Petroleum and Coal

SELECTION OF ADSORBENTS FOR DIFFERENT APPLICATIONS AND PROCESSES: A REVIEW

Sepehr Sadighi[1]*, Masood Sheikh Alivand[2], Morteza Faghihi[2]

[1] *Research Institute of Petroleum Industry (RIPI), Catalysis Technologies Development Division, P.O. Box 14665137, Tehran, Iran*
[2] *Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box 113659465, Tehran, Iran*

Abstract

Adsorption is one of the most sophisticated separation processes widely used in oil, gas and petrochemical facilities, and there is no doubt in the environmental and technological significant of this technology. But, the key to design an efficient adsorption service is to accurately select a suitable adsorbent that strongly dependent to the feed composition, product specification, and operating conditions. During the last 30 years, different classes of solid adsorbent have been manufactured; but, they should be meticulously chosen accordingly. In this paper, the specification and main characteristics of adsorbents generally used in oil, gas and petrochemical processes including activated alumina (AA), silica gel (SG), activated carbon (AC) and molecular sieves (MSs) are reviewed. Then, a novel adsorption selection diagram (ASD) is introduced to accurately choose adsorbents for various gas and liquid services. By using the proposed ASD, the suitable adsorbents are selected for some industrial plants to verify its validity.

Keywords: Adsorption; Adsorbent; Selection diagram; Molecular sieve.

1. Introduction

According to environmental legislation, mercaptanes, H_2S, CO_2 and water should be removed from effluent streams and fuel gas. Mercaptans are organic compounds with –SH in their structures which are corrosive, toxic and poisonous for the catalyst. Therefore, mercaptans content of fuels, especially for propane and butane is so significant [1]. H_2S is the main acid gas component which should be removed immediately because of its corrosion affinity. CO_2 and water are two main impurities that are the crucial cause for blockage in cryogenic systems. To reach these goals, absorption process is installed using different solvents such as amines for acid gas removal, glycol for dehydration and caustic for mercaptan removal. The main problems of these absorption processes are as follows:

(1) These solvents are pollutants of environment;
(2) In many cases, product stream should be purified at very stringent level which needs huge equipment and high circulation flow rate of solvent, and
(3) High capital and operating cost for a product with high purity is needed [2].

To tackle with these problems, adsorption processes are widely developed based on diffusing a specific molecule with low molecular diameter into the internal surface of adsorbent pores [3]. Due to the wide variety of molecules and demands for separation and purification, different types of synthetic adsorbents with spread pore diameters and physical properties are synthesized [4-5]. For a long time, adsorption process has been used as an effective method to remove impurities from gas and liquid streams in different services. Nowadays, different types of adsorbents are broadly used for various demands including bulk separation (such as hydrogen separation, nitrogen production and oxygen production) [6-9], and impurity removal application (such as dehydration, desulfurization, hydrogen purification, CO_2 and mercury removal) [10-15].

But, validated documents and knowledge for selection and application of various kinds of adsorbents are scarce. This vacuity promotes us innovate a method which can be applied as a comprehensive and trustworthy way for the selection of adsorbents for different services. In this paper, according to the literature and practical observations, a novel adsorption selection diagram (ASD) is proposed which is reliably used to choose suitable adsorbents for various gas and liquid services.

2. Adsorbents

Two traditional shape form of adsorbents are extrudate (such as pellet or granule) and spherical (bead type). Spherical adsorbents have some benefits compared to extrudate adsorbents including:
- Lower pressure drop (in the same range of mesh size) [16]
- Higher attrition resistance.
- Better particle flow performance.

According to the pore size, three main categories are classified as follows [17]:
- Macropore (> 500 Å) to improve molecules diffusion into the pores.
- Mesopore (20- 500 Å) that is filled with medium size molecules.
- Micropore (< 20 Å) to accommodate small molecules like water.

Almost similar ranges for these definitions can be found in other references [18]. Among commercial adsorbents, activated alumina (AA), silica gel (SG), molecular sieve (MS) and activated carbon (AC) are widely used in gas, petrochemical and refining industries.

