

CO₂ adsorption on zeolite X/activated carbon composites

Jinghong Ma · Chengming Si · Yixiao Li · Ruifeng Li

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Abstract Two series of zeolite X/activated carbon composites with different ratios of zeolite and activated carbon were prepared through a combination process of CO₂ activation of the mixtures of elutrilite and pitch and subsequent hydrothermal crystallization in alkaline solution. An additional surface modification was achieved in diluted NH₄Cl solution. CO₂ and N₂ uptakes on the composites before and after modification were determined for pressures up to 101 kPa at 273 and 298 K, respectively. Langmuir-Freundlich and Toth adsorption models were used to describe the adsorption isotherms of CO₂ and the corresponding heats of adsorption were estimated with the Clausius-Clapeyron equation. Both before and after modification, all composites exhibited a remarkable preferential adsorption of CO₂ compared to N₂, with the modified composites showing a higher adsorption selectivity to CO₂ over N₂ than the unmodified composites. With an increasing ratio of zeolite in the composites, adsorption capacity and adsorption heat of CO₂ on the composites increased simultaneously. Lower adsorption heat was observed both before and after modification especially at the low-loading region and when there was less energetic heterogeneity on the surface of the modified composites. The results may be attributed to the elimination of strong basic sites on the modified composites, which is favorable for desorption of CO₂ on the adsorbents and application in pressure swing adsorption processes.

Keywords Zeolite/activated carbon composite · Surface modification · Adsorption heat · Heterogeneity

1 Introduction

Since fossil fuel is still the world's primary energy source, its combustion is one of the major sources of the green house gas carbon dioxide (CO₂). CO₂ has been known as one of the causes of global warming, but the purified and concentrated CO₂ stream can be used as an important carbon source to synthesize clean fuels and fine chemicals. Due to the easy applicability of CO₂ over a relatively wide range of temperatures and pressures and its high-energy efficiency, the pressure-swing adsorption (PSA) process has become a preferred technology in the recovery of CO₂ from gas mixture streams. Using this technology, gas species are separated from a mixture of gases under pressure according to their molecular characteristics and affinity for an adsorbent material. A key aspect in separating CO₂ of PSA is to identify a suitable adsorbent. Although several types of adsorbents, such as zeolites, activated carbon, and silica, etc. may be employed for the adsorption of CO₂, the development of regenerable adsorbents with high selectivity and high adsorption capacity for CO₂ is a critical point for an efficient PSA process.

Zeolite has shown promising results for separating CO₂ from gas mixtures and can potentially be used in the PSA processes (Gomes and Yee 2002; Siriwardane et al. 2005). On the basis of the advanced analysis of several important studies concerning CO₂ adsorption using zeolites (Bonenfant et al. 2008; Walton et al. 2006), it appears that the surface basicity and pore size of zeolites, as well as the strength of the electric fields caused by the presence of exchangeable

J. Ma · C. Si · R. Li (✉)
Institute of Special Chemicals, Taiyuan University of Technology,
Taiyuan 030024, China
e-mail: ruifeng_li@hotmail.com

Y. Li
School of Chemical Engineering, Tianjin University,
Tianjin 300072, China

cations in the frameworks and cavities of zeolites are the essential factors for the CO₂ adsorption on zeolites. Synthetic consideration of all of these factors seems to be necessary to optimize an appropriate zeolite for CO₂ adsorption. It has been found that zeolite 13X (common name of zeolite NaX) with large pore diameter of 0.74 nm and Na/Si ratio of close to 1.5 is one of the most suitable zeolite adsorbents for the recovery and capture of CO₂ due to its high adsorption capacity, high selectivity and rapid mass transfer (Harlick and Handan-Tezel 2004). Alternatively, activated carbon is also proposed to be a suitable candidate for CO₂ capture because of its high adsorption capacity at ambient pressures, easy regeneration and low-cost (Schell et al. 2012). Activated carbon materials can be obtained from almost any carbonaceous product through carbonization followed by an activation step. The adsorption capacity of activated carbon is mainly governed by its textural property, but also strongly influenced by its surface chemistry (Shafeeyan et al. 2010). In general, zeolites have higher adsorption capacities for CO₂ as well as a higher equilibrium selectivity for CO₂ over N₂ than activated carbons, but the heat of adsorption of CO₂ on activated carbons is lower than on zeolites, so that the use of activated carbon in the PSA process may result in less severe heat effects on the PSA performance (Chue et al. 1995; Siriwardane et al. 2001). Desorption by pressure swing is often economical if the heat of adsorption is less than about 30 kJ per mole of adsorptive (Bart and von Gemmingen 2005). The temperature excursion due to heats of adsorption and desorption is detrimental to the separation performance of PSA process (Yang and Cen 1986).

