Adsorption of Methane on Poly Vinyl Alcohol

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Abstract

The adsorption studies of methane as environmental pollutant gas on PVA surface was discussed as one of the gas-solid application and removed it from the atmosphere .The adsorption ability of the methane gas at temperature rate 20 , 30, 40 and 50 ^{o} C was investigated .The results revealed that the relation between the gas concentration versus adsorption capacity obeys Freundlich isotherm .The a & n values were calculated was increases with the decreases of the temperatures ,this referred that the adsorption was physical adsorption .The adsorption isotherms was investigated from the relation between 1/T versus ln x furthermore the ΔH values was calculated according to Clauses-Clapeyron equation in these range of temperatures.

Keywords: Methane ; Poly Vinyl Alcohol; Freundlich isotherm

Introduction

In recent years, the adsorption process of removing and recovering organic chemicals from air has attracted a special interest as a means of protecting the environment from the pollution, at present, adsorption is widely accepted in environmental treatment applications throughout the world. , the adsorption process of removing and recovering organic compounds in trace levels from air has attracted special interest as a means of protecting the environment from air pollution. Gas–solid adsorption systems are based on the ability of certain solids to preferentially concentrate specific substances from air onto their surfaces. This principle can be used for the removal of pollutants, such as methane, ethane, CO, CO_2 from the atmosphere. Natural gas (NG) is a non-renewable natural resource still available in great amounts and sub-utilized in its energetic potential. NG has about 90% of methane; it is cheap and has a relatively clean combustion when compared to other fossil fuels such as gasoline and diesel. However, it has a major drawback as fuel: the high transportation costs due to the difficulty of achieving high energy densities in appropriate containers. The adsorption of natural gas in porous materials, in which case the gas may be stored (ANG) under moderate pressures (between 3.5 and 4.0 MPa), has been studied as an alternative for its storage and transport (Rafael B. Rios et al. 2009 ; Parkyns et al. 1995; Sun et al. 1996; Lozano-Castelló et al. 2002a, 2002b;

Azevedo et al. 2007; Bastos-Neto et al. 2005; Walton et al. 2005; Zhang et al. 2008; Prauchner and Rodriguez-Reinoso 2008). According to Cook et al. (1999).

Experimental

Adsorption of CH_4 was carried out in a plug flow bed reactor, the adsorbent being supported on a silica wool bed near the bottom of one side of a glass U-shaped reactor. The gas flow of CH_4 was introduced through a mass flow controller. Analysis was performed on-line by means of a Varian 3300 GC using a manual sampling valve, Rt-QPLOT column, FID, and helium carrier gas. Temperatures were measured using an in situ thermocouple, the experiments being carried out between 20-50 ^{o}C. The temperatures were obtained by putting the reactor in a water bath. The CH_4 gas used in this work had purity higher than 99.5%, supplied by (KOAC). The adsorbent used was a poly vinyl alcohol in the form of fine powder, supplied by Fluka. Adsorption experiments were performed by passing gas mixtures through a column packed with the adsorbent. The degassing process was obtained for 180 min. by evacuated the sample at 100 ^{O}C before each experiment.

Adsorption capacity of methane

The initial concentrations of methane and amount of PVA used were kept constant in order to make a comparative study. Each experiment on different temperature 20°C, 30°C, 40°C and 50°C was stopped when the adsorbent was exhausted. The results of methane adsorption on the PVA were presented in the form of breakthrough curves which showed the outlet methane concentrations as a function of time. The adsorption capacity at different temperature was determined by the equation (1).Then the adsorption isotherms of methane adsorption on the PVA were made based on adsorption capacity. The formula of adsorption capacity is expressed, as in (1).

$$X= (F\ C_o t - C) /\ m \quad \text{------------------} \quad 1$$

Where X is adsorption capacity (*mmol/gm*), F is gas flow rate (*ml/min*), t is adsorption time (*min*), m is adsorbent quantity (g), C_0 and C are the initial and final methane concentrations (*mmol/l*) respectively.

