AN INVESTIGATION ON THE OXYGEN AND NITROGEN SEPARATION FROM AIR USING CARBONACEOUS ADSORBENTS

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Abstract

Adsorption equilibria of pure oxygen and nitrogen were investigated in two different carbonaceous adsorbents such as activated carbons (ACs) and Multi-walled carbon nanotubes (MWCNTs). To improve the surface characteristics of MWCNTs for adsorption operations, the chemical pretreatment operations were performed. The equilibrium adsorption of oxygen and nitrogen on adsorbents were measured at different pressure values ranged from 0 to 50 bar at different temperatures. Due to the different surface structures of these adsorbents, the selectivity was different. A comparison between the separation factors of MWCNTs and ACs showed that oxygen was adsorbed on MWCNTs better than nitrogen. However, the lowest separation factor obtained was 2.7 for oxygen and nitrogen adsorption on chemically pretreated MWCNTs demonstrating that the chemically pretreated MWCNTs enhanced the preferential adsorption of oxygen to nitrogen.

Keywords: Adsorption, Separation factor, MWCNTs, ACs, Pretreatment, Uptake amount.

1. Introduction

Cryogenic distillation and pressure swing adsorption (PSA) are two conventional methods for separation of oxygen and nitrogen from outdoor air. The first work for separating desirable gases from air was performed in Europe in the 19th century and several years later, in the 1970s, the PSA technique was developed. The latter technique does not liquefy air to produce oxygen and nitrogen and instead, uses adsorbents for air separation at normal temperatures. Comparing between these two methods confirms that PSA is more economical than cryogenic distillation method.
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in small or medium size air separation plants [1]. By improving the adsorption processes and enhancing the characteristics of adsorbents, PSA process is considered to be useful even in large-quantity productions [1-4].

Air separation by adsorption of oxygen is desirable and several researches are being performed to develop adsorbents that adsorb oxygen preferentially to nitrogen to use in industrial adsorption systems. Zeolites and carbon molecular sieves are usually proposed as adsorbents for gas separation and adsorption processes [2, 5, 6]. To design a PSA system, it is crucial to have the adsorption isotherm information [7].

Carbon nanotubes (CNTs) as a new generation of carbonaceous materials, are very interesting as porous media [8, 9] due to their unique characteristics for gas adsorption and separation processes. After the discovery of CNTs [10], many researchers investigated synthesis, treatment, and physical properties of CNTs [11-13]. Although there are numerous works dedicated to the synthesis of CNTs, a limited number of studies investigated oxygen and nitrogen adsorption on CNTs [14-17]. Yulong et al. investigated the methane adsorption on MWCNTs and achieved to optimal value of 11.7% of mass storage capacity at room temperature and the pressure of 10.5 MPa [14]. Delavar et al. studied the equilibria and kinetics of natural gas adsorption on CNTs and indicated these adsorbents are potential materials for natural gas uptake [15]. In other works done by this group, the effect of chemical treatment on natural gas adsorption by multi-walled carbon nanotubes has been investigated. They report increased adsorption capacity of MWCNTs for natural gas adsorption [17].

There is the lack of knowledge about oxygen and nitrogen adsorption on MWCNTs. Also, little research has been done on the enhancement of adsorption capacity of CNTs material by chemical operation and their application on air separation. The main purpose of this study was to investigate the adsorption isotherms of oxygen and nitrogen at different operating conditions as well as the effect of chemical treatment operation on adsorption characteristics of MWCNTs. Furthermore, the separation factor of oxygen and nitrogen from air and the selective adsorption of various adsorbents were studied.

2. Materials and Methods

The Multi-Walled Carbon Nanotubes (MWCNTs) used in this work were synthesized by Chemical Vapor Deposition (CVD) method. The purity of MWCNTs was more than 95%. The Coal-based, extruded Activated Carbons (ACs) (2mm diameter tubes) were used in this study. Oxygen and nitrogen with purity of 99.99% were purchased from Technical Gas Services, UAE.

The adsorbents were characterized with respect to their wall thickness, diameter and length by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The physical properties of adsorbent surfaces such as specific surface area (SSA), mean pore diameter and total pore volume were measured by the Brunauer, Emmett and Teller (BET) technique employing N₂ adsorption isotherm at 77 °K to determine surface area, average pore diameter and pore volume.

