Preparation of Carbon Molecular Sieves from Pistachio Shell and Walnut Shell for Kinetic Separation of Carbon Monoxide, Hydrogen, and Methane

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ABSTRACT: *In this study, two Carbon Molecular Sieves using the Pistachio shell (CMS P) and Walnut shell (CMS W) were prepared by a chemical vapor deposition method and used for pressure swing adsorption and separation of CO/H_2 and CO/CH_4. The adsorption isotherms of gases obtained for both CMS's. The Dubinin-Radushkevich isotherm model was used for comparing pore volume of CMS's. The obtained isotherms for both CMS were compared with Langmuir and Freundlich isotherms. It was observed that Freundlich equation can better correlate the experimental data. The adsorption capacity of each CMS, and selectivity of them for separation of CO/H_2 and CO/CH_4 were obtained with the aid of kinetic studies. In comparison with CMS W, CMS P showed higher adsorption capacity values for gases, but lower selectivity for separation of them. Finally by fitting experimental data to a pseudo second-order equation, adsorption capacities at equilibrium were obtained for abovementioned gases on both CMS's.*

KEYWORDS: *Adsorption; CMS; Separation; Kinetic study.*

INTRODUCTION

Separation and purification of gases is essential to produce suitable hydrogen and carbon monoxide for using as feedstock in petrochemical processes and a variety of methods have been developed to achieve this separation. These methods include physical and chemical adsorption, membrane separation, cryogenic separation and chemical conversion [1]. Of major interest, adsorption process, a surface phenomenon by which a multi-component fluid mixture is adsorbed to the surface of a solid via physical or chemical interaction is recognized as the most efficient, promising and widely used fundamental approach in separation processes because of its low energy requirement, easy operation, and low maintenance [2-6].

A notable trend in the development of CMS, a microporous carbon adsorbent with a selective adsorption capacity of certain components of a mixture, large porous surface area, controllable pore structure and thermo-stability has been reported [7-10]. CMS is commonly prepared from

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a variety of carbonaceous materials such as cellulosic materials [11], coals [12], carbon fibers [13, 14], resins [15], etc [16-18].

There are two main methods to prepare CMS: the first one is based on the controlled pyrolysis of carbon precursors and the other is the modification of existing porosity of an activated structure through carbon deposition technique [19-21]. In the controlled pyrolysis process, the produced sample has usually low adsorption capacities and this may impose serious limitations on the performance of the CMS [22]. Carbon deposition technique, which aims to designing pore apertures to match the size of the desired adsorbate, has become an attractive area of adsorption for many gaseous systems [19]. Several carbon sources that can be used as carbon deposition agents are acetylene [23], benzene [24] and methane [25]. Benzene has been widely applied because it does not produce intermediate species in the cracking process, which makes the deposition control easier. Numerous experimental studies have been carried out for separation of different gases on CMS over a wide range of thermodynamic conditions [26-29].

In this work, carbon molecular sieves were prepared by using of locally available pistachio and walnut shells which carbonization followed by steam activation occurred before the carbon deposition step. The equilibrium adsorption study of CO, H_2 and CH_4 on the CMS samples has been investigated under the same conditions. Moreover, the adsorption values were compared with each other by using of Langmuir and Freundlich models.

EXPERIMENTAL SECTION

Materials

High purity source of all the gases (>99.99%) were obtained from the Roham Gas Co (Iran). Benzene (Merck, analytical grade) was used in this work as carbon source for deposition step.

Adsorbents preparation

Adsorption isotherms of CO, H_2 and CH_4 on CMS P and CMS W pistachio shells (CMS P) and walnut shells (CMS W) were prepared by a conventional method of carbonization followed by steam activation. Activation under the steam atmosphere was chosen because it can lead to produce the carbon molecular sieves with greater micropore volumes [30]. The carbonization and activation apparatus and the preparation procedure have been described in the reference [31]. The pistachio shells and walnut shells were ground and sieved to a particle size between1.0 and 2.0 mm. In a typical procedure, the walnut shell (300 g) and pistachio shell (300 g) was carbonized at 700 ^oC for 140 min under nitrogen flow. After the cooling of the reactor to room temperature, carbon deposition from pyrolysis of benzene was carried out in a stainless steel reactor equipped with a pre-heater by exposing 20.0 g of each activated samples at the stream of 20% benzene and temperature of 700 ^oC. The deposition time and nitrogen flow rate were fixed at 40 min and 20 mL/s, respectively. After benzene deposition step, the reactor was flushed with nitrogen to cool down to room temperature.

