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Research Article

Modification & Characterization of Activated Carbon Impregnated with KCl, Na_2S, and KI for Enhancing Mercury (Hg) Removal from Natural Gas

Abstract

Modified activated carbon (MAC) has been synthesized and characterized to enhance mercury (Hg) removal from natural gas. MAC was modified by impregnating it into KCl, Na_2S, and KI to introduce Cl-, S-, and I- elements. The SEM-EDX, FTIR, and SAA were used to characterize the AC & MAC. The isothermal and adsorption capacity were studied using the mercury gas standard. The results of SEM-EDX analysis show that the impregnation method is proven to produce MAC containing elements Cl, S, and I with mass % of 2.78% Cl, 0.76% S, and 39.60% I. The surface area is 421.91 m^2/g, total pore volume is 0.386825 cc/g, and the average of pore size is 1.83369 nm. Group functions are O-H, C=O, and C-O, and there are vibrations at the wavelength number 617.81 cm^{-1}, which are ions formed by the impregnation agent. The mechanism for absorbing mercury gas into MAC follows Freundlich isothermal model, with a coefficient of determination (R2) of 0.996. The adsorption capacity on MAC increased 57 times compared to unmodified activated carbon (AC) from 5540.60 to 315730.64 ng/g, with an efficiency maximum of 100%. The MAC has been proven to enhance mercury adsorption in natural gas with an efficiency of 78.3%.

Keywords: modified activated carbon, isothermal, adsorption capacity, natural gas, mercury.

1. INTRODUCTION

Mercury (Hg) known as hazardous and toxic materials in the form of heavy metals that are liquid, silver-white in color, and volatile at room temperature, where they are usually in the form of organic and inorganic compounds that are persistent and bio accumulative. Mercury occurs naturally in nature in several forms, such as metal (elemental mercury), inorganic mercury, and organic mercury [1].

The increasing exploration and production of hydrocarbon compounds has also caused mercury contamination to increase. Starting from health risks, safety, equipment contamination, catalyst damage, toxicity of emissions to the environment, and damage caused by mercury contamination in heat exchangers of LNG (liquified natural gas) plants [2].

Mercury is abundant in natural gas wells with varying levels, and its content needs to be removed to prevent damage to aluminum heat exchangers and other plant equipment. Most of natural gas has a small amount of mercury content (trace). The presence of mercury in natural gas, even in small amounts, is considered detrimental because it can cause corrosion to equipment and process facilities in the oil and gas industry [3].

The most common method developed to remove mercury in natural gas is activated carbon adsorption using Fixed-bed reactors (MRUs) [4]. The activated carbon surface can be efficiently modified by chemical impregnation methods to increase the adsorption capacity. According to the adsorbate's nature, activated carbon's surface can be modified by forming acidic or basic groups [5]. Many adsorbents have been developed commercially, most of which are sulfur-impregnated activated carbon [6,7].

The research data shows activated carbon impregnated with chloride (Cl) can absorb mercury by 96% [8]. Other studies reached 91.4% with a mercury adsorption capacity of 13.14 mg/g [9]. Mercury absorption capacity for Sulphur-impregnated activated carbon (AC-S) was 21 mg/g, chloride-impregnated activated carbon (AC-Cl) 38 mg/g, and combined impregnated activated carbon (AC-Cl+S) of 77 mg/g [10]. The adsorption of iodine-impregnated activated carbon (KI-AC) produced an efficiency of 98-100% [11].

Most of the research involved only one or two impregnation chemicals; there have been limited studies concerned on combined impregnation with three of impregnation chemicals. Meanwhile, adsorption using activated carbon impregnated by three impregnates, Sulphur (S), chloride (Cl), and iodine (I), offers the potential to enhance mercury removal from natural gas [8]. Therefore, this study aims to modify and investigate the characterization of modified activated carbon to promote a combination groups of Cl, S, and I elements, as well as isothermal and adsorption capacity, and its application to natural gas.

