MERCURY REMOVAL FROM WASTEWATER BY ELECTROCOAGULATION

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ABSTRACT

In the present study, electrocoagulation was used for the treatment of synthetic solutions containing mercury (II). Study was performed based on synthetic petrochemical waste contaminated with mercury and heavy metals. The objectives of this study are to investigate the efficiency of electrocoagulation in removal of synthetic mercury through and Aluminium electrode and to remove mercury ion from mercury synthetic by electrocoagulation using Aluminium as electrode. In this study equipment such as electrocoagulation OT-1 was used to run the experiment. Three parameters were investigated in this research, which are the effects of the distance between the electrodes, charge loading on the removal efficiency and flowrate. Determination of the Mercury (II) ions was performed by Mercury Analyzer. In this research, in was found that the electrocoagulation result was contribute 99% above removal by using Aluminium as electrode. The research showed the applicability of electrocoagulation to treat water contaminated by mercury. More than 99% of the pollutant was eliminated by using Aluminium as electrodes. The distance between the electrodes gives highest removal was 5 cm. While the lowest concentration is 2ppm with the highest charge loading will be contributes to the higher percentage of removal of mercury up to 99.18%.

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LIST OF SYMBOL/ABBREVIATIONS

Hg	-	Mercury
$HgCl_2$	-	Mercury Chloride
NaCl	-	Sodium Chloride
HCL	-	Hydrochloric acid
ppm	-	Part per million
H_2SO_4	-	Sulfuric acid
Co	-	Concentration mercury ion before treatment
C	-	Concentration mercury ion after treatment
A	-	Ampere
V	-	Voltage

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Industrial, agricultural, and domestic wastes can contribute to the pollution of water, and water pollutants can damage human and animal health. One of the most important categories of water pollutants is inorganic pollutant. Heavy metal is one of source of inorganic pollutants always found in industrial that mostly produced through the wastewater. Inorganic pollutants and in particular heavy metals create a serious threat for the environment. These heavy metals can cause serious long term diseased such as teratogenic and carcinogenic. (Mahvi, et al, 2010). Mercury is carcinogenic, mutagenic, teratogenic and promotes tyrosinemia. High-concentration of mercury causes impairment of pulmonary and kidney function, chest pain and dyspnousea (Fu-sheng et al.,2004). Examples manufacturing that produced such amount of heavy metals in waste are batteries and accumulators that made up of mercury (II) oxide in waste, paints that containing mercury (II) sulphate, pharmaceutical products like mercurochrome (antiseptic) and clinical thermometers. (X.Zhu, et al, 2006). Pollutant containing mercury can cause a water disaster. The first great pollution of great scale caused by this element is known to be the water disaster of Minamata (Japan) in 1953 which devastated more than 200 people who consumed fish contaminated by methyl mercury. (Ullruich, et al, 2001)

Mercury is one of the heavy metals that been produced by heavy industrials such as batteries industry. Mercury is not only known as heavy metals wastewater for certain industries but also important element or substances to produce some chemical in manufacturing processes.

Examples of mercury in manufacturing processes are:

1. Chlorine Production
2. Portland cement
3. Mining – i.e. gold mining
4. Caustic Soda
5. Sulfuric Acid

In recent years, there has been a growing need to eliminate hazardous pollutants from waters. Mercury pollution has been recognized as a primary environmental issue and public health problem (http://www.newmoa.org). Mercury, which is included in the list of priority pollutants of the US EPA, has been paid great attention for many years. The permitted discharge EPA limit of wastewater for total mercury is 10 ppb, and the limit for drinking water is 2 ppb (USEPA, 2001). Related limits established by the Ministry of the Environment of Japan are, however, 5 and 0.5 ppb (Takahashi et al., 2001) respectively. Meanwhile, the Word Health Organization (WHO) recommends 1 ppb as the maximum acceptable concentration in drinking water (USEPA, 2001).

Mercury is usually found in inorganic or organic forms. In the inorganic form, it usually exists in various physical states: liquid (HgO) or solid (salts of Hg^{2+}, Hg_2^{2+} ions or oxide). However, inorganic mercury can combine with organic compounds to give organometallics, and sometimes methyl mercury under the action of bacteria for instance. In this final form, mercury is much more toxic and labile compared to its free form. In general, mercury contamination is favored by its high volatility which can make its inhalation through air, its high reactivity readily allows mercury to combine with various other elements, leading to quite stable species, and that can accumulate in sea products. Ingestion of the products constitutes another way of contamination of human beings.