RESULTS AND DISCUSSION

Adsorption isotherms

The experiment temperature of methane adsorption isotherms on the PVA was 20°C, 30°C, 40°C and 50°C. The gas flow (F) was *10 ml/min.* the amount of adsorbent (*m*) was *2.5 gm.* Time of adsorption was *180 min.* The adsorption isotherms of methane adsorption based in different temperatures were shown in Fig.1.
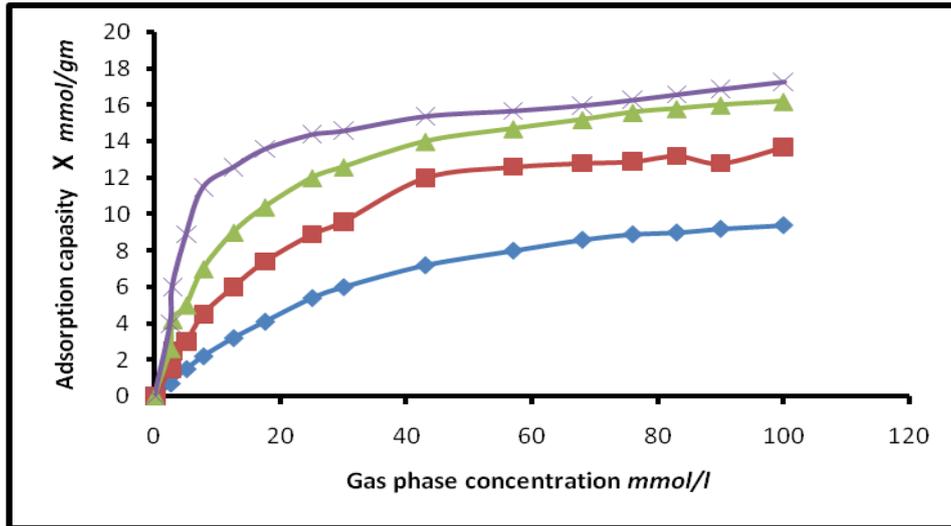
$*$ 50 ^{o}C , ▲40 ^{o}C, ■ 30 ^{o}C ,♦ 20 ^{o}C

Fig. -1: Adsorption isotherm's of methane at different temperatures

The adsorption capacity of the PVA was decreased with the increasing of temperature at 20-50°C. The adsorption of methane on PVA was only physical adsorption at this rang of temperature.

Adsorption isotherm equation

The adsorption isotherms of methane adsorption approximately followed Freundlich equation. The formula of Freundlich equation is expressed as in (2).

$$X = a\, C_e^{1/n} \qquad \text{- - - - - - - - - - - - - - - - -} \qquad 2$$

The logarithm formula of (2) is expressed as in (3).

$$ln\, X = ln a + (ln C_e)/n \qquad \text{- - - - - - - - - - - - - - - - -} \qquad 3$$

Where X is adsorption capacity (*mmol/gm*), C_e is the equilibrium concentration of methane (mmol/*l*), a and n are equation parameters which obtained from the equation curve fitting. Then using the experimental data of adsorption isotherm equation was plotted with *ln*X as Y-axis against *ln*C_e as X-axis. Fig.2.

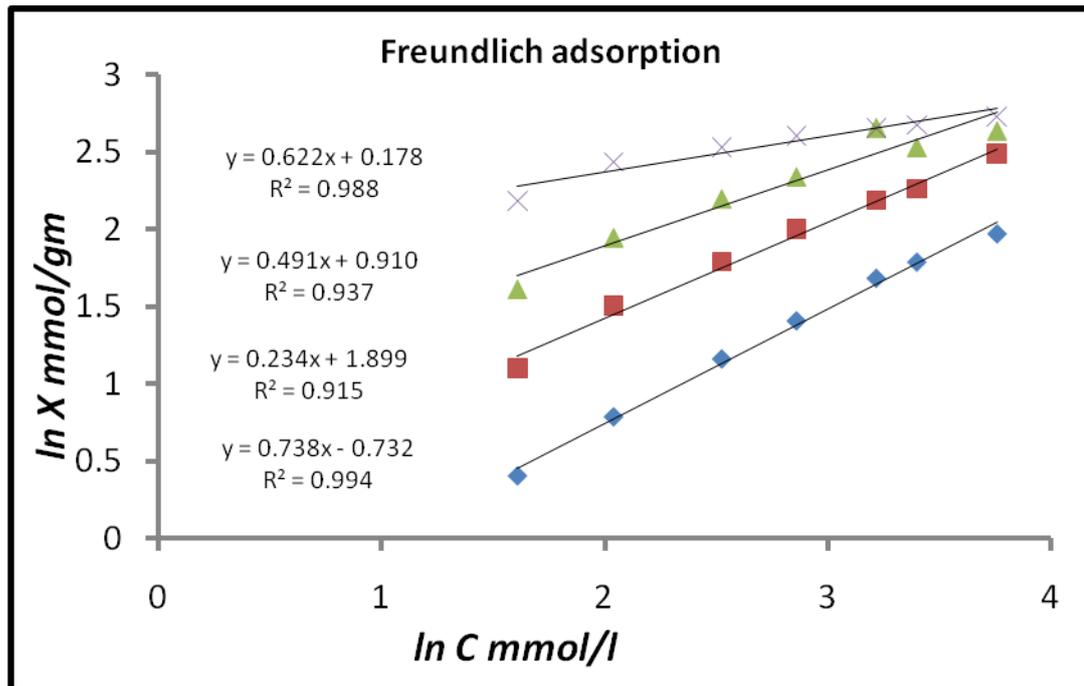Fig.-2: Freundlich adsorption equation of methane

The equation parameters of Freundlich equation at different temperature were at Table-1.

$$ln\,X = ln\,a + (\,ln\,C_e\,)/n \quad \text{- - - - - - - - - - - - - - - - -} \quad 3$$

Table-1: Adsorption equation's parameters

Temprature °C	Ln a	1/n	R^2	Freundlich equation
20	-0.6847	0.651	0.9941	$X= 0.5066\ C_e^{\,0.651}$
30	0.1788	0.453	0.9151	$X= 1.1943\ C_e^{\,0.594}$
40	0.8435	0.394	0.9373	$X= 2.3231\ C_e^{\,0.453}$
50	1.6904	0.233	0.9889	$X= 5.4191\ C_e^{\,0.233}$

In Fig.2 and Table1, The adsorption isotherms for methane could be well fitted by Freundlich equation at different temperature. At the temperatures range (20-50°C), the value of a and n was decreasing with the improvement of reaction temperature. The reason was that the adsorption of methane on PVA was only physical adsorption. So the adsorption capacity of methane on PVA was increased with the improvement of reaction temperature.

