Morphological based mechanism for adsorption of Hg from natural gas using solid supported ionic liquids

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Abstract

Mercury is a highly toxic element that is released in oxidized, particulate and elemental forms both naturally and as a result of human activity. Natural gas sector could be a significant source of both global mercury supply and emissions. The magnitude of mercury emissions from natural gas processing plants depends on the mercury content of the gas before processing and whether mercury removal has been conducted. Eastern/Central Europe, North Africa, and Southeast Asia are generally considered the hotspots for mercury in natural gas since concentrations there are routinely above $100\mu g/m^3$. Most of the mercury in natural gas is elemental mercury whereas quantities of inorganic (including mercuric chloride), organic (including dimethyl mercury and diethylmercury) and organo-ionic compounds are also present. The presence of mercury in refinery hydrocarbon streams not only results in detrimental effects, including catalyst poisoning, corrosion, safety issues but also anthropogenic increase of mercury level in environment, has provoked the search for environmental friendly techniques to capture the mercury from process streams. Solid supported ionic liquids (SSILs) is a promising, eco-friendly technique to remove mercury from natural gas stream with high efficiency and causing no deteriorating impact on gas processing plant. In this study, the fixed bed reactor has been used to investigate the mechanism of mercury adsorption based on morphological study using SSILs. The understanding of mechanism would help to further increase the overall mercury adsorption efficiency in the presence of different contaminants.

Keywords: Mercury, Natural gas, Solid Supported Ionic Liquids, Morphology

Introduction

Mercury (Hg) is a highly volatile transition metal found in the environment in trace quantities in both elemental (Hg^0) form and as highly toxic organo-mercury compounds [1]. Hg is a naturally occurring contaminant in geological hydrocarbons and is distributed freely throughout production, processing, transportation and consumption systems [2]. The toxic contaminants from these activities can enter into the environmental cycle and food chains easily, through emission during processing stages or unregulated disposal of wastes or accidents, causing various diseases and disorders to animals and humans [3]. As shown in figure 1, hydrocarbons from different geological locations contain Hg in microgram levels. The values shown are estimations and may change from time to time, depending on geological factors and production practices [4].
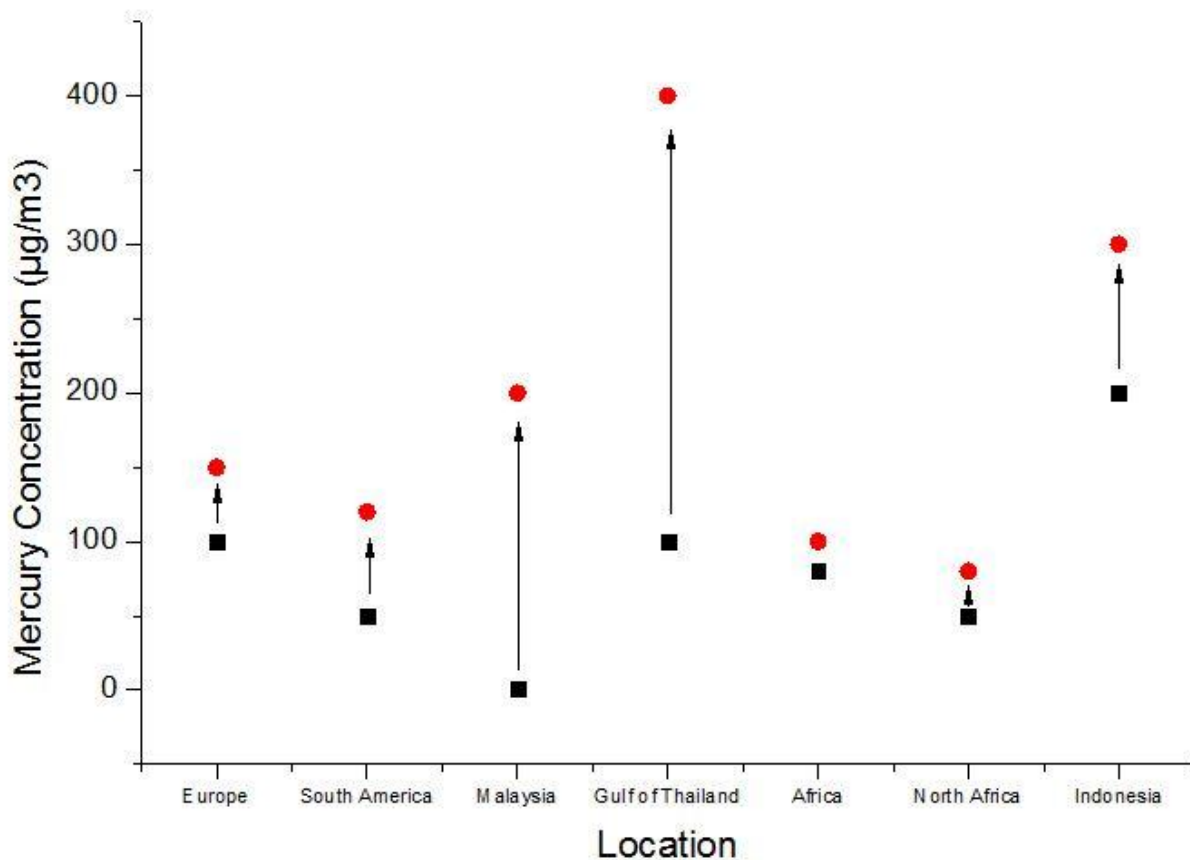

