

CATALYTIC OXIDATIVE CHEMICAL TREATMENT FOR THE REMOVAL OF
ELEMENTAL MERCURY ON CARBON STEEL (SAE J429) SURFACE

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Specially for my beloved family and friends

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ABSTRACT

In this study, mercury contaminated carbon steels was prepared using droplet and physisorption methods. Various oxidants were applied to oxidize the mercury element and the oxidized mercury and the iron leaching were analyzed using Atomic Absorption Spectrometer (AAS) for data collections. The effect of oxidant system of KI/I₂, peracetic acid, different conditions of experiment namely heating, stirring, left at room temperature, the presence of catalysts and the addition of imidazoline based corrosion inhibitor were investigated. The experiment revealed the oxidant system of 1H₂O₂:1CH₃COOH (peracetic acid) ratio as the best to remove 96.43% physisorbed Hg and 96% droplet Hg from carbon steel surfaces under ambient temperature and soaking for 5 hours. The total iron leached detected under the optimum condition from used carbon steel contaminated with physisorp Hg and droplet Hg were 21.45 ppm and 22.98 ppm respectively. Interestingly, the presence of Ru/Mn (25:75)/Al₂O₃ catalyst calcined at 1000°C with peracetic acid as oxidant could further remove 99% of Hg for CS-physisorbed-Hg and 98.71% for CS-droplet-Hg resulting in 19.71 ppm and 19.62 ppm respectively iron leached in 3 hours. FESEM illustrated the catalyst surface is covered with small and dispersed particles with undefined shape. From FESEM-EDX analysis, Mn species were detected in all the catalysts tested. The X-Ray Diffraction (XRD) analysis revealed that the catalyst is crystalline and Mn species is believed to be the active species for the catalysts. Nitrogen Gas Adsorption (NA) analysis showed that both fresh and spent catalysts are of mesoporous material with Type IV isotherm and type H₃ hysteresis loop.

ABSTRAK

Dalam kajian ini, keluli karbon tercemar merkuri telah disediakan menggunakan teknik titisan dan fizijerapan. Berbagai bahan pengoksida diaplikasikan untuk mengoksida elemen merkuri dengan menggunakan sistem pengoksidaan KI/I_2 dan asid perasetik. Kondisi eksperimen yang berbeza iaitu pemanasan, pengacauan, dibiarkan pada suhu bilik, dengan kehadiran pemangkin dan penambahan perencat kakisan berasaskan imidazolin juga dikaji. Merkuri yang teroksida dan ferum terlarut telah dianalisa menggunakan Spektroskopi Serapan Atom (AAS) untuk pengumpulan data. Eksperimen membuktikan bahawa sistem pengoksidaan $1H_2O_2:1CH_3COOH$ (asid perasetik) adalah yang terbaik untuk menyingkirkan 96.43% Hg-fizijerapan dan 96% Hg-titisan daripada permukaan karbon keluli pada suhu bilik dan direndam selama 5 jam. Ferum terlarut bagi Hg-fizijerapan adalah 21.45 ppm dan 22.98 ppm bagi Hg-titisan. Menariknya, kehadiran mangkin $Ru/Mn (25:75)/Al_2O_3$ yang telah dikalsinkan pada suhu $1000^\circ C$ dengan asid perasetik sebagai bahan pengoksida boleh menyingkirkan 99% Hg bagi Hg-fizijerapan manakala bagi Hg-titisan adalah 98.71% dengan ferum terlarut sebanyak 19.71 ppm dan 19.62 ppm selama 3 jam. Mikroskop Pengimbas Elektron Emisi Medan (FESEM) menunjukkan permukaan pemangkin diselaputi dengan zarah-zarah halus yang mempunyai bentuk yang pelbagai. Daripada analisis Spektroskopi Sinar-X Penyebar Tenaga (EDX) spesis Mn telah dikesan bagi semua mangkin yang telah diuji. Analisis Pembelauan Sinar-X (XRD) pula menunjukkan mangkin adalah dalam bentuk kristal dan spesis Mn adalah spesis aktif bagi mangkin-mangkin tersebut. Penyerapan Nitrogen (NA) menunjukkan mangkin yang baru dan yang telah digunakan masing-masing mempunyai ciri bahan mesoporous dan *Isotherm Jenis IV* juga histerisis lengkokkan H_3 .