2.1. Activated alumina

Alumina is one of a popular adsorbent due to its high mechanical strength and thermal stability [19-20]. This material is a hydrated form of aluminum oxide (Al_2O_3), and in natural state is called Bauxite [21]. But, the commercial AA adsorbent is generally manufactured by the following steps:
1. Aluminum tri-hydroxide ($Al(OH)_3$) is thermally decomposed at a temperature about 400°C to partially dehydrate alumina.
2. The activated powder is bonded using water to form desired size and shape such as spheres or granules [22-23].
3. The formed particles are thermally treated to produce the final products [16].

The typical chemical composition and physical properties of AA are shown in Tables 1 and 2, respectively.

Table 1. Typical chemical compositions of AA [16]

Chemical	Composition (wt.%)
SiO_2	0.02
Fe_2O_3	0.02
Na_2O	0.36
LOI (Loss on ignition)	6.0
Al_2O_3	93.6

Table 2. Typical physical properties of AA [16]

Physical properties	Value
Surface area (m^2/g)	320-360
Pore volume (cm^3/g)	0.4-0.5
Bulk density (kg/m^3)	770-840
Crush strength (N)	140-320
Static sorption at 60% RH (%)	20-22

Adsorption of molecules on AA surface is done through chemisorption, physisorption and capillary condensation. Chemisorption is occurred through the reaction between water molecules with aluminum oxide surface sites (single layer). Then, physisorption is promoted by hydrogen bonding (Van der Waals' forces), forming multiple layers in alumina pores. Finally, multi-layers of water grow by capillary condensation [24].

2.2. Silica gel

Silica gel (SG) mainly consists of silicon dioxide (SiO_2) with a representative formula of $SiO_2.nH_2O$, and it is manufactured in the forms of powder, granule, and spherical beads in different sizes [25]. There are more than 25 types of SG that has specific and unique adsorption characteristics. Generally, common SGs can adsorb moisture up to 40% [26-27].

SG is produced by reacting of sodium silicate with sulfuric acid. The produced material is called hydrogel which is washed to remove sodium sulfate. Then, hydrogel is dried to produce the commercial SG, a porous adsorbent with high surface area (approximately 700-800 m^2/g), and it adsorbs polar molecules such as water [25]. The low concentration of alumina in SG merits low catalytic activity to this adsorbent [28]. This feature is desirable in adsorption of hydrocarbon streams due to minimization of coke formation of cracked hydrocarbons during regeneration [29].

Two main commercial types of SGs widely used in gas dehydration process are Sorbead R and W. The Sorbead R has higher activity than the Sorbead W adsorbent, and it is used for removal of heavy hydrocarbons from natural gas stream. Sorbead W can persist against water droplets [16], and it is appropriate for dehydration services. Typical chemical analysis of commercial SG is shown in Table 3.

Table 3. Typical chemical composition of commercial SG [16]

Chemical element	Content (wt. %)
SiO_2	99.71
Fe_2O_3	0.03
Al_2O_3	0.10
TiO_2	0.09
Na_2O	0.02
CaO	0.01
ZrO_2	0.01
Other elements	0.03

2.3. Molecular sieve

Molecular sieves (MS) can be categorized as an extensively applied adsorbents which are used in petrochemical industries from the past three decades. The main portion of MS contains zeolite powder and other parts consist of binder and some additives.

MS has the large surface area with specific uniform pore dimensions among the solid adsorbents. Additionally, it can separate molecules, based on its uniform pores. Moreover, MS is a crystalline material with positive and negative charges which traps polar molecules into its pores. Due to distribution of charges, an electrostatic attraction for polar molecules such as water is available in its structure [30].

Additionally, MS has some better properties compared to AA and SG such as uniform pore size, high adsorption capacity and high affinity for un-saturated and polar components. Zeolites are stable in the pH range of 5-12. Up to now, more than 150 different types of zeolite structures have been discovered but only two synthetic types are used in conventional applications including zeolite A and Faujasite (or Zeolite X) [31-32].

