A COMPARATIVE STUDY OF VARIOUS POROUS ADSORBENTS FOR CO_2 ADSORPTION

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Abstract: Zeolites, metal organic frameworks (MOFs), carbon nanotubes, polymers, and activated carbons have been commonly used as porous adsorbents for CO_2 adsorption. The objective of the study was to prepare low-cost activated carbon from carob stones and compare its adsorption capacities for CO_2 with that of commercial mesoporous silica and four zeolites (zeolite, 4A zeolite, ammonium Y and sodium Y zeolites). CO_2 adsorption on these porous adsorbents was investigated by using volumetric adsorption apparatus, TriStar II 3020 at room temperature and at pressures up to 900 mmHg. The CO_2 adsortion capacities (wt%) were determined using the values of the quantity adsorbed at 900 mmHg. It could be confirmed that chemical activation plays an important role in determining the porous structure and amount of CO_2 adsorbed.
Keywords: Carob stones, zeolite, 4A zeolite, ammonium Y zeolite, sodium Y zeolite, mesoporous silica, activated carbon.

Introduction

Climate change is the result of increasing CO_2 and other greenhouse gases (such as CH_4, HFCs and F_6) emissions. Various technigues (cryogenic separation, absorption and adsorption) for removing CO_2 from gas and thus reducing its impact on climate change have been investigated. Adsorption is most commonly used method for the capture and separation of CO_2 because of low energy requirements and high adsorption capacity (Liu et al. 2011; Liu et al. 2015; Goel et al. 2016) . Activated carbon, carbon nanotubes, zeolites, mesoporous silica, metal organic frameworks (MOFs), polymers have been commonly used as adsorbents for CO_2 adsorption. Activated carbon is produced from variety of raw materials such as cherry stones, apricot stones, cornelian cherry stones, olive stones, wood and coal. Activated carbons can be produced by chemical activation. Chemical activation is a single step method for the preparation of raw material in the presence of chemical agent such as KOH, NaOH, LiOH, $ZnCl_2$ and H_3PO_4 (Erdogan 2016; Erdogan and Erdogan 2016). There are several study for CO_2 adsorption in the literature. Boyjoo et al. (2017) produced activated carbon from Coca Cola® for CO_2 adsorption. They found the adsorption capacity of the KOH activated carbon as 5.22 mmol/g. Ramli et al. (2014) investigated the effect of pressure and temperature on the adsorption of CO_2 on MCM-41. Sayari et al. (2011) exhibited a high CO_2 adsorption capacity 1.55 mmol7g at 55 C. Zeolite like metal organic frameworks with sod and rho topologies have been investigated for CO_2 adsorption by Chen et al. (2011). They found the adsorption capacities of sod-zeolite like metal organic framework and rho-zeolite like metal organic framework as 53 and 51 mg/g, respectively. Osler et al. (2017) reported that impregnating chitosan onto multiwalled carbon nanotubes increased their CO_2 adsorption capacity by 650%. The main objects of this study are: (i) to study the feasibility of using the activated carbon produced from carob stones as a low-cost adsorbent for CO_2 adsorption, (ii) to compare its CO_2 adsorption capacity with that of six commercially available typical adsorbents with different porosity and texture, i.e. activated carbon, mesoporous silica and four types zeolites (zeolite, 4A zeolite, ammonium Y and sodium Y zeolites).

Materials and Methods

In this study, carob stones were obtained from Antalya in Turkey. The precursor, carob stones were first air dried, then crushed. Then, carob stones were contacted with dilute a 15 vol.% sulfuric acid solution for 12 hours and washed with hot distilled water. Zeolite (Z), 4A zeolite (4AZ), ammonium Y (AYZ) and sodium Y zeolites (SYZ) and mesoporous silica (MCM-41) were purchased from Sigma-Aldrich.

