SYNTHESIS, CHARACTERIZATION, ADSORPTION AND THERMODYNAMIC STUDIES OF PURE AND BINARY CO$_2$-N$_2$ MIXTURES ON OXYGEN ENRICHED NANOSTRUCTURED CARBON ADSORBENTS

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Abstract - Oxygen enriched porous carbons have been synthesized by a nanocasting technique using mesoporous zeolite as template and epoxy resin as precursor. Characterization results show the effect of the nanocasting technique on the development of heterogeneous surface, high basicity, and high surface area of 686.37 m$^2$ g$^{-1}$, beneficial for CO$_2$ adsorption. Pure component adsorption isotherms were correlated with Langmuir, Sips, and dual-site Langmuir (DSL) models and found that Sips and DSL isotherm models fitted well, indicating the heterogeneous nature of the adsorbent surface. Dynamic breakthrough data for the binary system CO$_2$-N$_2$ were obtained using a fixed-bed column at different adsorption temperatures (30-100 °C) and CO$_2$ feed concentrations (5-12.5% by volume). The developed adsorbent shows high adsorption capacity with complete regenerability over four adsorption/desorption cycles. Prediction of binary components (CO$_2$-N$_2$) was made by using extended Sips, extended DSL and IAST (ideal adsorbed solution theory) by utilizing pure component adsorption isotherm data. Experimental and predicted equilibrium data were compared with breakthrough curve data and it was found that the extended forms (Sips and DSL) indicated under-predicted CO$_2$ adsorption equilibria because of differences in adsorptive strengths of CO$_2$ and N$_2$ molecules. Also, adsorption equilibria were closely predicted using IAST theory. Asymmetric x-y diagrams from Raoult’s law indicated positive deviation, implying that as the CO$_2$ gas phase molar fraction increases, total adsorbed amounts increase. Negative values of molar Gibbs free energy change suggested feasibility of the adsorption process. Formation of a more ordered configuration of CO$_2$ molecules on the adsorbent surface was seen as a higher heat of adsorption was exhibited for CO$_2$ as compared to N$_2$.

Keywords: Nanocasting, extended sips; Extended DSL; IAST; Selectivity.

INTRODUCTION

Nowadays, the world is facing tremendous challenges due to the increase in greenhouse gas emissions (mainly carbon dioxide), which causes a major global warming problem. The concentration of CO$_2$ has risen to 409 ppm level and continues to increase (2018). This increase in level is further affecting the global temperature, rise of sea levels as well as marine life. Measures required to be taken for the reduction of CO$_2$ concentration have turned out to be a necessity for our environment. Carbon capture and sequestration (CCS) is one of the effective and important technologies for controlling the increase in CO$_2$ concentration. Absorption, adsorption, membrane separation and cryogenic processes are
the various technologies that are being used for CCS. The conventional amine absorption technology for capture of CO₂ is efficient but presents a series of drawbacks like high energy requirements, equipment corrosion, and low efficiency. Many research groups, to improve adsorption capacity and CO₂ selectivity, modified the adsorbents by amine modification, but this has drawbacks. Modification caused blocking of adsorbent pores and adsorbents possess poor stability due to amine degradation. Alternatively, adsorption by solid adsorbents has gained attention due to its reduced energy penalty, high adsorption capacity, selectivity and fast kinetics coupled with good thermal and mechanical stability. Zeolites (Deng et al., 2012), activated carbons (Wang et al., 2012; Yoo et al., 2013), metal-organic frameworks (Bastin et al., 2008; Sumida et al., 2012), amine supported mesoporous materials (Melloa et al., 2011; Xu et al., 2009) are potential candidates used so far, but among these, carbon based adsorbents have been studied extensively due to their better properties like well-developed porous structures, high adsorption capacities, easy regenerability, fast kinetics coupled with high thermal and chemical stability. Moreover, the preparation of these carbon adsorbents can be carried out by using low-cost precursors and by using various preparation techniques like sol-gel, carbonization of carbon containing precursor and nanocasting techniques. Among the preparation techniques, nanocasting developed the materials having controlled pore structure used in this study. It is possible to improve the textural properties, it is less time-consuming and it is possible to control pore structure characteristics. In this technique, precursor is introduced into the template pores, carbonized and lastly the template is removed. Further, using heteroatoms like nitrogen, oxygen etc. (Tiwari et al., 2017a) in the carbon matrix increases their uptake capacity as well as improves the surface property and selectivity of the adsorbent towards CO₂. Therefore, carbon adsorbents obtained from high oxygen containing epoxy resin and using as template mesoporous MCM-41 can act as a potential adsorbent for selectively capturing CO₂.

Nitrogen-doped porous carbon monoliths synthesized by Hao et al. (2010) using pyrolysis of a copolymer of resorcinol, formaldehyde and lysine exhibited static CO₂ uptake of 3.13 mmol g⁻¹ at 25 °C under a pure CO₂ atmosphere. N-enriched carbon adsorbents synthesized by Pevida et al. (2008) using melamine-formaldehyde resin showed CO₂ uptakes of 2.25 and 0.86 mmol g⁻¹ at 25 °C and 75 °C, respectively, under a pure CO₂ environment. Literature shows that synthesis using direct carbonization of nitrogen/oxygen containing precursors shows poor textural properties of the adsorbent. Also, CO₂ adsorption capacities were determined under static conditions, which showed higher CO₂ uptake values but do not have much relevance to practical application in CO₂ capture. Therefore, this study, using a nanocasting technique and an adsorption study in a dynamic fixed bed adsorption system, is more relevant for flue gases.