2. RESEARCH METHODS

2.1 Material

Chemicals used in this research are commercial activated carbon pro analysis (Merck KGaA No. 1.02186, M=12,01 g/mol, for analysis), sodium sulfide (Merck, M=78.04 g/mol, for analysis), potassium chloride (Merck, M=74.55 g/mol, for analysis), potassium iodide (Merck, M=166.00 g/mol, for analysis), mercury standard box (MB-1 NIC), tedlar bag capacity of 5 l, natural gas from liquefied natural gas (LNG) plant.
Instrumentation applied in this research are Fourier-transform infrared spectrometer (FTIR) Thermo Nicolet IS 10 (Sample measured on KBr pelleted that scanned over the wavenumber 400-4000 cm^{-1}), Scanning Electron Microscope & Electron Dispersive X-Ray (SEM-EDX) JEOL JED-2300 Analysis Station, Surface Area Analysis (SAA) St 3 on NOVA touch 4LX Quanta chrome, Mercury analyzer NIC- WA5.

2.2 Methods

Activated carbon is an adsorbent commonly used in the process of absorbing mercury (Hg) in natural gas [2], so adding active groups of Chloride (Cl), Sulphur (S), and Iodide (I) to activated carbon can increase the absorption of mercury in natural gas.
This research aims to determine the characteristics of modified activated carbon (MAC) using SEM-EDX, FTIR, and SAA. Then, the isothermal and adsorption capacity were determined using the mercury gaseous standard, and its application to natural gas from LNG (Liquefied natural gas) plant was examined.

2.2.1 Preparation of activated carbon (AC)

10 g of commercial activated carbon heated at 120℃ for 3 hours, then cooled again in a desiccator. It is labeled as unmodified activated carbon (AC). The AC then characterized using SEM-EDX, SAA, and FTIR for the initial characterization.

2.2.2 Modification of activated carbon (MAC)

10 g of commercial activated carbon is soaked using 100 ml of 5% KCl solution at room temperature, stirring at 100 rpm for 12 hours. Then, the KCl-impregnated activated carbon is filtered, and the filtered activated carbon is heated up at 120℃ for 3 hours and then cooled again in a desiccator. It was then soaked using 100 ml of 5% Na_2S solution at room temperature, stirring at 100 rpm for 12 hours [12]. Na_2S-impregnated activated carbon is filtered, and the filtered activated carbon is heated up at 120℃ for 3 hours and then cooled again in a desiccator. After Na_2S impregnation, the activated carbon above is soaked again using 100 ml of 5% KI at room temperature, stirring at 100 rpm for 12 hours [13]. Finally, the activated carbon impregnated KCl + Na_2S + KI are filtered and heated at 120℃ for 3 hours, then cooled again in a desiccator. It is labeled as modified activated carbon (MAC). The MAC then characterized using SEM-EDX, SAA, and FTIR.

2.2.3 Determination of isothermal and mercury adsorption capacity

The procedure was performed by preparing each 0.010 g of AC & MAC and mercury gas standard with variation 4.99; 24.96; 49.92; 74.88; 99.83; 249.58 ng/l. Then, the adsorption process for all variations was carried out at the room temperature & flow of 1 l/min according to Figure 1, and the gas standard being adsorbed was measured by Mercury analyzer WA-5, then calculated % removal efficiency, isothermal and adsorption capacity. The amount of mercury removal efficiency was calculated following equation (1) [14,15].

$$\%R = \frac{(C_o - C_i)}{C_o} \times 100 \tag{1}$$

Where, %R = removal efficiency, C_o & C_i = Hg ion concentration at before and after adsorption (ng/l).

Langmuir isothermal is shown as the following equation (2) [14,16].

$$\frac{1}{q_e} = \frac{1}{K_L\, q_{max}} x \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (2)$$

Where, the q_e = amount of adsorbate uptake at equilibrium (mg/g), q_{max} = the maximum adsorption capacity (mg/g), and K_L = Langmuir isothermal constant (l/mg), and C_e = the equilibrium concentration (mg/l). The separation factor (R_L) is shown as the following equation (3) [17,16].

$$R_L = \frac{1}{1 + C_i\, x\, K_L}$$

Where, R_L = Langmuir isothermal separation factor which show the adsorption possibility.
Freundlich isothermal is expressed as the following equation (4) [14,16].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where, K_f = Freundlich constant and used to calculate the Freundlich adsorption capacity.