Characterization

The characterization of the materials was accomplished by N_2 (77 K) and CO_2 (273 K) adsorptions in a Micromeritics ASAP 2010 volumetric adsorption apparatus. The results showed that the CMS samples were not able to adsorb nitrogen at 77 K. From CO_2 adsorption data, specific BET surface area of CMS W and CMS P samples were estimated to be 409 m^2/g and 443 m^2/g, respectively. In addition, micropore volumes were calculated from CO_2 adsorption data at 273 K [$V_{DR}(CO_2)$] using the Dubinin–Radushkevich equation (DR) [2]. $V_{DR}(CO_2)$ for CMS W and CMS P were 0.189 cm^3/g and 0.176 cm^3/g, respectively. Pore size distribution (PSD) was obtained from Dubinin Astakhov (DA) analysis. The adsorption isotherm curves of CO_2 and the pore size distribution of both CMS at 273 K are given in Fig. 1 and Fig. 2, respectively. The average pore sizes were obtained 0.72 nm for CMS W and 0.74 nm for CMS P.

Adsorption setup

Determining equilibrium data is a very significant step toward designing separation processes by adsorption technology. Two types of static experimental techniques are used for measurement gas-solid equilibrium data: gravimetric and volumetric methods.

The volumetric method is the most reliable technique for measurement gas-solid equilibrium data and was used in this work. In fact, most of the data reported in the literature have been obtained by this method.

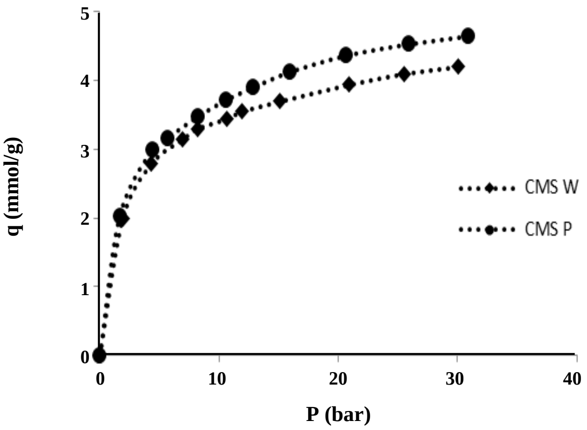

Fig. 1: Adsorption isotherms of CO_2 on CMS P and CMS W at 273 K.

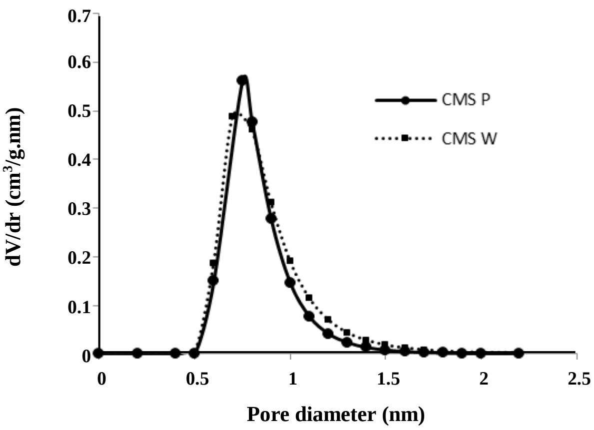

Fig. 2: Pore size distribution of CO_2 on CMS P and CMS W at 273 K.