Before performing the chemical treatments, the nanotubes were sonicated in a proportion of 50 mg MWCNTs in 500 mL ethanol for 40 min to eliminate the amorphous phase. Then, resulting solution was filtered and dried for 2 hours in a
vacuum oven at 90 °C. The acidic treatment of MWCNTs in the presence of a concentrated nitric acid solution (70%) was carried out. To this end, the prepared MWCNTs were doused in 200 ml concentrated nitric acid 63% for 2 hours under sonication at 30°C. Then the acidic concentrated solution was refluxed for 4 hours at 90°C. Resulting solution was adequately filtered and resulting CNTs washed with deionized water until the pH of the filtered water reached 7, then dried at 100°C for 8 hours in a vacuum oven [10, 12, 13]. After drying, the samples were taken out of the filters and applied as adsorbents in oxygen and nitrogen adsorption experiments. Surface characteristics of the pristine untreated MWCNTs as well as chemically pretreated MWCNTs sample used as adsorbent were determined. Table 1 shows the physical properties of pristine and chemically pretreated MWCNTs used in this study. For the ACs, the specific surface area and the apparent density were determined to be 822 m²/g and 0.66 g/cm³, respectively.

Table 1. Specifications of MWCNTs before and after chemical treatment obtained from BET analysis.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pristine MWCNTs</th>
<th>Treated MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²/g)</td>
<td>293.86</td>
<td>346.69</td>
</tr>
<tr>
<td>Mean pore diameter (nm)</td>
<td>4.67</td>
<td>3.68</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.62</td>
<td>0.69</td>
</tr>
</tbody>
</table>

**Adsorption measurement**

The adsorption experiments for oxygen and nitrogen were performed using volumetric technique at pressures ranging from 0 to 50 bar at different temperatures. The adsorbents were heated at 393 K for 5 hours to remove undesirable gases. The amount of adsorbed gases was calculated using material balance at equilibrium conditions. The nonideality of gas phase was corrected using the SRK equation. The material balance equation for calculation of adsorbed amount is shown below:

\[
\left( \frac{PV}{zRT} \right)_{1}\frac{1}{z_{1}} + \left( \frac{PV}{zRT} \right)_{2}\frac{1}{z_{2}} = \left( \frac{PV}{zRT} \right)_{1}\frac{1}{z_{1}} + \left( \frac{PV}{zRT} \right)_{2}\frac{1}{z_{2}} + nM
\]

where P, T and V are pressure, temperature and volume, respectively; R is the gas constant; M is the adsorbent mass; z is the gas compressibility factor (obtained from SRK state equation); n is the adsorbed amount; 1 and 2 represent for the state before and after the adsorption equilibrium, respectively.

By calculating the adsorbed amount of oxygen and nitrogen on carbonaceous adsorbents at different equilibrium conditions, the adsorption isotherms were obtained.

3. Results and Discussion

3.1. Characterization

Figure 1 shows the TEM image of MWCNTs and SEM images of MWCNTs and activated carbons, respectively. The TEM analysis was used to determine the
characteristics of Pristine MWCNTs such as multiwall structure, inner and outer diameter and length. The MWCNTs were 15-20 nm in outer diameter, about 4 nm in inner diameter and about 30 µm in length.

Fig. 1. Transmission electron microscopy of MWCNTs (A), Scanning electron microscopy of MWCNTs (B) and ACs (C).
Figure 2 shows the SEM images of MWCNTs before and after chemical pretreatment. The structural characteristics of the MWCNTs have been changed considerably after acidic treatment and ultrasoniating in the concentrated solution. The acidic treatment caused break down in nanotube structure (reducing its length) and created defects in its network. The shortening of MWCNTs length can be clearly seen in Fig. 2. Similar observations were reported using SEM images by other researchers [18]. According to the values of Table 1, the acidic treatment led to considerable increase in the specific area and decrease in mean pore diameters. The formation of cavities and defects in MWCNs structure led to increasing the surface area by opening of the closed ends as it can be observed in Fig. 2. The major change obtained in chemically pretreated MWCNTs structure promoted its capacity for oxygen and nitrogen storage, compared to pristine MWCNTs. Optimum values of oxygen and nitrogen adsorption capacity for chemically pretreated MWCNTs were estimated to be 30 mmol/g and 28 mmol/g at 283.15°C and 50 bar, respectively. The overall results show that the amounts of oxygen and nitrogen uptake on chemically pretreated MWCNTs were obviously higher than the ones on ACs and pristine MWCNTs.