Adsorption heat

Using the adsorption isotherm equation, the adsorption capacity at different temperature could be calculated. Then on the condition of equal adsorption capacity, the linear equation of (4) was plotted with $ln(C_e)$ as Y-axis verses 1/T as X-axis. The adsorption heat of methane on PVA could be obtained by calculating the linear equation's slope. The adsorption capacity of methane on PVA was decreased with the improvement of reaction temperature at 20-50°C, The adsorption isotherms of methane on PVA was shown in Fig.3.
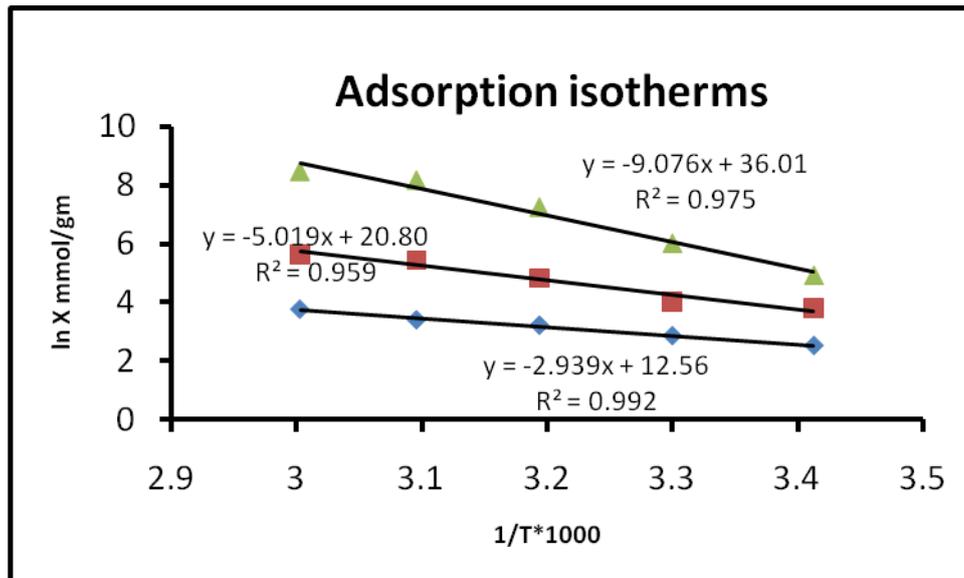
▲300mg, ■ 200 mg , ♦100 mg

Fig .-3: Adsorption isotherms of methane on PVA at (303-323 K)

Using the Clausius- Clapeyron equation, the adsorption heat of methane on PVA could be obtained by calculating the linear equation's slope. The adsorption isotherm's parameter and adsorption heat were shown in Table- 2.

Table -2: Adsorption isotherm parameters and adsorption heat

Temperature °C	Capacity	Adsorption Isotherm	Adsorption Heat
20-50	100 mg.g^{-1}	y = -2.939x + 12.56	15.59 KJ.mol^{-1}
20-50	200 mg.g^{-1}	y = -5.019x + 20.80	19.23 KJ.mol^{-1}
20-50	300 mg.g^{-1}	y = -9.076x + 36.01	23.71 KJ.mol^{-1}

Thus, to sum up the points which we have just calculated above, the adsorption of methane on the PVA was physical adsorption at 20-50°C .The physical adsorption was caused by the intermolecular force .The adsorption heat in experiment was 15- 23KJ/mol at 20-50°C .

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الخلاصة

تمت دراسة امتزاز غاز الميثان الملوث للبيئة على سطح دقائق الكحول متعدد الفاينيل PVA كأحد تطبيقات امتزاز غاز- صلب لهذا الغاز السام في الهواء الجوي .تضمن البحث دراسة قابلية الامتزاز وفي مدى درجات حرارية 20، 30 ، 40 و 50 ^{o}م . أظهرت النتائج أن العلاقة بين تركيز الغاز وسعة الامتزاز تطيع معادلة وايسوثيرم فراندليش فضلا عن أيجاد قيم كل من   a   و n والتي تزداد بتناقص درجات الحرارة والتي أعطت مؤشرا واضحا على أن الامتزاز هو امتزاز فيزياوي. ومن العلاقة بين 1/T و ln x   تم الحصول على أيسوثيرمات الامتزاز ،وتم الحصول على قيم   ΔH   للامتزاز في مدى درجات الحرارة المذكورة من تطبيق علاقة كلاوسيس – كلابيرون.