



# CHARACTERIZATION OF 3A MOLECULAR SIEVE USING TRISTAR MICROMERITICS DEVICE

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**SUMMARY:** Equilibrium adsorption was studied for nitrogen and carbon dioxide on 3A molecular sieve zeolite at constant temperature by using a new advanced device, called TriStar Micromeritics. In this regard, TriStar II 3020 (licensed by Micromeritics Company) was used for characterizing the desired 3A molecular sieve. Results demonstrated that the BET isotherm was suitable for fitting equilibrium data of nitrogen adsorption on the 3A molecular sieve. But, Langmuir isotherm had no ability to predict the equilibrium data correctly. However, other isotherms such as Langmuir-Freundlich could be more useful and suitable to predict multilayer adsorption capability of zeolite 3A molecular sieve in nitrogen adsorption. The experiments also showed that 3A molecular sieve zeolite had more affinity with nitrogen than carbon dioxide at selected temperature which varies for each of them. Additionally, it was confirmed that there were extended macropore and mesopore distribution inside the shaped product to regulate the CO<sub>2</sub> adsorption of the 3A molecular sieve. Although general procedure for forming the powder of 3A molecular sieves has been reported, this research proposed burning organic materials to produce the extended macropores.

**Keywords:** 3A molecular sieve, Adsorption, TriStar II, Zeolite

## 1. INTRODUCTION

Various types of the adsorbents were used to remove or adsorb toxic and dangerous materials in oil, gas & petrochemical industries. Recent developments in the production and in the use of adsorbents have greatly increased the necessity of determining characteristics and dependable design procedures of them. In this regard, the molecular sieves are considered as one of the main adsorbent materials because they are porous solids containing channels and cavities with pore diameters in the range of 0.3-2.0 nm [1, 2].

There are different categories to classify the molecular sieves that they include different material types such as carbon molecular sieve (CMS), activated alumina, silica gel, zeolites, etc. Any of these sieves has unique application and feature due to its morphology and structure. For example, unlike activated alumina, silica gel, activated carbon, and carbon molecular sieves (characterized by pore size distributions), aluminosilicate (zeolites) and aluminophosphate molecular sieves possess a uniform pore size which is responsible for the sieving effect exerted on gaseous molecules on the basis of steric considerations [3]. Due to their compositional variety, uniform pore space, and structural symmetry, zeolites have high surface areas, and are able to sieve molecules based on size, shape, and internal physicochemical properties [2, 3].

A common classification of molecular sieves divides them into four categories based on pore size including 3A, 4A, 5A, and 13X. Researches show that 3A and 4A molecular sieves have analogous crystal structure, and demonstrate similarities in adsorptive capacity and selectivity [4, 5]. The characteristics of these molecular sieves include fast adsorption speed, frequent regeneration ability, good crushing resistance and pollution resistance. These features can improve both the efficiency and lifetime of the sieve. From the industrial viewpoint, 3A molecular sieves (with a pore size of three angstrom,



the smallest size currently available in the market) are the necessary desiccant in petroleum and chemical industries for oil refining, polymerization, and chemical gas-liquid depth drying [6].

It can be concluded that determination of adsorption rates is essential for the design of adsorption-based gas separation processes by molecular sieves. Adsorption rates of molecular sieves are generally limited due to the mass transfer occurring by a variety of possible mechanisms including micropore and macropore diffusion (ordinary diffusion, Knudsen diffusion or Poiseuille flow), transport across a surface barrier, and external mass transfer. As each of these mechanisms differs in its dynamic behavior, the study of adsorption rates includes both the identification of the mass transfer mechanisms and the measurement of relevant model parameters [7]. Therefore, by determining the molecular sieve characteristics, it is possible to design, simulate and model the adsorption units. By the consideration of this important capability, molecular sieves are extensively used in a wide variety of applications including catalysis, gas separation, and drying agents [8-10]. As pointed out by Chiou et al [9], 3A molecular sieve is made by substituting potassium cations for the inherent sodium ions of 4A structure. Since the pore size of the 3A sieve is very close to the critical diameter of a water molecule (2.65Å), it has a very strong affinity for the polar water molecule [9].