Electrocoagulation is an electrochemical technique whereby anodes (aluminium or iron electrodes) corrode to release active coagulants into solution. It is an alternative technology for wastewater treatment and recovery of chemicals from wastewater. The main advantages of electrocoagulation over other conventional techniques such as chemical coagulation and adsorption are "*in situ*" delivery of reactive agents and compactness. Many studies have reported the potentials of electrocoagulation in treating a variety of wastewater including removing suspended solids removing dyes, heavy metals, breaking oil emulsions in water, removing complex organics, removing bacteria, viruses and cysts. (C.Phalakornkule et al., 2010)

For conventional method, which is chemical coagulation method, the chemicals most widely used coagulants are:

1) Ferrous sulphate
2) Sodium Aluminate
3) Silicon Derivatives
4) Lime
5) Synthetic Organic Polymers
6) Aluminium Sulphate

(http://www. fibre2fashion.com)

Chemical also added in drinking water to adjust its hardness or softness, pH, and alkalinity. Water that is acidic is very corrosive to the pipes and materials with which it comes into contact. The addition of sodium hydroxide can reduce corrosively and extend the service life of pipelines, storage tanks, and building plumbing systems. Pipes may also be coated with chemicals to prevent metals like copper from dissolving in the water. (Abuzaid, et al.1998)

1.2 Problem statement

Coagulation of Petrochemical waste is an important process in water treatment that helps to produce clear, finished water which is aesthetically acceptable to the consumer. Much of the suspended matter in water is colloidal (1 mm to 1 m) and negatively charged. Because of their large surface area and electrical charge, colloidal particles settle very slowly. Aluminum or iron salts are used to neutralize these surface charges and to cause the colloids to combine and become large enough so that they will readily settle. But the conventional method which is chemical coagulation used to reducing the effects caused by the presence of mercury will increase the amount of sludge production. Other problems are permanent water hardness, water salts like sodium, annual high operation costs, sediment formation on membrane, which require an effluent post treatment and disposal of residual sludge. In order to overcome this, an alternative method like electrocoagulation may help to improve Hg^{+} removal.

1.3 Objective

I. To investigate the efficiency of electrocoagulation in removal of synthetic mercury through and Aluminium electrode.

II. To remove mercury ion from mercury synthetic by electrocoagulation using Aluminium as electrode.

1.4 Scope of study

I. Study the effect of flowrate on removal efficiency.

II. Study the effect of charge loading on removal efficiency.

III. Study the effect of distance between the electrodes on removal efficiency.

1.5 Significant of study

Chemical coagulant method will cause problems such as permanent water hardness, water salts like sodium, annual high operation costs, sediment formation on membrane, which require an effluent post treatment and disposal of residual sludge while Electrocoagulation utilizes methods that precipitate out large quantities of contaminants in one operation; the technology is the distinct economic and environmental choice for industrial, commercial and municipal waste treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Mercury

Mercury (Hg) has an atomic number of 80. Mercury is also known as quicksilver or hydrargyrum. Mercury (Hg), naturally-occurring element is a silver-white liquid at room temperature. With a freezing point of -38.83^0C and boiling point of 356.73 °C, mercury has one of the narrowest ranges of its liquid state of any metal. (http://www.lenntech.com)

Mercury applications has been use in thermometers, barometers, manometers, float valve, some electrical switches and other scientific apparatus is used though concerns about the element's toxicity have led to mercury thermometers and sphygmomanometers being largely phased out in clinical environments in favor of alcohol-filled, galinstan-filled, digital, or thermistor-based instruments. It remains in use in scientific research applications and in amalgam material for dental restoration.

Mercury has a wide variety of uses in industry: medicine, dentistry, batteries, science, and military applications. The burning of fossil fuels and medical waste ineration accounts for more than 80% of all anthropogenic sources (Guangliangn, et al, 2012.) Fifty-five percent of the total consumption of mercury is by chloralkali synthesis (used in electrodes), the wood pulping industry, paint, and electrical equipment. It has been estimated that the global reservoir of atmospheric mercury has increased by a factor of 2 to 5 since the beginning of the industrial revolution. Atmospheric contamination by industry has recently decreased, but mining is still a significant contributor to the contamination of ground and surface waters.

2.1.1 Forms of Mercury

Mercury is usually found in inorganic or organic forms. In the inorganic form, it usually exists in various physical states: liquid (HgO) or solid (salts of $Hg^{2}+$, $Hg_2{}^{2}+$ ions or oxide). However, inorganic mercury can combine with organic compounds to give organometallics, and sometimes methyl mercury under the action of bacteria for instance. In this final form, mercury is much more toxic and labile compared to its free form. In general, mercury contamination is favored by its high volatility which can make its inhalation through air, its high reactivity readily allows mercury to combine with various other elements, leading to quite stable species, and that can accumulate in sea products.

