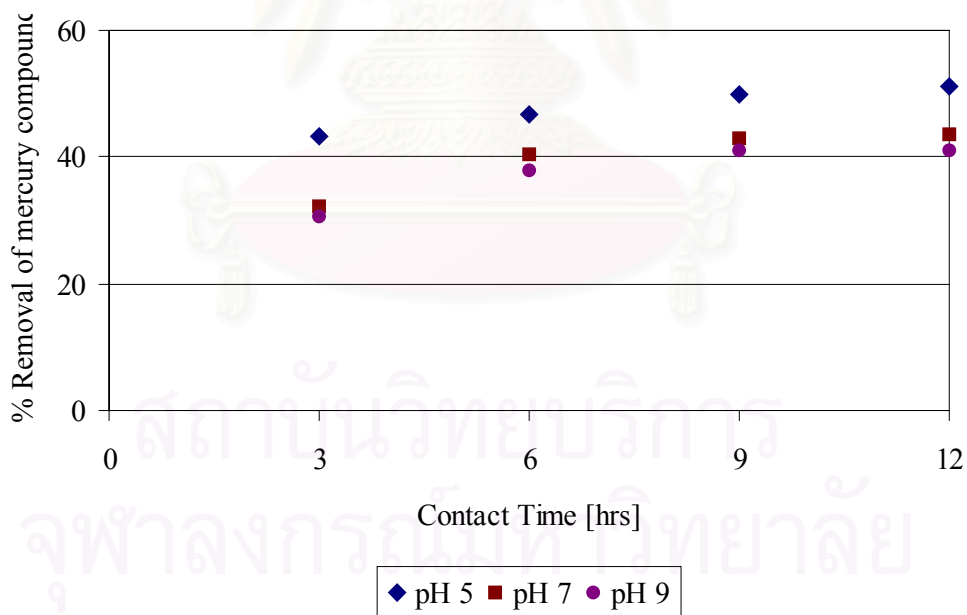
Figure 4.4 Effect of contact time on adsorption of phenylmercuric acetate using
chitosan dry beads

It is shown that the percent removal of mercury compounds depends on the
adsorption period. Percent removal of mercury compounds increases rapidly during the

first 9 hours of the experiment and then it maintains at constant value until 12 hours. From this set of experiments, the contact time is considered. It is decided that the suitable adsorption period is 9 hours and used for subsequent studies.

4.1.2 Adsorption Experiment and Experimental Results

This section describes adsorption experiment and experimental results. The adsorption experiment conducted in order to find effects of initial pH of solution, temperature, concentration of chitosan solution, and types of chitosan bead. The operating conditions of all experiments are summarized in Table 4.3.

Table 4.3 Operating conditions of all experiments.

Solution weight (g)	150
Adsorbent weight (mg)	15
Solution concentration (ppm)	10
Pressure (atm)	atmospheric
Contact time (hour)	9
Mercury compound	Mercuric Chloride and Phenylmercuric Acetate
Initial pH of solution	5, 7, 9
Temperature (^{o}C)	30, 40, 50
Type of chitosan beads	Gel and Dry
Chitosan concentration in acetic acid solution (%)	2, 3, 4

The results are shown in Appendix A and are used for calculation of percent removal of mercury compounds presented in Table 4.4.

Table 4.4 Percent removal by adsorption of mercury compounds

Types of Bead	Conc.of chitosan in acid solution (%)	Temp. (°C)	Removal of Mercury Compounds (%)					
			Mercuric Chloride			Phenylmercuric Acetate		
			PH 5	PH 7	pH 9	pH 5	pH 7	pH 9
Gel	2	30	56.56	39.38	35.95	37.20	35.98	34.79
		40	61.85	48.91	42.19	50.51	45.29	27.55
		50	61.53	49.69	46.95	39.85	36.82	35.35
	3	30	50.98	38.53	38.72	43.77	42.00	39.76
		40	65.13	40.83	40.39	52.12	44.91	38.72
		50	68.07	55.58	45.32	45.32	34.31	34.73
	4	30	53.76	41.33	41.88	61.32	55.32	41.13
		40	58.55	47.02	43.76	54.29	43.77	38.04
		50	58.84	49.41	44.88	52.38	41.47	37.48
Dry	2	30	51.50	45.53	36.54	50.05	43.10	40.99
		40	53.87	47.01	41.52	43.37	36.61	33.36
		50	63.91	54.48	43.01	39.21	35.30	31.11
	3	30	37.48	35.72	21.04	47.01	36.44	26.02
		40	49.79	48.54	24.69	30.97	27.43	23.59
		50	58.31	53.25	28.29	23.94	17.78	16.15
	4	30	29.23	26.21	23.64	28.78	26.38	24.45
		40	45.50	30.62	25.36	27.95	22.02	19.00
		50	46.94	36.21	35.19	26.73	18.05	16.68

4.2 Adsorption Behavior of Mercury Compounds on Chitosan Adsorbent

4.2.1 Ionization of Mercury Compounds

Aqueous solutions containing mercury compounds are prepared by adding mercuric chloride or phenylmercuric acetate in powder forms into demineralized water. Upon dissolving of these compounds, it is possible that the compounds may be dissociated in the solution.

Ciavatta and Grimaldi (1968) proposed that mercuric chloride, when it is dissolved in water, can dissociate by the following Equation.

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+ \text{ , } \log k_1 = 6.72 \pm 0.02 \quad ....(4.1)$$

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2 \text{ , } \log k_1 k_2 = 13.23 \pm 0.02 \quad ....(4.2)$$
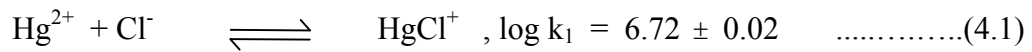
The formation constants in Equations 4.1 and 4.2 showed that the concentration of Hg^{2+} is negligibly small. In addition, Ciavatta and Grimaldi (1968) also proposed the following reactions.

$$HgCl_2 + H_2O \rightleftharpoons HgClOH + H^+ + Cl^- \text{ , } \log k = -9.56 \pm 0.05 \quad ....(4.3)$$

$$HgCl_2 + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+ + 2Cl^- \text{ , } \log k' = -19.6 \pm 0.1 \quad ....(4.4)$$
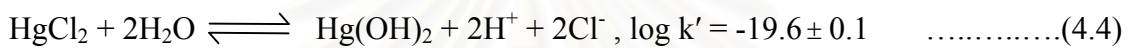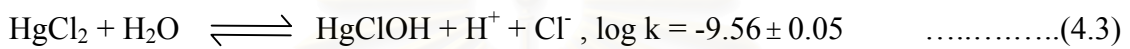
In the case of single-solute system of $HgCl_2$, the dissociation constants (k and k') denote that $HgCl_2$ does not dissociate at all in the aqueous phase because of the dissociation constants of Equations 4.3 and 4.4 are small. Therefore, the concentration of any ionized or dissociated species from $HgCl_2$ is negligibly small. It is concluded that $HgCl_2$ does not dissociated in aqueous solution.

Tezuka and Tonomura (1976) studied the dissociation of phenylmercuric acetate in water and proposed that it dissociated by enzyme catalyst in water. Phenylmercuric acetate in water reacted with organomercurial lyase and dissociated in three groups as Hg^{2+}, phenyl group and acetate group. In demineralized water used in this study, enzyme should not be existed in the solution, so dissociation of phenylmercuric acetate through enzyme is impossible.

Chemical Notification and Assessment (2000) reported that the dissociation constant of phenylmercuric acetate can not be determined. The notified chemical of phenylmercuric acetate should be soluble in water and dissociate completely. In this study, the dissociation of phenylmercuric acetate in demineralized water can not be identified.

4.2.2 Adsorption Behavior

Mercuric chloride can be adsorbed on chitosan in various forms upon the conditions of solution. Kawamura et al. (1993) studied the adsorption of $HgCl_2$ on cross-linked chitosans in single-solute system of mercuric chloride and showed that $HgCl_2$ can be adsorbed on the cross-linked chitosan not by ion exchange but by complex formation reaction as followed

$$
\begin{array}{ccc}
R_1 & & R_1 \\
| & & | \\
R\!-\!N \;+\; HgCl_2 & \rightleftharpoons & R\!-\!N\!-\!HgCl_2 \\
| & & | \\
R_2 & & R_2
\end{array}
\quad\text{..............(4.5)}
$$
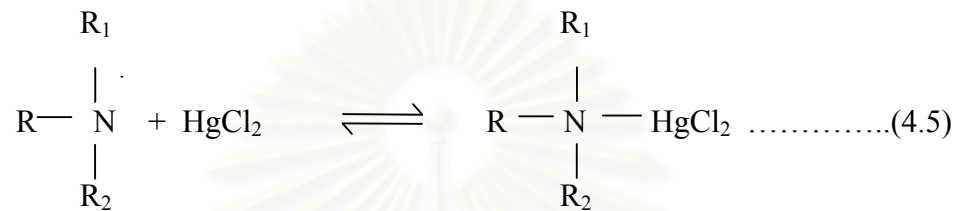
Where, R   denotes the network of the resin.

