PHILIPPINE ENGINEERING JOURNAL
PEJ 2014; Vol. 35, No. 2: 1-8

HG REMOVAL FROM MERCURY-CONTAMINATED GAS BY AG-IMPREGNATED ACTIVATED ALUMINA ADSORBENTS

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ABSTRACT

Natural gas, a mixture of gaseous hydrocarbons, is used as fuel in various industrial and domestic applications. Unprocessed natural gas typically contains 1–400 $\mu g/m^3$ *toxic mercury vapor which damages pipes and equipment walls. In this study, novel silver-impregnated activated alumina (Ag/AcAl) adsorbents were synthesized via ultrasound-assisted wet process. The adsorbents were used to remove elemental mercury* (Hg^0) *from mercury-contaminated gas. Static adsorption experiments were carried out to evaluate the effects of dopant-to-support ratio, reaction temperature and contact time on* Hg^0 *removal. At 55°C, up to 147.51 mg of* Hg^0 *was removed per g of the 15% Ag/AcAl adsorbent after 40 days of static adsorption. In addition, dynamic adsorption experiments were conducted to compare the performance of the Ag/AcAl adsorbent and commercial activated carbon in removing elemental mercury from mercury-contaminated gas stream. Results showed that Ag/AcAl was superior to activated carbon throughout the entire dynamic testing duration. This study demonstrates the potential of Ag/AcAl adsorbents for mercury removal from natural gas.*

1. INTRODUCTION

Natural gas remains one of the major energy sources used worldwide including the Philippines. It is mainly utilized as fuel for electricity generation and also used for transportation, domestic cooking, and other industrial and agricultural processes. About 20% of worldwide energy consumption is from processed natural gas [3].

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Received: August 26, 2014
Accepted: December 15, 2014

In the Philippines, 15% of the total power generation comes from natural gas, the equivalent volume of which is approximated at 2.8 billion m^3 [1,12]. The demand for natural gas is expected to increase as the country's population and economy continue to grow. Figure 1 shows the actual [1,3,12] and projected natural gas consumptions in the local and global setting.

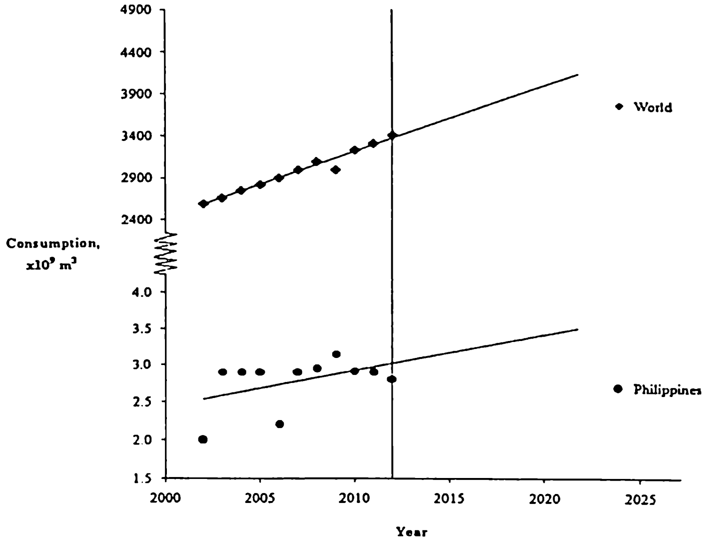


Figure 1. Actual and projected natural gas consumptions

Unprocessed natural gas contains a number of impurities: water, sulfur species, diluents (*i.e.* CO_2, H_2S and N_2), radioactive materials, oxygen, and trace quantities of mercury mostly Hg^0 and some lesser amount of $Hg(CH_3)_2$ [6,12]. The amount of mercury in natural gas depends primarily on geological factors and production practices. The concentration of mercury in natural gas varies widely. Fields in the Gulf of Mexico usually contain low mercury concentrations (< 1 μg/m^3) while those in the Gulf of Thailand have relatively higher concentrations (100–400 μg/m^3) [9].

Removing mercury from natural gas streams provides several advantages. It increases the fuel heating value by 0.37 J per cubic meter of natural gas. It will minimize the corrosion of brazed-aluminum heat exchangers and other equipment used for gas processing operations. It will eliminate the contamination of treatment processes such as dehydration units and amine acid gas removal systems. It will also minimize the risks to human and animal health. It is known that daily exposure to 20 μg/m^3 of mercury vapor causes mild nervous system toxicity, increased protein in the urine leading to kidney failure, and other serious illnesses like the Minamata disease and acrodynia disease [15].