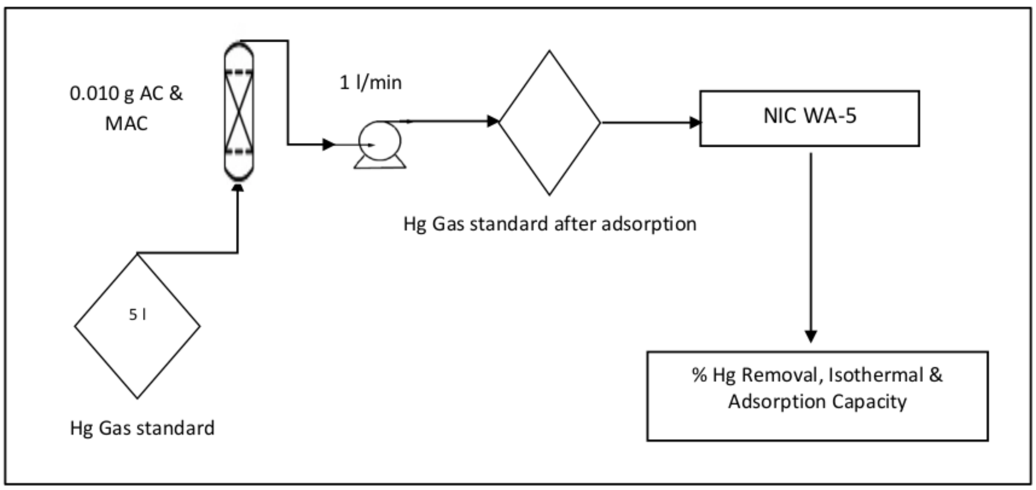

Figure 1. Adsorption scheme for determining isothermal & adsorption capacity

The MAC then implemented to natural gas, which was taken from the Unit feed gas inlet on the LNG plant into tedlar bags with a capacity of 5 l. Tedlar bags were subjected to adsorption tests using 0.010 g of MAC as per shown in Figure 1. The natural gas being adsorbed was then calculated the %R.

3. RESULTS AND DISCUSSION

3.1 Characterization of Activated Carbon

The activated carbon's surface morphology was examined using SEM-EDX analysis [18]. Figure 2 displays the SEM data, and Table 1 displays the EDX results.