R_1 and R_2 are hydrogen or cross-linking reagent

Vichit (2002) showed the XRD result of adsorption of phenylmercuric acetate. The result indicated that phenylmercuric acetate adsorbed on chitosan in $C_4H_6HgO_4$ form. The most possible compound having this formula is mercury (II) acetate. The adsorption of phenylmercuric acetate on chitosan may be ligand adsorption on amino group fixed on chitosan particles.

$$
R\!-\!NH_2 + Hg(COOCH_3)_2 \rightleftharpoons R\!-\!NH_2\!-\!Hg(COOCH_3)_2 \quad\text{.......(4.6)}
$$
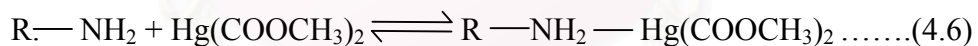
4.3 Effect of Adsorption Conditions

4.3.1 Effect of pH on Adsorption of Mercury Compounds

Effect of pH on adsorption of mercury compounds is discussed in this section. Initial pH of mercury compound solutions are 5, 7, and 9 representing acid, neutral, and basic solutions, respectively. Chitosan gel and dry beads are used as adsorbents. The results are presented in Table 4.4 and plotted in Figures 4.5 to 4.8.
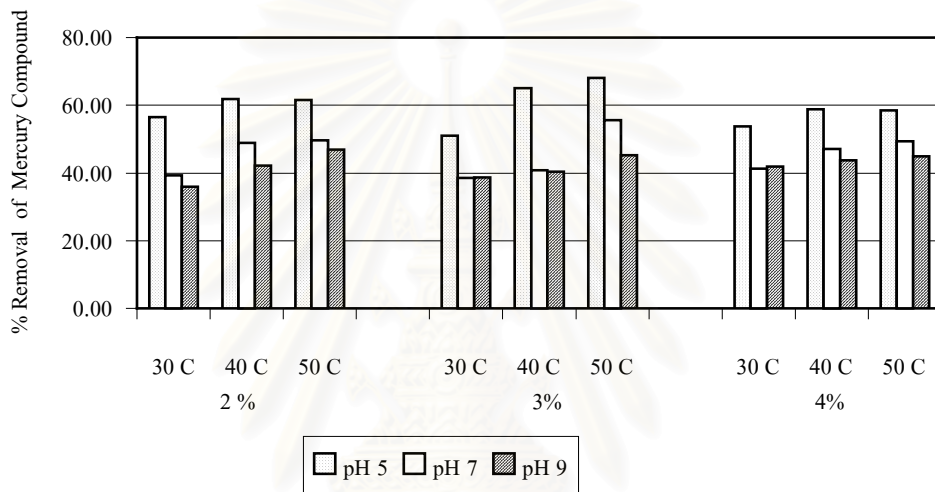
Figure 4.5   The comparison of initial pH of feed in adsorption of $HgCl_2$ using chitosan gel beads
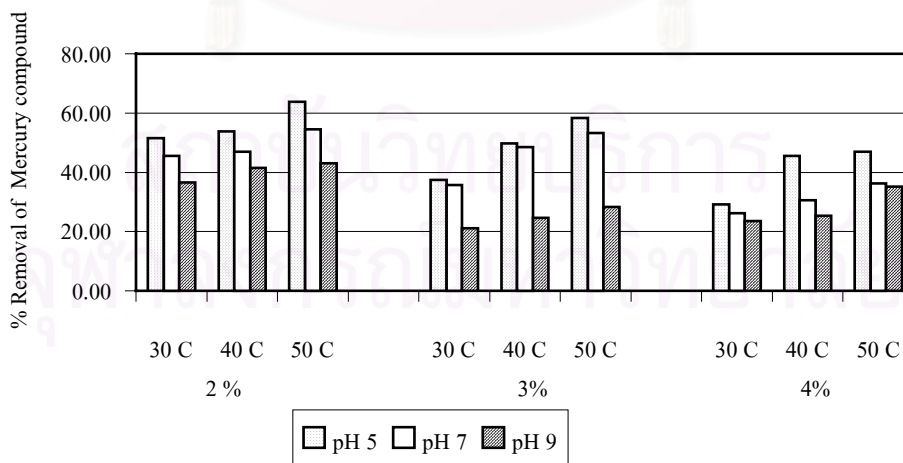
Figure 4.6   The comparison of initial pH of feed in adsorption of $HgCl_2$ using chitosan dry beads
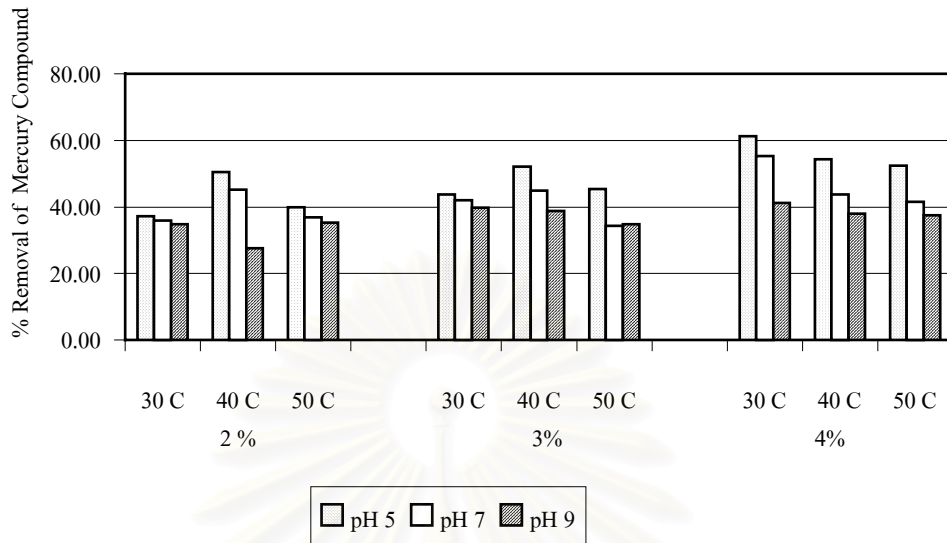
Figure 4.7 The comparison of initial pH of feed in adsorption of PMA using chitosan
gel beads
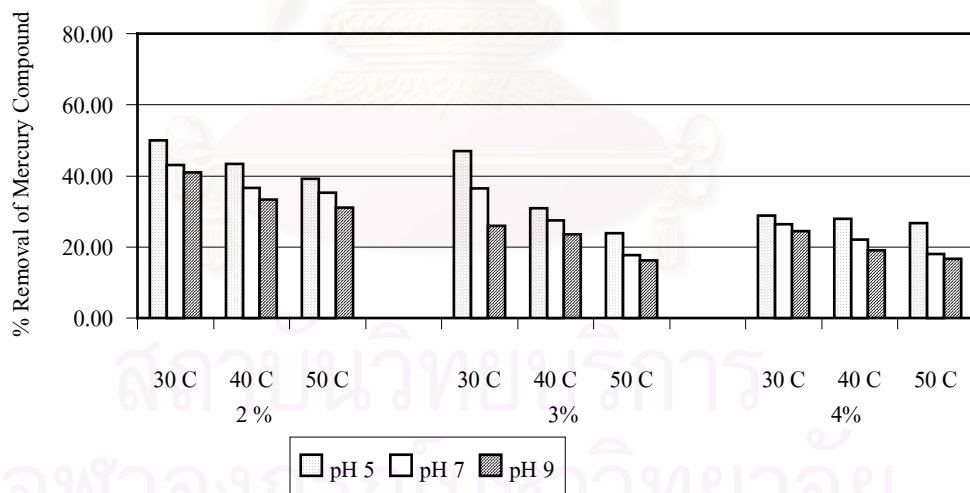
Figure 4.8 The comparison of initial pH of feed in adsorption of PMA using chitosan
dry beads

The adsorption ability of chitosan is presented in percent removal of
mercury compounds. The results indicate that percent removal of mercuric chloride,
adsorbed by chitosan gel beads and chitosan dry beads adsorbents, decreases with
increasing initial pH of solution at all operating temperature.

It is disscussed earlier that mercuric chloride is adsorbed on chitosan as $HgCl_2$ species. When initial pH of mercuric chloride is adjusted to neutral or basic solution, pH 7 or pH 9, sodium hydroxide is used as a chemical compound to adjust the pH. When sodium hydroxide is added to water, it dissociates to Na^+ and OH^-. The OH^- species reacts with $HgCl_2$, as followed.

$$HgCl_2 + OH^- \rightleftharpoons HgClOH + Cl^- \qquad \ldots\ldots\ldots\ldots(4.7)$$

$$HgCl_2 + 2OH^- \rightleftharpoons Hg(OH)_2 + 2Cl^- \qquad \ldots\ldots\ldots\ldots(4.8)$$
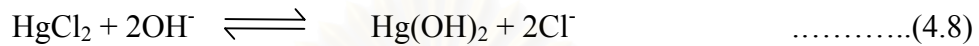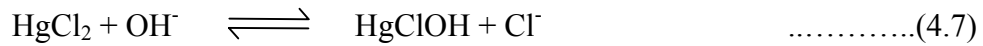
The reaction shift to the right when OH^- is present, resulting in decreasing of $HgCl_2$ in the solution. Since mercuric chloride adsorbs on chitosan as a $HgCl_2$ molecule, decreasing in the amount of $HgCl_2$ in the solution would also decrease the amount of $HgCl_2$ adsorbed on chitosan.