Over the last decade, mercury removal studies from gaseous media focused on the flue gas of coal combustion. The two main strategies employed are: (i) oxidation of Hg^0 to Hg^{2+} and (ii) adsorption of Hg^0. The former utilizes catalysts to convert Hg^0 into Hg^{2+} which readily forms a compound that is generally reactive, water soluble and more effectively captured by pollution control devices of coal-fired power plants. The latter, on the other hand, involves a wide range of adsorbents for mercury vapor capture including commercial and synthesized activated carbon, activated coke, biomass gasification chars, pyrolyzed petroleum coke, synthetic sorbents, bamboo-based sorbents, zeolite, and wood char [2,4,7,8,10,11,13,16]. Adsorbent modification by loading a metal oxide into the support activated carbon has also been conducted [13].

In this study, mercury-contaminated gas was simulated by mixing nitrogen gas with elemental mercury vapor. Silver metal–doped activated alumina was synthesized by wet impregnation method and used to remove elemental mercury from contaminated gas. Mercury removal was expected from the reaction of elemental mercury with silver metal to form amalgam on the surface of Ag-doped activated alumina. Static and dynamic adsorption experiments were conducted to evaluate the performance of the silver metal doped activated alumina for elemental mercury removal.

2. METHODOLOGY

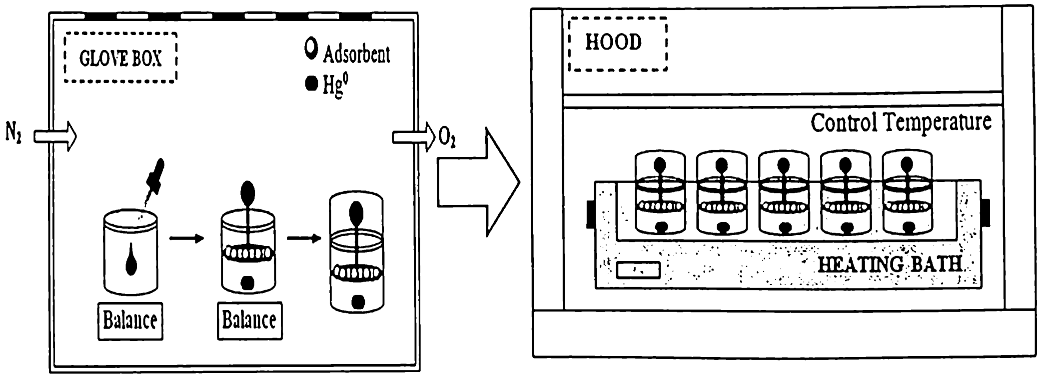
A. Materials and adsorbent synthesis

Activated alumina (Al_2O_3, 0.5-1.2 mm, WHA-104) obtained from Pingxiang Huihua Packing Co., Ltd was used as the metal oxide support while silver nitrate ($AgNO_3$), purchased from Carlo Erba Reagents, was used as dopant.

Silver-impregnated activated alumina adsorbents were synthesized by incorporating known amount of $AgNO_3$ (% w/w) into activated alumina by wet impregnation method. The doped activated alumina was subjected to ultrasound irradiation for 3 h and dried in an oven at 80°C for at least 6 h. The dried powder was calcined in a muffle furnace for 3 h at 480°C at a heating rate of 10°C/min to remove the nitrate ion [4]. The ensuing adsorbent powder was pelletized depending on the desired application. For static adsorption experiments, each pellet weighed 50 mg while for dynamic adsorption, the powder was pelletized for 1 mm sieves.

B. Static adsorption experiments

Figure 2 shows the schematic diagram of the static adsorption set-up. The adsorbents were placed in static glass cylinders containing liquid mercury (Figure 2a). The preparation of the static adsorption set-up was done in a glove box that is constantly purged by nitrogen gas to eliminate oxygen contamination. Static adsorption tests were carried out at different temperatures. The glass sets containing the adsorbents and liquid mercury were placed inside a heating bath (Figure 2b). Samples were taken and analyzed after 5, 10, 20 and 40 days. The amount of Hg^0 in the adsorbent was analyzed by Lumex-RA915$^+$ mercury analyzer.



(a) (b)

Figure 2. Static adsorption test set-up

C. Dynamic adsorption experiments

The schematic diagram of the flow adsorption set-up is shown in Figure 3. Mercury vapor was produced from liquid mercury in a saturator by controlling the temperature in the heating bath. The temperature of the water bath as well as the temperature of the air inside the hood was maintained constant at 30°C.