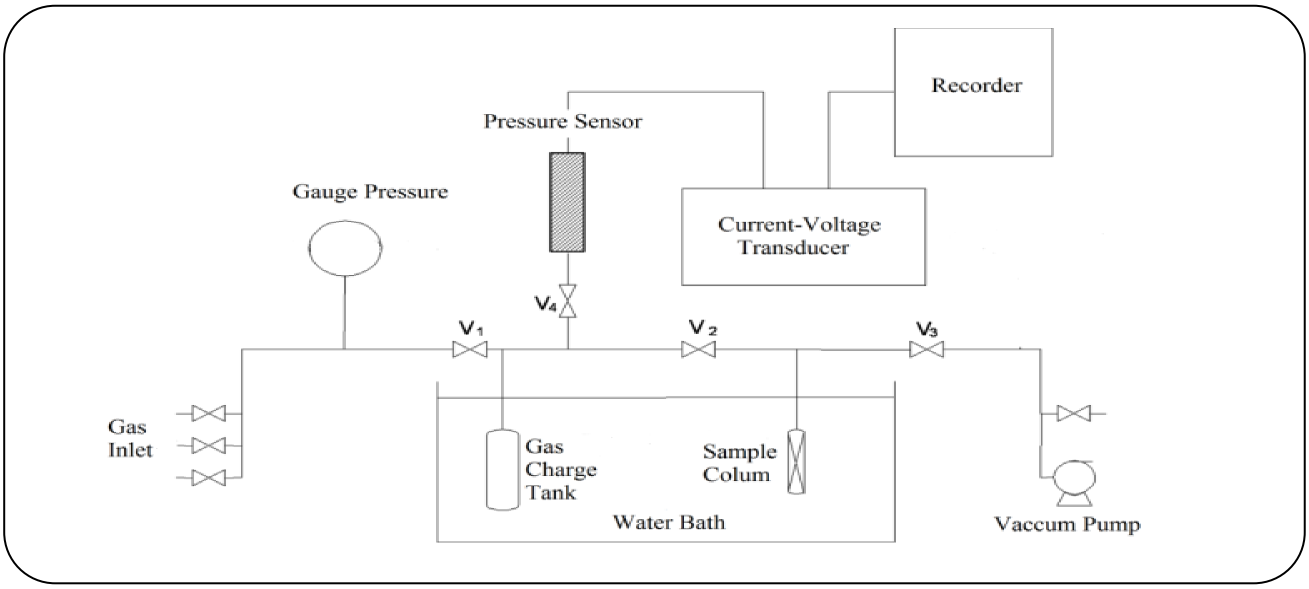

Fig. 3: Schematic diagram of adsorption system.

The schematic flow diagram of the experimental setup is shown in the Fig. 3. Two gram of the CMS adsorbents was placed in the sample column attached to the setup. The system was connected to a vacuum line and the sample column was heated for 2 h at 200 °C in order to have all the preadsorped gases desorbed. To carry out the tests in the constant temperature, the gas charge tank and the sample column were placed in a water bath of 20 °C temperature. When the thermal equilibrium was reached, valves V_2 and V_4 were closed and the gas sample was injected from the gas container to the gas charge tank. The initial gas pressure was read by closing valve V_1 and then with opening valve V_2 to let the gas sample into the sample column, and from then the changes in the gas pressure was plotted versus time until the pressure reached a fixed value. A blank test was conducted with He gas. Performing the experiment with helium revealed that part of the pressure drop is related to the gas expansion after opening V_2 and since there is no relation between this pressure drop and gas adsorption, as it has to be subtracted from the total pressure drop. To evaluate the gases adsorption value, the Z factor was calculated using the SRK equation [32]. All the experiments were carried out under atmospheric pressure up to about 35 bar.

Table 1: Physical properties of the studied adsorb.

	CH_4	H_2	CO
Molecular weight (g/mol)	16.043	2.016	28.01
Critical point (K)	190.6	33.2	132.9
Kinetic diameter (nm)	0.38	0.289	0.36

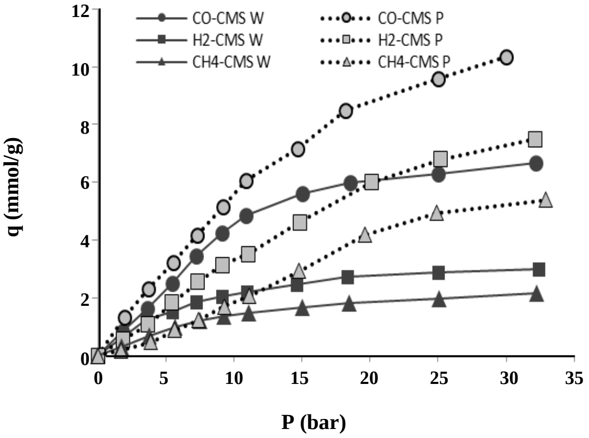

Fig. 4: Adsorption isotherms of CO, H2 and CH4 on CMS P and CMS W at 293 K.