In adsorption of phenylmercuric acetate, the results are presented in Figures 4.7 to 4.8. The results indicate that percent removal of phenylmercuric acetate adsorption using chitosan gel beads and chitosan dry beads adsorbents are slightly decrease with decreasing initial pH of phenylmercuric acetate solution. Mercury (II) acetate can adsorb on chitosan (as described previously). When pH of solution increase, the OH^- species may react with mercury (II) acetate result in decreasing of mercury (II) acetate in the solution. Since phenylmercuric acetate adsorbs on chitosan as mercury (II) acetate species, decreasing in the amount of mercury (II) acetate in the solution would also decrease the amount of phenylmercuric acetate adsorbed on chitosan.

4.3.2 Effect of Temperature

Effect of temperature on adsorption of mercury compounds in presented and discussed in this section. Temperatures used in this experiment are 30 ºC, 40 ºC, and 50 ºC. Percent removal of mercury compounds in each experiment are plotted as function of temperature in Figures 4.9 to 4.12
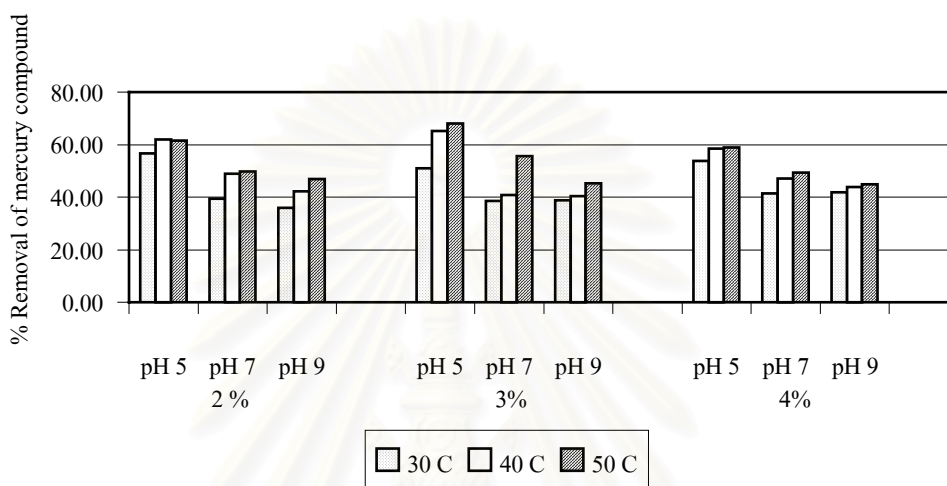
Figure 4.9   The comparison of temperature in adsorption of $HgCl_2$ using chitosan gel beads.
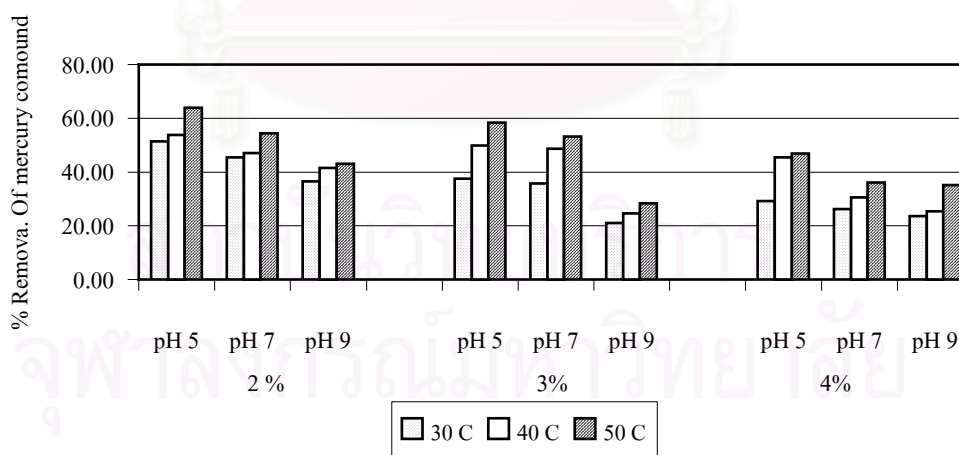
Figure 4.10 The comparison of temperature in adsorption of $HgCl_2$ using chitosan dry beads.
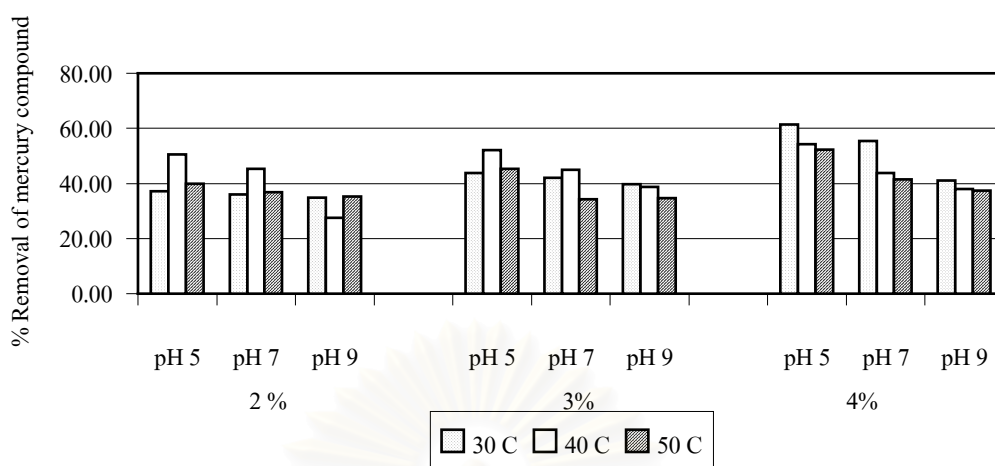
Figure 4.11 The comparison of temperature in adsorption of PMA using chitosan gel beads
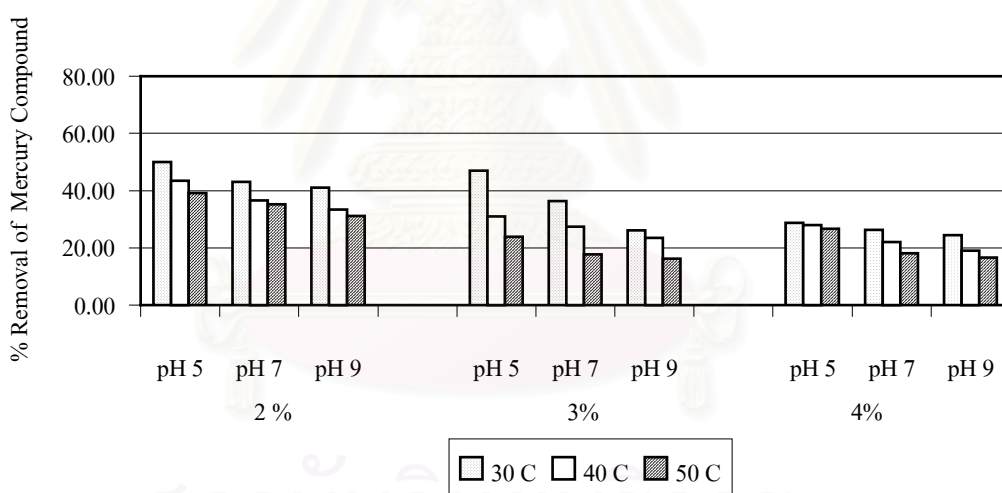
Figure 4.12 The comparison of temperature in adsorption of PMA using chitosan dry beads

Figures 4.9 to 4.10 show the comparison of percent removal of mercuric chloride using chitosan gel beads and dry beads, respectively. The results indicate that the removal of mercuric chloride, by both of gel beads and dry beads depends on temperatures. The percent removal slightly increases with increasing operating temperatures.

It is described earlier in Chapter II that external mass transfer resistance and intraparticle mass transfer resistance are major controlling stages of adsorption ability. Mass transfer resistances are function of the diffusivity coefficient according to Stokes-Einstein equation (James R, Welty, 1984) as follow

$$D_{AB} = kT/6\pi r\mu_B \qquad\qquad \text{............(4.9)}$$

D_{AB} = Diffusivity

k = Boltzmann constant

T = Temperature

r = solute particle radius

μ_B = solvent viscosity

It is shown from Equation 4.9 that diffusivity coefficient increases with increasing temperature. When diffusivity coefficient increases the amount of mass transferred from bulk of liquid solution to the surface of the adsorbent also increases which would also increase adsorption ability of chitosan beads.

