

CHAPTER II

LITERATURE REVIEW

This chapter concern with the literature reviews of method to remove mercury compounds. The literatures are divided into four sections. The first section concerns with properties and disadvantages of mercury. The second section described the properties of chitosan. The third section described the method that used to remove mercury compounds and adsorption methods. The last section is literature summary.

2.1 Properties and Disadvantages of Mercury Compound

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 II B groups of periodic table. All of the elements in IIB group lose two electrons to form ions. The Oxidation State of mercury is 1 and 2. Atomic number of mercury is 80 while atomic weight is 200.59. The capable of mercury is reaction to hundreds of compounds which its own properties. Mercury metal has a high vapor pressure at ordinary temperature.

2.1.2 Disadvantages of Mercury in Wastewater

Most mercury compounds are extremely toxic and two mercury compounds that most used in industry and agriculture is mercuric chloride and phenylmercuric acetate.

Mercuric Chloride

Domestic garbage contains a large amount of mercury, which originates from disposed thermometers, fluorescent lamps, mercury batteries, and other sources. When the garbage is burned in a refuse incinerator, mercury vaporizes into the flue gas (Kawamura et al. 1998). The flue gas is cleaned using an electric dust corrector, bag filter, and then washing with HCl aqueous solution using a scrubber. The effluent contains HgCl_2 and HCl. In commercial, it is one of the most important mercury

compounds. It is used in the manufacture of dry cells. Mercuric chloride was the strong soluble in water and so easily soluble in alcohol or benzene.

Phenylmercuric Acetate

Phenylmercuric acetate is the most important organomercurial of commerce. PMA is sparingly soluble in water but soluble in many organic solvents. In agricultural, PMA used as a foliage fungicide and herbicide. Extremely toxic, the probable oral lethal dose for human is 5-50 mg/kg, between 7 drops and 1teaspoonful for a 70 kg (150 lb.) person. It is a powerful vesicant agent; painful blistering of the skin will results about 8 hours after contact.

2.2 Properties of Chitosan

Chitosan (poly (1→ 4)-2-amino-2-deoxy-β-D-glucan) is a crystalline, structural polysaccharide generally obtained from natural chitin after deacetylation by alkaline treatment. Chitin (poly-β-(1→ 4)-N-acetyl-D-glucosamine), 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 yeasts, etc. Molecular structure of cellulose, chitin and chitosan are illustrated in Figure 2.1. Advantages of chitosan include availability, low cost, high biocompatibility, biodegradability; ease of chemical modification and it is also nontoxic (Li et al. 1992).

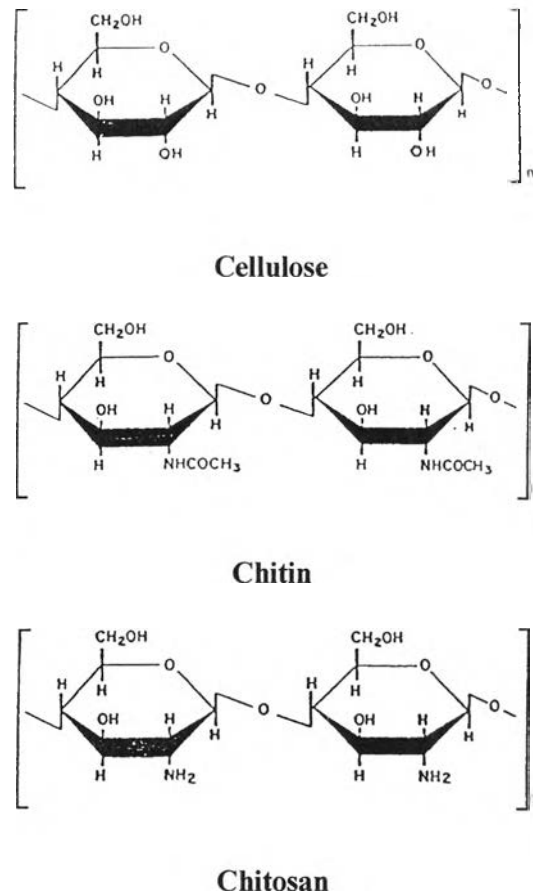


Figure 2.1 Comparison of the molecular structure of cellulose, chitin and chitosan.