Preparation of the activated carbon: 20 g of dried carob stones (<2 mm) was mixed in a beaker with 200 mL of KOH solution which corresponded to an impregnation ratio of 4:1 (weight of impregnation reagent/weight of carob stones) for 10 hours at 65°C. The mixtures were immersed in the ultrasonic bath for 120 minutes at 65°C and then the impregnated sample was then dried over a night in a moisture oven at 120°C. Then, the impregnated sample was carbonized in a tube furnace (Protherm STF) under N_2 flow at a heating rate of 10°C/min up to 700°C for 1 hour. After the activation, the sample was allowed to cool down to the room temperature under N_2 flow before its removal from the furnace. The activated sample was washed several times with HCl and hot distilled water to remove residual chemicals until it did not give chloride reaction with $AgNO_3$. The activated sample was dried for 6 hours at 120ºC. Activated sample was stored in a sealed flask and labelled. The pores of activated carbon were characterized by analysis of N_2 adsorption–desorption isotherms at 77 K using Micromeritics ASAP 2020 (Erdogan 2018c).

Characterization of porous adsorbents and CO_2 adsorption measurement:The surface physical properties of adsorbents were characterized with an automated gas sorption apparatus (Micromeritics TriStar II 3020 and ASAP 2020) using N_2 as adsorbate at -196 °C. Prior to measurements, the porous adsorbents were degassed for 4 hours under vacuum at 300 °C. The BET surface area was calculated using nitrogen adsorption data in the relative pressure (P/P_0) range of 0.04 to 0.2. The total pore volume was calculated from the amount of adsorbed nitrogen at P/P_0=0.99. The micropore volume of the porous adsorbents was calculated by using the t-method analysis (Erdogan 2017a; 2018a). CO_2 adsorption-desorption isotherms of the produced activated carbon and commercially porous adsorbent samples were measured using a Micromeritics TriStar II 3020 instrument, which is a static volumetric apparatus. The equilibrium experiments were conducted at 25 °C and at pressures up to 900 mmHg. The CO_2 adsorption capacities were determined using the values of the quantity adsorbed at 900 mmHg.

Results and Discussion

The N_2 adsorption-desorption isotherms of the activated carbon (AC) is shown in Fig. 1. It can be seen that, activated carbon possessed a combination of type I and type IV isotherms according to IUPAC classification. Appearance of hysteresis loop indicates the presence of mesopores. The isotherm reveals mesoporosity but also strong signs of microporosity