Nitrogen gas, used as carrier gas of the mercury vapor, flowed into 2 separate lines with a combined flow rate of 75 mL/min: (i) the mercury line which passed through the saturator and carried the mercury vapor with it, and (ii) the dilution line which diluted the mercury line.

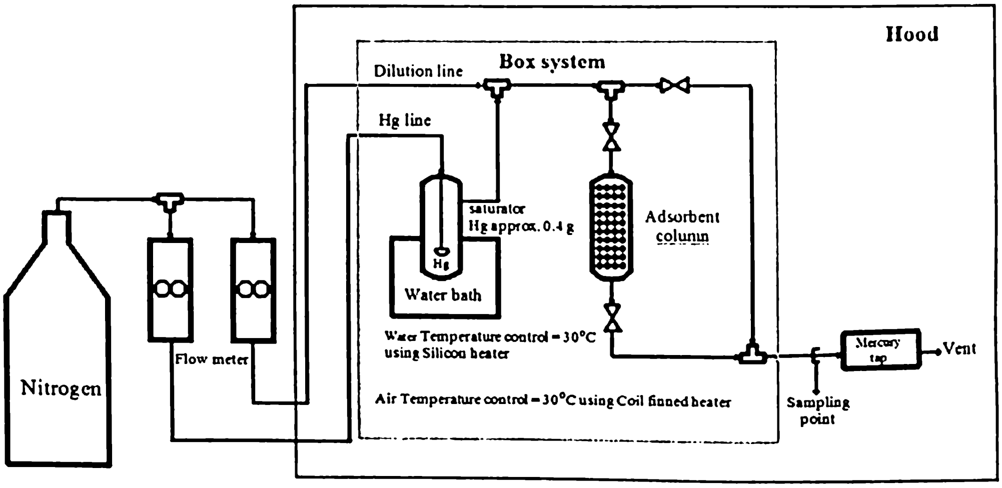


Figure 3. Schematic diagram of dynamic adsorption

The nitrogen with mercury vapor was allowed to bypass the adsorbent column for several days to stabilize the concentration of mercury that will eventually pass through the column. When the mercury-containing nitrogen gas started flowing through the adsorbent column, the effluent gas was analysed for mercury concentration daily.

3. RESULTS AND DISCUSSION

A. Static adsorption

The adsorption capacity versus time profiles of the activated alumina adsorbents are shown in Figures 4a and Figure 4b for static adsorption at 40°C and 55°C, respectively. As shown, negligible elemental mercury (0.005 – 0.03 mg Hg/g adsorbent) was removed by pure activated alumina t the end of the 40-day static adsorption.

On the other hand, silver-doped activated alumina gave higher mercury removals at higher amount of doped silver metal and higher reaction temperature. At the end of the 40-day duration, the amount of elemental mercury adsorbed by the silver-doped activated alumina which contained 15% silver (w/w) was approximately twice that removed by the doped adsorbents which contained 5% silver (w/w). At higher dopant concentration, more silver metal is available to react with elemental mercury to form amalgam.