Surface area and porosity are important physical properties that influence the quality and utility of many materials and products. Therefore, it is critically important that these specifications can be accurately determined and controlled. In this work the innovative studies on 3A adsorbent carried out by using a TriStar II device (licensed by Micromeritics Company, United State) are presented. This device was installed and started up in Hengye Middle East production complex (Nitel Pars and Fateh group, Shiraz, Iran). The presented methodology in this research follows three main targets: 1. Measurements of adsorptive capacity of 3A molecular sieves, 2. Determination of the characteristics of 3A molecular sieve i.e. pore size distribution, surface area, porosity, etc., and 3. Investigation and introduction of the TriStar II 3020 as an important instrument for determining the properties and characteristics of adsorbent materials which are used in oil, gas and petrochemical industries.

## 2. EXPERIMENTAL OBSERVATIONS

### 2.1 Materials

The 3A molecular sieve in the form of beads with the approximate diameter of 2.5 mm (manufactured by Hengye Middle East, Shiraz, Iran) was used for this research. Some basic physical properties of zeolite 3A adsorbent are: equivalent particle diameter of 2.59 mm, bulk density of 800 kg/m<sup>3</sup>, crush strength of 52.7 N, attrition loss of 0.04 wt.%, moisture content at 550 °C (1hr) of 0.21 wt.%, and static water adsorption at 20 °C (RH=50%) of 20.14 wt.%.

### 2.2 Analysis and measurements

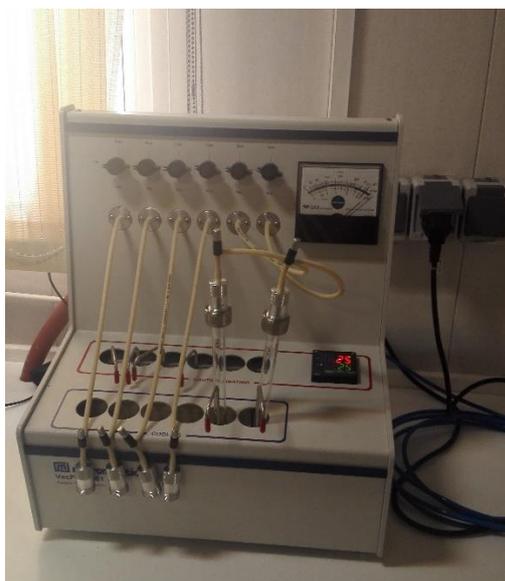
As mentioned earlier, the Micromeritics TriStar II 3020 was used to characterize 3A molecular sieve in N<sub>2</sub> and CO<sub>2</sub> adsorption process. This instrument (see Fig. 1) can be used for characterizing the micropores below 10 angstroms within 8 hours using nitrogen, argon, carbon dioxide, or other non-corrosive gases such as butane, methane, etc. The TriStar II 3020 is an automated gas adsorption analyzer with three ports allowing up to three samples to be analyzed simultaneously. Some benefits and features of this analyzer are as follows [11]:

- Surface areas as low as 0.01 m<sup>2</sup>/g can be measured using nitrogen and as low as 0.001 m<sup>2</sup>/g with the krypton option.
- Up to 1000 data points can be collected allowing the observation of minute details of the isotherm.
- Up to four analyzers can be operated with one computer.
- The system consists of the analyzer, an optional SmartPrep degasser for preparing samples, a vacuum pump, and a computer for entering analysis and report options.
- Isotherms from gas adsorption can be determined at specified temperature.
- User selectable data ranges through the graphic interface allows direct modeling for BET, t-plot, Langmuir, DFT, and interpretation.
- User-defined reporting options allow direct modeling.



Figure 1. Image of TriStar II 3020

To do the experiments, the 3A molecular sieve (about 0.359 mg) was firstly weighted. Then, this sample was placed in the sample tube (Fig. 2a), and consecutively, it was connected to the vacuum pump (Fig. 2b), which allowed degassing and achieving ultra-high vacuum. The sample tube was then placed, and nitrogen liquid (for N<sub>2</sub> adsorption) or water (for CO<sub>2</sub> adsorption) was applied to control the temperature (Fig. 3). After reaching equilibrium of the mass value, the isotherms were measured in the pressures up to ambient pressure.