Also, understanding of pure component adsorption isotherms is very crucial for assessing the capture capability of these adsorbents. Along with this, further knowledge of binary gas adsorption equilibria is important as it plays an important role in designing an economically feasible adsorption system for CO₂ capture. In the present study, using adsorption isotherm models and pure component adsorption equilibria data, adsorption equilibria of binary gas can be predicted (Do, 1998). This approach is preferred, otherwise it takes a lot of time for experimentation. To date, very few studies are available for predicting mixed-gas adsorption equilibria on carbon-based adsorbents from pure component adsorption. The few which have been studied are of pre-combustion CO₂ capture conditions like equilibrium CO₂ adsorption capacity and breakthrough time evaluated by García et al. (2011) on a commercial activated carbon adsorbent for the ternary system of CO₂/N₂/H₂ (pre-combustion CO₂ capture). In other work (Schell et al., 2012), pure component adsorption equilibria of CO₂, H₂, N₂ and binary equilibria of CO₂/H₂ and CO₂/N₂ were obtained gravimetrically on commercial activated carbon.

In this work, predicted binary gas adsorption data for CO₂ and N₂ on oxygen enriched nanostructured carbon pertaining to post-combustion capture conditions is compared with the experimental breakthrough data. For this, pure component (CO₂ and N₂) adsorption equilibria on prepared carbon were measured volumetrically at four different temperatures (30-100 °C). Langmuir, Sips and dual-site Langmuir (DSL) are the three different adsorption isotherm models used to fit the experimental data. Also, binary gas adsorption equilibria data, obtained from a fixed-bed adsorption system, were compared with the predicted data obtained from extended forms of pure component isotherm models. The present study is much more effective because it was performed in a dynamic fixed bed system in which we have evaluated CO₂ uptake from room temperature to high adsorption temperature along with regenerability.

MATERIALS AND METHODS

Materials

Oxygen enriched nanostructured carbon adsorbent (EZ-700) approximately ~ Rs 15,000 per kg, prepared from epoxy resin Lapox L-12 is DGEBA (Di Glycidyl Ether of Bisphenol-A) as polymeric precursor, was supplied by M/s Atul Ltd., Gujarat, India. The density and viscosity of resin are 1.1-1.2 g cm⁻³ and
9000-12000 mPa.s, respectively. Mesoporous zeolite (MCM-41) as template having a surface area of 800 m$^2$ g$^{-1}$ and pore diameter of 3 nm (purchased from Tianjin Chemist Scientific Ltd., China) was used for the synthesis of adsorbents. Pure N$_2$ (99.995%) and CO$_2$ (99.999%) gases, procured from M/s Sigma Gases and Services (India), were used for pure and binary gas adsorption studies. Non-adsorptive gas, helium (He) of high purity (99.999%) from Sigma was used for outgassing the sample.

Characterization

Adsorbent preparation

The epoxy resin (80 g) and the template mesoporous zeolite (20 g) were mixed in 150 ml of pure ethanol followed by removal of excessive solvent by heating at 120 °C for 3 h to obtain templated resin. After this, carbonization and activation at 700 °C under N$_2$ and CO$_2$ atmospheres at a heating rate of 10 °C/ min was performed. Flow of gases at 60 ml min$^{-1}$ was maintained throughout the carbonization-activation. Then it was cooled to room temperature followed by dissolution of the sample in 40 wt.% NaOH solution for at least 24 h to remove the template. The obtained sample after washing is denoted as E-T, where $T$ denotes the carbonization and activation temperature.

Adsorbent characterization

Elemental analysis (CHN) and oxygen content (determined by difference) was performed using a Thermo Scientific Flash 2000 organic elemental analyzer. Micrometrics ASAP 2020 sorption analyzer was used to obtain surface area and pore volume of the obtained sample. From N$_2$ isotherms, the specific surface area ($S_{BET}$) was calculated by using the Brunauer-Emmet-Teller (BET) equation. TEM images of samples were recorded on a JEOL JEM-2100 transmission electron microscope at operating voltage of 200 kV. The surface morphology of the samples was examined using a JEOL JSM-6510 LV scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were made to identify nitrogen moieties on samples in a Kratos axis ultra DLD system with an Al K$_\alpha$ source. The anode potential and emission current were 15 kV and 10 mA, respectively.

Methods

Pure component adsorption measurement

Adsorption measurements of pure gases (CO$_2$ and N$_2$) on the nanostructured carbon adsorbent were performed using a Micrometrics ASAP 2010 volumetric analyzer at four different adsorption temperatures (30, 50, 75 and 100 °C) and pressures ranging from 0 to 1 atm using high purity CO$_2$ and N$_2$ gases. Before the analysis, carbon sample was degassed for 12 h under vacuum at 200 °C.

Binary component adsorption measurement

Binary equilibrium adsorption data were obtained using a fixed gas adsorption setup (Fig. 1) whose detailed description and procedure were reported in the previous paper (Tiwari et al., 2017b). The adsorption experiments were performed at approx. 1 atm in the fixed bed tests.

Adsorption/desorption experiments were performed by packing 2g of adsorbent in the fixed-bed column (internal diameter of 0.939 cm and height of 30 cm). Before this, adsorbent was kept overnight in the oven to remove moisture and other pre-adsorbed gases. Pretreatment of adsorbent under N$_2$ atmosphere (50 mL min$^{-1}$) was performed for 2 h at 200 °C in the column before carrying out adsorption. After this, adsorption was carried out by reducing the temperature to the desired adsorption temperature (30 to 100 °C) by passing different gas mixtures of CO$_2$ and N$_2$ at a total flow rate of 80 mL min$^{-1}$ (evaluated at NTP), with varying CO$_2$ volumetric concentrations ranging from 5% to 12.5%. The exit CO$_2$ concentration was monitored by GC until the exit CO$_2$ concentration became equal to the inlet CO$_2$ concentration. At the end of the adsorption column, a gas chromatograph (GC 7890A, Agilent Technologies, US) is used to periodically monitor the CO$_2$ and N$_2$ concentrations. After performing the adsorption study, desorption was carried out by increasing the temperature to 200 °C under pure N$_2$ flow (50 mL min$^{-1}$).