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
BET	-	Brunauer–Emmett–Teller
CI	-	Corrosion inhibitor
CS-droplet-Hg	-	Carbon steel droplet Hg
CS-physisorbed-Hg	-	Carbon steel physisorbed Hg
DOE	-	Department of Environment
DOC	-	Dissolved organic carbon
di-PAA	-	Diperacetic acid
EDX	-	Energy dispersive X-ray spectroscopy
FESEM microscopy	-	Field emission scanning electron
LME	-	Liquid metal embrittlement
MHS-AAS Absorption	-	Mercury-Hydride System, Atomic Spectroscopy
PAA	-	Peracetic acid
SAMMS	-	Self-assembled mercaptan groups on mesoporous silica
SS	-	Sewage sludge
TBHP	-	Tert-butyl hydroperoxide
XPS	-	X-Ray photoelectron spectroscopy
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 History of Mercury

Mercury concentrations in natural gas can range from below 1 ng m^{-3} to greater than $1000 \text{ } \mu\text{g m}^{-3}$ depending on the location, the well or the process and is measured using amalgamation atomic fluorescence spectrometry. Mercury is of great concern receiving a major focus due to its unique high toxicity, volatility, and persistence in the environment and easiness of bioaccumulation. Organic forms of mercury are more toxic than inorganic forms, but it is possible for inorganic mercury to be biologically methylated. Methyl mercury has high affinities for fatty tissues in organisms and can accumulate through food chain to higher toxic levels within those organisms. Therefore, it is important to have a strict control on inorganic mercury leaching from mercury-containing wastes (Jian *et al.*, 2002).

Elemental mercury (Hg^0), although is a metal, at normal temperatures, it is in liquid form. Thus, because of this unique property, plus its high specific gravity and electrical conductivity, has brought about its various types of laboratory equipment and instruments extensive use in the industries. The elemental mercury is also extremely dense which is 13.5 times denser than liquid water under ambient conditions. This high density, low saturation vapor and high surface tension control

the immediate behavior of the releasing of elemental mercury on land surface (Turner, 1992).

Mercury can exist in three oxidation states, which is Hg° (metallic), Hg_2^{2+} (mercurous) and Hg^{2+} (mercuric). These oxidation states will determine the properties and behavior of the mercury. Mercury (Hg), is one of the most toxic heavy metals commonly found in the global environment including lithosphere, hydrosphere, atmosphere and biosphere. Cycle of three-oxidation states of Hg to the environment is allowed by a series of complex chemical transformations allows. Most of the Hg encountered in all environmental media (water/soil/sediments/biota) is in the form of inorganic mercuric salts and organomercurics, with the sole exception of atmosphere. The mercuric salts HgCl_2 , $\text{Hg}(\text{OH})_2$ and HgS are the prevalent forms existing in the environment and CH_3HgCl and CH_3HgOH are main forms of organic compounds, together with other organomercurics (eg: dimethylmercury and phenylmercury) existing in small fractions (USEPA, 1997)

1.2 Mercury Flow through Petroleum and its Scenario to Environment

The mercury from industries and power plants is emitted primarily as mercury vapour. This vapor consists mainly of elemental mercury and dimethyl mercury. It is difficult to say which volatile compound dominates the discharge process. Mercury species other than elemental Hg and $(\text{CH}_3)_2\text{Hg}$ can also contribute. Most mercury is emitted as dimethyl mercury with a relatively fast degradation to elemental mercury taking place in the air. Hg (O) is mobilized to the atmosphere where it is subjected to atmospheric oxidation processes to yield water soluble forms, subsequently scavenged by wet or dry deposition (Elisabeth *et al.*, 2000)..

Petroleum products carry mercury from a geological reservoir and distribute mercury to the environment along their passage. This section describes the flow and trend of mercury as carried by petroleum products. More work with the more

sensitive analytical methods developed in the past few years should be performed to confirm these numbers.