Figure 1: Hg concentration in gas for different regions [4, 5]. (The arrows between black and red dots are representing the range)

As Hg presents in many natural gas streams, even low levels of mercury need to be removed to avoid detrimental impacts on gas processing operations [6]. The presence of Hg in hydrocarbon is problematic due to its toxicity. In addition, Hg is corrosive towards hydrocarbon processing equipment, such as that used in oil and gas refineries. Hg can react with aluminum components of

hydrocarbon processing equipment to form amalgam, which can lead to equipment failure. Hg in gas plant products affects downstream processes. Gas plant 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 [2].

Adsorption by activated carbons [7], particularly those impregnated with sulfur (S) [8], chloride (Cl) or Iodine (I) [9] is being employed for the removal of Hg^0 from the natural gas but these adsorbent have less efficiency to remove Hg^0 for longer period of time [6]. Moreover, to meet the outlet speciation, bulk quantity of these adsorbent are being used which may increase the cost and create disposal issue of bulk quantity of adsorbent [10].

Recently, solid supported ionic liquids have proven greater ability to remove Hg from gas streams than conventional adsorbent [11]. However, there is still need to understand the immobilization of ILs on solid support through morphological study that will help researchers to understand the role of solid support and improve the efficiency of adsorbent as well. In the present study, 1 butyl 3 methyl imidazolium chloride [Bmim]Cl was immobilized along with oxidizing agent potassium permanganate ($KMnO_4$) on activated carbon to study the morphological changes upon immobilization of ionic liquid and performance against adsorption of Hg^0 vapor.

Materials and Chemicals

The [Bmim]Cl were purchased from Merck, whereas activated carbon named AC Nangjing was provided by PETRONAS Research sdn bhd, Malaysia. Dicholromethane and $KMnO_4$ were obtained from Fischer Scientific. The physical immobilization was performed as discussed by Ji et al. [10] . 3.3125 g of [Bmim]Cl was dissolved in 80 ml dichloromethane (DCM), after that 2.9375 g of $KMnO_4$ was added to the solution. The final solution was added to the flask having 22.5 g of activated carbon. The mixture was stirred at 300rm for 24 hours to get the homogenous immobilization of ionic liquid on activated carbon and then DCM was removed using vacuum rotary evaporator at 33°C. The adsorbent was dried in oven at 90°C overnight to remove any further moisture.