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption equilibrium isotherms of CO, H_2 and CH_4 on the two CMS samples at 293 K are presented in Fig. 4. Ten tests were carried out for each gas at the pressure range of 2-35 bar. From Fig. 4, all curves can be classified as type-I according to the IUPAC classification. Early gas adsorption rises with increasing the pressure, notwithstanding, this increase is limited at higher pressures and the slopes of absorption curves decrease gradually due to the saturation of the adsorbent.

The adsorption capability of gases on the two CMS samples were increased in the following order: CH_4<H_2<CO. The substantially higher uptake of CO under the same thermodynamic conditions reflects the strength of interaction with the substrate due possibly to the higher quadrupole interaction energy. CO and H_2 possess relatively high quadrupole moment, which gives rise to additional interactions among the specific moment and the substrate (CMS). Moreover, as shown in Table 1, the effect of the subcritical adsorption temperature and the kinetic diameter should account for the reason of high adsorption capacity of CO. Although CH_4 has the highest subcritical adsorption temperature and kinetic diameter among the other gases, it indicates the existence of weaker interactions with the substrates in comparison with the two other gases. The reason may be that CH_4 exhibits an octopole as the first no vanished moment.

As one can see from Fig. 4, the measured adsorption capacity of CO, H_2, and CH_4 on CMS W at 293 K and 25 bar were determined 6.30, 2.91, and 2.02 mmol/g, and 9.65, 6.82, and 4.95 mmol/g for CMS P, respectively.

The adsorption capacity of the gases for CMS W is less than CMS P. This behavior can be explained in terms of the pore structures of the CMS samples by fitting the Dubinin-Radushkevich isotherm model to the actual experimental data if it fits. The Dubinin-Radushkevich isotherm model is expressed in a linear form as [2]:

$$\ln(V)=\ln(V_0)-\left(\frac{RT}{E_D}\right)^2\left(\ln\left(\frac{P_0}{P}\right)\right)^2 \qquad (1)$$

where P (bar), P_0 (bar), V (cm^3/g), V_0 (cm^3/g), R (kJ/mol.K) and E_D (kJ/mol) are the equilibrium pressure, the saturation vapor pressure of the gas at the analysis temperature (T), the volume adsorbed at the equilibrium pressure, the pore volume , the gas constant and the free energy of adsorption, respectively. This model has been developed to describe subcritical adsorption. Above the critical temperatures, the saturation pressure is undefined; a different standard state has to be chosen. In this work, saturation pressure is obtained with Clausius equation according to:

$$\ln\left(\frac{P_s}{P_0}\right)=\frac{ML_v}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right) \qquad (2)$$

where T_0 (K), P_S (bar), M (kg/mol), L_v (J/kg) and R (J/mol.K) are the boiling temperature of gas at pressure P_0, the saturation vapor pressure, molecular weight, latent heat of evaporation and the gas constant, respectively. The saturation pressure of CO, H_2 and CH_4 were achieved 613, 154 and 239 bar respectively.

Table 2: Parameters of Dubinin-Radushkevich equation.

Adsorbent	Sample gas	V_0 (cm^3/g)	E_D (kJ/mol)	R^2
	CO	0.6770	8.3066	0.971
CMS W	H_2	0.6408	8.2117	0.983
	CH_4	0.4607	8.1265	0.978
	CO	1.9564	8.2117	0.996
CMS P	H_2	1.7454	6.1284	0.995
	CH_4	1.3661	6.5574	0.996

The parameters of Dubinin-Radushkevich isotherm equation for CO, H_2 and CH_4 are represented in Table 2. The values of parameters and regression coefficients (R^2) were calculated by using of corresponding mathematical methods. The value of regression coefficients were close to 1 and the adaptability of the isotherm models could be evaluated. The R^2 values are calculated from the following equation [2]:

$$R^2 = 1 - \frac{\sum\left(q_{exp} - q_{cal}\right)^2}{\sum\left(q_{exp} - Y\right)^2} \quad , \quad Y = \frac{1}{N}\sum\left(q_{exp}\right) \tag{3}$$

Where N is the number of experimental points and q_{exp} and q_{cal} are corresponded to the amounts of each experimental point in isotherm curve and the amount calculated by equations, respectively.