Crude petroleum is identified to contain small but measurable amounts of mercury. About 16 to 18 million barrels (672 to 756 million gallons) of crude oil are consumed daily in the United States. At an average concentration of 0.41 ppm mercury and an average density for crude oil of 6.9 lbs per gallon, the lowest total amount of mercury vaporized daily is therefore 1,901 lbs. This value represents an annual discharge of 347 tons of mercury nationwide, assuming that all of the oil is combusted. As very large volumes of oil consumed, even a small concentration of mercury clearly represents a major source of atmospheric deposition of mercury.

Some natural gas regulators made before 1961 contained Hg^0 , which was sometimes spilled when the regulators were removed. After a large Hg^0 spill, the hazard can persist for a long time. In the case of natural gas regulator spills, monitoring found elevated airborne $\text{Hg}^0 > 10$ years after it was spilled. Spilled Hg^0 forms small beads, which spread, making a thorough cleanup difficult.

1.3 Techniques of mercury removal

Chemical leaching where the chemical separation is based upon the reactivity of mercury and employs solution leaching of the mercury-contaminated materials can do removal of mercury from metal surfaces. Solution leaching may be used to remove both elemental and inorganic forms of mercury. Most common used leaching solutions are the oxidizing acids such as nitric acid, hypochlorous acid and sulfuric acid. These oxidizing acids are used because of their ability to readily dissolve elemental and inorganic mercury (Foust, 1993). Preferred oxidizing agents are those, which are characterized as being mild, and which do not react with any of the solid material to form oxidation products, which complicate separation contamination of the solid material. In this case, iodine is a most preferred oxidant.

Removal of mercury from solid waste can be conducted by using a lixiviant consisting an aqueous solution of potassium iodide/iodine (KI/I₂) (Ebadian, 2011a). Mercury in contaminated solid wastes in the form of oxides, sulfides, elemental, and adsorbed phases is mobilized by the KI/I₂ lixiviant through oxidation and complex-forming reactions. Iodine, which is an oxidizing agent, is capable to oxidize various species of mercury including elemental mercury to mercuric iodide. While potassium iodide is a complexing agent, thus it can react with mercuric iodide to form a water-soluble compound, which has the formula of K₂HgI₄.

In addition, in order to increase mercury solubility for absorption, oxidizers such as sodium hypochlorite and hypochlorous acid have been applied to transform insoluble Hg⁰ to very soluble Hg²⁺ which can then be easily moved through aqueous scrubbing (Zhao *et. al*, 2008a). Elemental mercury absorption in hypochlorous acid was found to be much more reactive than hypochlorite but the mercury removal reactivity of hypochlorite increased in the presence of sodium or potassium chloride and potassium hypochlorite was found to be more reactive than sodium hypochlorite (Zhao *et. al*, 2008b and Lynn *et. al*, 1999). NaOCl strongly absorbs elemental Hg vapor even at high pH. At low pH, high concentrations of chlorine⁻ and high temperature favor mercury absorption.

One of the most established approaches on removing mercury from wastewater is precipitation and coagulation/co-precipitation technology (Ebadian, 2001b). Sulfide is added to the waste stream to convert the soluble mercury to the relatively insoluble mercury sulfide form:



The process usually combined with pH adjustment and flocculation, followed by solid separation. The sulfide precipitant is added to the wastewater in a stirred reaction vessel, where the soluble mercury is precipitated as mercury sulfide. The precipitated solids can be removed by gravity settling in a clarifier. Sulfide precipitation can achieve 99% removal for initial mercury levels exceeds of 10 mg/L

(Patterson, 1985). Approximately 10 to 100 $\mu\text{g/L}$ are the lowest achievable effluent mercury concentration that appeared for various initial concentrations even with polishing treatment such as filtration. Sulfide precipitation appears to be the common practice for mercury control in many chlor-alkali plants. A 95 to 99.9% of removal efficiencies were reported well-designed and managed mercury treatment systems (Perry, 1974).

Numerous studies have been conducted on the mercury removal from aqueous medium but the most preferable technique is to use photocatalyst. Photocatalytic processes use electron-hole pairs photogenerated in semiconductors to promote redox reactions. The photocatalytic treatment for mercury (II) produces metallic mercury that deposits on the photocatalysts (Aguado *et. al*, 1995).