In recent years, zeolite/activated carbon composites have been prepared and their environmental application for gas separation and wastewater treatment have been explored to overcome inherent drawbacks of the sole zeolite and activated carbon in adsorptive properties (Foo and Hameed 2011). Elutrilite is a kaolinite-rich gangue containing mainly aluminosilicate and organic carbons. It is found that such novel porous composite of zeolite A/activated carbon extrudates can be prepared from elutrilite based on its mineralogical and chemical composition. Moreover, the ratio of zeolite to activated carbon in the composites can be adjusted by addition of pitch powder into elutrilite as a raw material (Ma et al. 2010).

The objective of this work is to study the adsorption of CO₂ on a series of zeolite X/activated carbon composites and to examine the effects of the relative proportion of zeolite X and activated carbon in the composites and their surface modification upon CO₂ adsorption in order to develop a novel CO₂ adsorbent with the advantages of both zeolite and activated carbon. The composites of zeolite X/activated carbon are prepared from elutrilite by adding solid silicon dioxide and pitch powder as an additional silica and carbonaceous source, respectively. Through a two-step process

of CO₂ activation followed by hydrothermal transformation in an alkali-solution, the composites are surface modified by ammonium chloride solution. After obtaining unmodified and modified composites, CO₂ and N₂ adsorption isotherms on two series of the composites before and after modification at 273 and 298 K up to 101.3 kPa are measured, and fitted with the Langmuir-Freundlich and Toth models, respectively, so that corresponding heats of adsorption can be calculated.

2 Experimental

2.1 Preparation of zeolite X/activated carbon composites

The composition of Elutrilite employed was 41.0 wt% SiO₂, 35.5 wt% Al₂O₃ and 7.0 wt% carbon. It was ground to below 200 meshes and mixed with SiO₂ and pitch powder to make up a final composition of 25, 35, or 50 wt% carbon with a SiO₂/Al₂O₃ molar ratio of 4.5. The resulting mixture was kneaded with water and extruded to a cylinder shape with dimensions of Ø2.0 mm × 6.0 mm. The extrudates were dried overnight and thereafter placed inside a tubular furnace for calcinations and activation. The samples were heated to 450 °C for 2 h and then to 850 °C for an additional 2 h under N₂ flow to carry out the carbonization; after which, the nitrogen gas was shut off and the activating agent CO₂ was introduced into the furnace. The total duration of activation was 24 h. The activated samples were treated in a NaOH hydrothermal system (Na₂O/SiO₂ = 1.5, H₂O/Na₂O = 3). When crystallization was finished, the samples were removed from the reactor, filtered and washed with hot water until the pH of the filtrate reached 6–7. The composite materials obtained were denoted as ZCC-*n* (*n* = 1, 2, 3), in which the mass percentage of activated carbon in each composite is 12.5 %, 18.4 % and 29.4 %, respectively.

The surface modification of the composites was carried out by using 0.3 mol/L ammonium chloride solution. Approximately 5 g of powder was treated with 125 ml of the solution for 0.5 h under constant agitation at 340 K. The treated samples were filtered and washed with distilled water and activated in a tube furnace at 623 K under vacuum. The corresponding samples after modification were denoted as MZCC-*n* (*n* = 1, 2, 3).

2.2 Characterization of composites

The phase of the samples was checked by X-ray powder diffraction (XRD-6000, Shimadzu) using Cu K α radiation operated at 40 kV and 30 mA. The BET specific surface area (S_{BET}) was calculated by N₂ adsorption isotherms measured

on an automatic adsorption instrument (Nova1200e, Quantachrome) at 77 K. The total pore volume (V_{total}) was calculated from the amount of N_2 adsorbed at $P/P_0 = 0.98$. Micropore volume (V_{mic}), and surface area (S_{mic}) were determined by using the t -plot method. The external surface area (S_{ext}), which includes the contribution of mesopores, macropores and the external surface of the particles, was obtained from the difference between BET and microporous surface area. The mass percent of carbon in the sample was analyzed on a TG209/3/F Thermogravimetric Analyzer (Netzsch). The analysis was carried out with a ramp of $10^\circ\text{C}/\text{min}$ in air atmosphere.