The difference between chitin and chitosan lies in the degree of deacetylation. Most publications use the term chitosan when the degree of deacetylation is more than 70%. The degree of deacetylation is one of more important chemical characteristics of chitosan that determines the content of free amino groups. The molecular weight of commercial chitosan products fall between 100,000 and 1,200,000 (Li et al. 1992). Molecular weight may vary widely because many factors in the manufacturing process.

Chitosan is insoluble in water, alkali and organic solvents, but soluble in most solutions of organic acid when the pH of solution is less than 6. Acetic acid and formic acid are two of the most widely used acids for dissolving chitosan. Some diluted inorganic acid such as hydrochloric acid, nitric acid, perchloric acid and phosphoric acid can also be used to prepare chitosan solution (Onsoyen et al. 1990), (Bassi et al. 2000). Chitosan is also a well-known adsorbent, effective in the uptake of transition metals since the amine groups on a chitosan chain can serve as chelation sites for metals (Guibal et al. 1999).

2.3 Study of Mercury Removal in Wastewater

Several methods for removal of mercury have been studied and proposed for many years. It can be classified into three methods i.e. physical treatment, chemical treatment and adsorption.

2.3.1 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 settling, filtration, or dissolved air flotation. These latter steps improve the removal of the precipitated mercury sulfide, but do not enhance the efficiency of precipitation of the soluble mercury itself. 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 ug/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 ug/l, other drawbacks of this method include (1) the formation of soluble mercury sulfide complexes at high levels of excess sulfide, (2) the difficulty of monitoring excess sulfide levels, and (3) the problem of toxic sulfide residual in the treated effluent.

2.3.2 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. In wastes where chloride is not high, cation exchange resins are effective. Although information on the cation exchange behavior of mercury is scarce, Amberlite IR-120 and Dowex-50W-X8 are both reported to be effective. Resins that contain mercapto groups (R-S-H) such as polythiostyrene are

highly specific for mercuric ion. Thiol resin is widely used for cationic mercury removal in Europe. 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 appears to yield an effluent of 1-5 ug/l. Most effective treatment results from two-stage treatment, at neutral to slightly acidic pH.

Coagulation Treatment

Removal of mercury by coagulation has been reported for a variety of mercury containing wastewaters. 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 ug/l by 94-98%. Lime coagulation treatment, applied at a higher mercury level of 500 ug/l, provided 70% removal with filtration. The results have been reported in another study, which also found that increasing coagulant dosage to 100-150 mg/l did not improve mercury removal.

Reduction Processes

Inorganic ionic mercury can be converted to the metallic form by reduction and separated by filtration or other solids separation techniques. A variety of reducing agents are available, including aluminum, zinc, hydrazine, stannous chloride, and sodium borohydride. The main advantage claimed for reduction is that mercury can be recovered in the metallic state. However, the results have been reported indicate that reduction processes cannot effectively achieve mercury level below 100 ug/l.

2.3.3 Adsorption

The disadvantage of chemical reaction in removing mercury is the contamination of chemicals that use for remove of mercury to the product. Adsorption is a high efficiency method for removing of mercury. The adsorption method comprises contacting the adsorbent with an aqueous phase at various conditions, depending on type of adsorbent used. Mercury compounds are adsorbed and remained in adsorbent. There are many studies about adsorbed of Hg and others heavy metal by chitosan.

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 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

Kawamura et al. (1993) studied the removal of heavy metal in aqueous solution using chitosan resin. The single-solute system was used solution containing 100 ppm of HgCl_2 . The sample was stirred with the chitosan resin at temperature of 25°C , pH of 7 for 72 hours. The results indicated that a mercury content was decreased to about 5 ppm, selectivity for adsorption of metal ions on the resin at pH of 7 was $\text{Hg (II)} > \text{UO}_2 \text{ (II)} > \text{Cd (II)} > \text{Zn (II)} > \text{Cu (II)} > \text{NI (II)}$. The selectivity depended on the pH of each metal solution.

