

Mercury Removal Techniques for Industrial Waste Water

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Abstract—The current work focuses on rephrasing the harmful effects of mercury that is being released from a number of sources. Most of the sources are from the industrial waste water. Different techniques of mercury removal have been discussed and a brief comparison among these has been made. The experimental work has been conducted for two most widely used methods of mercury removal and comparison in terms of their efficiency has been made.

Keywords—Mercury, Waste Water, Adsorption.

I. INTRODUCTION

MERCURY is a metal having atomic number 80 and is liquid at standard temperature and pressure. It has $-38.83\text{ }^{\circ}\text{C}$ freezing point and $356.73\text{ }^{\circ}\text{C}$ boiling point. Mercury deposits are usually found in the form of mercuric sulfide. It is highly toxic if inhaled. Mercury poisoning could also result from exposing to soluble forms of mercury like mercuric chloride or methyl mercury. Mercury makes amalgams with other metals such as gold, zinc. On heating, mercury forms mercury oxide by reacting with oxygen in air. Mercury is one of the toxic pollutants that must be controlled. Sodium mercury amalgam is the main compound in the electrolysis of brine during production of caustic soda. Inorganic mercury compounds can accumulate in the drinking water and are possible health hazards [1].

A. Applications

Mercury is extensively used in many temperature measuring instruments. Gaseous mercury is used in fluorescent lamps. Other uses of mercury are in the production of a number of industrial chemicals. The elemental mercury is an important ingredient for dental amalgams. The example is Thiomersal, an organic compound used in vaccines as preservative. Merbromin, a topical antiseptic, is applied to minor cuts and scrapes. The major application of mercury is in the form of mercury cell (Castner-Kellner process). Metallic sodium is deposited as an amalgam on the cathode of mercury which further reacts with water to form sodium hydroxide. At times, liquid mercury was also applied as a cooling media for nuclear reactors. It is now being replaced with sodium due to the high density of mercury which needs more power to circulate as a cooling medium.

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B. Environmental issues

The major sources of mercury release are from Chlor-alkali industry and serve as a threat to aquatic life as well as for drinking water. Mercury in the organic form becomes more hazardous when converted to methyl mercury, ethyl mercury and butyl mercury. One of the natural sources of mercury is the volcanoes that produce almost half of the mercury emissions released in atmosphere. The rest half is being generated by humans by various means including 65% in combustion, 11% in the production of gold, 6.8% in the production of non-ferrous metal, 6.4% in the production of cement, 3.0% in the waste disposal including municipal waste, and 3.0% in the production of caustic soda.

C. Health Issues

Mercury could be inhaled and absorbed through the body skin. The mercury could be toxic in the form of organic compounds as well as inorganic compounds. Mercury could cause chronic as well as acute poisoning. River and lake water in the nearby industries may contain mercuric discharges which are fatal for the aquatic as well as human life. These discharges could accumulate in the stomach and remain non digestible resulting in the formation of cancerous diseases. Long time exposure to mercury could cause serious damage to nerve, brain, kidney, lung irritation, eye irritation, skin rashes, vomiting and diarrhea [2, 3].

II. EXPERIMENTAL OBJECTIVES

Our key objective is to remove these mercury entities, if in any case the removal is not possible then there should be mechanism in reduction of contamination. In this work some removal techniques will be discussed and at the end there will be a short description about process comparison. The decrease in concentration is up to the parts per million levels or in some techniques it should be in parts per billion levels.

The acceptable mercury concentration for the initiation of removal process is above 2 parts per billion. This is the least amount of concentration that could be detected with any of the available composition analyzer.

The reduction in mercury concentration from various process streams includes

- Discharge liquid waste from electrolytic cells.
- Drinking water

Any residual mercury entertained due to breakage of any of the following instrument:

- Barometer
- Manometer
- Gauge glasses

Experimental work includes the following techniques:

- Chemical Precipitation
- Adsorption using Activated Carbon

The removal techniques for mercury are as follows:

- Adsorption (carbon, coal and some other adsorbents)
- Coagulation (using ferric chloride and others)
- Filtration (cross flow micro filter and sand bed filter)
- Bio Films (acetobater cellulose xyllinum)
- Reverse Osmosis
- Chemical precipitation (using aluminum sulfate and some others)

A. Removal of Mercury through Adsorption

In this process, contaminated gas molecules are absorbed over the surface of the activated carbon. Carbon is a preferred adsorbent due to its large surface area. The sources of carbon include coal, wood and coconut shells. The activation is carried out at high temperature under controlled oxidation process. The adsorption efficiency depends upon the characteristics of the contaminant, the temperature and the concentration of the contaminant. The adsorption capacity of any contaminant depends upon the amount of the contaminant that could possibly be adsorbed on a unit mass of activated carbon. Moderately adsorbed compounds show adsorption capacity in the range of 5 to 30 % of the mass of the carbon.