Removal of phenylmercuric acetate shows opposite results. When chitosan dry beads was used to adsorb phenylmercuric acetate, adsorption ability of chitosan dry beads decreases with increasing temperature. This may be the result of polarity complication of molecule of phenylmercuric acetate and the structure may be changing when temperature increased because it is organic substance. Adsorption ability of chitosan gel beads on adsorption of phenylmercuric acetate, as shown in Figure 4.11, can not be conclude.

4.3.3 Effect of Chitosan Concentration

Effect of concentration of chitosan solution on adsorption of mercury compounds in aqueous solutions is discussed in this section. The concentrations of chitosan solution in this experiment are 2, 3, and 4 percent by weight of chitosan in 1 M acetic acid, respectively. The results are plotted in Figures 4.13 to 4.16.
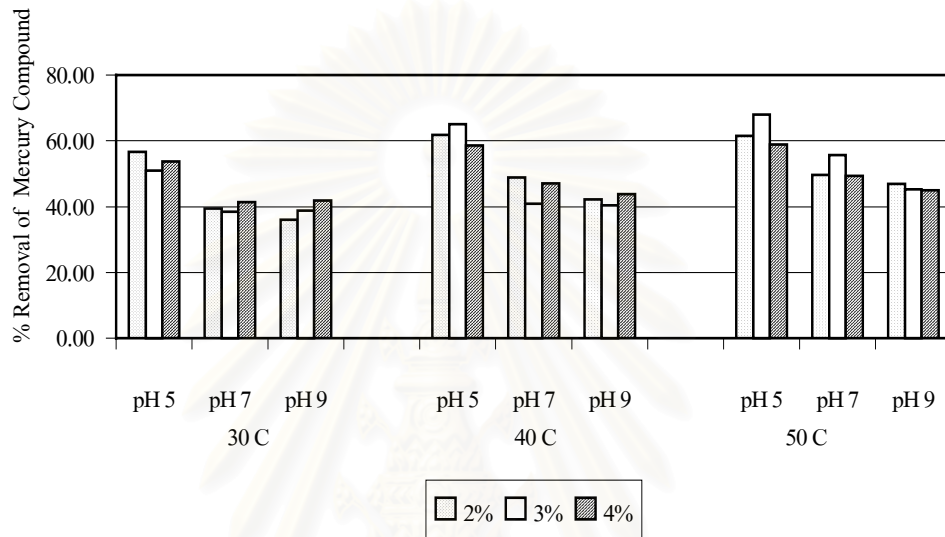
Figure 4.13 The comparison of chitosan concentration in adsorption of HgCl$_2$ using chitosan gel beads
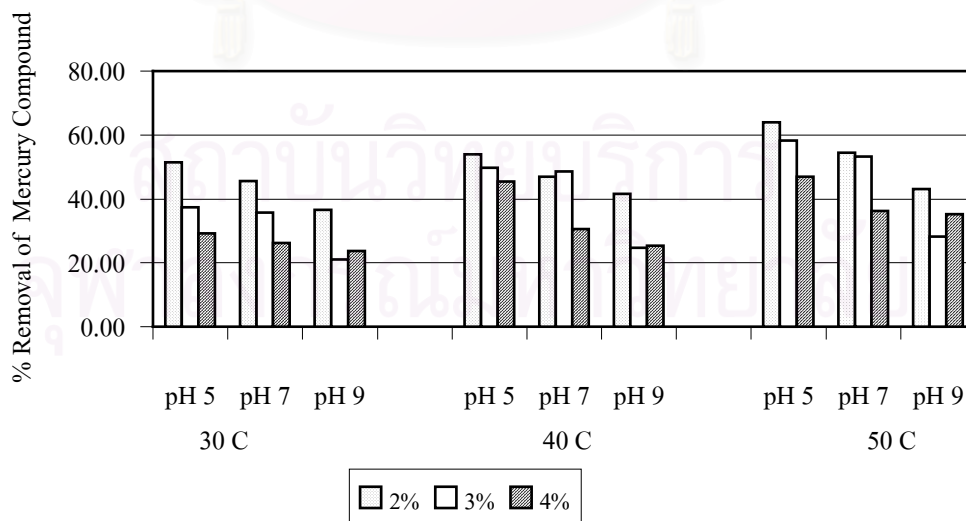
Figure 4.14 The comparison of chitosan concentration in adsorption of HgCl$_2$ using chitosan dry beads
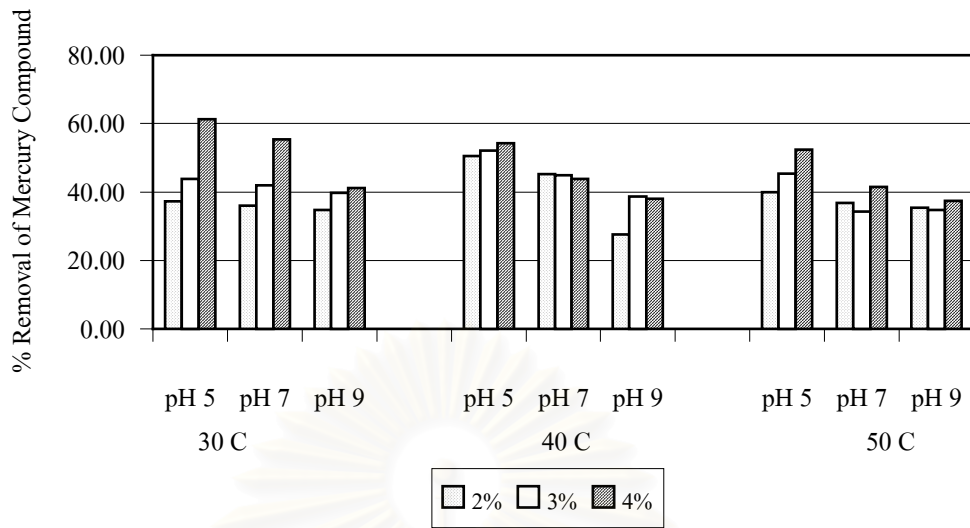
Figure 4.15 The comparison of chitosan concentration in adsorption of PMA using chitosan gel beads
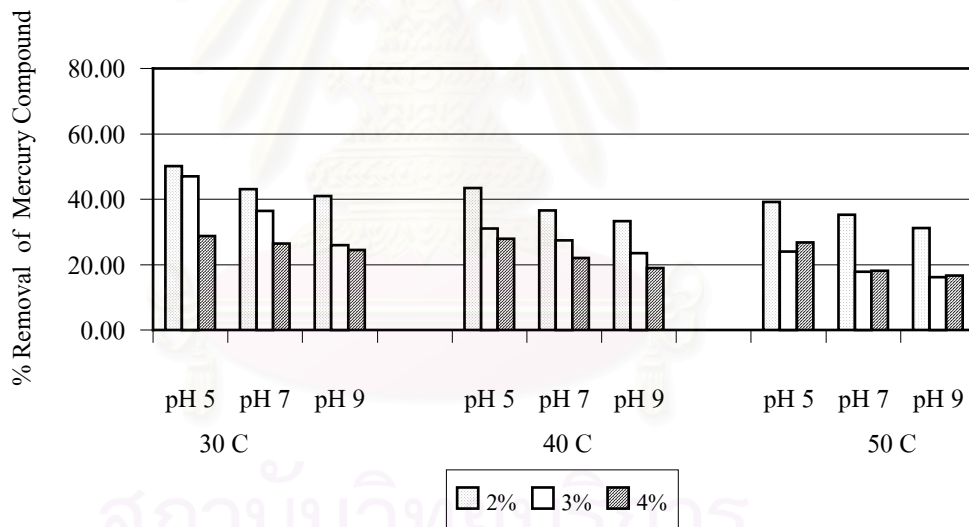
Figure 4.16 The comparison of chitosan concentration in adsorption of PMA using chitosan dry beads

Comparison of mercury compounds removal using chitosan gel beads prepared from different concentrations of chitosan solutions is shown in Figures 4.13 and 4.15. The results did not show any changing pattern or any relationship. Adsorption of mercuric chloride on chitosan gel beads seems to be independent of concentrations of chitosan solution. It is possible that chitosan gel beads contains large amount of water in its structure during formation. When high concentrations of

chitosan solution are used to prepare chitosan gel beads, the formation of the beads would be more densely which change the mass transfer resistance of the system. Mechanism of adsorption of mercury compounds on chitosan gel beads prepared from different concentrations of chitosan solution has not yet been explained and the results in this study are scattered, so effect of concentration of chitosan solution ca not be conclude yet.