1.4 Problem Statement

Crude oil and unprocessed gas condensate can contain significant amount of mercury. Elemental mercury Hg^0 is independently quantified as volatile species evaporated from a single crude oil using selective trapping. Steel sorbs mercury in considerable quantity. Hg^0 both adsorbs and chemisorbs to metal surfaces.

Mercury is common and naturally occurring component of petroleum. Petroleum processing often is accompanied by generation waste streams contain some mercury. These waste streams become problematic when the mercury concentration in process feeds exceeds a few ppb because of the highly toxic nature of mercury.

In gas processing, mercury damages equipment and fouls cryogenic exchangers. Pipelines that carry fluids that contain mercury can become contaminated over time and thus require special attention. The interactions of mercury with pipe surfaces affect worker health and safety strategies and impacts

operational procedures. Therefore, the wastes that contain mercury must be disposed in safe manner so that the world will not be a dangerous place to live for another generations (Wilhelm, 1999).

There are few solution used in industry to solve mercury metal presence on material surface, mostly by using inorganic acid, but it reacts with the metal surface and became corrode. Recently, technologies claimed lixiviant chemical is potential to remove mercury from metal surfaces, but it reacts with the material for example, carbon steel. The critical successfulness of the technique should be no or acceptable reaction towards the material surface, instead reacts with Hg metal. Thus, this research is proposed to suggest the most effective way to treat mercury on metal surfaces so that it can be used in the industry.

1.5 Significance of Study

In this research, peracetic acid with the addition of a potential catalyst can be used to enhance the removal of elemental Hg presence on the metal surfaces.

The removal technique via this oxidant and catalyst can remove elemental mercury that is hazardous to the environment. This will help to prevent mercury, which has been known to be causing serious impact on human health, animals, plants and also the environment. Mercury was found to produce several impacts on gas processing production. These includes, it forms amalgams with several metals, particularly carbon steel, which leads to LME. This is prevelant in pipeline welds, cryogenic components, heat exchangers and hydrogenation catalysts. Besides, it may be necessary to avoid the corrosion and clogging to the delivery pipeline. This cleaning method will certainly improve the quality and quantity of Malaysian oil manufacturing company. The utmost important, the oxidant and potential catalyst will contribute to the growth of the national economy and create green and sustainable environment. This proposed technique enables to conduct treatment of elemental mercury in the internal pipeline system.

The oxidant and the catalyst are easily prepared and environmental friendly. All the ingredients in the fabrication of both oxidant and catalyst are easily available, cheap and stable. It requires minimum modification to the already existing system and offers cost effective operating system.

1.6 Objective of Study

The objectives of this research are:

1. To develop the oxidizing agent, potential for the treatment of mercury metal presence on metal surface
2. To test the catalytic activity of the prepared catalyst for elemental mercury removal from metal surfaces
3. To optimize the catalytic oxidative reaction for elemental mercury removal
3. To characterize the prepared catalysts utilizing various analytical techniques

1.7 Scope of Research

The removal of mercury from metal surfaces will be done using five different types of oxidizing agents, which are iodine/iodide lixiviant (KI/I_2), sodium hypochlorite ($NaOCl$), diperacetic acid ($di-PAA$), peracetic acid (PAA), and tert-butylhydroperoxide ($TBHP$). Next, a series of alumina-supported catalyst based on ruthenium oxide doped with noble metal were prepared using wetness impregnation techniques. Meanwhile, adding the prepared catalysts to the oxidants carried out catalytic testing. Carbon steel physisorbed Hg (CS -physisorbed-Hg) and Carbon steel droplet Hg (CS -droplet-Hg) will be used in this experiment. The batch experiments will be carried out in a 100 ml glass beaker. Then, the samples that contain mercury will be analyzed using Mercury-Hydride System, Atomic Absorption Spectroscopy

(MHS-AAS) as the quantitative analytical method to determine the level of mercury after the treatment of the samples. Lastly, characterization of the catalysts will be carried out by various techniques including X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray Analysis (EDX).

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