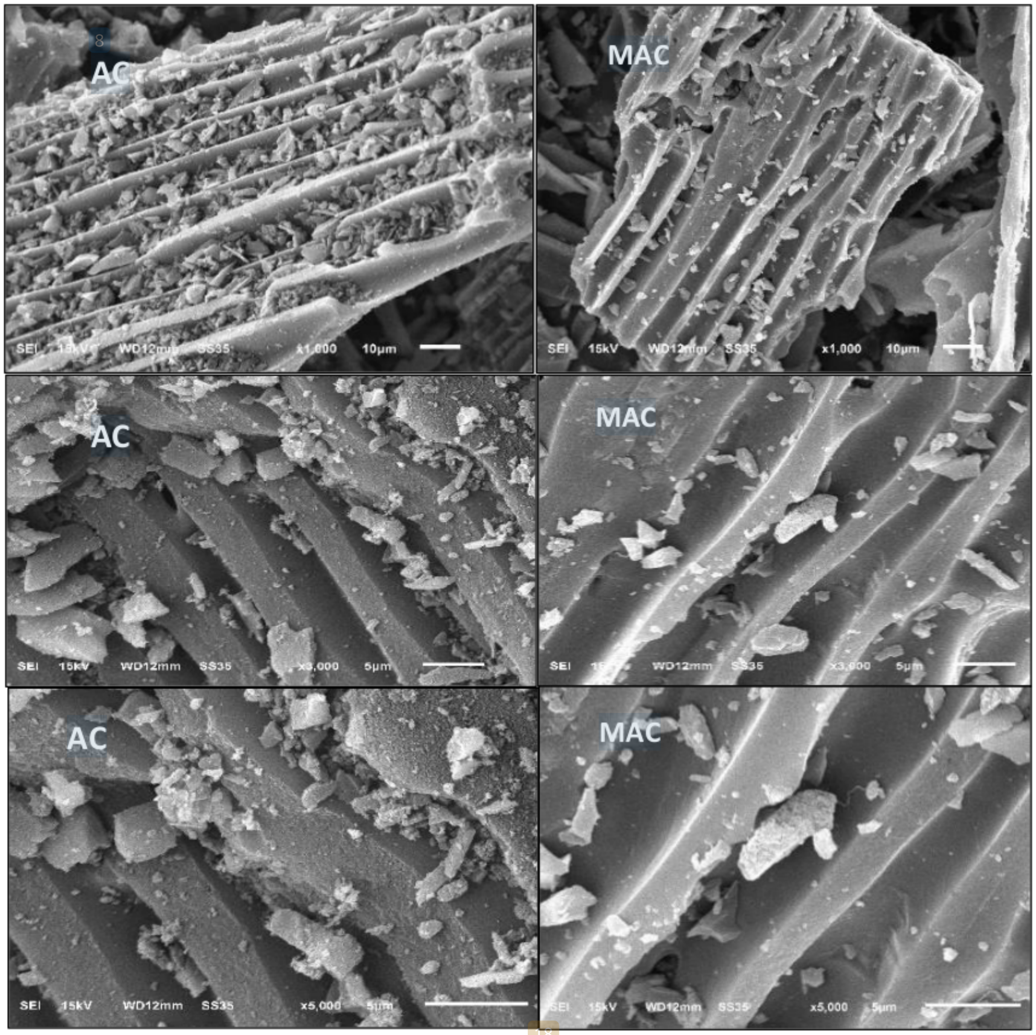

Figure 2. Morphology of unmodified (AC) & modified activated carbon (MAC)

Figure 2 shows that the surface at magnifications of 1000, 3000, and 5000x for the AC has a rough surface shaped like a tunnel, and many small particles cover the surface. Meanwhile, the MAC has a smoother surface, and the porosity can be seen. The findings of this research are consistent with those of the Zhu et al. (2009)[19], which showed a rough surface and contained irregular particles and macropores on activated carbon before impregnation, while impregnated activated carbon showed a smooth surface. Another study by Sreńscek-Nazzal et al. (2016)[20], obtained similar results that commercial activated carbon before treatment produced a rough surface, there were many fractures and irregularities, while after treatment, it produced a smoother surface and visible porous cavities.

The EDX spectra showed the elements in AC and MAC (Table 1). The impregnation process using KCl, Na_2S, and KI has been shown to produce MAC containing the elements Cl, S, and I with a composition of 2.78% Cl; 0.76% S; and 39.60% I; respectively.

Table 1. EDX result of unmodified activated carbon (AC) & modified activated carbon (MAC)

Adsorbent	Elements (%mass)						
	C	O	Cl	S	I	Na	K
AC	72.12	26.91	0.98	-	-	-	-
MAC	37.68	8.80	2.78	0.76	39.60	3.75	6.64

A surface area analyser (SAA) is used for assessing the pore size, pore volume, and surface area of a porous material. These characteristics, which are listed in Table 2, are crucial to its use.

Table 2. SAA analysis result of unmodified activated

No	Adsorbent	Surface area (m^2/g)	Total pore Volume (cc/g)	Average pore size (nm)
1	AC	708.28	0.568061	1.60406
2	MAC	421.91	0.386825	1.83369

Table 2 shows that activated carbon surface area and porosity size decreased after impregnation. This is because impregnation is a process of total saturation of certain substances so that active ion salts will diffuse to fill the pores of activated carbon [21]. Activated carbon will experience a reduce in surface area and porosity size after impregnation and change its physical and chemical properties [22].

The International Union of Pure and Applied Chemistry defines the pore size classification as micropore < 2 nm, mesopore 2-50 nm, and macropore > 50 nm. This classification is the basis for the pore size classification scheme [23]. This research led to the classification of AC and MAC as micropores.

As seen in Figure 3, adsorption and desorption isotherms were also evaluated using nitrogen at 77.35 K. The adsorbed gas at relative pressure (P/Po), where P is the gas's vapour pressure and Po is the adsorbent's saturation pressure, was described using the adsorption isotherms. Figure 3 shows AC and MAC have similar isothermal curves type II, monolayer-multilayer adsorption. From the beginning of the curve to the middle of the isotherm, it is almost linear, often used to indicate the stage where monolayer coverage has been completed and multilayer adsorption will begin soon [24,25].