Elemental mercury is initially released into the atmosphere, captured by precipitation and ultimately deposited in the sediments of lakes and oceans. This process leads to the second type of the transport and distribution of mercury. It involves the deposition of mercury in the sediments of lakes and oceans and its transformation to a methylated species by anaerobic bacteria. The amount of methyl-mercury produced by anaerobic bacteria may be decreased by demethylation reactions and volatilization of dimethylmercury. (Boszke 2002)

2.1.2 Sources of Mercury

Alkali and metal processing, incineration of coal, and medical and other waste, and mining of gold and mercury contribute greatly to mercury concentrations in some areas, but atmospheric deposition is the leading source of mercury over most of the landscape. Once in the atmosphere, mercury is widely dispersed and can flow for years, accounting for its wide-spread distribution. Natural sources of atmospheric mercury include volcanoes, geologic deposits of mercury, and volatilization from the ocean. Although all rocks, sediments, water, and soils naturally contain small but varying

amounts of mercury, scientists have found some local mineral occurrences and thermal springs that are naturally high in mercury. (http://www.clu-in.org)

2.2 Health Effect

2.2.1 Human Effect

The toxic effects of mercury depend on its chemical form and the route of exposure. Mercury does affects the immune system, alters genetic and enzyme systems, and damages the nervous system, including coordination and the senses of touch, taste, and sight. Methyl mercury is one of dangerous and it's toxic form mercury. It is because, it particularly damaging to developing embryos, which are five to ten times more sensitive than adults. Ingestion is easily exposure to methyl mercury. Methyl-mercury poses a serious human health risk which was first realized during the 1950 and 1960's at Minamata Bay, Japan where more than 1000 people were killed and 5000-6000 suffered permanent neurological damage from the consumption of mercury contaminated seafood. Contamination at Minamata Bay resulted from organic mercury overflow produced by an acetaldehyde facility. Mercury poses such a huge threat to human health because once it enters the body the destruction that occurs is usually irreversible.(Ullrich 2001)

Elemental mercury, Hg (0), this form of mercury is the only common metal that is liquid at room temperature. Because it is highly volatile, it is easily converted into gaseous form. Elemental mercury form released from broken thermometers can cause tremors, gingivitis, and excitability when vapors are inhaled over a long period of time. Although it is less toxic than methyl mercury, elemental mercury may be found in higher concentrations in environments such as gold mine sites, where it has been used to extract gold. If elemental mercury is ingested, it is absorbed relatively slowly and may pass through the digestive system without causing damage. Ingestion of other common forms

of mercury, such as the salt HgCl2, which damages the gastrointestinal tract and causes kidney failure, is unlikely from environmental sources**.** (www.clu-in.org)

2.2.2 Environmental Effects

Figure 2.1 Distribution of mercury within the environment (http://rydberg.biology.colostate.edu)

This reveals that more than half of the mercury released into the environment today is from human impact sources. Mercury cannot be degraded either biologically or chemically, and besides, it can be converted into more toxic compounds in the environment. The biogeochemical cycle of mercury is well established, conversion of inorganic forms such as Hg (II) into organomercury through biomethylation being perhaps the most important transformation given the dramatic toxic effects caused by the

latter to living organisms. Many international organizations have limited maximum allowable contents of mercury in water and food. (Sandra 2006)

Thus, the US environmental protection agency (EPA) has limited mercury concentration in water for human consumption to 0.002 mg/L (ppm) in accordance to the primary drinking water standard while the European Community has indicated a maximum mercury concentration of 0.001 mg/L (ppm) in drinking water Mercury is its strong absorption into biological tissues and slow elimination from them. (Sandra 2006)

2.3 Chemical Properties and Physical Characteristic of Mercury

The chemical and physical characteristics of mercury are shown in Table 2.1 and Table 2.2 respectively.

Table 2.1 Chemical properties of mercury *(http://www.lenntech.com)*

Atomic number	80
Atomic mass	200.59 $g.mol^{-1}$
Density	13.6 g.cm-3 at 20°C
Melting point	- 38.9 °C

Table 2.2 Physical Characteristic of Mercury *(http://www.lenntech.com)*

Color	Bright silvery metallic
Luster	Metallic
Transparency	Opaque
Specific Gravity	13.5 (very dense)

2.4 Material Safety Data Sheet (MSDS) of Mercury

MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the further information about physical and chemical properties of mercury, for further review, see at Appendices.