(a)



(b)

Figure 2. (a) Sample tube of TriStar device (b) Vacuum pump



Figure 3. The sample compartment

### 3. MATHEMATICAL AND MODELING

The Langmuir isotherm is the simplest, and yet one of the most useful isotherms for both physical and chemical adsorption on porous solids [10]. The Langmuir isotherm is derived based on the concept of dynamic equilibrium between the rates of condensation (adsorption) and evaporation (desorption), as follows (Eq. 1):

$$\frac{q}{q_m} = \frac{BP_i}{1 + BP_i} \quad (1)$$

where  $q$  is the adsorbed phase ( $N_2$ ) concentration (mmol/g),  $q_m$  is the saturated adsorbed phase concentration (mmol/g),  $P_i$  is the partial pressure of the adsorbate (Pa), and  $B$  is the Langmuir adsorption constant.

In situations where the temperature is below the critical temperature of the adsorbate gas, the isotherms like the Langmuir cannot properly predict the adsorption rates [12]. In this case, there is a multi-layer of adsorbate buildup well before a complete monolayer is formed. To take into account this phenomenon, a two-parameter isotherm was developed by Brunauer, Emmett, and Teller (BET) which was essentially an extension of the Langmuir model for multi-layer adsorption [10,12]. It is assumed that the heat of adsorption beyond the first layer is constant and equals the heat of liquefaction. In addition, the ratio of the adsorption ( $\alpha$ ) and desorption ( $\beta$ ) constants is also assumed constant for layers beyond the first one. By summing over all layers, the BET equation is obtained as follows:

$$\frac{P}{q(P_0 - P)} = \frac{1}{q_m C} + \frac{C - 1}{q_m C} \left(\frac{P}{P_0}\right) \quad (2)$$

The values  $q_m$  and  $C$  (dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the molecular sieve sample) are determined experimentally, and are significant parameters affecting both adsorption capacity of zeolite adsorbents and adsorption process kinetics.

### 4. RESULTS AND DISCUSSION

The equilibrium adsorption of nitrogen vapor on zeolite 3A is presented in Fig. 4. According to these results, constants of BET adsorption isotherm were estimated. The comparison between the simulated equilibrium data points versus the actual values is demonstrated in Fig. 5.

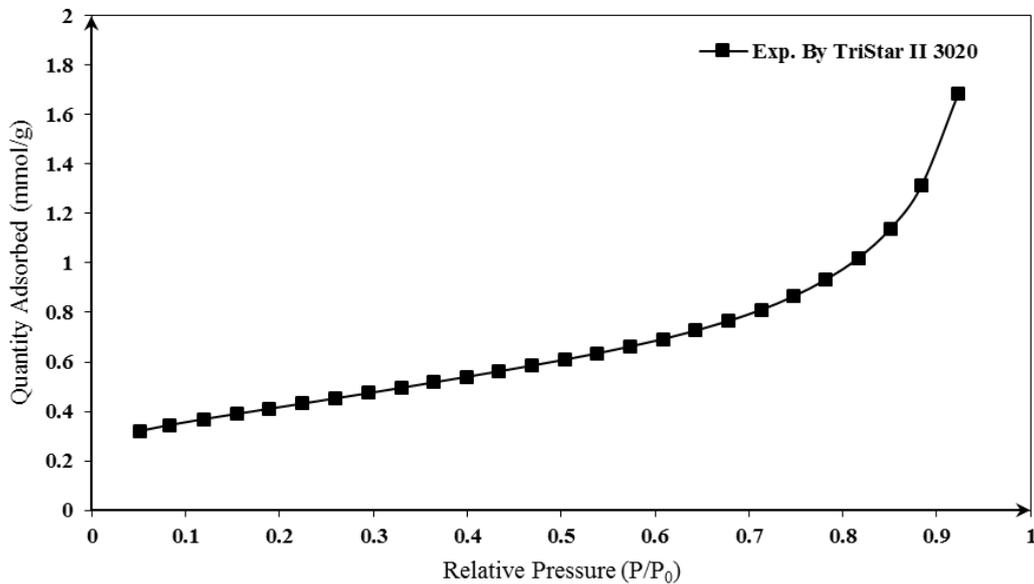


Figure 4. The equilibrium adsorption of nitrogen vapor on zeolite 3A at -195.85°C