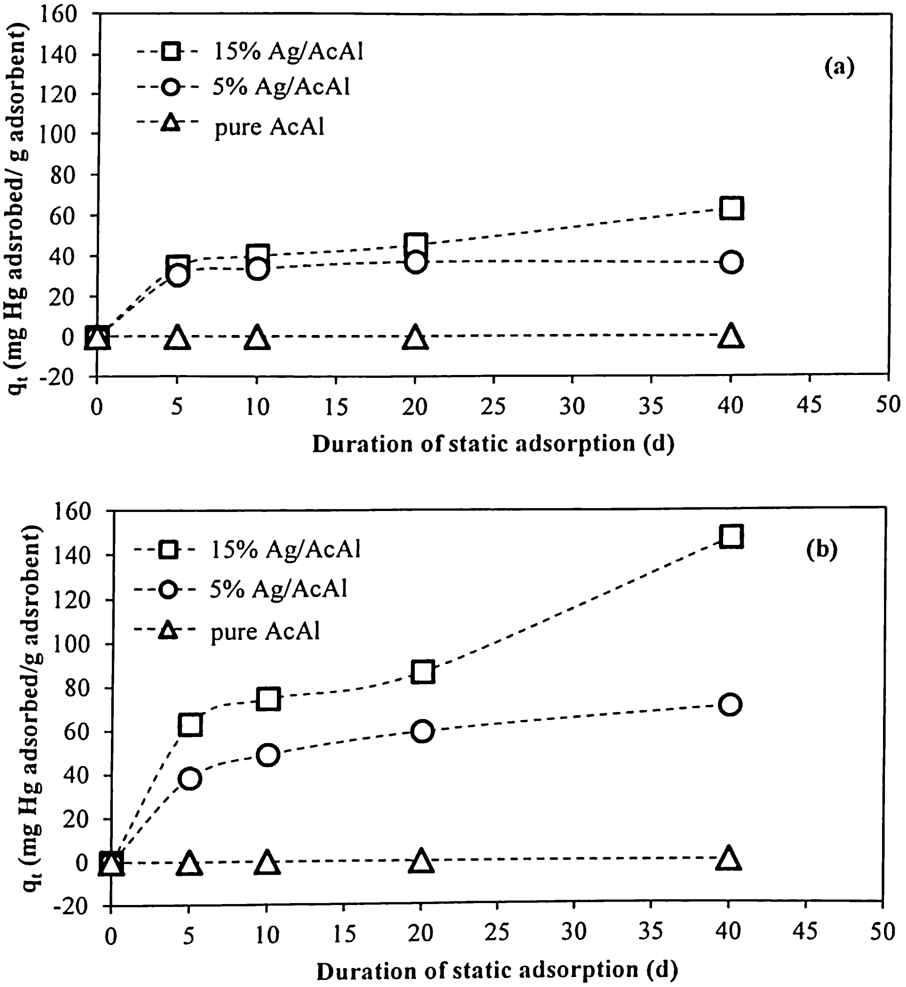


Figure 4. Adsorption capacity versus time profiles at (a) 40°C and (b) 55°C

For the doped activated alumina containing 15% silver (w/w), mercury removals of up to 62.49 mg Hg/g adsorbent and 147.51 mg Hg/g adsorbent were reached at the end of the 40-day static adsorption duration for reaction temperatures of 40°C and 55°C, respectively.

For both temperatures, the 5% silver-doped adsorbent was near saturation at the end of 40 days. For the same duration, however, adsorbent saturation was not reached by the doped activated alumina which contained 15% silver (w/w).

B. Dynamic adsorption

The results of the 48-day dynamic adsorption experiments are shown in Figure 5. Although both adsorbents were not able to reach their respective exhaustion points at the end of the dynamic adsorption duration, silver-doped activated alumina removed more elemental mercury at a faster rate compared to commercially available Norit activated carbon. Elemental mercury concentration ratios of 0.2 and 0.3 achieved for silver-doped activated alumina and Norit activated carbon, respectively after 48 days.

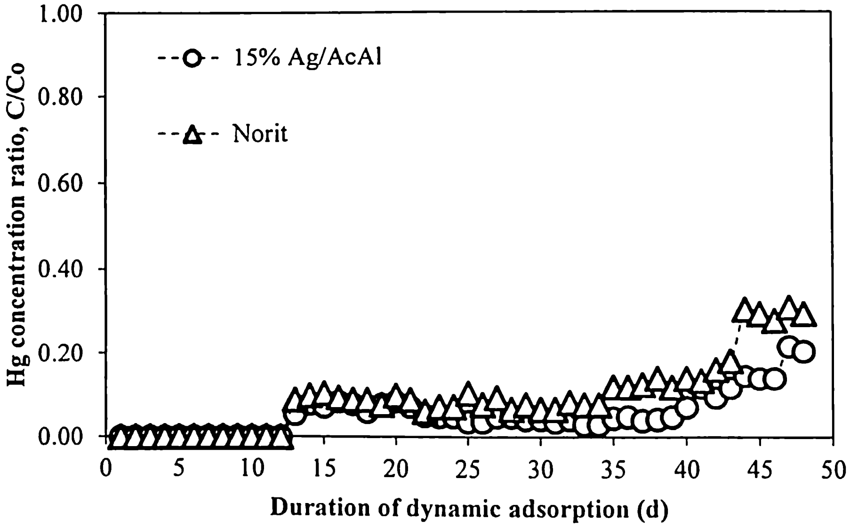


Figure 5. Elemental mercury removal during dynamic adsorption

4. CONCLUSIONS

The present study demonstrates the effectiveness of silver-impregnated activated alumina in removing elemental mercury from contaminated gas streams. Elemental mercury vapor formed amalgams with the silver metal doped on the surface of the metal oxide. Silver-impregnated activated alumina can be incorporated into the activated carbon matrix to improve its mercury removal ability.

ACKNOWLEDGMENTS

The authors are grateful for the assistance and cooperation of the Catalysis and Adsorption Laboratory of the Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Thailand; the Energy Enginering Program, the Department of Mechanical Enginering, the Department of Chemical Engineering of the College of Engineering, University of the Philippines, Diliman, Republic of the Philippines; and the Engineering Research and Development for Technology Program of the Department of Science and Technology, Republic of the Philippines.

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