Characteristics of Adsorbent

The surface area and pore size of fresh activated carbon and coated carbon was analyzed by using Micromeritics' ASAP 2020. Field Emission Scanning Electron Microscopy (FE-SEM) was performed on (Zeiss-SUPRA 55VP) at 5000X to investigate the morphological changes in adsorbent and confirm the homogenous immobilization of [Bmim]Cl and KMnO4. Energy-dispersive X-ray spectroscopy (EDX) was used to perform elemental analysis and mapping in the case of spent adsorbent.

Mercury Removal from Gas

A laboratory scale fixed-bed continuous flow adsorber was used to evaluate the performance of adsorbent as shown in figure 2. The flow rate of carrier gas was maintained 60ml/min through

rotameter and average concentration of mercury vapor in the gas stream was 15 -17 ppm. 0.1 gram of adsorbent was loaded in the adsorber.

Figure 2: Mercury adsorption facility

Results & Discussion

BET surface area (Fresh activated carbon and [Bmim]Cl + KMnO₄ coated carbon)

The structural properties (pore size, pore volume, and BET surface area) of fresh activated carbon and coated activated carbon were characterized with a Micromeritics ASAP2020 using liquid nitrogen. The surface area was calculated from the adsorption isotherms using the BET method. The pore-size distribution (PSD) was obtained from the adsorption branch of the isotherm using the BJH method. The results are shown in table 1. It was noticed that micropore area was reduced upon immobilization of [Bmim]Cl by blocking the micropores, leading to less surface area. The pore size was reduced from 7.25 nm to 6.37 nm but still the in range of mespores.

Table 1: Surface area, pore volume and pore size of adsorbent

Adsorbent	BET surface area (m²/g)	t-Plot Micropore Area (m²/g)	BJH Pore volume (cm³/g)	t-Plot micropore volume (cm³/g)	Pore Size (nm) (average pore diameter)
Fresh activated carbon	640.93	549.25	0.027	0.22	7.25

[Bmim]Cl + KMnO$_4$ coated carbon	448.85	226.93	0.034	0.10	6.37

Mercury Removal from Gas Stream

After 72 hours, the adsorbent were taken out and digested. The mercury content was measured by using mercury analyzer PE-1000. The PE-1000 mercury analyzer uses atomic florescence spectrometry (AFS) detector and able to detect mercury down to pico gram level. For liquid samples, it's able to detect down to 0.01 ppbv (ug/l), depending on the volume injected, for gas samples, it can detect as low as 0.001 ppbv (ng/m^3).The capacity of adsorbent was found 6.8 mg/g. The capacity of adsorbent could be more than of that as the complete saturation of adsorbent is not studied.