As seen in Fig. 5, the BET isotherm can be fairly applied to fit equilibrium data of nitrogen adsorption on the 3A molecular sieve due to the type of isotherm plot obtained by TriStar II 3020 (Fig.4). Furthermore, it was found that Langmuir isotherm has no ability to predict the N<sub>2</sub> equilibrium data correctly. This procedure was also performed for CO<sub>2</sub> adsorption on the zeolite 3A molecular sieve at constant temperature (25°C). The main results obtained from the TriStar II 3020 such as surface area and saturated adsorbed phase concentration, for BET isotherm is presented in Table 1. It can be deduced that the other isotherms such as Langmuir-Freundlich can be more useful and suitable to predict multilayer adsorption capability of zeolite 3A molecular sieve in nitrogen adsorption, instead of Langmuir model.

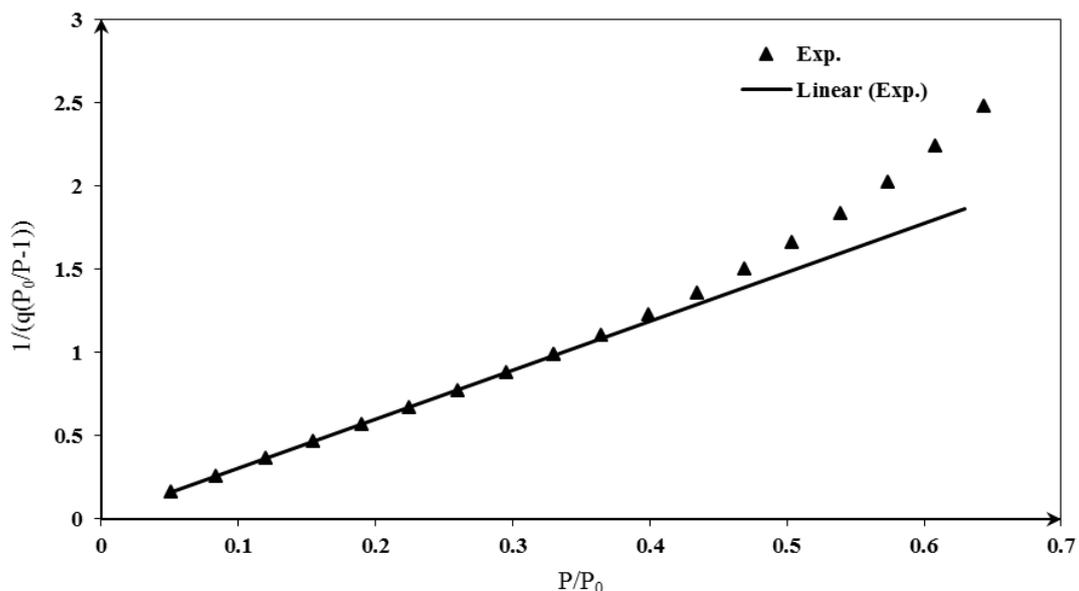


Figure 5. Fitted plot of BET adsorption isotherm for nitrogen on zeolite 3A molecular sieve at -195.85°C



**Table 1. Fitted and other constants of BET adsorption isotherm obtained by TriStar**

BET macropore surface area (m <sup>2</sup> /g)	Saturated adsorbed concentration (mmol/g)	Molecular cross-sectional area (nm <sup>2</sup> )	Dimensionless constant
33.2774	0.3411	0.162	158.597

The method of Barrett, Joyner, and Halenda (BJH) is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. It applies only to the mesopore and small macropore size range. The BJH calculation determines the mesopore volume/area distribution which accounts for both the change in adsorbate layer thickness and the liquid condensed in pore cores. Another capability of TriStar II 3020 is to generate pore size distribution using BJH method from adsorption and desorption data points. In this regard, the BJH calculation and cumulative pore volume of zeolite 3A molecular sieve is shown in Fig. 6. Furthermore, according to the CO<sub>2</sub> adsorption on the understudy 3A molecular sieve, 0.0368 weight percent of CO<sub>2</sub> at 258.4 mmHg absolute pressure was recorded (completely satisfying) whereas the 3A powder (before shaping) had shown about zero weight percent of adsorption.