It can be shown from Table 2 that CMS P has the higher pore volume for all the gases rather than CMS W and it can be concluded that the higher pore volume of CMS P is the cause of the higher ability adsorption of the gases on CMS P rather than CMS W.

Langmuir and Freundlich isotherms

Several mathematical models are available for describing equilibrium studies of the adsorption of gases on solid surfaces. Langmuir and Freundlich models are frequently applied to calculate the adsorption isotherms that can fit the experimental data. Langmuir model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [33]. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) [34], with no transmigration of the adsorbate in the plane of the surface [35]. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance. Whereas, Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In this perspective, the amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process. Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves [36].

In this work, both models were used to describe the experimental data obtained at 293 K on both CMS samples. In nonlinear forms of the models (Table 3), q (mmol/g) is the amount of adsorbed gas per gram of adsorbent, q_m (mmol/g) is the maximum capacity of adsorbent, P (bar) is the pressure of the gas, b is the affinity constant which is related to the apparent energy of adsorption, and n and k are equation parameters which are dependent on the nature of the gas. Table 3 illustrates the obtained results for CO, H_2, and CH_4 from the adsorption modeling. The values of parameters and regression coefficients were calculated by using of corresponding mathematical methods

Adsorption isotherm curves have been plotted for the two equations in Fig. 5 and Fig. 6. Comprising the R^2

Table 3: Langmuir and Freundlich model constants for the adsorption of CO, H_2 and CH_4.

Isotherm	Parameter	Expression	CMS W			CMS P		
			CO	H_2	CH_4	CO	H_2	CH_4
Langmuir	B		0.090	0.013	0.001	0.095	0.058	0.025
	q_m	$\frac{q}{q_m}=\frac{bP}{1+bP}$	8.950	3.800	2.900	12.500	10.200	11.150
	R^2		0.953	0.967	0.965	0.950	0.960	0.946
Freundlich	k		1.150	0.135	0.050	1.330	0.670	0.400
	1/n	$q=kP^{1/n}$	1.850	2.560	2.040	1.631	1.408	1.282
	R^2		0.976	0.971	0.978	0.977	0.987	0.981

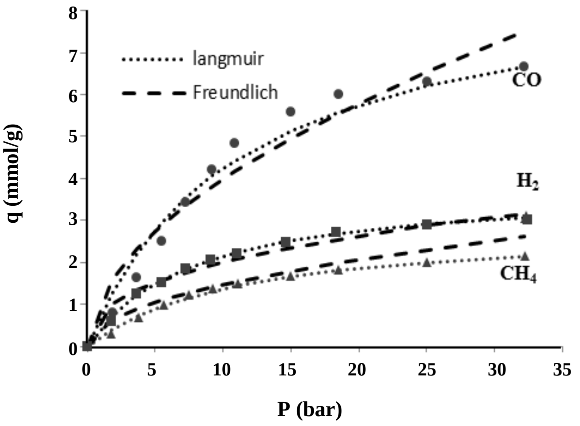

Fig. 5: Comparison of Langmuir and Freundlich isotherm for the adsorption of CO, H_2 and CH_4 on CMS W.