2.3 Measurement of adsorption isotherms

The adsorption isothermal data of carbon dioxide on the composites were measured using a NOVA 1200e instrument that is a static volumetric type of apparatus. Prior to the adsorption measurement, the samples were activated under vacuum at 623 K for at least 4 h. Isotherms were obtained at two temperatures (273 K and 298 K) to determine the isosteric heat of adsorption.

3 Results and discussion

3.1 Characterization of composites

Figure 1 shows the representative XRD patterns and N_2 adsorption/adsorption isotherms of the zeolite X/activated carbon composites before and after modification, respectively. From the XRD patterns, it can be seen that all samples exhibit characteristic peaks of zeolite X without other impurity phases. Upon surface modification by the diluted ammonium chloride solution, there is a relative decrease in the intensity of the peaks, indicating a slight loss of crystallinity during modification. The decrease in intensity is almost 18 %. In addition, the N_2 adsorption/desorption isotherms of the composites before and after modification at 77 K display a combination of type I and IV isotherms (Yoo et al. 2012), reflecting the coexistence of micropores and mesopores in the composites. The characterization from XRD and N_2 adsorption shows the formation of zeolite X/activated carbon composites with developed microporous and mesoporous porosity from elutriite by adding pitch powder and solid SiO_2 . Table 1 lists the pore structure parameters of the zeolite X/activated carbon composites before and after modification with different ratios of zeolite X and activated carbon. Because zeolite X is the sole microporous and activated carbon and its hierarchical porosity ranges from micropore to mesopore, the microporous surface area of the composites decreases with the increase of the proportion of activated carbon in the composites, whereas the external surface area and $S_{\text{ext}}/S_{\text{BET}}$

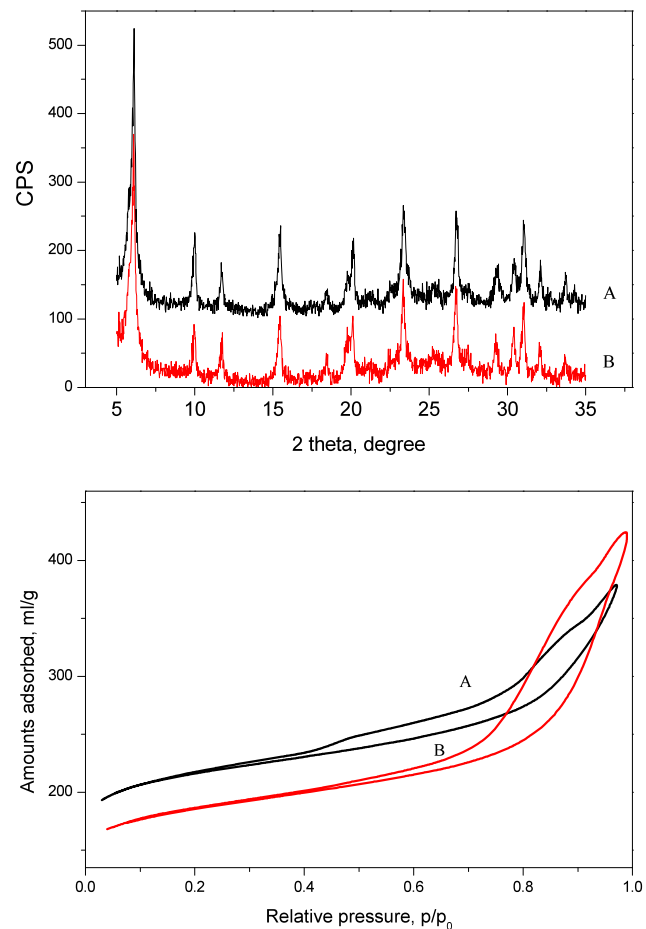


Fig. 1 XRD patterns and N_2 adsorption/desorption isotherms of ZCC-2 (A) and MZCC-2 (B) zeolite X/activated carbon composites

Table 1 The parameters of pore structure for zeolite X/activated carbon composites