**Figure 1.** Schematic diagram of the CO$_2$ adsorption/desorption setup.

RESULTS AND DISCUSSION

Characterization of adsorbent

The prepared adsorbent shows an effect of template in development of nanostructured carbon in the range of 2-6 nm (TEM, Fig. 2a). SEM shows a nanocasting effect which is seen from the developed porosity having irregular and heterogeneous type pores (Fig. 2b) that can facilitate transport of CO$_2$ molecules towards the inner side of the adsorbent. N$_2$ adsorption/desorption show Type I and Type IV isotherms (Fig. 2c), showing...
the presence of micro and mesopores with highest surface area of 686.37 m$^2$ g$^{-1}$. The oxygen content of the sample was 47.51% due to the presence of a higher amount (46.79 area %) of O2 (ether, alcohol) at binding energy of 532.92 eV (Fig. 2d) indicating higher basicity and selectivity towards CO$_2$.

**Adsorption isotherm study**

**Pure component isotherms**

Fig. 3 shows pure component adsorption-desorption (symbols) and the model predicted isotherms (as lines) on prepared oxygen enriched carbon adsorbent as a function of pressure at different adsorption temperatures (30-100 °C). It is seen that the adsorption of CO$_2$ and N$_2$ increases as pressure increases, while it decreases as temperature increases. CO$_2$ was found to adsorb more strongly on the adsorbent as compared to N$_2$ at all temperatures. Three pure component isotherm models (Langmuir, Sips and DSL) at different adsorption temperatures were used for fitting the experimental pure component adsorption data of CO$_2$ and N$_2$ on EZ-700. The corresponding model parameters along with SSE (sum of the squared relative errors) values are reported in Tables 1, 2 and 3.

The Langmuir adsorption isotherm model exhibits the correct asymptotic behavior as it approaches Henry’s law in the low pressure range and is thermodynamically sound. However, this model is not able to explain well the adsorption behavior of CO$_2$ on EZ-700 at all adsorption temperatures as its SSE lie in the range of 19-22%. It deviated from experimental data at all pressures. On the other hand, both Sips and DSL isotherm models fit well as compared to Langmuir isotherm model as indicated by the SSE values (Sips <9.7% and DSL <3.24%). This signifies surface heterogeneity of the adsorbent. Similar results of conformity of these two models with CO$_2$ adsorption on carbon materials were shown by several research groups (Caldwell et al., 2015; García et al., 2013).

N$_2$ adsorption was well explained by all the three isotherm models and only a small difference is found between them. This is because of the linear shape
Synthesis, Characterization, Adsorption and Thermodynamic Studies of Pure and Binary CO$_2$-N$_2$ Mixtures on Oxygen Enriched...

Brazilian Journal of Chemical Engineering, Vol. 36, No. 03, pp. 1319 - 1332, July - September, 2019

Figure 3. Experimental adsorption isotherms of (a) CO$_2$ and (b) N$_2$ on EZ-700 at different temperatures and their corresponding isotherm model fits.

Table 1. Langmuir isotherm model parameters for pure component adsorption on EZ-700 at different temperatures.

| Component | Parameter | Temperature (°C) |
|-----------|-----------|------------------|
|           |           | 30   | 50   | 75   | 100  |
| CO$_2$    | $q_m$ (mmol g$^{-1}$) | 1.45 | 1.23 | 0.93 | 0.68 |
|           | $b$ (atm$^{-1}$)     | 3.89 | 2.03 | 2.25 | 1.97 |
|           | SSE (%)             | 22.31| 19.83| 19.65| 19.20|
|           | $b_0$ (atm$^{-1}$)  | 0.09 |      |      |      |
|           | $B$ (kJ mol$^{-1}$) | -9.36|      |      |      |
| N$_2$     | $q_m$ (mmol g$^{-1}$) | 1.37 | 0.70 | 0.55 | 0.43 |
|           | $b$ (atm$^{-1}$)     | 0.15 | 0.12 | 0.08 | 0.03 |
|           | SSE (%)             | 4.02 | 5.66 | 6.84 | 7.55 |
|           | $b_0$ (atm$^{-1}$)  | 0.0005|      |      |      |
|           | $B$ (kJ mol$^{-1}$) | -14.35|      |      |      |

Table 2. Sips isotherm model parameters for pure component adsorption on EZ-700 at different temperatures.