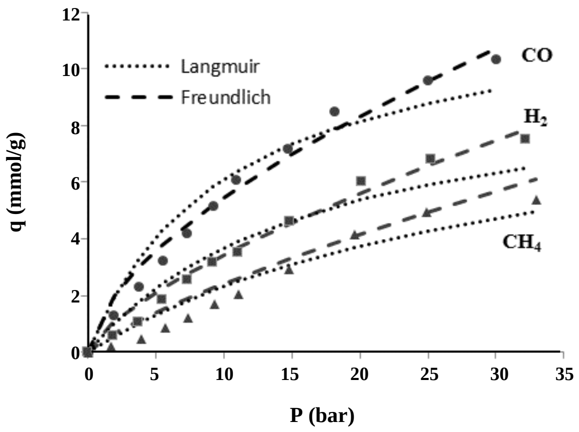

Fig. 6: Comparison of Langmuir and Freundlich isotherm for the adsorption of CO, H_2 and CH_4 on CMS P.

values obtained from Langmuir and Freundlich models, one can found that the Freundlich and Langmuire equations do not perfectly correlate the CO, H_2 and CH_4 adsorption values, however the Freundlich equation can better correlate the CO, H_2 and CH_4 adsorption values rather than Langmuire equation.

Kinetic studies

In order to effectual designing and to judge the suitability of an adsorbent for the desired separations, it is useful to plot the variation of gases adsorption capacity with time. Adsorption kinetic was studied for two pairs of gases; CO-H_2 and CO–CH_4 (Fig. 7 and Fig. 8). Two samples adsorbed all gases very rapidly within 15 s. Table 4 is listed for representing a better picture of kinetic adsorption for the two pairs of gases by both CMSs at the pressure of 8 bar. While CMS P demonstrated the highest adsorption capacity for all gases, it did not show any noticeable selectivity for both CO/H_2 and CO/CH_4. An almost twofold increase in the selectivities is observed for sample prepared by walnut shell (CMS W) compared to sample prepared by pistachio shell (CMS P). The separation selectivity for mixtures of CO/H_2 and CO/CH_4 on CMS W were estimated to be 2.42 and 3.41, respectively. This suggests that CMS W is more efficient for CO/CH_4 separation under modest pressures in a PSA process.

Adsorption rate constant study:

To obtain the adsorption kinetic rates of CO, H_2 and CH_4 on the CMS samples, the following pseudo second-order equation was used:

$$\left[\frac{t}{q_t}\right]=\frac{1}{k_{ad}q_e^2}+\frac{1}{q_e}(t) \qquad (4)$$

Table 4: Adsorption capacity values for CO, H_2 and CH_4 and selectivity at 60 s.

Sample	capacity value (mmol.g^{-1}) at 60 s			S_{60}	
	CO	H_2	CH_4	CO/H_2	CO/CH_4
CMS P	1.91	1.44	1.17	1.32	1.62
CMSW	0.75	0.31	0.22	2.42	3.41

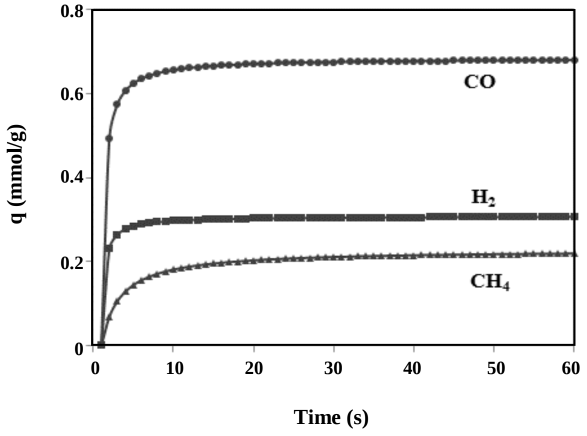

Fig. 7: Adsorption kinetics of CO, H_2 and CH_4 at 293 K and 8 bar on CMS W.

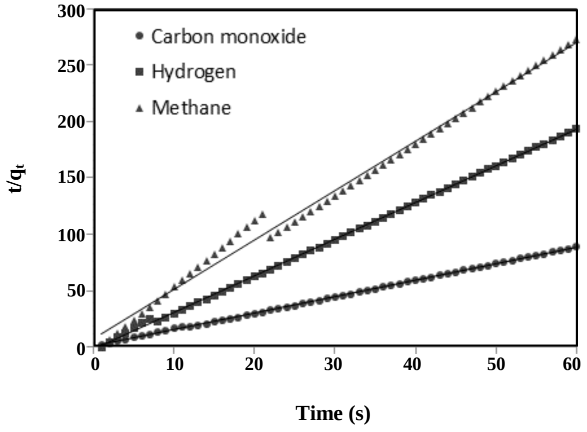

Fig. 9: Pseudo second-order adsorption kinetic of CO, H_2 and CH_4 on CMS W.