Surface Morphology of Fresh and Spent Adsorbent

FESEM-EDX is a scanning electron microscopy to determine the micro structure of a material including texture, morphology, composition and christallography particle surface. EDX (Energy Dispersive X-ray), is a material characterization method using x-ray emission. It was noticed that the surface of activated carbon became smooth as compared to fresh activated carbon due to the immobilization of ionic liquid. Through morphology of adsorbent, it is clear that ionic liquid blocked the micro, not meso or macro pores (yellow highlighted in figure 3) and that does not have much ability to capture mercury from gas stream. The EDX mapping confirms that Cl contents of [Bmim]Cl was distributed uniformly on the surface of adsorbent. The morphology of spent adsorbent was changed due to the bond formation between mercury and ionic liquid on the surface as shown in figure 4 (red highlighted). It may due to the oxidation of Hg^0 to Hg^{2+} by KMNO$_4$ following the formation of HgCl$_2$. Moreover, it was clear from morphology of spent adsorbent that meso or macropores were not filled by Hg^0 (yellow highlighted in figure 4), showing that they does not have ability to capture Hg^0 vapor.
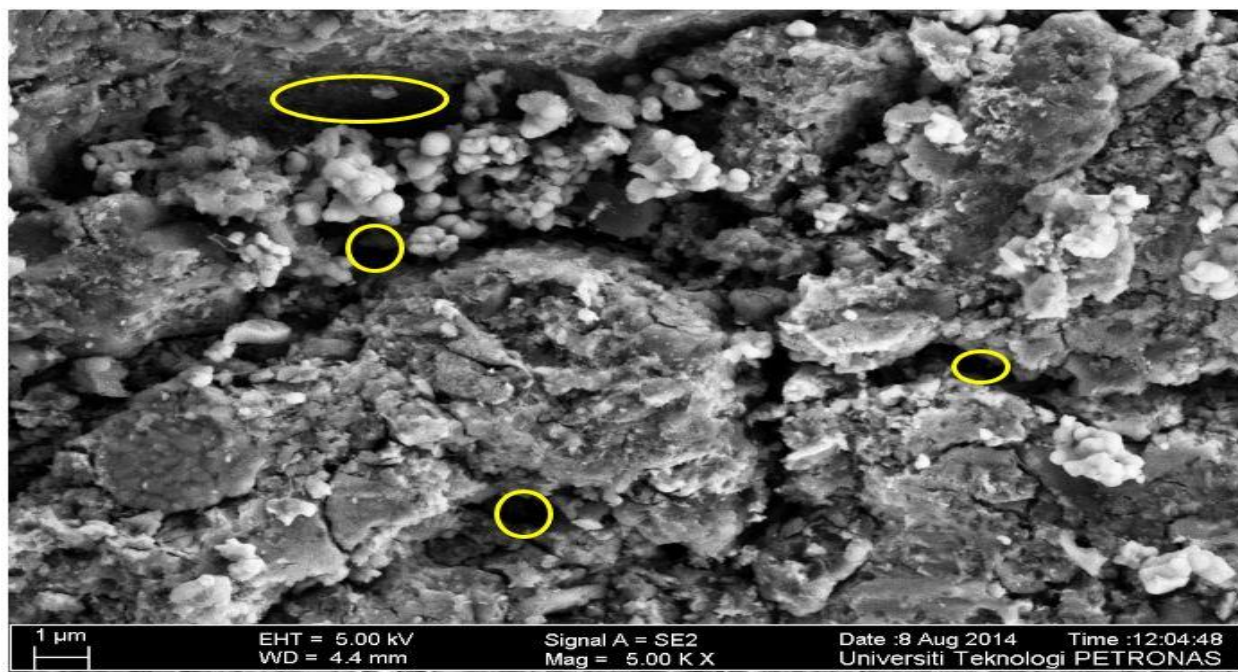
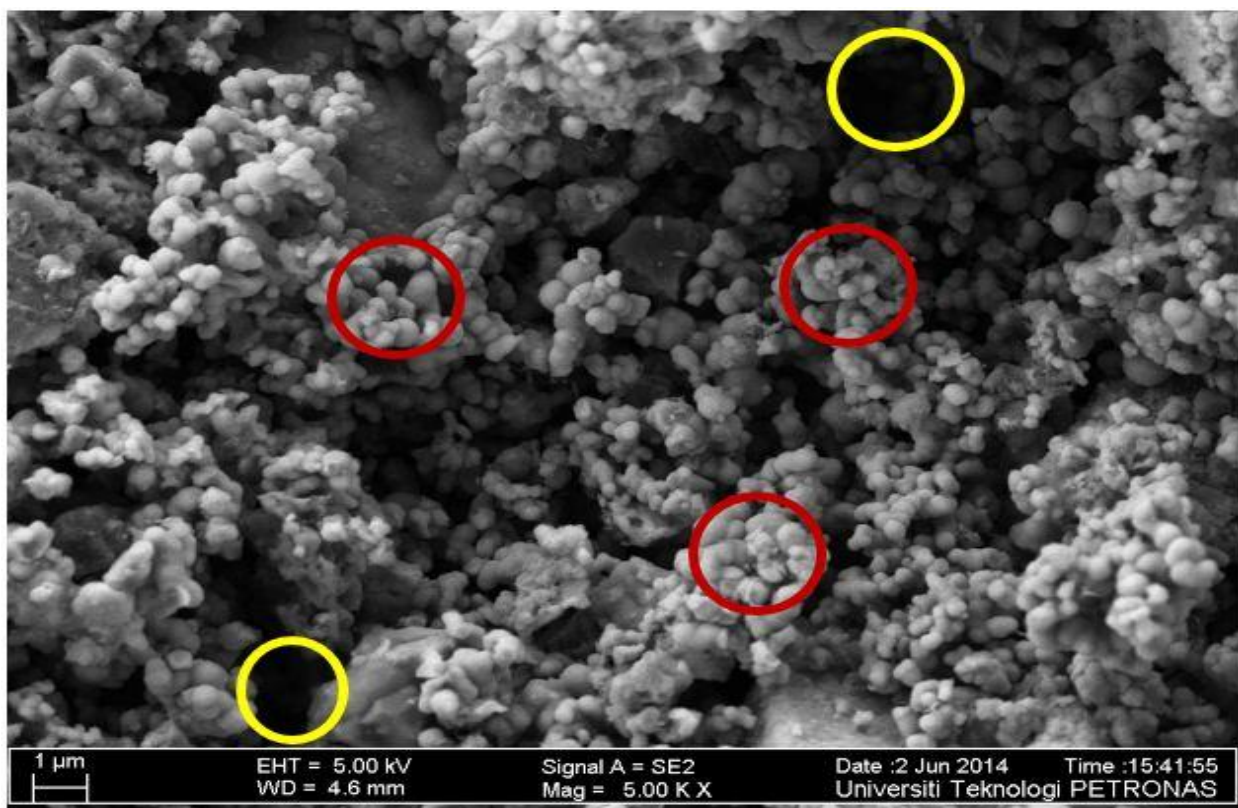Figure 3: Morphology of [Bmim]Cl and KMnO₄ coated activated carbon (fresh adsorbent) at 5000X