Samples	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	$S_{\text{ext}}/S_{\text{BET}}$ (%)	V_{Total} (cm^3/g)
ZCC-1	657	494	163	24.8	0.537
ZCC-2	655	465	190	29.0	0.585
ZCC-3	622	411	211	33.9	0.657
MZCC-1	594	409	185	31.1	0.592
MZCC-2	567	351	217	38.3	0.673
MZCC-3	553	284	269	48.6	0.702

ratio increases. Additionally, modification by NH_4Cl results in some changes in pore distribution between the micropores and mesopores of composites, i.e., the microporous surface area decreases while the external surface area increases thereby resulting in an $S_{\text{ext}}/S_{\text{BET}}$ ratio increase.

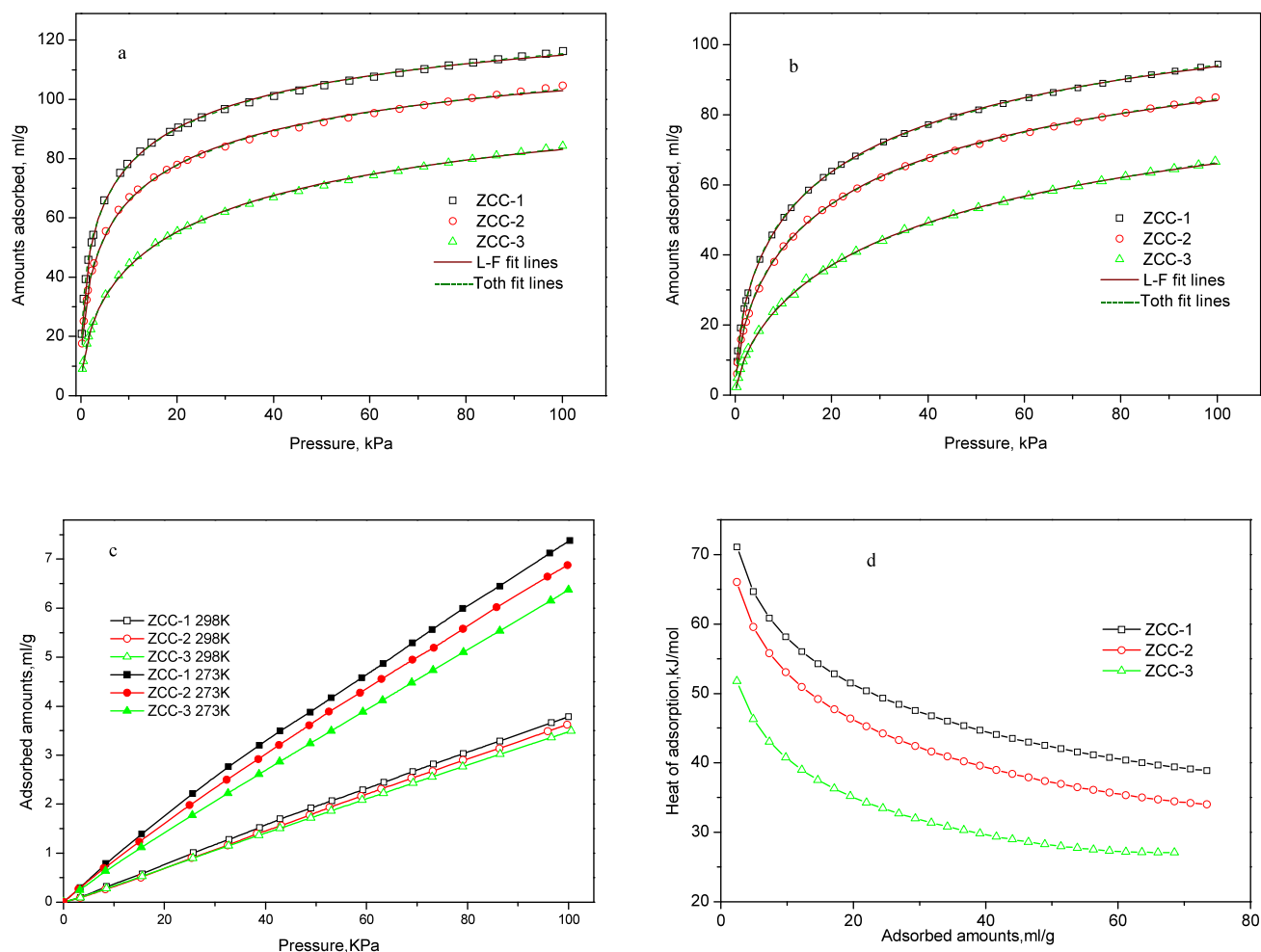


Fig. 2 Adsorption isotherms of ZCC-*n* (a) CO₂ at 273 K, (b) CO₂ at 298 K, (c) N₂ and (d) corresponding heats of adsorption for CO₂