Comparison of mercury compounds removal using chitosan dry beads prepared from different concentrations of chitosan solution are shown in Figures 4.14 and 4.16. The results show that percent removal of chitosan decrease with increasing chitosan concentration. Analysis of surface area and pore volume of chitosan dry beads show that after freeze drying chitosan beads, surface area and pore diameter of chitosan dry beads decrease with increasing concentration of chitosan solution. This may explain that increasing concentration of chitosan solution do not change the particle size results in the density of chitosan beads increases with concentration of chitosan solution. Therefore high concentration of chitosan has a small cavity, when it collapse after drying resulted in small pore size and decrease surface area according the result of this experiment. In adsorption behavior, increasing in size of the pores control the diffusion of mercury ions by decreasing the intraparticle diffusion resistance (M.Ruiz et al., 2001). In addition, adsorption ability increases with increasing surface area of adsorbents resulted in chitosan concentration had effect of mercury compounds adsorption on chitosan.

4.3.4 Effect of Chitosan Beads Types

Effect of chitosan bead types, gel and dry beads, on adsorption mercury compounds are discussed. Chitosan gel bead is a wet chitosan that contain large amount of water in the bead. Chitosan dry bead is a gel bead which water is removed using freeze-drying method. Figures 4.17 to 4.22 present comparison of both type of beads.
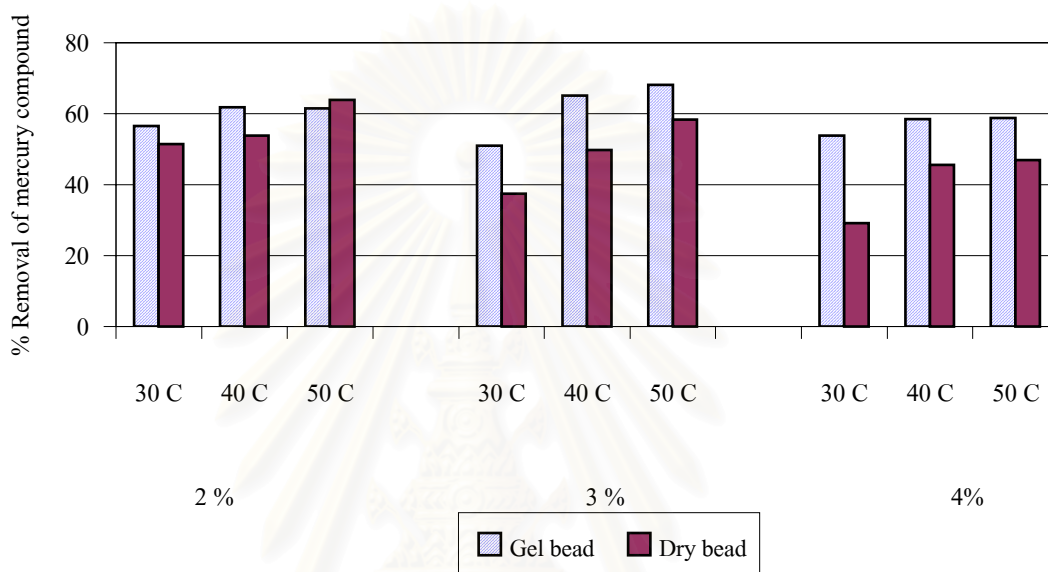
Figure 4.17 The comparison of chitosan gel bead and dry bead in adsorption ability of $HgCl_2$ at pH 5
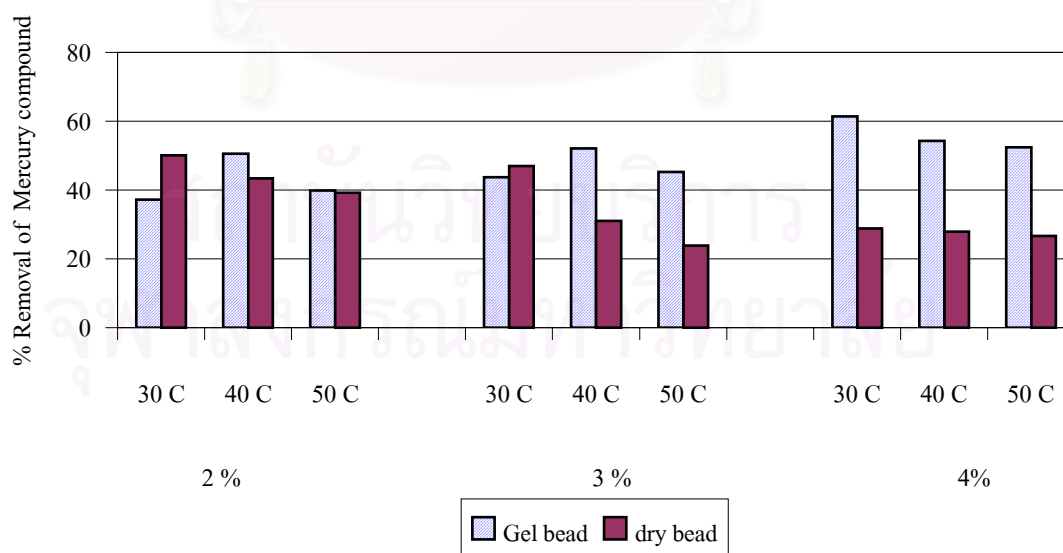
Figure 4.18 The comparison of chitosan gel bead and dry bead in adsorption ability of PMA at pH 5
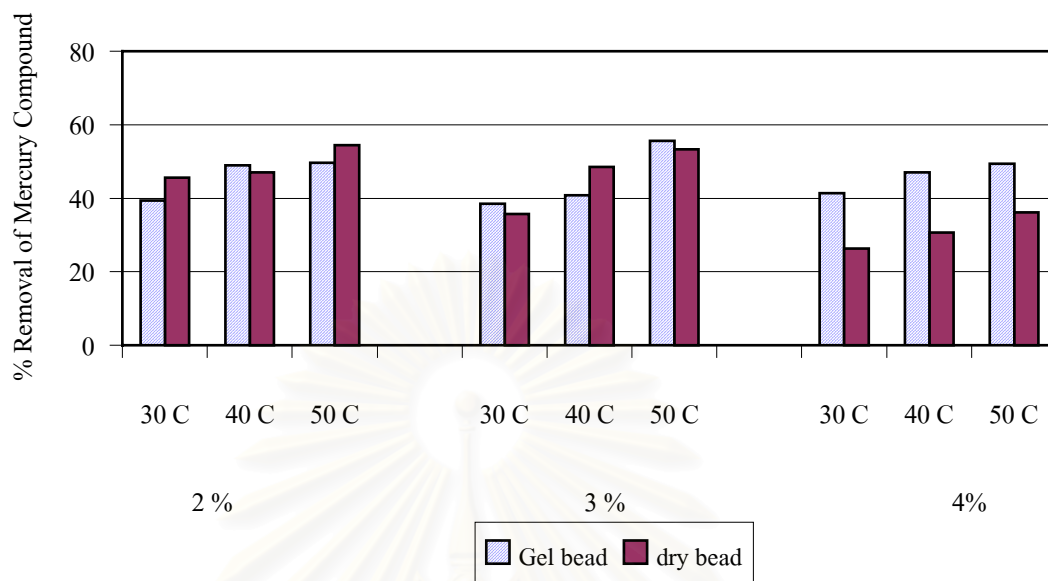
Figure 4.19 The comparison of chitosan gel bead and dry bead in adsorption ability
of HgCl$_2$ at pH 7
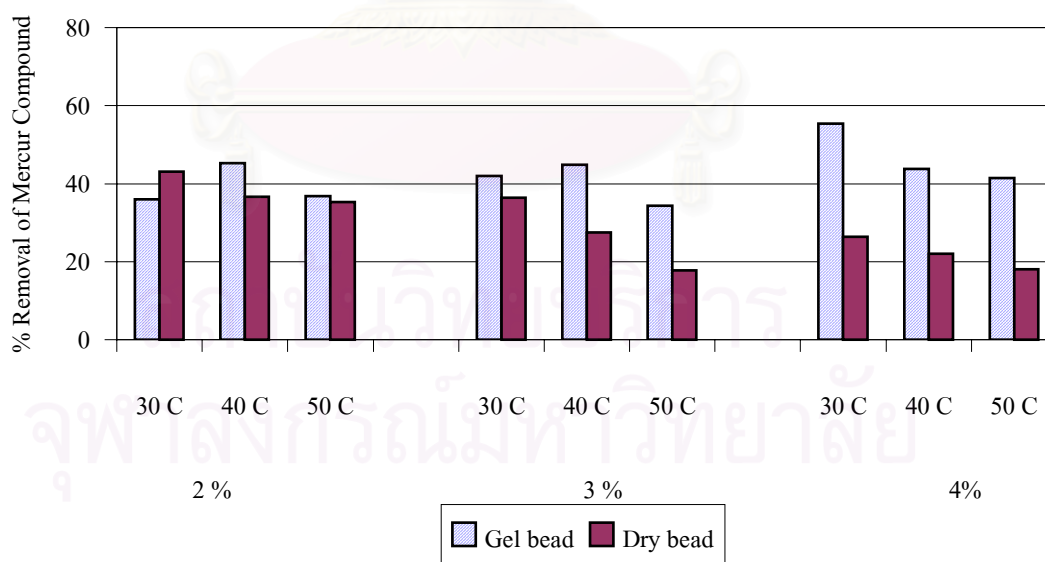
Figure 4.20 The comparison of chitosan gel bead and dry bead in adsorption ability
of PMA at pH 7
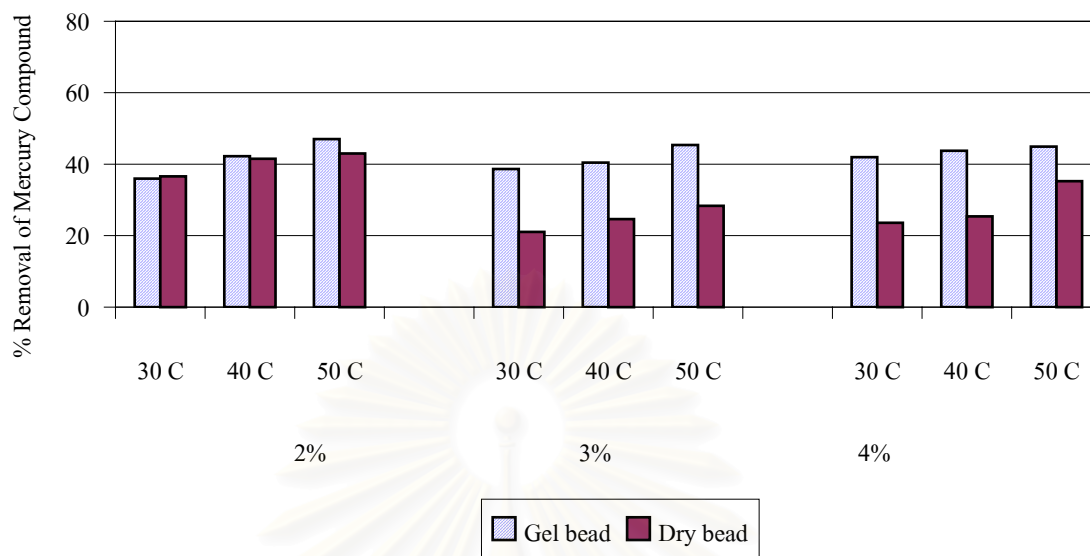
Figure 4.21 The comparison of chitosan gel bead and dry bead in adsorption ability
of $HgCl_2$ at pH 9
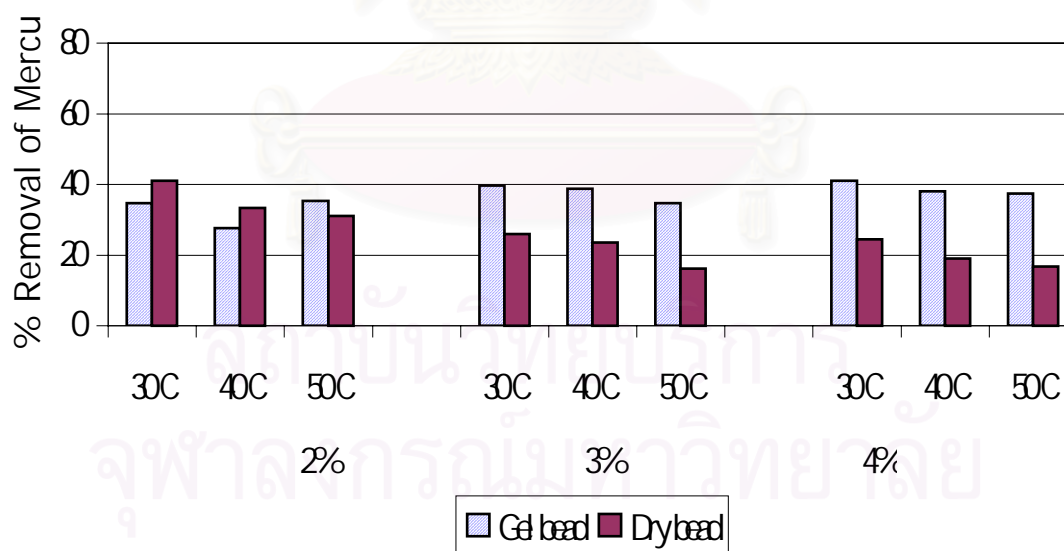
Figure 4.22 The comparison of chitosan gel bead and dry bead in adsorption ability
of PMA at pH 9