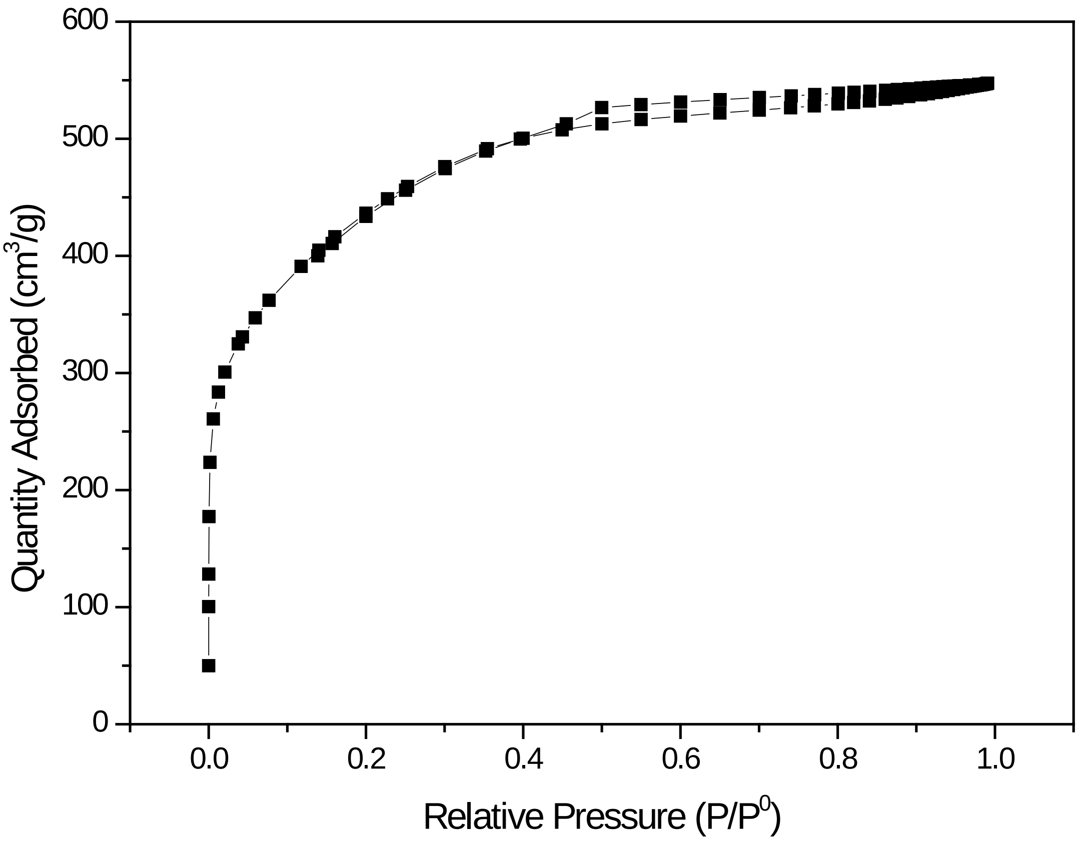

Figure 1. The adsorption-desorption isotherms of activated carbon sample (AC).

Average pore widths and pore volumes were calculated from the nitrogen adsorption isotherm data by t-method analysis. Table 1 gives the values of the BET surface areas, Langmuir surface areas, total pore volumes, micropore volumes and average pore widths which were calculated by using the nitrogen adsorption-desorption data obtained at 77 K. The BET and Langmuir surface areas were found for the AC produced with KOH activation, as 1480.96 and 2288.31 m^2/g, respectively. In our previous studies we have reported that the BET surface areas and pore volumes and average pore widths of MCM-41 (Oguz Erdogan and Erdogan 2018), AYZ and SYZ (Erdogan 2018a), Z, 4AZ (Erdogan 2018b). BET surface areas of MCM-41, AYZ, SYZ, Z and 4AZ adsorbents were found as 689.32, 736.92, 766.61, 6.874 and 18.09 m^2/g, respectively. Average pore widths for MCM-41 and 4AZ were found as 4.32 ve 19.391 nm, respectively and it was reported that these absorbents have mesoporous structure. Average pore widths for AYZ, SYZ and Z were found as 1.945, 1.918 ve 1.255 nm, respectively and it was reported that these absorbents have microporous structure.

Table 1: Physical characteristics of the activated carbon sample (AC).

BET surface area (m^2/g)	1480.96
Langmuir surface area (m^2/g)	2288.31
Total pore volume (cm^3/g)	0.845
Micropore volume (cm^3/g)	0.140
Average Pore Width (nm)	2.283

CO_2 Adsorption: Figure 2 represents the carbon dioxide adsorption-desorption isotherms of these six porous adsorbents at 25 °C. The adsorption isotherms indicate that the CO_2 adsorption capacity at 900 mmHg for SYZ is higher than the other porous adsorbents. The chemically activated carbon sample (AC) showed better CO2 adsorption capacity as compared to the commercial Z, AYZ, 4AZ and MCM-41.