3.2 CO₂ adsorption on composites

3.2.1 CO₂ adsorption on synthetic composites

Families of isotherms for CO₂ and N₂ adsorption on zeolite X/activated carbon composites before modification with different ratios of zeolite X and activated carbon at temperatures of 273 K and 298 K are presented in Fig. 2(a, b) and (c). The isotherm for CO₂ is much higher than that for N₂ indicating that there is a preferential adsorption of CO₂ on the composites. The CO₂ experimental isotherms obtained for the three samples are the combination of type I and IV according to the IUPAC classification. With the increase of CO₂ pressure, the adsorbed CO₂ volume increases sharply at low pressures before a slower increase occurs in the medium- and high-pressure ranges, especially for ZCC-1 with its higher proportion of zeolite. This result suggests that a CO₂ molecule preferably adsorbs at the high binding energy sites in micropores of the composite. Moreover, adsorbed CO₂ volume decreases when

the adsorption temperature is increased. However, it is remarkable that the difference in adsorbed CO₂ volume at different temperatures is small under the low-pressure region yet it becomes obvious under the high-pressure region, and the temperature affects the volume adsorbed at a higher surface coverage where CO₂ may adsorb on the external surface of the composites with multilayer coverage. On the other hand, it is also shown that the adsorbed CO₂ volume decreases with an increasing of the relative proportion of activated carbon in the composites at 273 K and 298 K over the entire range of pressure studied. The corresponding CO₂/N₂ selectivity is summarized in Table 2. The highest adsorption capacity and CO₂/N₂ selectivity are obtained for ZCC-1, which is in agreement with it having the highest proportion of zeolite in the composites.

It is well known that an accurate correlation of experimental data for the equilibrium adsorption isotherms of carbon dioxide in adsorbents is required for the reliable modeling and simulation of the different PSA separations.

Table 2 Langmuir-Freundlich and Toth fitting parameters of CO₂ adsorption isotherms on ZCC-*n* samples

Samples	CO ₂ /N ₂ selectivity ^a	L-F model			Toth model			
		<i>Q_m</i> (ml g ⁻¹)	<i>b</i> (kPa ⁻¹)	<i>n</i>	<i>Q_m</i> (ml g ⁻¹)	<i>b</i> (kPa ⁻¹)	<i>t</i>	<i>K_H</i>
273 K								
ZCC-1	15.8	148.8	0.356	2.04	173.4	4.655	0.321	807
ZCC-2	15.1	138.0	0.282	1.96	164.7	2.535	0.326	418
ZCC-3	13.2	125.5	0.144	1.76	170.3	0.582	0.328	90
298 K								
ZCC-1	16.0	133.8	0.156	1.70	170.7	0.525	0.361	90
ZCC-2	14.8	124.1	0.125	1.63	163.0	0.324	0.371	53
ZCC-3	12.7	109.4	0.067	1.47	158.5	0.094	0.396	15

^a Estimated at 101.3 kPa as a ratio of the CO₂ adsorbed over N₂

ration processes of CO₂. The collected experimental adsorption isotherm data need to be fitted to an isotherm model to extend its utility. In this work, conventional Langmuir-Freundlich (Eq. (1)) and Toth (Eq. (2)) adsorption models were used to fit experimental data of CO₂ adsorption onto various composites at different temperatures.

$$q = q_m b p^{1/n} / (1 + b p^{1/n}) \tag{1}$$

$$q = q_m b p / (1 + (b p)^t)^{1/t} \tag{2}$$

where *q* is the amount adsorbed and *p* the pressure; *q_m* the maximum adsorption capacity, and *b*, *n* and *t* are model parameters to be determined by a data fitting method, *b* is the adsorption affinity, and *n* is a parameter that qualitatively characterizes the heterogeneity of the adsorbate-adsorbent system, and the deviation of *n* from unity may be taken as a measure of the deviation from the Langmuir isotherm.