The results show that removal of mercury compounds, using chitosan gel and dry beads prepared from 2 percent by weight of chitosan solution, are almost identical. The differences of percent removal of mercury compounds are within error limit of this study.

When the beads are prepared using concentrations of chitosan solutions of 3 and 4 percent, percent removal of mercury compounds using chitosan gel beads are higher than chitosan dry beads. The difference of adsorption ability between chitosan gel and dry beads increase with increasing chitosan concentration. Chitosan gel beads contain large amount of water in the bead, solutions containing mercury compounds can diffuse easily through intraparticle of chitosan gel beads. When the gel beads are dried, intraparticle diffusion resistance was strongly increased because of a restriction in the porous in the beads and a decrement in the size of the pores.

CHAPTER V

CONCLUSIONS

The following conclusions are drawn from this study;

1. The results showed that chitosan beads adsorbents can be used effectively in the removal of mercury compounds in aqueous solution.
2. Adsorption ability of chitosan beads on mercuric chloride and phenylmercuric acetate decreased with increasing initial pH of solution.
3. Mercuric chloride can be adsorbed better with increasing operating temperature but phenylmercuric acetate showed an opposite result.
4. It is also found that chitosan gel beads can be used to remove mercury compounds more effectively than chitosan dry beads.
5. Concentration of chitosan solution does not affect adsorption ability of mercury compounds but adsorption ability of chitosan dry beads decreased with increasing concentration of chitosan solution.

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    <u>Analytical Sciences</u> 16 (2000) : 1303-1308.

APPENDICES

Appendix A

Table 1A Conditions and results of each experiment.

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (^{o}C)	Time (hrs)	Hg content (ppm)	% Removal
1	HgCl$_2$	2	Gel	10.76	5	30	3	6.09	43.36
2	HgCl$_2$	2	Gel	10.76	7	30	3	7.40	31.21
3	HgCl$_2$	2	Gel	10.76	9	30	3	7.71	28.3
4	PMA	2	Gel	11.25	5	30	3	7.60	32.45
5	PMA	2	Gel	11.25	7	30	3	7.84	30.26
6	PMA	2	Gel	11.25	9	30	3	8.00	28.89
7	HgCl$_2$	2	Gel	10.76	5	30	6	5.31	50.61
8	HgCl$_2$	2	Gel	10.76	7	30	6	6.63	38.37
9	HgCl$_2$	2	Gel	10.76	9	30	6	7.32	31.95
10	PMA	2	Gel	11.25	5	30	6	7.42	34.03
11	PMA	2	Gel	11.25	7	30	6	7.36	34.54
12	PMA	2	Gel	11.25	9	30	6	7.59	32.51
13	HgCl$_2$	2	Gel	10.47	5	30	9	4.55	56.56
14	HgCl$_2$	2	Gel	10.47	7	30	9	6.35	39.38
15	HgCl$_2$	2	Gel	10.47	9	30	9	6.71	35.95
16	PMA	2	Gel	11.42	5	30	9	7.17	37.2
17	PMA	2	Gel	11.42	7	30	9	7.31	35.98
18	PMA	2	Gel	11.42	9	30	9	7.45	34.79
19	HgCl$_2$	2	Gel	10.47	5	30	12	4.48	57.25
20	HgCl$_2$	2	Gel	10.47	7	30	12	6.27	40.13
21	HgCl$_2$	2	Gel	10.47	9	30	12	6.61	36.88
22	PMA	2	Gel	11.42	5	30	12	7.11	37.8
23	PMA	2	Gel	11.42	7	30	12	7.28	36.3
24	PMA	2	Gel	11.42	9	30	12	7.33	35.8

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (^{o}C)	Time (hrs)	Hg content (ppm)	% Removal
25	HgCl$_2$	2	Dry	10.18	5	30	3	6.68	34.35
26	HgCl$_2$	2	Dry	10.18	7	30	3	7.87	22.72
27	HgCl$_2$	2	Dry	10.18	9	30	3	8.81	13.42
28	PMA	2	Dry	11.42	5	30	3	6.47	43.36
29	PMA	2	Dry	11.42	7	30	3	7.74	32.21
30	PMA	2	Dry	11.42	9	30	3	7.94	30.50
31	HgCl$_2$	2	Dry	10.18	5	30	6	5.52	45.76
32	HgCl$_2$	2	Dry	10.18	7	30	6	6.49	36.27
33	HgCl$_2$	2	Dry	10.18	9	30	6	7.27	28.61
34	PMA	2	Dry	10.91	5	30	6	5.82	46.61
35	PMA	2	Dry	10.91	7	30	6	6.51	40.37
36	PMA	2	Dry	10.91	9	30	6	6.77	37.95
37	HgCl$_2$	2	Dry	10.69	5	30	9	5.18	51.50
38	HgCl$_2$	2	Dry	10.69	7	30	9	5.82	45.53
39	HgCl$_2$	2	Dry	10.69	9	30	9	6.78	36.54
40	PMA	2	Dry	10.91	5	30	9	5.45	50.05
41	PMA	2	Dry	10.91	7	30	9	6.21	43.10
42	PMA	2	Dry	10.91	9	30	9	6.44	40.99
43	HgCl$_2$	2	Dry	10.69	5	30	12	5.00	53.19
44	HgCl$_2$	2	Dry	10.69	7	30	12	5.81	45.61
45	HgCl$_2$	2	Dry	10.69	9	30	12	6.66	37.67
46	PMA	2	Dry	10.91	5	30	12	5.32	51.21
47	PMA	2	Dry	10.91	7	30	12	6.16	43.51
48	PMA	2	Dry	10.91	9	30	12	6.42	41.13