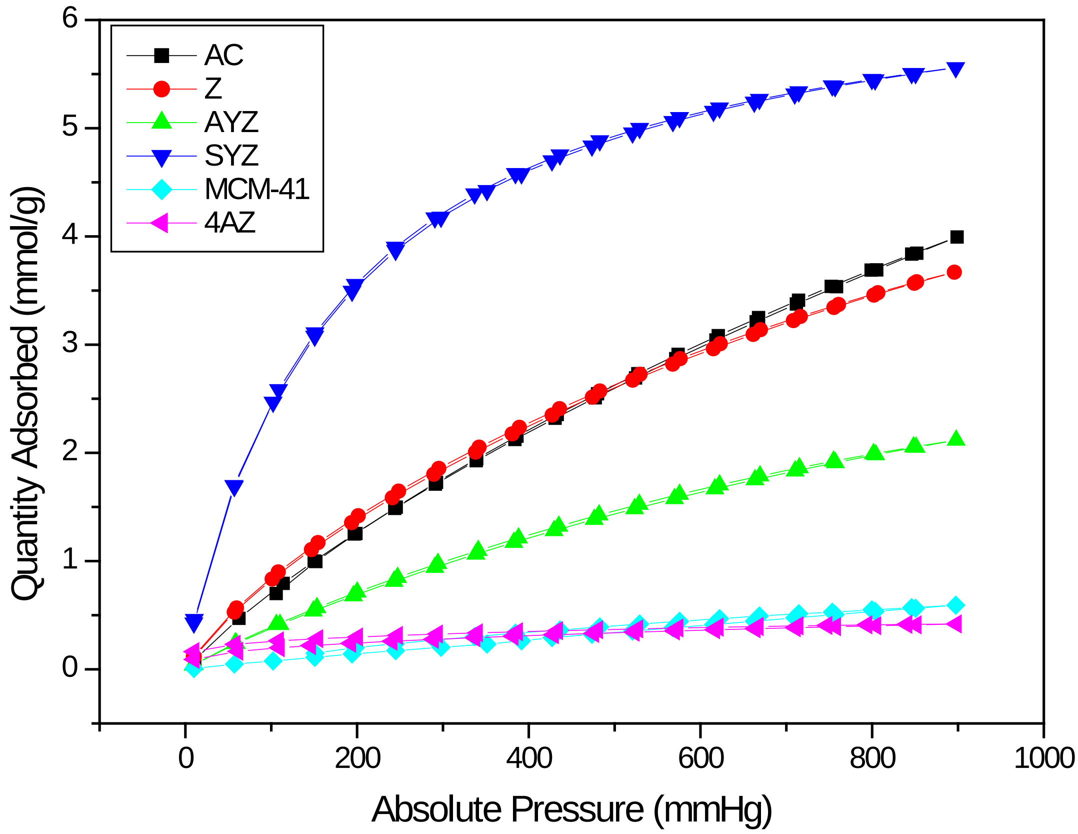

Figure 2. The adsorption-desorption isotherms of CO_2 on the porous samples.

The CO_2 adsorption capacities of these porous adsorbents are shown in Figure 3 and Table 2. The CO_2 adsorption capacities of the SYZ, AC, Z and AYZ were found as 19.657, 14.951, 13.905 and 8.524 wt %, respectively.