The isothermal model is relevant to the mercury adsorption isothermal test results found on Figure 5 & 6 that show the mercury adsorption process on AC and MAC occur in a complex monolayer and multilayer manner [26].

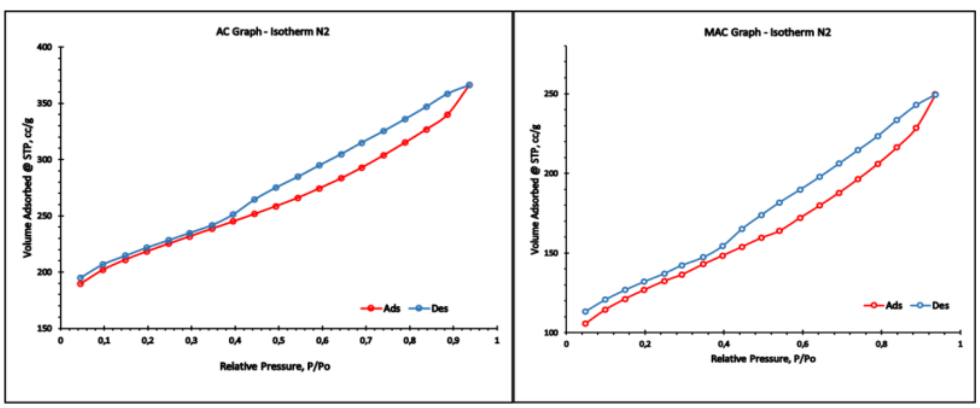

Figure 3. Isothermal curve of unmodified (AC) & modified activated carbon (MAC) measured using nitrogen at 77.35 K at relative pressure (P/Po)

FTIR analysis is to identify functional groups found in activated carbon [19]. FTIR scanning using KBr with a measurement range of 4000 – 400 cm^{-1} (Figure 3). As shown in Figure 3, the results of the FTIR spectrum, which are similar between AC and MAC. The absorption area of wavenumbers 3421.44 & 3417.57 cm^{-1} indicate the existence of hydroxyl groups (-OH) obtained from the existence of water molecules in activated carbon; this can be seen from the shape of the high and asymmetric peak at the beginning of the absorption area of wavenumbers indicating the presence of hydrogen bonds [27].

At the wavenumbers 1563.56 & 1561.53 cm^{-1}, as carboxyl groups (C=O), and wavenumbers 1126.79 & 1101.57 cm^{-1} as Esters, ether or phenol groups (C-O) [28]. In the FTIR spectrum of MAC, there is a vibration at wavenumbers 617.81 cm^{-1}, which AC does not exist. These are the ions resulting from the impregnation of KCl, Na_2S, and KI. These results are similar to those obtained in the research of Cai et al. (2014)[29], which produced a new absorption area in KI and KBr-impregnated activated carbon, namely in the absorption area of wave numbers 793 – 453 cm^{-1}.