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (°C)	Time (hrs)	Hg content (ppm)	% Removal
49	HgCl₂	2	Gel	11.35	5	40	9	4.33	61.85
50	HgCl₂	2	Gel	11.35	7	40	9	5.80	48.91
51	HgCl₂	2	Gel	11.35	9	40	9	6.56	42.19
52	PMA	2	Gel	11.62	5	40	9	5.75	50.51
53	PMA	2	Gel	11.62	7	40	9	6.36	45.29
54	PMA	2	Gel	11.62	9	40	9	8.42	27.55
55	HgCl₂	2	Gel	11.35	5	50	9	4.37	61.53
56	HgCl₂	2	Gel	11.35	7	50	9	5.71	49.69
57	HgCl₂	2	Gel	11.35	9	50	9	6.02	46.95
58	PMA	2	Gel	11.62	5	50	9	6.99	39.85
59	PMA	2	Gel	11.62	7	50	9	7.34	36.82
60	PMA	2	Gel	11.62	9	50	9	7.51	35.35
61	HgCl₂	3	Gel	10.58	5	30	9	5.19	50.98
62	HgCl₂	3	Gel	10.58	7	30	9	6.50	38.53
63	HgCl₂	3	Gel	10.58	9	30	9	6.48	38.72
64	PMA	3	Gel	10.22	5	30	9	5.75	43.77
65	PMA	3	Gel	10.22	7	30	9	5.93	42.00
66	PMA	3	Gel	10.22	9	30	9	6.16	39.76
67	HgCl₂	3	Gel	10.58	5	40	9	3.69	65.13
68	HgCl₂	3	Gel	10.58	7	40	9	6.26	40.83
69	HgCl₂	3	Gel	10.58	9	40	9	6.31	40.39
70	PMA	3	Gel	10.22	5	40	9	4.89	52.12
71	PMA	3	Gel	10.22	7	40	9	5.63	44.91
72	PMA	3	Gel	10.22	9	40	9	6.26	38.72

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (°C)	Time (hrs)	Hg content (ppm)	% Removal
73	HgCl$_2$	3	Gel	10.31	5	50	9	3.29	68.07
74	HgCl$_2$	3	Gel	10.31	7	50	9	4.58	55.58
75	HgCl$_2$	3	Gel	10.31	9	50	9	5.64	45.32
76	PMA	3	Gel	10.22	5	50	9	5.59	45.32
77	PMA	3	Gel	10.22	7	50	9	6.71	34.31
78	PMA	3	Gel	10.22	9	50	9	6.67	34.73
79	HgCl$_2$	4	Gel	10.31	5	30	9	4.77	53.76
80	HgCl$_2$	4	Gel	10.31	7	30	9	6.05	41.33
81	HgCl$_2$	4	Gel	10.31	9	30	9	5.99	41.88
82	PMA	4	Gel	10.22	5	30	9	3.95	61.32
83	PMA	4	Gel	10.22	7	30	9	4.57	55.32
84	PMA	4	Gel	10.22	9	30	9	6.02	41.13
85	HgCl$_2$	4	Gel	9.60	5	40	9	3.98	58.55
86	HgCl$_2$	4	Gel	9.60	7	40	9	5.09	47.02
87	HgCl$_2$	4	Gel	9.60	9	40	9	5.40	43.76
88	PMA	4	Gel	10.28	5	40	9	4.70	54.29
89	PMA	4	Gel	10.28	7	40	9	5.78	43.77
90	PMA	4	Gel	10.28	9	40	9	6.37	38.04
91	HgCl$_2$	4	Gel	9.60	5	50	9	3.95	58.84
92	HgCl$_2$	4	Gel	9.60	7	50	9	4.86	49.41
93	HgCl$_2$	4	Gel	9.60	9	50	9	5.29	44.88
94	PMA	4	Gel	10.28	5	50	9	4.90	52.38
95	PMA	4	Gel	10.28	7	50	9	6.02	41.47
96	PMA	4	Gel	10.28	9	50	9	6.43	37.48

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (°C)	Time (hrs)	Hg content (ppm)	% Removal
97	HgCl$_2$	2	Dry	10.35	5	40	9	4.77	53.87
98	HgCl$_2$	2	Dry	10.35	7	40	9	5.48	47.01
99	HgCl$_2$	2	Dry	10.35	9	40	9	6.05	41.52
100	PMA	2	Dry	10.41	5	40	9	5.90	43.37
101	PMA	2	Dry	10.41	7	40	9	6.60	36.61
102	PMA	2	Dry	10.41	9	40	9	6.94	33.36
103	HgCl$_2$	2	Dry	10.35	5	50	9	3.74	63.91
104	HgCl$_2$	2	Dry	10.35	7	50	9	4.71	54.48
105	HgCl$_2$	2	Dry	10.35	9	50	9	5.90	43.01
106	PMA	2	Dry	10.41	5	50	9	6.33	39.21
107	PMA	2	Dry	10.41	7	50	9	6.74	35.3
108	PMA	2	Dry	10.41	9	50	9	7.17	31.11
109	HgCl$_2$	3	Dry	10.68	5	30	9	6.68	37.48
110	HgCl$_2$	3	Dry	10.68	7	30	9	6.87	35.72
111	HgCl$_2$	3	Dry	10.68	9	30	9	8.43	21.04
112	PMA	3	Dry	10.41	5	30	9	5.52	47.01
113	PMA	3	Dry	10.41	7	30	9	6.62	36.44
114	PMA	3	Dry	10.41	9	30	9	7.70	26.02
115	HgCl$_2$	3	Dry	10.68	5	40	9	5.36	49.79
116	HgCl$_2$	3	Dry	10.68	7	40	9	5.50	48.54
117	HgCl$_2$	3	Dry	10.68	9	40	9	8.04	24.69
118	PMA	3	Dry	10.41	5	40	9	7.19	30.97
119	PMA	3	Dry	10.41	7	40	9	7.55	27.43
120	PMA	3	Dry	10.41	9	40	9	7.95	23.59

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (°C)	Time (hrs)	Hg content (ppm)	% Removal
121	HgCl$_2$	3	Dry	10.56	5	50	9	4.40	58.31
122	HgCl$_2$	3	Dry	10.56	7	50	9	4.94	53.25
123	HgCl$_2$	3	Dry	10.56	9	50	9	7.57	28.29
124	PMA	3	Dry	9.29	5	50	9	7.07	23.94
125	PMA	3	Dry	9.29	7	50	9	7.64	17.78
126	PMA	3	Dry	9.29	9	50	9	7.79	16.15
127	HgCl$_2$	4	Dry	10.56	5	30	9	7.47	29.23
128	HgCl$_2$	4	Dry	10.56	7	30	9	7.79	26.21
129	HgCl$_2$	4	Dry	10.56	9	30	9	8.06	23.64
130	PMA	4	Dry	9.29	5	30	9	6.62	28.78
131	PMA	4	Dry	9.29	7	30	9	6.84	26.38
132	PMA	4	Dry	9.29	9	30	9	7.02	24.45
133	HgCl$_2$	4	Dry	10.43	5	40	9	5.68	45.50
134	HgCl$_2$	4	Dry	10.43	7	40	9	7.24	30.62
135	HgCl$_2$	4	Dry	10.43	9	40	9	7.78	25.36
136	PMA	4	Dry	9.29	5	40	9	6.69	27.95
137	PMA	4	Dry	9.29	7	40	9	7.24	22.02
138	PMA	4	Dry	9.29	9	40	9	7.52	19.00
139	HgCl$_2$	4	Dry	10.43	5	50	9	5.53	46.94
140	HgCl$_2$	4	Dry	10.43	7	50	9	6.65	36.21
141	HgCl$_2$	4	Dry	10.43	9	50	9	6.76	35.19
142	PMA	4	Dry	9.29	5	50	9	6.81	26.73
143	PMA	4	Dry	9.29	7	50	9	7.61	18.05
144	PMA	4	Dry	9.29	9	50	9	7.74	16.68

Table 1A Conditions and results of each experiment. (continued)