Figure 4: Morphology of [Bmim]Cl and KMnO₄ coated activated carbon (spent adsorbent) at 5000X.

To confirm the presence of mercury on the surface of adsorbent, EDX mapping was performed. It confirmed the presence of mercury on the surface as shown in figure 5, which may be due to the formation of Hg-ionic liquid ([Bmim]Cl) complex i-e $HgCl_2$.
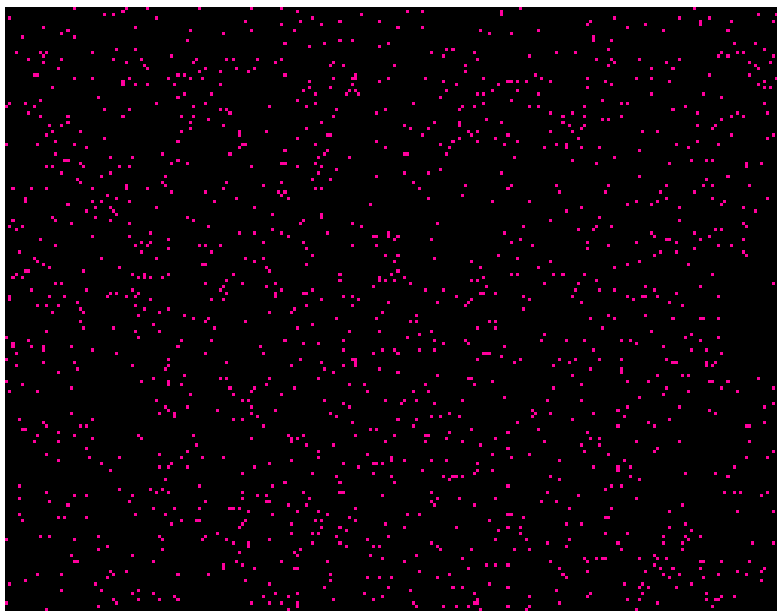