B. Some Flocculants for Removal of Mercury

Flocculants are chemicals that cause flocculation of particles suspended in liquids to aggregate and forming a floc. Flocculants are widely applied for waste water treatment processes for the purpose of improving the sedimentation or filterability of small particles. Flocculants could be employed in swimming pool or drinking water to help in the removal of mercury metal that would be the cause of water turbidity. A number of flocculants are cations of aluminum, iron, calcium or magnesium. These cations interact with anions to facilitate the process of aggregation. A number of such chemicals with appropriate pH, and temperature react with water to produce insoluble hydroxides. These hydroxides on precipitation form long chains and trap the small particles in the form of larger floc.

C. Removal of Mercury by Blue PRO reactive filtration process

The Blue PRO reactive filtration process could lower particulate as well as dissolved species of mercury using multiple removal mechanisms. Blue PRO is a tertiary wastewater treatment process and capable of doing co-precipitation and adsorption, overcoming diffusion limitations within a continuous backwash filter, and filtering of particulates. Hydrous ferric oxide (HFO) adsorptive media is used to be regenerated inside the filter, removing mercury to ultra-low levels. Blue PRO is cost effective compared to other tertiary wastewater treatment processes for mercury removal to lower levels. It is attributed to lower capital and operating

costs compared to membrane, reverse osmosis, granular activated carbon and coagulation systems.

D. Removal of Mercury Using Bio Films

A bio film consists of a complex structure of microorganisms that grows on a solid substrate. Formation of a bio film is attributed to the fixation of microorganisms to a surface. Initially, they adhere to the surface due to weak van der Waals forces. In case of not being separated immediately from the surface, they could adhere to the surface permanently using cell adhesion molecules.

The bio films are very efficient in removing high molecular metallic species like mercury in the waste water from chlor alkali plant. The most important thing about these bio films is the environment friendly operation with ease in regeneration with latest techniques. The growth of these bio films on a large scale for efficient removal of mercury. These bio films provide millions of sites for mercury adsorption and could be a leading process in the near future. Japan is using this technique on a medium scale in the chlor alkali plants.

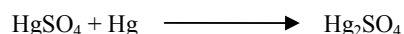
E. Removal of Mercury by Reverse Osmosis

Reverse Osmosis (RO) system consists of granular activated carbon pre-filters, a RO membrane, a storage tank, and a faucet for the delivery of the low concentration liquid stream. Commonly used RO membranes are Thin Film Composite (TFC) and Cellulose Triacetate (CTA). TFC membranes are relatively more efficient compared to CTA membrane. Both have a very high rejection rate for mercury types as well as its different contaminants. These are also cheap and cost about 5 cents per gallon of pure water.

F. Removal of Mercury by Chemical Precipitation

Bolken Process

Mercury is captured using HgSO_4 that is being generated as a result of reaction of mercury with the sulfuric acid. The process starts with acid concentration of 80% H_2SO_4 at temperature lower than 50°C . The second stage is carried out in a conventional tower operating at 93% H_2SO_4 . Later, the reaction of mercury with the acid forms mercurous sulfate as shown below:



This is much quite method and also not using very expensive chemicals to remove the mercury.

Sulfide Precipitation

Colloidal sulfur can be generated by adding sodium thiosulfate in the acid as shown below.



Firstly, the sulfur reacts with the Hg to form crystalline mercury sulfide (HgS). Sulfur also reacts with other metal contaminants in the acid to produce insoluble metal sapphires. The technique works on acid concentrations of less than 85%

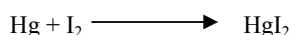
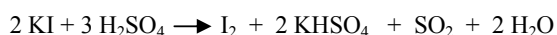
H₂SO₄. Higher acid concentrations could result in the oxidation of sulfur to form sulfur dioxide (SO₂). The product acid also contains sodium sulfate that is not desirable in the product acid. Sodium thiosulfate dosage must also be controlled otherwise it produces mercury sulfide that is not easy to filter. By the use of this method, the mercury concentration could be decreased from 15 ppm to 0.5 ppm in an hour. Hydrogen sulfide could be one of the important source of sulfide for the precipitation of mercury along with other metals. This technique is preferred when the sodium sulfate is not desirable in the end product. At neutral pH, the process is more efficient. The process efficiency starts to decrease as pH goes above 9. In the chlor alkali plant, this process could be a better option with the efficiency of 95 to 99%.