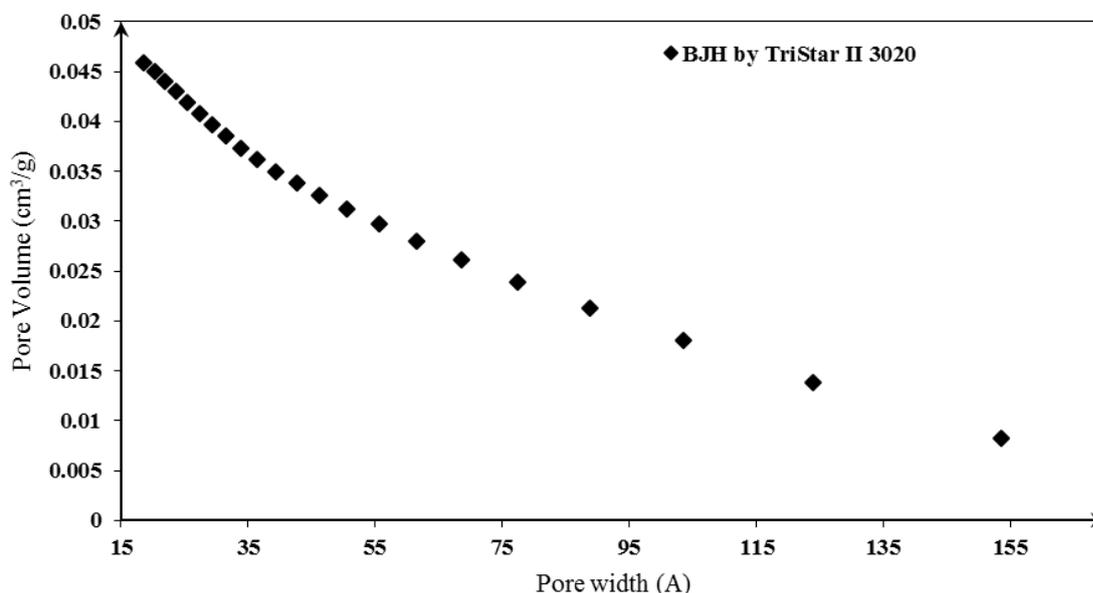


Figure 6. The BJH adsorption cumulative pore volume (cm<sup>3</sup>/g) obtained from TriStar II 3020

As seen from Fig.6, in addition to micropore size distribution, there are extended macropore and mesopore distribution inside the shaped product to regulate the CO<sub>2</sub> adsorption of the 3A molecular sieve. Although general procedure for forming the powder of 3A molecular sieves has been reported, the proprietary details not available even in patents remain secret. These include details of adding pore making agents (Porogen), water, binder and special additives [13]. Accordingly, method of pore control may be divided into three categories. The first is to regulate particle size which is primarily related to interparticle spacing. The second is to widen interparticle distance by decreasing surface tension by utilizing vapor pressure of water when heated. The third is to give pores by burning out or by leaching organic materials. In this research, the last option was chosen, and lignosulfonate (0.5-1 wt.% of final adsorbent) was added to produce the extended macropores. As previously mentioned, the low value of CO<sub>2</sub> adsorption (0.0368 weight percent of CO<sub>2</sub> at 258.4 mmHg absolute pressure) confirms the appropriate selection of pore making method.



## 5. CONCLUSIONS

The investigation and determination of molecular sieve characteristics and their adsorption properties are the most important effective factors which should be studied prior to any designing and manufacturing of adsorption systems. In this study, the experiments are performed by TriStar Micromeritics device which is a modern, and advanced new device playing a pivotal role in pre-adsorption processing. This device can be used in the laboratories related to oil, gas, petrochemical and pharmaceutical industries.

Results showed that the BET isotherm can be used to fit equilibrium data of nitrogen adsorption on the 3A molecular sieve whereas the Langmuir isotherm is not an appropriate model to estimate the equilibrium points. Moreover, Langmuir-Freundlich is suitable to predict multilayer adsorption capability of zeolite 3A molecular sieve in nitrogen adsorption.

Moreover, BJH calculations for pore size distributions confirm that the 3A molecular sieve has 0.0368 weight percent of CO<sub>2</sub> adsorption at 258.4 mmHg absolute pressure which is completely satisfying to be used as water adsorbent in industrial plants. It can be concluded that the method of making pores during manufacturing process (adding lignosulfonate) has been successful to produce extended macropores.

## 6. ACKNOWLEDGMENTS

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