| Component | Parameter | Temperature (°C) |
|-----------|-----------|------------------|
|           |           | 30   | 50   | 75   | 100  |
| CO$_2$    | $q_m$ (mmol g$^{-1}$) | 1.60 | 1.14 | 0.29 | 0.07 |
|           | $b$ (atm$^{-1}$)     | 0.29 | 1.65 | 0.92 | 0.07 |
|           | SSE (%)             | 22.31| 19.83| 19.65| 19.20|
|           | $b_0$ (atm$^{-1}$)  | 0.18 | 1.26 | 0.93 | 0.88 |
|           | $c$               | 2.72 | 2.70 | 2.64 | 3.24 |
|           | $b_{0,1}$ (atm$^{-1}$) | 0.273|      |      |      |
|           | $b_{0,2}$ (atm$^{-1}$) | 0.00017|      |      |      |
|           | $B$ (kJ mol$^{-1}$) | 48.06|      |      |      |
|           | $E_2$ (kJ mol$^{-1}$) | -30.15|      |      |      |
| N$_2$     | $q_m$ (mmol g$^{-1}$) | 0.68 | 0.35 | 0.28 | 0.21 |
|           | $b$ (atm$^{-1}$)     | 0.68 | 0.35 | 0.28 | 0.21 |
|           | SSE (%)             | 2.02 | 4.66 | 3.84 | 4.55 |
|           | $b_{0,1}$ (atm$^{-1}$) | 0.32|      |      |      |
|           | $b_{0,2}$ (atm$^{-1}$) | 0.00046|      |      |      |
|           | $B$ (kJ mol$^{-1}$) | 43.676|      |      |      |
|           | $E_2$ (kJ mol$^{-1}$) | -14.35|      |      |      |

Table 3. Dual-site Langmuir isotherm model parameters for pure component adsorption on EZ-700 at different temperatures.

| Component | Parameter | Temperature (°C) |
|-----------|-----------|------------------|
|           |           | 30   | 50   | 75   | 100  |
| CO$_2$    | $q_{0,1}$ (mmol g$^{-1}$) | 1.60 | 1.14 | 0.29 | 0.07 |
|           | $q_{0,2}$ (mmol g$^{-1}$) | 0.29 | 1.65 | 0.92 | 0.07 |
|           | $b_1$ (atm$^{-1}$)     | 55.34| 32.49| 21.08| 11.08|
|           | SSE (%)             | 2.72 | 2.70 | 2.64 | 3.24 |
|           | $b_{0,1}$ (atm$^{-1}$) | 1.04 |      |      |      |
|           | $b_{0,2}$ (atm$^{-1}$) | 0.00017|      |      |      |
|           | $B$ (kJ mol$^{-1}$) | 48.06|      |      |      |
|           | $E_2$ (kJ mol$^{-1}$) | -30.15|      |      |      |
| N$_2$     | $q_{0,1}$ (mmol g$^{-1}$) | 0.68 | 0.35 | 0.28 | 0.21 |
|           | $q_{0,2}$ (mmol g$^{-1}$) | 0.68 | 0.35 | 0.28 | 0.21 |
|           | $b_1$ (atm$^{-1}$)     | 0.15 | 0.12 | 0.06 | 0.03 |
|           | SSE (%)             | 2.02 | 4.66 | 3.84 | 4.55 |
|           | $b_{0,1}$ (atm$^{-1}$) | 0.32|      |      |      |
|           | $b_{0,2}$ (atm$^{-1}$) | 0.00046|      |      |      |
|           | $B$ (kJ mol$^{-1}$) | 43.676|      |      |      |
|           | $E_2$ (kJ mol$^{-1}$) | -14.35|      |      |      |

of the N$_2$ isotherm that can be fitted well with all aforementioned isotherm models (Caldwell et al., 2015).

CO$_2$ affinity towards the adsorbent surface is higher as compared to N$_2$ as observed from higher values of $b$ in Tables 1, 2 and 3. Moreover, higher $q_m$ values of CO$_2$ adsorption than N$_2$ were obtained with all three isotherm models. N$_2$ considers both the adsorption sites as equal free-energy sites which are confirmed by similar values of the parameters $b_1$ and $b_2$ in the DSL isotherm. Therefore, there will be no energetic site-matching issue and CO$_2$ (component 1) will see site 1 as high free energy site and site 2 as low free energy site. So, there will be only one value of adsorbed amount for an adsorbate at a given temperature and gas composition conditions. It is seen that the parameter $b$ (Langmuir and Sips model) and $b_1$ and $b_2$ (Dual-site Langmuir) values decreased with increasing temperature, signifying the exothermic nature of the adsorption process. The Sips isotherm model parameter value $c$ shows a deviation in value from unity, indicating heterogeneity of the adsorption process.

**Binary component isotherms**

Sips and DSL isotherm models were used for binary component adsorption as these models properly explain the pure component adsorption behavior. Also, IAST
Deepak Tiwari et al.

Brazilian Journal of Chemical Engineering

Partial and total adsorbed amounts of CO$_2$ and N$_2$ on EZ-700 at different adsorption temperatures are shown in Fig. 5. Sips, DSL, IAST-Sips and IAST-DSL isotherm predictions and experimental values of CO$_2$ adsorbed are presented in Table 4.

Figure 5. Binary adsorption isotherms for CO$_2$-N$_2$ mixtures on EZ-700 at (a) 30 °C, (b) 50 °C, (c) 75 °C, and (d) 100 °C (symbols represent experimental data and lines represent model predicted data).
Table 4. Comparison of experimental and predicted binary system CO₂ adsorption capacities on EZ-700 based on binary component adsorption isotherms.