Figure 5: Presence of Hg on the surface of adsorbent

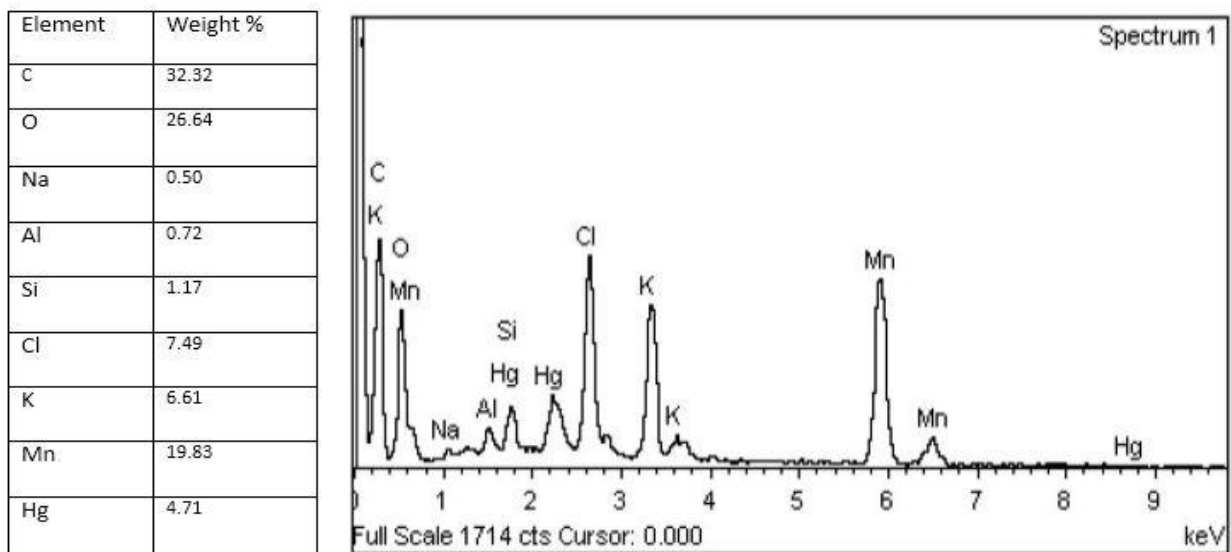The elemental composition of spent adsorbent was also investigated by EDX as shown in figure 6.

Element	Weight %
C	32.32
O	26.64
Na	0.50
Al	0.72
Si	1.17
Cl	7.49
K	6.61
Mn	19.83
Hg	4.71

Figure 6: Elemental composition and EDX spectra of spent adsorbent

The presence of Cl, K, Mn and O is due to the immobilization of [Bmim]Cl and KMnO$_4$, whereas Na, Al, Si are the impurities of activated carbon.

Conclusion

[Bmim]Cl and KMnO$_4$ were successfully immobilized on activated carbon to adsorb Hg^0 from gas stream. It was found that the surface area and pore size of adsorbent were reduced due to micropore blockage by the immobilization of ionic liquid. The carbon coated with [Bmim]Cl and KMnO4 showed promising ability to capture Hg from gas stream. The capacity of Hg removal was found 6.8 mg/g of adsorbent in 72 hours (gas flow rate and Hg^0 vapor concentration were 60ml/min and 15ppm). A change in surface morphology was noticed due to the formation of Hg complex with [Bmim]Cl i-e HgCl$_2$. Furthermore, it is clear from the morphology and EDX mapping of spent adsorbent that Hg was uniformly attached on the surface of adsorbent due to chemisorption with [Bmim]Cl.

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