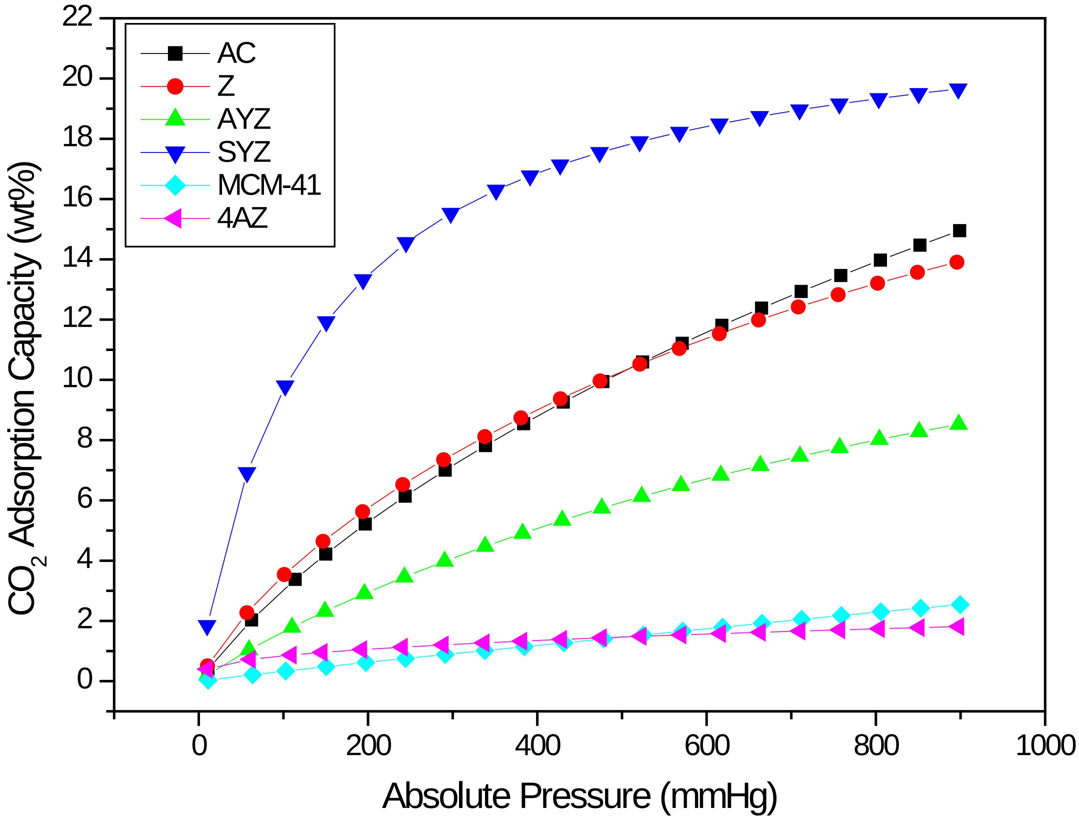

Figure 3. The CO_2 adsorption capacity (wt%) collected at 298 K for the AC, Z, AYZ, SYZ, MCM-41 and 4AZ.

The CO_2 adsorption capacities of the MCM-41and 4A zeolite were found as 2.540 and 1.811 wt %, respectively. The highest CO_2 adsorption capacities of 19.657 and 14.951 wt % were achieved with SYZ and AC, respectively. It could be confirmed that KOH activation plays an important role in determining the porous structure and amount of CO_2 adsorbed. A similar phenomenon was reported in previous studies (De Andres 2013; Boyjoo et al. 2017).

Table 2: CO_2 adsorption capacities (wt%) of porous adsorbents.

Adsorbents	CO_2 adsorption capacities (wt%)
AC	14.951
Z	13.905
AYZ	8.524
SYZ	19.657
MCM-41	2.540
4AZ	1.811

Conclusion

We have investigated the adsorption process for CO_2 on six typical adsorbent with different texture, surface area and porosity. The CO_2 adsorption capacities of the SYZ, AC, Z, AYZ, MCM-41 and 4AZ were found as 19.657, 14.951, 13.905, 8.524, 2.540 and 1.811 wt %, respectively. Microporous zeolites and AC showed higher CO2 adsorption capacities than the mesoporous MCM-41 and 4A zeolite. The CO_2 adsorption capacity of commercial 4A zeolite was found to be 1.811wt%, while CO_2 adsorption capacity of the KOH activated carbon (AC) was found to be 14.951wt%. This correspound to 8.26 times increase in the CO_2 adsorption capacity. The adsorption capacity of activated carbon sample obtained from carob stones for carbon dioxide was higher than the investigated four commercial porous adsorbents. It can be said that chemical activation plays an important role in determining the porous structure and amount of CO_2 adsorbed. This study revealed that carob stones based activated carbon can be used as a highly efficient and economically viable adsorbent for carbon dioxide adsorption.

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