| Temperature | CO₂ mole fraction in feed | Experimental CO₂ adsorption capacity (mmol g⁻¹) | Sips model | DSL model | IAST-Sips model | IAST-DSL model |
|-------------|---------------------------|-----------------------------------------------|------------|-----------|----------------|----------------|
| 30 °C       |                           |                                               |            |           |                |                |
| 0.050       | 0.30                      | 0.29                                          | 0.36       | 0.38      | 0.31           | 0.30           |
| 0.075       | 0.39                      | 0.35                                          | 0.36       | 0.38      | 0.31           | 0.37           |
| 0.100       | 0.49                      | 0.41                                          | 0.41       | 0.45      | 0.45           | 0.42           |
| 0.125       | 0.65                      | 0.64                                          | 0.64       | 0.63      | 0.64           | 0.67           |
| 0.050       | 0.21                      | 0.23                                          | 0.23       | 0.25      | 0.25           | 0.23           |
| 0.075       | 0.30                      | 0.28                                          | 0.29       | 0.31      | 0.31           | 0.29           |
| 50 °C       |                           |                                               |            |           |                |                |
| 0.100       | 0.41                      | 0.34                                          | 0.34       | 0.39      | 0.39           | 0.37           |
| 0.125       | 0.49                      | 0.38                                          | 0.38       | 0.50      | 0.50           | 0.46           |
| 0.050       | 0.19                      | 0.12                                          | 0.11       | 0.19      | 0.19           | 0.16           |
| 0.075       | 0.27                      | 0.16                                          | 0.14       | 0.26      | 0.26           | 0.24           |
| 75 °C       |                           |                                               |            |           |                |                |
| 0.100       | 0.33                      | 0.19                                          | 0.17       | 0.36      | 0.36           | 0.34           |
| 0.125       | 0.39                      | 0.21                                          | 0.19       | 0.40      | 0.40           | 0.35           |
| 0.050       | 0.16                      | 0.09                                          | 0.07       | 0.15      | 0.15           | 0.13           |
| 0.075       | 0.22                      | 0.11                                          | 0.08       | 0.25      | 0.25           | 0.21           |
| 100 °C      |                           |                                               |            |           |                |                |
| 0.100       | 0.28                      | 0.13                                          | 0.09       | 0.26      | 0.26           | 0.22           |
| 0.125       | 0.32                      | 0.15                                          | 0.13       | 0.27      | 0.27           | 0.29           |

It can be seen that both Sips and DSL show different predicted values of CO₂ adsorbed amount. The predicted value of CO₂ obtained from the Sips equation as compared to the DSL equation is higher at 75 and 100 °C. On the other hand, IAST-Sips shows higher value of the CO₂ adsorbed amount as compared to IAST-DSL at all temperatures. However, the IAST forms of these two isotherm models show somewhat similar values for the CO₂ capacity obtained experimentally. Similar kinds of observations were seen for predicted N₂ uptake values by these isotherm models. Therefore, it can be concluded that, IAST forms of these isotherm models show similar predicted CO₂ capacities as those of experimental data obtained from binary breakthrough curves. Total and partial adsorbed amounts were highly under predicted by all these models with maximum under-estimation by Sips and IAST based Sips isotherm models for CO₂ and N₂ adsorption, respectively.

Experimental and model predicted molar fractions of CO₂ in the adsorbed phase vs. mole fraction of CO₂ in gas phase at different adsorption temperatures for the CO₂-N₂ binary system were determined and shown in Fig. 6. Maximum deviation for the DSL model at
100 °C and for Sips at 100 °C in predicting $x$ for a given $y$ is observed. However, for IAST based models, except at 30 °C (under predicted), they followed closely the experimental data for CO$_2$ mole fraction. Also, symmetric $x$-$y$ diagrams along with rising total adsorbed amount with mole fraction in the gas phase are exhibited by gas mixtures showing ideal behavior at equilibrium (Bakhtyari and Mofarahi, 2014). Adsorption of the CO$_2$-N$_2$ gas mixture on EZ-700 does not show a symmetric $x$-$y$ diagram, though total adsorbed amount increased with gas phase mole fraction. This suggests that carbon dioxide and nitrogen do not form ideal adsorptive mixtures on mesoporous carbon EZ-700.

Comparison of adsorption selectivity calculated experimentally from breakthrough curves under dynamic conditions and obtained from various isotherm models is also made. Experimental and predicted values of adsorption selectivity are shown in Table 5. Sips and DSL isotherm models show lower values, while IAST-Sips and IAST-DSL, except at 50 °C, show lower values of selectivity for CO$_2$ over N$_2$. This shows the inibility of binary component adsorption isotherms to predict mixed gas adsorption equilibria. It is also observed that, with the increase of CO$_2$ concentration, selectivity obtained from breakthrough curves increases, while for Sips and DSL it decreases. IAST-Sips and IAST-DSL show a smaller decrease in selectivity over the complete range of CO$_2$ concentration.

It is noted that the prediction of adsorption equilibria from IAST isotherm models for the binary component system was not correct because they vary in their size, polarity and most importantly they do not have the same equilibrium adsorption capacity. Also, in the case of heterogeneous adsorbents, IAST led to inadequate prediction of adsorption capacities. It provides relatively accurate multi-component behavior of systems such as CH$_4$-CO$_2$, CH$_4$-N$_2$, noble gases etc. (Walton and Sholl, 2015). CO$_2$ adsors more strongly as compared to N$_2$. Therefore, in the present study the difference in their adsorption levels is the main reason for under predicted adsorption behavior of the CO$_2$-N$_2$ system.

IAST has been extensively used by researchers for predicting mixed-gas adsorption equilibria, mostly in high pressure regions for pre-combustion capture application. Jeon et al. (2004), using NaX zeolite, studied CO$_2$ separation from a CO$_2$/N$_2$ mixture in a PSA system. The IAST model was able to predict proper behavior, but the extended Langmuir isotherm was unable to predict CO$_2$-N$_2$ adsorption behavior properly. Another study by Caldwell et al. (2015) was related to CO$_2$-N$_2$ equilibrium adsorption capacities obtained from breakthrough curves using fixed-bed experiments under high pressure conditions for CO$_2$ capture application. Sips and IAST-DSL models showed under predicted CO$_2$ uptake and the dual-site Langmuir isotherm model showed proper behavior for CO$_2$-N$_2$ system on activated carbons.