Exp. No.	Mercury Type	CTS Conc. (%)	Bead Tepe	Int. Conc (ppm)	Initial pH	Temp (°C)	Time (hrs)	Hg content (ppm)	% Removal
145	HgCl$_2$	2	Dry	10.76	7	30	9	6.01	44.19
146	HgCl$_2$	2	Dry	10.76	7	30	9	5.75	46.59
147	HgCl$_2$	2	Dry	10.47	7	30	9	5.70	45.56
148	HgCl$_2$	2	Dry	10.47	7	30	9	5.46	47.84
149	HgCl$_2$	2	Dry	10.18	7	30	9	5.25	48.43
150	HgCl$_2$	2	Dry	10.18	7	30	9	5.65	44.54
151	HgCl$_2$	2	Dry	10.69	7	30	9	6.04	43.52
152	HgCl$_2$	2	Dry	10.69	7	30	9	5.72	46.48
153	HgCl$_2$	2	Dry	11.35	7	30	9	6.27	44.80
154	HgCl$_2$	2	Dry	11.35	7	30	9	6.13	45.95
155	HgCl$_2$	2	Dry	10.58	7	30	9	5.46	48.44
156	HgCl$_2$	2	Dry	10.58	7	30	9	5.84	44.82
157	HgCl$_2$	2	Dry	10.31	7	30	9	5.39	47.74
158	HgCl$_2$	2	Dry	10.31	7	30	9	5.61	45.59
159	HgCl$_2$	2	Dry	9.60	7	30	9	5.11	46.73
160	HgCl$_2$	2	Dry	9.60	7	30	9	5.34	44.36
161	HgCl$_2$	2	Dry	10.35	7	30	9	5.46	47.22
162	HgCl$_2$	2	Dry	10.35	7	30	9	5.60	45.91
163	HgCl$_2$	2	Dry	10.68	7	30	9	5.83	45.39
164	HgCl$_2$	2	Dry	10.68	7	30	9	5.68	46.81
165	HgCl$_2$	2	Dry	10.56	7	30	9	5.57	47.23
166	HgCl$_2$	2	Dry	10.56	7	30	9	5.63	46.65
167	HgCl$_2$	2	Dry	10.43	7	30	9	5.39	48.37
168	HgCl$_2$	2	Dry	10.43	7	30	9	5.74	44.92

Appendix B
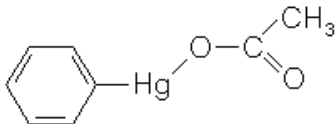
Table B – 1 Properties of Mercuric Chloride *

Formula	$HgCl_2$
Chemical Name	Mercuric Chloride
Physical Properties	
Molecular Weight	271.52
Status at 25 ^oC	Solid
Color	White
Boiling Point (^oC)	302
Melting Point (^oC)	277
Specific Gravity	5.44
Solubility	Soluble in Water
Purity	> 99%
Supplier	Fluka

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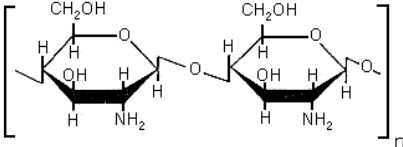
* From Encyclopedia of Chemical Engineering.

Table B – 2 Properties of Phenylmercuric Acetate *

Formula	$C_6H_5HgCOOCH_3$

Structure

Chemical Name	Phenylmercuric Acetate
Physical Properties	
Molecular Weight	336.74
Status at 25 ^{o}C	Solid
Color	White
Boiling Point (^{o}C)	-
Melting Point (^{o}C)	149
Specific Gravity	5.44
Solubility	soluble in water about 1700 ppm
Purity	> 97%
Supplier	Fluka

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* From Merck Index.

Table B – 3 Properties of Chitosan 95 % Degree of Deacetylation *

Structure	
Chemical Name	poly $(1\rightarrow 4)$-2-amino-2-deoxy-β-D-glucan
Appearance	Yellowish
Particle Size	Mesh No.18
Ash Content	0.15%
Moisture Content	9.0%
Deacetylation	95%
Solution (1% in 1% acetic acid)	
Insoluble	0.4%
Viscosity	648 cps
Heavy Metal	0 ppm
Microbial Content	
Total Plate Count	10 cfu/g
Yeast & Mold	10 cfu/g
E.coli & Salmonella	Nill

* From Seafresh Chitosan (Lab) Co., Ltd.

Table B – 4 Properties of Sodium Hydroxide *

Formula	NaOH
Chemical Name	Sodium Hydroxide
Physical Properties	
Molecular Weight	40.01
Status at 25 ^{o}C	Solid
Color	White
Boiling Point (^{o}C)	1390
Melting Point (^{o}C)	318
Specific Gravity	2.13
Solubility	Soluble in Water
Purity	48 - 51%
Supplier	Carlo Erba

* From Encyclopedia of Chemistry

Table B – 5 Properties of Nitric Acid *

Formula	HNO_3
Chemical Name	Nitric Acid
Physical Properties	
Molecular Weight	63.02
Status at 25 ^{o}C	Liquid
Color	Colorless
Boiling Point (^{o}C)	83
Melting Point (^{o}C)	- 41.59
Specific Gravity	1.502
Solubility	Soluble in Water
Purity	69.0 - 70.5%
Supplier	Merck

* From Merck Index.

Table B – 6 Properties of Sulfuric Acid *

Formula	H_2SO_4
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	98.09
Status at 25 ^{o}C	Liquid
Color	Colorless
Boiling Point (^{o}C)	~ 290
Melting Point (^{o}C)	10
Specific Gravity	1.84
Solubility	Soluble in Water
Purity	> 99%
Supplier	Merck

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* From Merck Index.

Table B – 7 Properties of Hydrochloric Acid *

Formula	HCl
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Status at 25 ^{o}C	Liquid
Color	Colorless
Boiling Point (^{o}C)	- 15.35
Melting Point (^{o}C)	- 83
Specific Gravity	5.44
Solubility	Soluble in Water and Alcohol
Purity	37%
Supplier	Merck

* From Encyclopedia of Chemical Engineering.

Table B – 8 Properties of Hydrofluoric Acid *

Formula	HF
Chemical Name	Hydrofluoric Acid
Physical Properties	
Molecular Weight	20.01
Status at 25 ^{o}C	Liquid
Color	Colorless
Boiling Point (^{o}C)	112.2
Melting Point (^{o}C)	- 83
Specific Gravity	1.155
Solubility	Soluble in Water
Purity	48 - 51%
Supplier	Carlo Erba

* From Encyclopedia of Chemical Engineering.

Table B – 9 Properties of Hydrogen Peroxide *

Formula	H_2O_2
Chemical Name	Hydrogen Peroxide
Physical Properties	
Molecular Weight	34.02
Status at 25 ^oC	Liquid
Color	Colorless
Boiling Point (^oC)	151.4
Melting Point (^oC)	0.89
Specific Gravity	1.13
Solubility	Soluble in Water, Acid and Ether
Purity	35 – 35.6%
Supplier	Merck

* From Encyclopedia of Chemical Engineering.

Table B – 10 Properties of Potassium Permanganate *

Formula	$KMnO_4$
Chemical Name	Potassium Permanganate
Physical Properties	
Molecular Weight	158.03
Status at 25 ^{o}C	Solid
Color	Dark Purple
Boiling Point (^{o}C)	-
Melting Point (^{o}C)	-
Specific Gravity	2.71
Solubility	Soluble in Water
Supplier	Carlo Erba

* From Merck Index.

Table B – 11 Properties of Potassium Persulfate *

Formula	K_2SO_8
Chemical Name	Potassium Persulfate
Physical Properties	
Molecular Weight	270.32
Status at 25 ^{o}C	Solid
Color	White
Boiling Point (^{o}C)	-
Melting Point (^{o}C)	-
Specific Gravity	-
Solubility	Soluble in Water
Supplier	Carlo Erba

* From Merck Index.

Table B – 12 Properties of Hydroxylamine-Hydrochloride *

Formula $NH_2OH*HCl$

Chemical Name   Hydroxylamine-Hydrochloride

Physical Properties

    Molecular Weight   69.49

    Status at 25 ^{o}C   Solid

    Color   White

    Boiling Point (^{o}C)   58

    Melting Point (^{o}C)   33

    Specific Gravity   1.20

    Solubility   Soluble in Water

    Purity   > 99%

Supplier   Carlo Erba

* From Merck Index.

Table B – 13 Properties of Sodium Chloride *

Formula	NaCl
Chemical Name	Sodium Chloride
Physical Properties	
Molecular Weight	58.54
Status at 25 ^{o}C	Solid
Color	White
Boiling Point (^{o}C)	804
Melting Point (^{o}C)	-
Specific Gravity	2.17
Solubility	Soluble in Water
Purity	> 99%
Supplier	Carlo Erba

* From Merck Index.

VITA

Miss Suchada Ampin was born on December 3, 1977 in Chonburi, Thailand. She received the Bachelor degree of Chemical Engineering from Faculty of Engineering, Burapha University in March 2000. She continued her Master's study at Chulalongkorn University in June 2000.