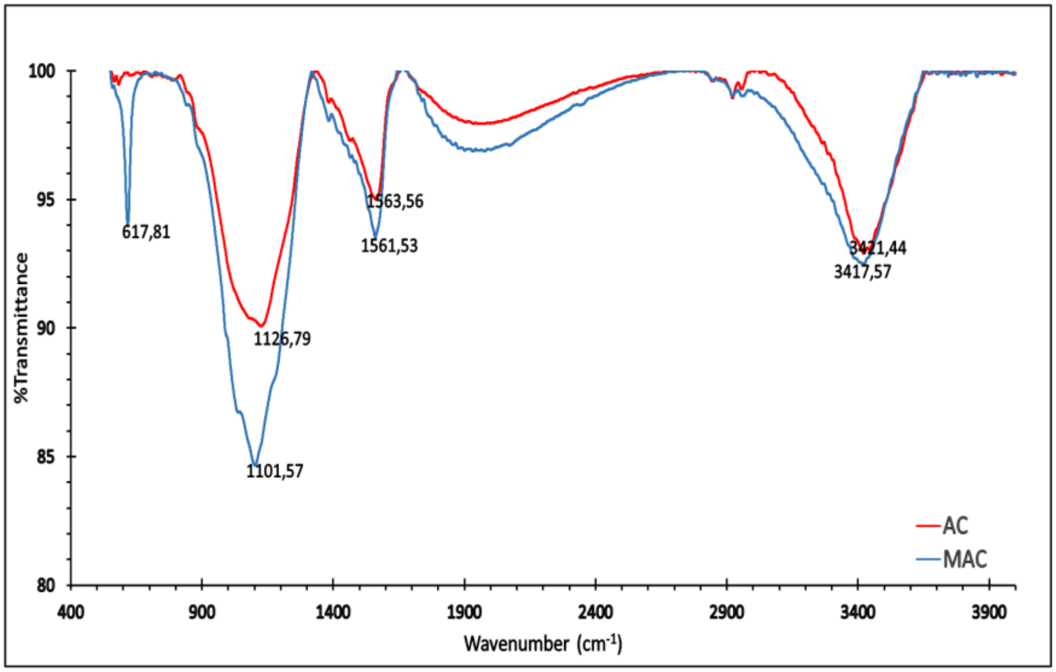

Figure 4. FTIR spectra of unmodified (AC) & modified activated carbon (MAC)

3.2 Adsorption test, Isothermal and mercury adsorption capacity

An adsorption test using standard gas aims to see the ability of adsorbent before and after modification to the efficiency of mercury gas absorption at various concentrations. It was obtained that the efficiency mercury removal of MAC increased significantly to 100 %; this is inversely proportional to AC, which experienced a decrease in efficiency from 98.31% to 43.40%, at a concentration of 4.99 ng/l to 249.58 ng/l, as in Table 3.

According to the other research by Jan et al. (2017)[30], activated carbon impregnated with KI, HCl, and Sulphur increased mercury absorption efficiency to 100%, while unimpregnated activated carbon only reached 60-80%. The results by Rosmayati (2012)[8], showed that activated carbon impregnated with chloride (Cl) could absorb 96% mercury (Hg). In another study Sano et al. (2017)[10], impregnation using K_2S and $CaCl_2$ can increase absorption efficiency up to 50-80 times compared to unimpregnated activated carbon. These results prove that activated carbon impregnated with KCl, Na_2S, and KI can increase the absorption efficiency of mercury gas up to 100%.

Table 3. Adsorption test at various concentration

No.	Initial concentration Hg (ng/l)	Residual concentration AC (ng/l)	Residual concentration MAC (ng/l)	Hg Removal AC (%)	Hg Removal MAC (%)
1	4.992	0.084	0.000	98.31	100.00
2	24.958	1.923	0.005	92.29	99.98
3	49.917	9.096	0.012	81.78	99.98
4	74.875	17.338	0.021	76.84	99.97
5	99.834	38.215	0.040	61.72	99.96
6	249.584	141.277	0.112	43.40	99.96

The results of determining the isothermal adsorption on AC are in Figure 5. Whereas, the isothermal adsorption on MAC are in Figure 6.