It is found that both equations provide a very good fit to the data over the entire pressure range studied. Table 2 lists fitted parameters for all composites before modification. By inspecting the table, it is apparent that *b* and *n* values decrease with an increasing proportion of activated carbon in the composites, indicating lower affinity and less heterogeneity of surface on the activated carbon than zeolite towards CO₂. In addition, Henry’s law constants *K_H* (= *q_mb*) derived from the Toth isotherm (Harlick and Handan-Tezel 2005) also decrease in the order of ZCC-1 < ZCC-2 < ZCC-3, implying their decreasing affinity of adsorption at low surface coverage.

The adsorption isotherms of CO₂ on the composites studied at 273 K and 298 K are employed for evaluating the adsorption enthalpy. For this purpose, the Clausius-Clapeyron equation is applied to the isotherm data for the purpose of calculating the isosteric heats of adsorption. The isosteric heat of CO₂ adsorption at different loadings on the three samples is shown in Fig. 2(d). In general, it is observed

that the heat of adsorption maintains a considerable dependence on surface coverage in the three composites due to surface energetic heterogeneity, and the heat of adsorption on the composites decrease with an increasing proportion of activated carbon in the composites over the entire range studied. The heat of adsorption is quite high and decreases rapidly at low surface coverage and then decrease gradually at high surface coverage, implying that the number of basic adsorption sites that can strongly interact with CO₂ is limited with the strong adsorption sites being saturated first. With an increase in loading, some weaker adsorption sites will be in operation resulting in a decrease in adsorption heat.

The comparison between the adsorption of CO₂ on molecular sieve 13X and activated carbon has shown preferential adsorption of CO₂ on the adsorption materials, but the amount of CO₂ adsorbed on the 13X zeolite is more than that of the activated carbon at pressures less than 50 psi indicating that the surface of 13X zeolite has a better affinity for CO₂ than that of activated carbon. Moreover, isosteric heat of adsorption of 13X zeolite decreases from 50 to 10 kJ/mol with increasing coverage from 1 to 5 mol/kg, and for the activated carbon, the isosteric heat of adsorption decreases from 28 to 11 kJ/mol with increasing coverage, indicating that the 13X zeolite has a strong and wide distribution of active sites for CO₂ adsorption (Siriwardane et al. 2001). As the above results show, it is reasonable for the amount of CO₂ adsorbed and the heat of adsorption on the zeolite X/activated carbon composites to vary with the proportion of activated carbon in the composites.

3.2.2 CO₂ adsorption on modified composites

The adsorption isotherms of CO₂ and N₂ on the modified composites at 273 K and 298 K are shown in Fig. 3(a, b) and (c). Preferential adsorption of CO₂ on the modified composites is also observed, and CO₂/N₂ selectivity of the samples is higher than that of the corresponding unmodified samples.