Toho Process

This process comprises of adding potassium iodide and mercury is then precipitated as mercuric iodide as shown below:

TABLE I
MERCURY REMOVAL BY ACTIVATED CARBON

Sample Concentration in ppm	Final Concentration in ppm	Temperature of the process stream in degree Celsius	Efficiency achieved by Activated Carbon in %age
540	48.6	50	91
533	10.13	100	98.1
535	7.33	124	99



Cuprous iodide is added along with the potassium iodide to form a more stable precipitate of Cu₂HgI₄. The separation of precipitated mercury is done by filtration [4, 5, 6, 7].

III. MATERIALS AND METHODS

The industrial mercury cell waste liquor contains large quantities of mercury and are released in the environment without any treatment of removal of mercury. These discharges are of high concentrations enough to produce lethal effects to human and aquatic life. The sample was the waste liquor of dimensional stable anode (Commonly known Mercury Cell). The sample contains mostly the elemental form and some in combined forms. Due to rigorous kinetics, we assume that the entire form of liquid waste is in elemental form of mercury.

A. Experimental Techniques

TABLE II
MERCURY REMOVAL BY TOHO PROCESS

Sample Concentration in ppm	Final Concentration in ppm	Temperature in degree Celsius	Efficiency in % age
529	37.03	25	93

In our experimental work these two techniques were performed in the laboratory scale to achieve satisfactory results.

- a. Activated Carbon Adsorption
- b. Chemical Precipitation using Toho process

i. Activated Carbon Adsorption

The method is generally applied for low mercury concentrations. 90% removal efficiency is normally achievable in lab and commercial scale. 1 gram of activated carbon could remove about 100 milligrams of mercury. The activated carbon bed was prepared in its highly porous divided form and the temperature of process stream was about 50°C. The exposure time was 15 minutes. The efficiency depends upon following factors:

- Exposure Time
- Activity of Carbon
- Temperature of Process Stream

Initially, the sample was having a concentration of mercury upto 540 ppm. After 15 minutes of exposure time, it was reduced to 48.6 ppm. Efficiency was 91 percent. Efficiency was quite good but in actual conditions of laboratory scale usually 97 percent efficiency could be achieved depending upon the factors listed above. However, when the temperature of process stream was increased to 124°C, the removal efficiency was 99 percent. However, at the temperature of about 100°C, the efficiency achieved was 98.1 percent. These results are presented in the Table I as shown below.

Discussion on Results

The experimental results are satisfactory for the laboratory scale as well as could be valid for commercial scale. Carbon adsorption systems are very useful for commercial scale and are used to remove several metallic traces including mercury. These systems could be a suitable solution in the chlor alkali waste streams to reduce the concentration up to the desired level in order to save the environmental damage. Environmental protection agency is not yet succeeded in forcing the chlor alkali industries to install the waste treatment units for mercury removal. An awareness program on harmful effects of mercury needs to be launched to control its concentration in the environment.

ii. Chemical Precipitation

The Toho process is the commercial process for removing mercury discharges up to satisfactory concentration. We used the laboratory solution of potassium iodide 5 percent on mass basis. The reaction was carried at room temperature in a beaker and the resultant precipitates were filtered using filter paper. The Table II below shows the result for experimental work.

Discussion on Results

Chemical precipitation is a very simple technique and involves the basic reaction and then filtration to remove the precipitates. Large scale of chemical precipitation could be done using the Toho's process which is very effective. In the laboratory scale the results are somewhat less efficient,

however, results up to 96 or 97 percent could be achieved using this process on commercial scale.

REFERENCES

- [1] L. Campanella, E. Cardarelli, T. Ferri, B.M. Petronio, Mercury removal from petrochemical wastes, *Water Research*, 20,1, January 1986, 63–65.
- [2] K. Anoop Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies, *Journal of Hazardous Materials*, 92,1- 2, 27 May.2002,161-183.
- [3] E Ekinci, T Budinova, F Yardim, N Petrov, M, Razvigorova, V Minkova, Removal of mercury ion from aqueous solution by activated carbons obtained from biomass and coals, *Fuel Processing Technology*, 77–78, 20 June 2002, 437–443.
- [4] Si-Hyun Lee, Young-Ok Park, Gas-phase mercury removal by carbon-based sorbents, *Fuel Processing Technology*, 84, 1–3, 15 November 2003, 197–206.
- [5] Sung Jun Lee, Yong-Chil Seo, Jongsoo Jurng, Tai Gyu Lee, Removal of gas-phase elemental mercury by iodine- and chlorine-impregnated activated carbons. *Atmospheric Environment*, 38, 29, September 2004, 4887–4893.
- [6] Mark Mullett, James TARDIO, Suresh Bhargava, Charles Dobbs, Removal of mercury from an alumina refinery aqueous stream, *Journal of Hazardous Materials*, 144,1–2, 1 June 2007, 274–282.
- [7] M. Zabihi, A. Haghighi Asl, A. Ahmadvour, Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell, *Journal of Hazardous Materials*, 174,1–3, 15 February 2010, 251-256.