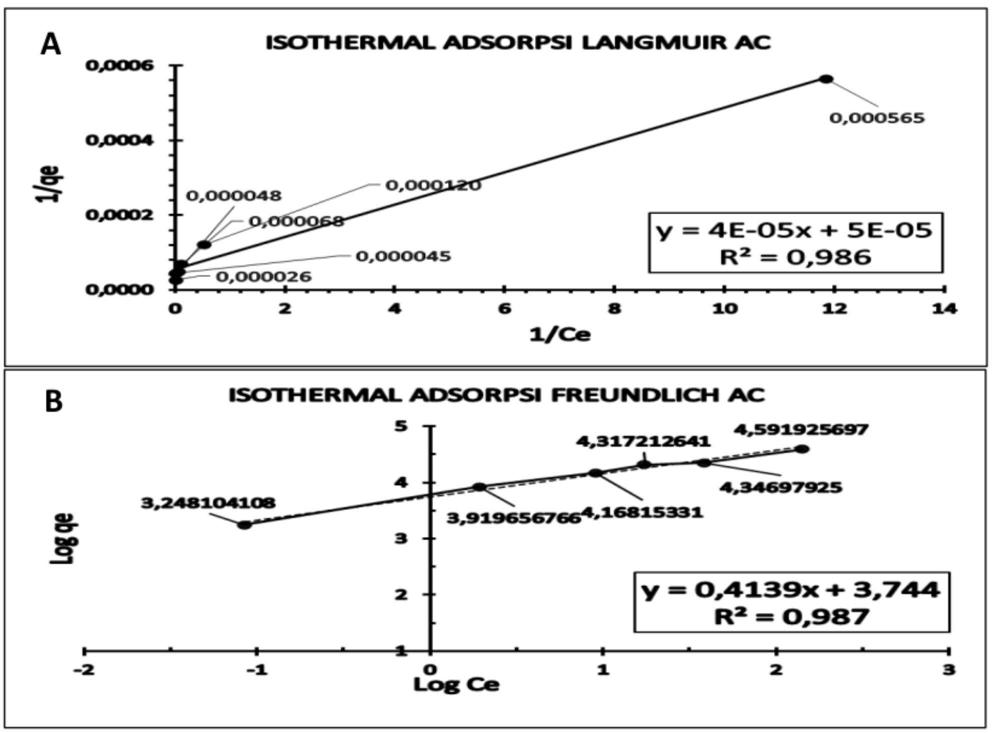

Figure 5. Langmuir (A) & Freundlich (B) isothermal of mercury adsorption on unmodified activated carbon (AC)

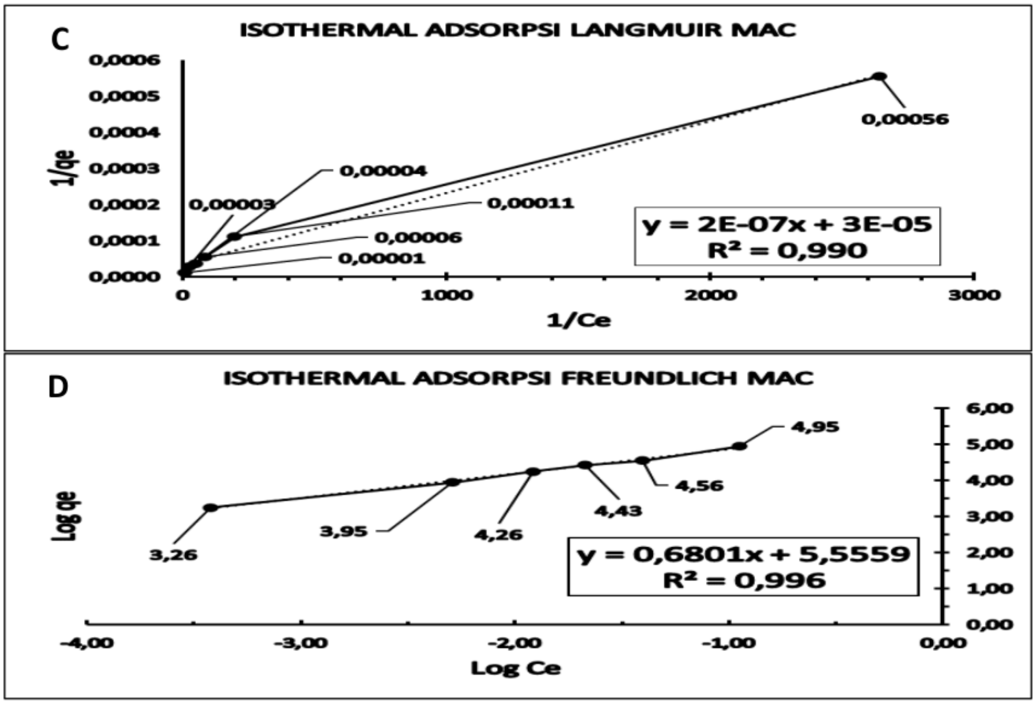

Figure 6. Langmuir (C) & Freundlich (D) isothermal of mercury adsorption on modified activated carbon (MAC)

Table 4 presents the overall isothermal parameters of mercury adsorption on AC and MAC. It is evident that the Freundlich isothermal model describes the mechanism of mercury gas absorption into adsorbents in both AC and MAC. This can be seen from the Langmuir coefficient of determination (R2) of 0.986 and 0.990. Meanwhile, in Freundlich are 0.987 and 0.996 for AC and MAC adsorbents.