**Thermodynamic study**

Using the Sips isotherm model and equations S(18-21), thermodynamic parameters for CO$_2$ and N$_2$ adsorption on EZ-700 were calculated numerically. Thermodynamic parameters for adsorption at 30 °C only are shown in Fig.7. The negative value of the integral molar Gibbs free energy change at all temperatures indicates feasibility and spontaneity of the process. A higher amount of isothermal work is required for packing more adsorbate molecules into the adsorbent’s cavity as compared to the initial adsorption, which was confirmed from the increase of pressure and fall in values of both CO$_2$ and N$_2$. At 0.08 mmol g$^{-1}$ coverage, $\Delta G$ on EZ-700 for CO$_2$ and N$_2$ were -2.13 and -2.57 kJ mol$^{-1}$, respectively, indicating less amount of work required for loading of CO$_2$ on EZ-700 than for N$_2$ (Yi et al., 2013).

**Table 5.** Experimental and isotherm model predicted selectivities for CO$_2$-N$_2$ binary system on EZ-700.

| Temperature | CO$_2$ mole fraction in feed | Selectivity |
|-------------|-----------------------------|-------------|
|             | Experimental | Sips model | DSL model | IAST-Sips model | IAST-DSL model |
| 30 °C       | 0.050       | 74.63      | 72.39      | 94.37       | 30.28       | 122.98    |
|             | 0.075       | 81.91      | 60.98      | 82.49       | 26.18       | 117.60    |
|             | 0.100       | 102.28     | 54.08      | 75.14       | 23.57       | 115.33    |
|             | 0.125       | 114.13     | 49.35      | 70.12       | 21.78       | 114.10    |
|             | 0.150       | 71.99      | 81.55      | 105.48      | 206.39      | 130.71    |
|             | 0.175       | 96.17      | 69.93      | 93.46       | 201.47      | 129.72    |
|             | 0.200       | 133.75     | 62.83      | 86.13       | 201.48      | 128.45    |
|             | 0.225       | 146.26     | 57.93      | 81.13       | 204.65      | 128.22    |
|             | 0.250       | 131.21     | 71.50      | 77.74       | 95.06       | 92.21     |
| 50 °C       | 0.075       | 131.93     | 61.95      | 69.04       | 102.76      | 87.15     |
|             | 0.100       | 160.30     | 56.05      | 64.26       | 108.63      | 85.98     |
|             | 0.125       | 155.22     | 51.95      | 61.20       | 114.39      | 85.21     |
|             | 0.150       | 140.37     | 79.80      | 30.28       | 123.39      | 90.06     |
|             | 0.175       | 133.68     | 68.47      | 26.18       | 117.16      | 81.30     |
|             | 0.200       | 150.60     | 61.53      | 23.57       | 113.43      | 77.90     |
| 75 °C       | 0.125       | 138.94     | 56.73      | 21.78       | 126.51      | 75.89     |
| 100 °C      | 0.100       | 150.60     | 61.53      | 23.57       | 113.43      | 77.90     |
Synthesis, Characterization, Adsorption and Thermodynamic Studies of Pure and Binary CO$_2$-N$_2$ Mixtures on Oxygen Enriched...

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Negative values of $\Delta S \times T$ over the complete pressure range at 30 °C indicate random to more orderly adsorption for CO$_2$ and N$_2$ on the adsorbent surface.

$\Delta S \times T$ for N$_2$ decreases with pressure and was almost constant for CO$_2$. A decrease in the cavity’s free space with increase in adsorbate molecule loading was also observed, signifying that N$_2$ adsorption on EZ-700 is homogenous. CO$_2$ adsorption on EZ-700 is heterogeneous which is seen from the small increase in the amount of entropy in the low pressure range (Deng et al., 2012; Zhou et al., 2012). At 0.08 mmol g$^{-1}$, $\Delta S \times T$ values for CO$_2$ and N$_2$ adsorption on EZ-700 at 30 °C are -14.22 and -8.53 kJ mol$^{-1}$, respectively, indicating a lower degree of disorder for CO$_2$ and higher for N$_2$. Lower degree of freedom of constrained CO$_2$ after it gets adsorbed onto carbon adsorbent is also confirmed from this. Efficient packing of CO$_2$ in the adsorbent cavity is because of localized adsorption, which is due to its higher quadruple moment than N$_2$. These quadruple moments of both CO$_2$ and N$_2$ interact with electrostatic-field gradients, thereby causing increased rotation and hence orientation of these molecules producing more efficient packing and this is more evident for CO$_2$ than N$_2$ due to its about three-fold larger quadruple moment than N$_2$ (Ridha and Webley, 2010).

Negative values of the integral molar enthalpy change confirmed the exothermic nature of the adsorption of CO$_2$ and N$_2$ on EZ-700 at 30 °C. A similar pattern was seen for molar enthalpy change and entropy change. With the increase of pressure from 0.01 to 1 atm, molar enthalpy changes of CO$_2$ on EZ-700 ranged from -11.58 to -23.20 kJ mol$^{-1}$, while for N$_2$ they varied from -6.61 to -11.21 kJ mol$^{-1}$. This indicates a more effective molecular packing, and higher amount of release of heat. Similar observations were seen for activated carbons like Maxsorb III (-20.37 kJ mol$^{-1}$) (Saha et al., 2011), coal based activated carbon (21.89 kJ mol$^{-1}$) (Yi et al., 2014), and activated carbon beads (-23.17 kJ mol$^{-1}$) (Shen et al., 2010).

As these parameters are calculated using the isotherm equation for each component, it is not possible to calculate them for binary system adsorption because there is no isotherm available to accurately predict the binary system equilibria.