Fig. 2. Scanning electron microscopy (SEM) images of MWCNTs before (A) and after (B) chemical pretreatment.
3.2. Equilibrium isotherms

Figure 3 shows the adsorption isotherms of pure oxygen and nitrogen on ACs, MWCNTs and pretreated MWCNTs, respectively. As shown, the MWCNTs adsorbents (pristine and pretreated) represent superior adsorption capacity for oxygen and nitrogen compared to ACs. This high-adsorption capacity is concluded from the unique surface properties of MWCNTs such as highly uniform pore size and high pore volume. Since the average size of oxygen and nitrogen molecules is 0.28 nm and 0.37 nm, respectively, they can be easily loaded within the MWCNTs with uniform pore size of about 4 nm, while the ACs contain a full range of micropores that most of total pores available in ACs are too large for latter gases molecules.
Fig. 3. Adsorption isotherms of oxygen and nitrogen on ACs (A), MWCNTs (B) and pretreated MWCNTs (C).

All the isotherms show that the amounts of oxygen and nitrogen uptake increase with an increased in the pressure. It can be seen that oxygen preferentially adsorbed in all adsorbents. Due to the chemically inert nature of the graphite surface, nonpolar and weakly polar molecules can be absorbed by carbonaceous material more strongly than other materials. The amount of adsorbed materials per unit weight of adsorbents can be explained as adsorption capacity. The adsorption capacity is the most important economical factor in adsorption processes and selectivity is the significant parameter in selective separation processes [19, 20], such as oxygen and nitrogen separation from air which was investigated in this study. As shown in Table 2, the selectivity of oxygen to nitrogen at 1bar and 298.15 K for activated carbons, MWCNTs and chemically pretreated MWCNTs were about 1.1, 1.3 and 1.45, respectively. As the molar compositions of oxygen and nitrogen in air are almost 0.21 and 0.79 at 298.15 K, respectively, the separation factor (SF) of oxygen to nitrogen can be calculated by dividing the amount of adsorbed nitrogen and oxygen by different adsorbents at 0.79 bar for nitrogen and 0.21 bar for oxygen. It is given by:

\[
SF = \frac{\text{amount of adsorbed nitrogen at 0.79 bar}}{\text{amount of adsorbed oxygen at 0.21 bar}}
\]  

As the ratio of the molar composition of nitrogen to oxygen in air is about 3.762, the separation factors higher than this value will result in no separation of nitrogen and oxygen from air. However, at separation factors lower than 3.762, oxygen will be adsorbed on adsorbents more selectively than nitrogen. As presented in Table 3, the calculated separation factor of activated carbons, MWCNTs and chemically pretreated MWCNTs were determined to be 3.65, 3.05 and 2.7, respectively. Therefore chemically pretreated MWCNTs were the best
adsorbent for oxygen and nitrogen separation from air among the examined adsorbents in this study because of their lowest separation factor [19].

### Table 2. Selectivity of oxygen to nitrogen (O\(_2\)/N\(_2\)) for different adsorbents at 298.15 K and 1 bar.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbed Oxygen (mmol/g)</th>
<th>Adsorbed Nitrogen (mmol/g)</th>
<th>Selectivity (O(_2)/N(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbons</td>
<td>0.16</td>
<td>0.14</td>
<td>1.1</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>0.71</td>
<td>0.55</td>
<td>1.3</td>
</tr>
<tr>
<td>Pretreated MWCNTs</td>
<td>0.95</td>
<td>0.65</td>
<td>1.45</td>
</tr>
</tbody>
</table>

### Table 3. Required data for calculation of separation factor at 298.15 K.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption of Nitrogen at 0.79 bar (mmol/g)</th>
<th>Adsorption of oxygen at 0.21 bar (mmol/g)</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbons</td>
<td>0.11</td>
<td>0.03</td>
<td>3.65</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>0.49</td>
<td>0.16</td>
<td>3.05</td>
</tr>
<tr>
<td>Pretreated MWCNTs</td>
<td>0.54</td>
<td>0.2</td>
<td>2.7</td>
</tr>
</tbody>
</table>

4. Conclusions

To evaluate an air separation process, three carbon-based adsorbents (ACs, MWCNTs and pretreated MWCNTs) were selected. Oxygen and nitrogen adsorption isotherms for aforementioned adsorbents revealed that their separation factors were different. By increasing the pressure and decreasing the temperature, the amounts of the oxygen and nitrogen adsorption enhanced for all adsorbents. The results confirm that chemical pretreatment operation enhances the selectivity of MWCNTs. Therefore, the pretreated MWCNTs are the most suitable adsorbent for air separation due to their porous structure and surface characteristics compared to ACs and pristine MWCNTs.

References