Table 4. Parameters of Langmuir & Freundlich isothermal parameters on mercury adsorption

Adsorbent	Langmuir			Freundlich		
	q_{max} (ng/g)	R_l	R^2	K_f (ng/g)	n	R^2
AC	16029.3	>1	0.986	5540.6	2.3322	0.987
MAC	24888.0	>1	0.990	315730.6	1.5198	0.996

The way to find out whether the experimental data follows the Langmuir or Freundlich equilibrium model can be stated in the value of the coefficient of determination (R2), if the plot results are close to 1, then the experimental data follows the equilibrium model [16]. Other evidence that states that the mercury adsorption process does not follow the Langmuir isothermal model is the separation factor (RL) value, which is more than 1 [31,32]. The RL value which is within the range of 0-1 suggests that the adsorption is favorable Langmuir isothermal model [33].
Another evidence can be seen from the adsorption intensity (n) value of 2.3322 and 1.5198 in the Freundlich isothermal; if the n value is between 1 - 10, then the adsorption is favorable and effective following the Freundlich isothermal [19,34]. If the value of 1/n is in the range of $0.1 < 1/n < 1$, then the Freundlich isothermal is favorable [17]. The Freundlich approach that the adsorbent surface is heterogeneous and adsorption forms multiple layers. This allows the adsorbate to move freely until the adsorption process occurs in many layers.
The adsorption of Hg^0 on the surface of the adsorbent can be classified into two types of absorption: physical absorption and chemical absorption. Adsorption of Hg^0 through physical absorption is considered reversible, occurring at low temperatures. On the other hand, chemical absorption is associated with a specific activation energy and occurs along with increasing temperature. So, the modified activated carbon in this study tends to follow physical absorption [29].

The predicted adsorption capacity of an adsorbent can be determined using the Langmuir and Freundlich isothermal equations. The q_{max} value indicates the Langmuir isothermal adsorption capacity. The K_f value indicates the Freundlich isothermal adsorption capacity [35]. The results showed that the adsorption capacity of MAC increased 57 times compared to the unmodified activated carbon (AC), from 5540.60 to 315730.64 ng/g.

3.3 Mercury (Hg) adsorption on natural gas

Modified activated carbon (MAC) was tested for mercury absorption on natural gas obtained from the LNG (Liquefied Natural Gas) plant. The adsorption results are presented in Table 5.

Table 5. Mercury (Hg) adsorption test on Natural gas

No.	Description	Hg Concentration (ng)	Hg Concentration (ng/nm^3)	Hg Removal (%)
1	Natural Gas Initial Concentration	0.005	1.38	78.3
2	Natural Gas after adsorption on MAC	0.001	0.30	

It can be seen that there was a decrease in mercury concentration after absorption using MAC from 1.38 to 0.30 ng/nm^3 with a percentage of mercury removal of 78.3%. This percentage could have increased due to the characteristics of the Natural gas sample from the LNG Plant used in this study having a very small mercury content so that the mercury concentration after MAC absorption had reached the instrument detection limit, which was 0.001 ng of mercury. This decrease in mercury concentration can be caused by the mercury contained in natural gas having bound to Cl, S, and I ions obtained from the modification process [36,37]. The results prove that MAC impregnated with KCl, Na_2S, and KI can reduce mercury concentration in natural gas.

4. CONCLUSIONS

The impregnation process using KCl, Na_2S, and KI has been proven to produce modified activated carbon (MAC) containing Cl, S, and I elements. The surface area is 421.91 m^2/g, total pore volume is 0.386825 cc/g, and average of pore size is 1.83369 nm. It has three of groups function O-H, C=O, and C-O, and there is a vibration at a wavenumber of 617.81 cm^{-1}, these are ions from the impregnation of KCl, Na_2S, and KI.
The mechanism of mercury gas absorption into impregnated activated carbon (MAC) follows the Freundlich isothermal model. The adsorption capacity on MAC increased 57 times compared to unmodified activated carbon (AC), from 5540.60 to 315730.64 ng/g. MAC has been proven to reduce mercury concentration from natural gas by 78.3% removal.

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BIBLIOGRAPHY