Isosteric heat of adsorption for the adsorption of pure CO$_2$ from equilibrium isotherms is calculated by using the Clausius-Clapeyron equation $\Delta S$ and is shown in Fig. 8. The average value of isosteric heat of adsorption ($Q_{st}$) for CO$_2$ on EZ-700 was calculated to be ca. 34.82 kJ mol$^{-1}$ which is in agreement with the available value in the literature for carbon adsorbents (Caldwell et al., 2015; Shen et al., 2010; Yi et al., 2014). An almost constant $Q_{st}$ value was seen at different surface loadings. This is in line with the assumption of the DSL adsorption model wherein $Q_{st}$ is independent of adsorbate loading on the adsorbent surface. Also, this supports the accurate prediction of CO$_2$ adsorption on EZ-700 by the DSL isotherm model.

![Figure 7. Thermodynamic functions ($\Delta G$, $\Delta H$ and $\Delta S \times T$) for CO$_2$ (closed symbols) and N$_2$ (open symbols) on EZ-700 at 30 °C](image)

CONCLUSIONS

Oxygen enriched nanostructured low-cost carbon having heterogeneous pores and high basicity is successfully developed using a nanocasting technique. Sips and DSL isotherm models provide the best fit over the entire pressure range. Adsorption equilibria of binary component CO$_2$ and N$_2$ at four different adsorption temperatures (30-100 °C) and CO$_2$ concentrations (5-12.5%) have been measured on EZ-700 using a fixed bed column. The adsorbent shows 0.636 mmol g$^{-1}$ adsorption capacity with complete regenerability over four adsorption/desorption cycles. For predicting binary component adsorption equilibria, extended Sips, extended dual-site Langmuir, IAST-based Sips and IAST-based DSL models have been

![Figure 8. Isosteric heat of adsorption of pure CO$_2$ from equilibrium isotherms on EZ-700](image)
used. Unlike Sips and DSL, IAST-based Sips and IAST-based DSL closely predicted the adsorption behavior of the binary component. Neither selectivity nor total adsorbed amount can be explained properly by these models because of high adsorption strength and the heterogeneous adsorbent surface of one component as compared to the other. Overall, it can be concluded that binary component adsorption equilibria are important for real systems. These help in better selecting the appropriate model for simulation of gas phase adsorption systems.

Molar Gibbs free energy change, entropy change, and enthalpy change for pure components signify a spontaneous, exothermic and feasible nature of adsorption process. Effective packing of CO$_2$ molecules in the cavities of carbon adsorbents has been confirmed by the higher amount of heat generation for CO$_2$. Higher chemical potential and higher pressure are required by N$_2$ as compared to CO$_2$ to load carbon on its surface.

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**APPENDIX - THEORY**

**Pure component isotherm**

Langmuir, Sips and Dual-site isotherm models were used to predict adsorption equilibrium of pure gases (CO₂ and N₂) on prepared oxygen enriched carbon.

**Langmuir isotherm**

\[
q_e = \frac{q_m b P}{1 + b P} \quad (A.1)
\]

where \(q_e\) (mmol g⁻¹) is the equilibrium adsorption capacity, \(q_m\) (mmol g⁻¹) is the maximum monolayer capacity, \(b\) (atm⁻¹) is the affinity of adsorbed molecules towards the adsorbent surface and \(P\) is the total pressure.

**Sips isotherm model**

\[
q_c = \frac{q_m b P^{1/c}}{1 + b P^{1/c}} \quad (A.2)
\]

**Dual-site Langmuir model**

\[
q_e = \frac{q_{1,m} b_1 P + q_{2,m} b_2 P}{1 + b_1 P + b_2 P} \quad (A.3)
\]

where \(q_{1,m}\) and \(q_{2,m}\) are the saturation capacities of the adsorbate at sites 1 and 2, respectively, \(b_1\) and \(b_2\) are the affinity parameters on sites 1 and 2, respectively.

**Temperature dependent parameter for Langmuir isotherm**

\[
b = b_o e^{-(B/RT)} \quad (A.4)
\]

where \(b_o\) is the adsorption affinity at the reference temperature, and \(B\) (J mol⁻¹) is the heat of adsorption.

**Temperature dependent parameter for Dual-site isotherm**

\[
b_j = b_{o,j} e^{E_j/RT} \quad (A.5)
\]

where \(j\) is the energy level of site 1 or 2, \(b_{o,j}\) is the adsorption affinity at the reference temperature and \(E_j\) is the corresponding adsorption energy.

**Error calculation**

\[
SSE(\%) = \sqrt{\frac{\sum (q_{e,exp} - q_{e,pred})^2}{N}} \times 100 \quad (A.6)
\]

where \(q_{e,exp}\) and \(q_{e,pred}\) are the experimental and model predicted amounts of adsorbate adsorbed, respectively, and \(N\) = total number of data points.

**Binary component isotherm**

In the present study, two approaches were used for the prediction of adsorption equilibria of the
binary system (CO$_2$ and N$_2$) using pure component adsorption isotherm parameters. In the first approach, the models which properly fitted the pure component data were extended to binary component adsorption isotherms and, in the other. ideal adsorbed solution theory (IAST) model was used to derive binary system isotherms from pure component adsorption isotherms. Further, these predicted isotherms are compared with the measured binary system isotherms.

**Extended Sips isotherm model**

$$q_{e,i} = \frac{q_{m,i} b_i P_i^{1/c_i}}{1 + \sum_{j=1}^{N} b_j P_j^{1/c_j}}$$

(A.7)

where $i$ is the component for which isotherm is evaluated, and $q_{e,i}$ is the equilibrium adsorption capacity of component $i$ in the mixture.