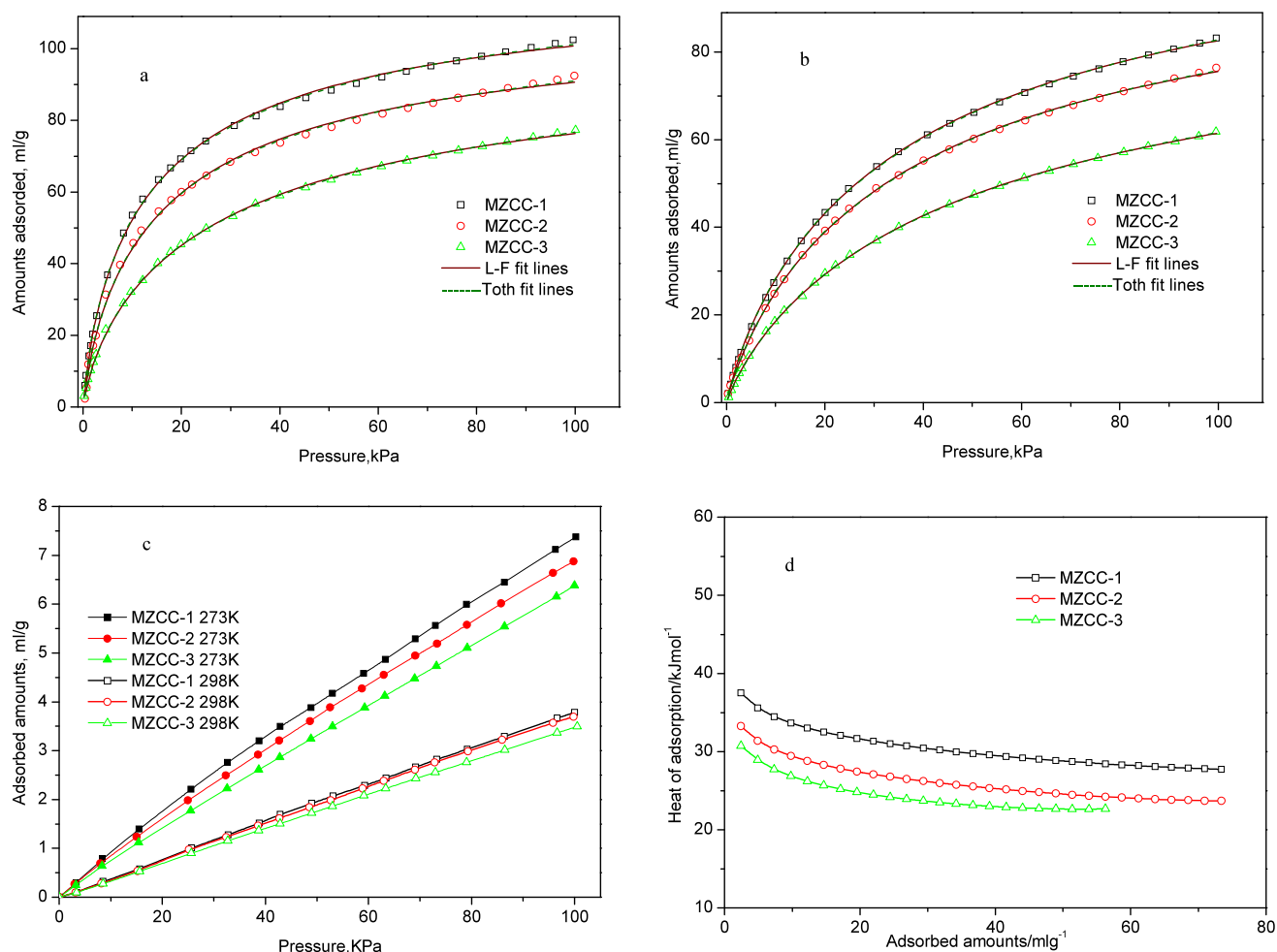


Fig. 3 Adsorption isotherms of MZCC-*n* (a) CO₂ at 273 K, (b) CO₂ at 298 K, (c) N₂ and (d) corresponding heats of adsorption for CO₂

However, the shapes of the isotherms CO₂ on the composites before and after modification appear to be very similar, i.e. CO₂ adsorption increases rapidly when the pressure is increased in the lower pressure regions while CO₂ adsorption at higher pressure regions increases gradually. However, the slopes of the isotherms in the low pressure range as well as the amounts of CO₂ adsorption on the modified composites are lower than that of the corresponding unmodified composites.

The results of an experimental adsorbent screening study for CO₂ removal from N₂ (Harlick and Handan-Tezel 2004) have shown that the most promising adsorbent characteristics are a near linear CO₂ isotherm. This is because a simple criterion for adsorbent selection in a PSA cycle is proposed based on the effective working capacities, i.e., the difference in the adsorption amounts between the high pressure adsorption step and the low pressure desorption step. A rectangular isotherm requires low pressure regeneration to realize a high effective working capacity, whereas a linear CO₂ isotherm may obtain a high effective working capacity at higher re-

generation (desorption) pressure in the PSA cycle, hence, the reducing CO₂ isotherm curvature, that is, a lower slope of the isotherm is more favorable to its use in a PSA process due to the greater regenerability of the adsorption materials.