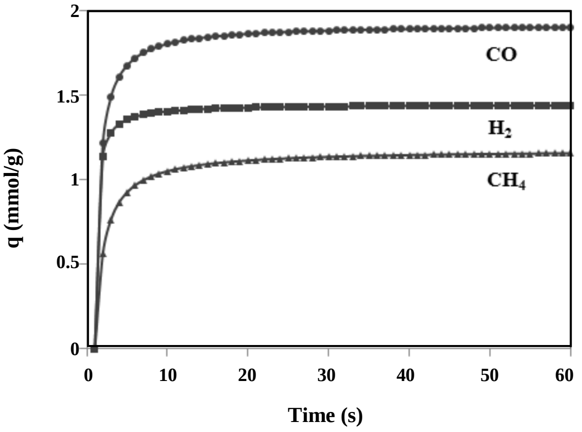

Fig. 8: Adsorption kinetics of CO, H_2 and CH_4 at 293 K and 8 bar on CMS P.

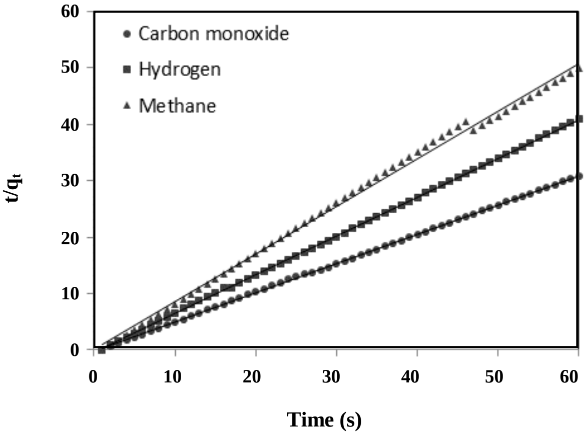

Fig. 10: Pseudo second-order adsorption kinetic of CO, H_2 and CH_4 on CMS P.

Where q_e (mmol/g) and q_t (mmol/g) are the adsorption capacity at equilibrium and at time t and k_{ad} (g/mmol.s) is the rate constant of pseudo second order.

Validity of the pseudo second-order model was checked by the fitted straight line presented in Fig. 9 and Fig. 10. The corresponding kinetic parameters and determination coefficients are summarized in Table 5. The high correlation coefficients were obtained for pseudo second-order model for both CMS's (R^2>0.99). These results show that the pseudo second-order equation provides a perfect theoretical line for CO, H_2 and CH_4 adsorption data on both CMS. Moreover, K_{ad} changed

Table 5: Adsorption rate constants of pseudo second-order at 293 K.

		Pseudo second-order model		
Adsorbent	Gas sample	q_e (mmol/g)	k_{ad} (g/mmol s)	R^2
CMS P	CO	1.92	0.9	0.999
	H_2	1.45	2.57	0.999
	CH_4	1.18	0.78	0.997
CMS W	CO	0.68	3.79	0.999
	H_2	0.31	9.61	0.999
	CH_4	0.23	1.89	0.993

in the order of H_2>CO>CH_4 that was expected because the kinetic diameter of H_2, CO and CH_4 are 0.289, 0.36, 0.38 nm, respectively.

CONCLUSIONS

The carbon molecular sieve prepared by the pistachio shell showed higher equilibrium adsorption capacity for CO, H_2, and CH_4 than the walnut shell adsorbent. CMS W was found to be more suitable for selective separation of CO/H_2 and CO/CH_4 by the kinetic effect. The adsorption capability of the gases on both CMS were increased in the following order CH_4<H_2<CO. The adsorption equilibrium data of CO, H_2 and CH_4 at 293 K were fitted to Langmuir and Freundlich isotherm models. The latter model could better describe the adsorption of the gases. The present study indicates that CMS W would be a promised candidate for the separation of CO/CH_4 and CO/H_2 systems.

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