2.5 Environmental Quality Regulation

Environmental quality is a set of properties and characteristics of the environment, either generalized or local, as they impinge on human beings and other organisms. Environmental quality is a general term which can refer to different characteristics that relate to the as well as the environment, such as air and water purity or pollution, noise and the potential effects which such characteristics may have on physical and mental health caused by human activities. In Malaysia, we apply the environmental quality regulation to ensure that the treatment we use to removal mercury always meet the Malaysia DOE, Standard (B) on Environmental Quality Act 1974. (www.doe.gov.my)

2.6 Petrochemical Wastewater Contains Mercury

In Petrochemical, mercury has several harmful impacts on petrochemical processing. For examples mercury deposits in cryogenic equipment sometimes cause cracking of welded aluminum heat exchangers. Mercury in products also affects downstream processes. Products used for chemical manufacture, especially olefins, ethylene, aromatics and MTBE, are at risk to mercury in process feeds due to the cited

equipment problems and due to catalyst poisoning. Mercury contaminates treatment processes such as molecular sieve and glycol dehydration units, and amine acid gas removal systems. Mercury sorbent materials used for gas or liquid treatment, when spent, constitute a generated hazardous waste that plant operators must store or process for disposal.

Sludge that containing mercury from water treatment systems, separators, reactors and heat exchangers will represents a toxic waste stream that can be difficult to store or process for disposal as shown in Figure 2.2. Wastewater streams that contain high levels of mercury must be treated to remove mercury prior to discharge thus adding significant costs to plant operational expense. (http://www.gec.jp)

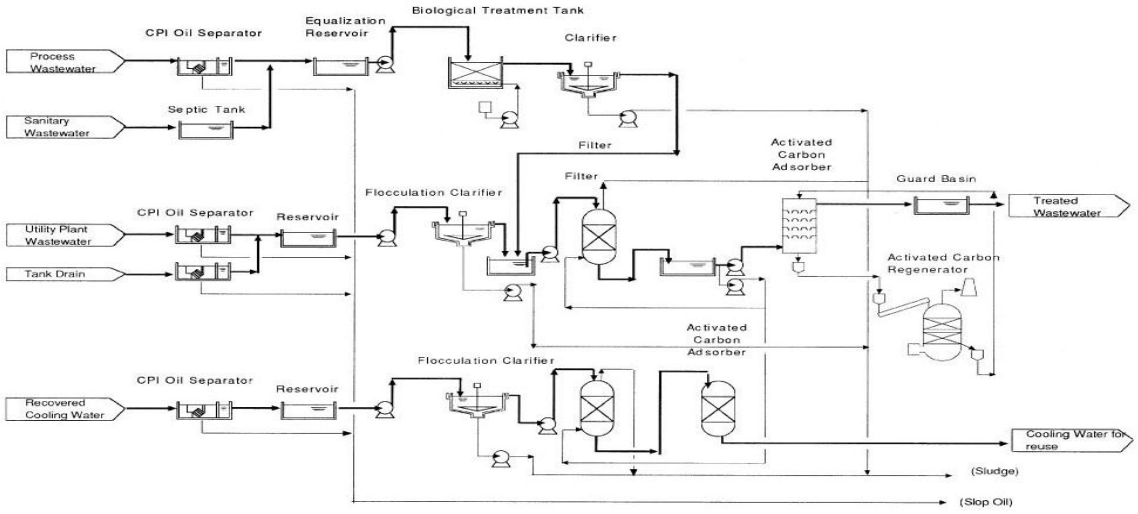

Figure 2.2 Example of a wastewater treatment system in petrochemical plant (http://www.gec.jp)

2.7 Examples Various Techniques Removal Mercury in Wastewater

There are various techniques for the removal of heavy metals in wastewater, such as chemical substances, membrane process, adsorption on activated carbon and ion exchange through a liquid-liquid membrane. These techniques also are used to reduce the effect caused by the presence of mercury and its derivatives in wastewater. All these technique are conventional methods that have been used in wastewater treatment. In order to improve the technique during the coagulation process, all these conventional method have been replaced with electrocoagulation method, which is more convenient and more economic. Advantages using these methods are not very expensive, do less impact on hazard in the environment and without increasing the salinity of the water.

2.7.1 Chemical Coagulation

Conventional method that mostly used in industry is chemical coagulation, which is chemical coagulation method, the chemicals most widely used coagulants are ferrous sulphate, Sodium Aluminate, Silicon Derivatives, Lime, Synthetic Organic Polymers and Aluminium sulphate. Chemical coagulation consists of the dosing of the coagulant solution to the wastewater in order to reduce the electrical repulsion that caused the combination of particles. To maintain the electro neutrality in the wastewater charged ions of hydroxyl (OH^-) or hydrogen ions (H^+) are attracted to the pollutant particles oppositely. (Peter et al., 2002). There are several disadvantages using chemical coagulation method. During this method, the sludge was increased and contributed high cost because the chemical have to supply continuously. (M.Malakootian, et al, 2010).