**Extended dual-site Langmuir isotherm model**

$$q_{e,i} = \frac{q_{m,1,i} b_{1,i} P_i + q_{m,2,i} b_{2,i} P_i}{1 + \sum_{j=1}^{N} b_{1,j} P_j + \sum_{j=1}^{N} b_{2,j} P_j}$$

(A.8)

**Ideal adsorbed solution theory (IAST)**

Another model, which is given by Myers and Prausnitz (1965), for prediction of adsorption equilibria of a binary system using pure component adsorption isotherms is Ideal adsorbed solution theory (IAST). This model depends on the concept of IAST in which adsorbed phase is in equilibrium with the gas phase.

We have also used IAST-Sips and IAST-DSL models, which were obtained by substituting pure component Sips and DSL isotherm equations into Eq. (10) followed by its integration. Eqs. (13) and (14) give the reduced spreading pressure for Sips and DSL models, respectively which are also equated for each component and the expressions for Sips and DSL models are given by Eqs. (15) and (16), respectively.

$$P y_i = P_i^0 (\pi^*) x_i$$

(A.9)

where $y_i$ is the mole fraction of component $i$ in gas phase, $x_i$ is the mole fractions of component $i$ adsorbed phase, $P$ is the total pressure of the mixture, $P_i^0 (\pi^*)$ is the equilibrium gas phase pressure corresponding to solution temperature and spreading pressure, $\pi^*$,

$$\pi^*_i = \frac{\pi_i A}{RT} = \int_0^{P_i^*} \frac{d\pi}{P_i^0}$$

(A.10)

where $\pi^*_i$ and $\pi_i$ are reduced spreading pressure and spreading pressure of component $i$ in the adsorbed phase, respectively, $A$ is the specific surface area of the adsorbent, $q_i^*$ is the pure component adsorption isotherm equation, and $P_i^0$ is the standard state pressure of pure component $i$ corresponding to spreading pressure of the mixture.

$$\frac{1}{q_T} = \sum_{i=1}^{N_C} \frac{x_i}{q_i^0 (P_i^0)}$$

(A.11)

$$q_i = x_i q_T$$

(A.12)

$$\pi^*_i = q_{m,i} c_i \ln \left(1 + b_i \left(\frac{P_i^0}{P_i^0} \right)^{1/c_i} \right)$$

(A.13)

$$\pi^*_i = q_{m,i} c_i \ln \left(1 + b_i \left(\frac{P_i^0}{P_i^0} \right)^{1/c_i} \right) + q_{m,i} c_i \ln \left(1 + b_i \left(\frac{P_i^0}{P_i^0} \right)^{1/c_i} \right)$$

(A.14)

$$q_{m,i} c_i \ln \left(1 + b_i \left(\frac{P_i^0}{P_i^0} \right)^{1/c_i} \right) = q_{m,1,i} c_1 \ln \left(1 + b_1 \left(\frac{P_1^0}{P_1^0} \right)^{1/c_1} \right)$$

(A.15)

$$q_{m,i} c_i \ln \left(1 + b_i \left(\frac{P_i^0}{P_i^0} \right)^{1/c_i} \right) + q_{m,2,i} c_2 \ln \left(1 + b_2 \left(\frac{P_2^0}{P_2^0} \right)^{1/c_2} \right)$$

(A.16)

A MATLAB program is used to calculate $x_i$, by solving the above mentioned equations implicitly.

**Selectivity**

Selectivity, which is one of the main characteristic properties of adsorbent, can also be determined for CO$_2$ over N$_2$ ($S_{CO_2}$) and is compared with the experimental data obtained from breakthrough curves.

$$S_{CO_2} = \frac{x_{CO_2}}{y_{CO_2}} \frac{x_{N_2}}{y_{N_2}}$$

(A.17)

where $x_{CO_2}$ and $S_{CO_2}$ are the mole fractions of CO$_2$ in the adsorbed phase, respectively, and $y_{CO_2}$ and $y_{N_2}$ are the molar ratios of CO$_2$ and N$_2$ in the gas phase, respectively.

**Thermodynamic study**

Three thermodynamic parameters, i.e., integral molar Gibbs free energy, integral molar enthalpy and integral molar entropy were calculated numerically, whose values tell the behavior of the adsorption process (Deng et al., 2012; Ridha and Webley, 2010):

**Integral molar Gibbs free energy change for the adsorption process**

$$\Delta G = \frac{\Omega}{q} \left[ -RT \int_0^P q d(\ln P) \right]$$

(A.18)
where $\Omega$ is the surface potential (kJ mol$^{-1}$), $R$ is the universal gas constant (kJ mol$^{-1}$ K$^{-1}$), $q$ is the amount of adsorbate adsorbed (mmol g$^{-1}$) and $T$ is temperature (K).

Integral molar enthalpy, $\Delta H$ (kJ mol$^{-1}$)

$$\Delta H = \left[ \frac{\partial (\Omega / T)}{\partial (1/T)} \right]_p$$  \hspace{1cm} \text{(A.19)}$$

Integral molar entropy change, $\Delta S$ (kJ mol$^{-1}$ K$^{-1}$)

$$\Delta S = \frac{-\frac{\partial \Omega}{\partial T}}{q}$$  \hspace{1cm} \text{(A.20)}$$

Isosteric heat of adsorption for CO$_2$, $Q_{st}$ (kJ mol$^{-1}$)

$$Q_{st} = -R \left[ \frac{\partial \ln P}{\partial \left( \frac{1}{T} \right)} \right]_{q_e}$$  \hspace{1cm} \text{(A.21)}$$