Similarly, as shown in Fig. 3(a, b), both the Langmuir-Freundlich and Toth models can also satisfactorily describe the experimental isotherm data of CO₂ adsorption on the modified composites. The fitted parameters are represented in Table 3. Comparing the values of parameter *b* and *n* from the unmodified and modified composites, the latter composites have lower *b* values and deviation of *n* from unity than the corresponding former composites, implying a weaker interaction between adsorbate and adsorbent, at least at low coverage, and a lower degree of surface heterogeneity of the adsorption centers on the modified composites. In addition, a lower value of Henry's law slope, *K_H*, for the modified composite also indicates a weaker interaction because at low coverage there is very little interaction between adsorbate molecules and adsorbents.

Table 3 Langmuir-Freundlich and Toth fitting parameters of CO₂ adsorption isotherms on MZCC-*n* samples

Samples	CO ₂ /N ₂ selectivity ^a	L-F model			Toth model			
		Q_m (ml g ⁻¹)	b (kPa ⁻¹)	n	Q_m (ml g ⁻¹)	b (kPa ⁻¹)	t	K_H
273 K								
MZCC-1	27.1	121.8	0.117	1.24	130.3	0.137	0.655	18.0
MZCC-2	25.0	112.2	0.100	1.23	121.3	0.112	0.653	14.0
MZCC-3	22.1	105.1	0.072	1.27	121.2	0.078	0.579	9.5
298 K								
MZCC-1	21.8	117.2	0.042	1.14	128.7	0.039	0.723	5.0
MZCC-2	20.2	107.5	0.040	1.13	118.3	0.037	0.733	4.4
MZCC-3	17.8	96.6	0.032	1.15	111.4	0.028	0.679	3.2

Moreover, isosteric heats of adsorption of CO₂ as a function of surface coverage on the modified composites are also calculated by adsorption isotherms at 273 K and 298 K using the Clausius-Clapeyron equation. As shown in Fig. 3(d), all modified composites show fundamentally the same trend in variation of adsorption heat with coverage. By comparing the curves of adsorption heats with the surface loading on the composites before and after modification, obvious differences are observed. First, the heat of adsorption presents a slower decrease in the low-loading region that remains essentially constant becoming nearly independent of loading, in the high-loading region. Second, the average heat of adsorption decreases after modification. These results indicate less surface heterogeneity and weaker adsorbate-adsorbent interactions on the modified composites than on unmodified ones. As a result of the above discussion, it can be noted that the modified composites are more promising judging from the shape of isotherms, equilibrium selectivity and heat of adsorption, though it is inferior with respect to adsorption capacity.

The amount of adsorption on an adsorbent depends on the available surface area and the affinity for an adsorption gas. Adsorbents used for gas separation should have the affinity based on physical interaction between the surface of the adsorbents and the adsorbate molecules since the adsorption-desorption processes should be reversible. Increasing physical affinity leads to the increase of adsorption capacity. Bonenfant et al. (2008) has summarized the influence of the structural characteristics of zeolites on the CO₂ adsorption, and it is considered that the basic properties of zeolites generated by the different electron densities of the framework oxygen allow strong adsorption of CO₂ acidic molecules (Bonenfant et al. 2008). This kind of adsorption usually involves a high heat of adsorption that is not desirable for CO₂ capture due to a high-energy demand for adsorbent regeneration in desorption. For synthetic zeolite X/activated carbon composites studied in the present work, which have been prepared through hydrothermal treatment in alkali-solution, they have stronger basic surfaces including either zeolite X and activated carbon in the composites, while modification

by the diluted NH₄Cl solution has resulted in the decrease of basicity on the composite surfaces.

4 Conclusions

Zeolite X/activated carbon composites with different ratios of zeolite and activated carbon were prepared and then modified by diluted NH₄Cl solution. The adsorption characteristics of CO₂ on the composites before and after surface modification have been investigated. Adsorption equilibrium data at 273 K and 298 K up to 101 kPa were measured and modeled successfully using Langmuir-Freundlich and Toth isotherms. As shown there is a higher capacity and steeper nature of the CO₂ isotherm on the unmodified composites and a lower capacity and lower slope of the isotherm on the modified composites. In general, the CO₂ adsorption capacity and corresponding adsorption heat on both unmodified and modified composites decreased with increasing activated carbon in composites, indicating a weaker interaction between CO₂ and activated carbon than with zeolite. After modification, higher adsorption selectivity of CO₂/N₂ and lower adsorption heat, especially in the low-loading regions, were obtained compared to unmodified composites which results in their favorable utilization in a PSA process.

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