Baba et al. (1998) studied the method for mercury removal using chitosan derivatives. The solution containing 200 ppm of HgCl_2 was shake with the chitosan derivatives at temperature of 30°C to achieve equilibration. The results indicated that the chitosan derivatives were high selectivity for mercury removal. All of the chitosan derivatives tested were found to be effective for the selective removal of nearly 80 – 100% of the initial mercury (II).

Kawamura et al. (1998) studied the removal of HgCl_2 from aqueous solution using chitosan beads. The solution containing 2000 ppm of mercury was passed in upflow direction through chitosan beads, which is packed in a column (1-cm i.d.), at temperature of 25°C and various pH of feed. The results showed that the adsorption capacity was 2500 mol/m^3 at pH of 7. The adsorption capacity was decreased with pH increasing.

Kawamura et al. (1998) proposed the concentration of sulfuric acid for desorb chitosan beads. The results indicated that at concentration of sulfuric acid 250 and 500

mol/m³, it was selectivity higher than at concentration of 1000 mol/m³, and at temperature of 35°C, chitosan beads desorbed greater than at temperature of 25°C.

Yang et al. (1999) studied the removal of mercury, lead, copper, cadmium and chromium using chitosan cross-linked. The solution containing 100 ppm of mercury was stirred with chitosan powder at pH 5.5. The adsorption capacity of mercury, lead, copper, cadmium and chromium was 0.22, 0.20, 0.26, 0.14 and 0.12 mmol/g of chitosan respectively.

Udaybaskar et al. (1990) studied the removal of hexavalent chromium in aqueous solution using chitosan flake. The initial solution containing 5 ppm Cr⁶⁺ was stirred with chitosan at various pH of feed. The first-order rate constant from chromium removal was calculated to be 1.92 h⁻¹. The results indicated that percent removal was decreased with increasing of pH of the feed. Adsorption was almost 90% at pH of 3 and at an initial chromium concentration of 5 mg/L, reduced to 10% at pH of 7 and above. Presence of electrolytes and chloride significantly affected the removal of chromium, indicating the electrostatic attraction as the main removal mechanism. Regeneration of the adsorbent with alkali was not very effective as only 88% of desorbed chromium could be recovered.

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 the lower degree of deacetylation.

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.

Guibal et al. (1999) studied the removal of molybdate and vanadate in aqueous solution using chitosan. The experiment operated at temperature of 25°C and various pH of feed. The results show that the maximum selectivity of adsorption was at pH of 3 and the spent adsorbent can be regenerated using phosphoric acid.

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 0.24 g/ 25 ml. of solution. Stir cloud not effects to removal of these metals and the maximum result in percent removal of zinc, copper, cadmium and lead was at pH 7.

2.4 Literature Summary

1. Mercury in wastewater is in elemental, inorganic and organic mercury.
2. Methods for mercury removal are classified into three methods: physical treatment, chemical treatment and adsorption.
3. The mercury that used to study removal of inorganic mercury was mercuric chloride.
4. Many studies indicated that chitosan could be adsorbed mercury in many forms of mercuric compounds such as HgCl_2 , HgCl_4^{2-} .
5. The study of factors that have effective to adsorption by chitosan was pH, temperature, pore structure, specific functional group and degree of deacetylation.

Table 2.1 Summary of Treatment Technology for Mercury

Technology	Lower Limit of Treatment Capability (Hg, ug/l)
Sulfide precipitation	10 - 20
Ion exchange	1 - 5
Alum coagulation	1 - 10
Iron coagulation	0.5 - 5
Activated carbon	
High initial Hg	20
Moderate initial Hg	2.0
Low initial Hg	0.25