2.3.1. Zeolite A

Pores of zeolite A are restricted by 8-membered oxygen rings (Figure 1a). This type has a crystalline structure with intra-crystalline voids where adsorption takes place. Zeolite A group consists of 3 conventional MS including 3A, 4A and 5A. The former is synthesized by replacing a large fraction of the sodium ions (approximately 75%) with potassium reducing its pore sizes to about 3 Å. This type is used for dehydration of streams such as natural gas, olefins and high polar alcohols. The equilibrium adsorption capacity of 3A zeolite at a given water vapor pressure increases by increasing K^+/Na^+ molar ratio; but, the opposite effect is reported by closing the vapor pressure to infinity [33]. 4A is sodium form of the MS which has the pore diameter of 4 Å. This type of MS is most common adsorbent for dehydration of air and paraffin streams. Compared to 3A type, 4A is cheaper and has more adsorption capacity. 5A (with approximately 5 Å openings) is formed when 75% of Na ions are exchanged with Ca ones, and is used to remove large molecules such as H_2S, CO_2, and light mercaptans [34-35].

2.3.2. Faujasite

In this framework, silicate-aluminate minerals pores are restricted by 12-membered oxygen rings (Figure 1b). Depending on the silica-to-alumina ratio, faujasite zeolites are divided into X and Y zeolites. In X zeolites, ratio is between 2 and 3, while in Y zeolites, it is 3 or higher. The former has different internal characteristics, especially crystalline structure compared to A type zeolites. The crystal structure of X type zeolite is built up by arranging the basic sodalite cages in a tetrahedral stacking (diamond structure) with bridging across the six-member oxygen atom ring. These rings provide opening pores with 9-10 Å in diameter [36-37].

Zeolite X can adsorb all molecules adsorbed by A type MS, and also it has higher adsorption capacity. 13X and 10X are two kinds of X type zeolite. 13X zeolite has pores with the diameter of 10 Å which consists Na ions. While 10X zeolite is produced from 13X by exchanging about 75% of Na ions with Ca ions [16]. In Figure 1, the structures of zeolite A and X types are shown.

(a) Structure of Zeolite A   (b) Structure of Zeolite X
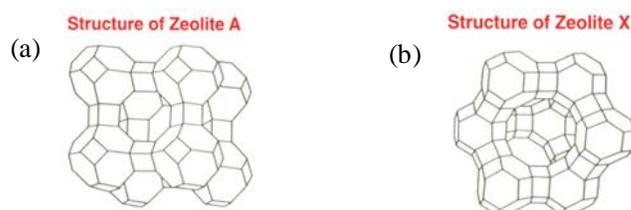
Figure 1. The structure of zeolite A and X type

Typical properties of 3A, 4A, 5A and 13X MSs are shown in Table 4. As seen, zeolite 4A is a general purpose adsorbent, and can uptake most typical molecules while H_2O capacity of 13X is the greatest among the others.

Table 4. Typical chemical composition of commercial MS [16]

Type of zeolite	Nominal pore diameter (Å)	Bulk density (g/cm^3)	H_2O capacity (wt.%)	Typical molecules adsorbed	Molecules excluded	Typical application
3A	3	0.75	20	H_2O, NH_3	Ethane and larger	Dehydration of unsaturated hydrocarbons
4A	4	0.72	22	H_2S, CO_2, SO_2, C_2H_4, C_2H_6, C_3H_6	Propane and larger	Static desiccant in refrigeration systems, drying saturated hydrocarbons
5A	5	0.69	21.5	n-C_4H_9OH	Iso-compounds, 4-carbons rings and larger	Separation of n-paraffins from branched and cyclic hydrocarbons
13X	10	0.61	28.5	Di-n-propyl-amine	$(C_4F_9)_3N$ and larger	Co-adsorption of H_2O, H_2S and CO_2

2.4. Activated carbon

Activated carbon (AC) is a highly porous material which is created by burning a suitable source in the absence of oxygen. Bituminous coal, lignite coal or coconut shell are the most common bases for AC manufacturing [38-39]. AC has wide applications in different industries such as oil and gas refineries, and petrochemical complexes [40]. Despite inorganic chemicals, AC can appreciably attract organic chemical compounds from vapor and liquid streams. Generally, there are a variety of ways to produce AC. But, here the most populated method is described. At first, the base material is heated to 900°C in the absence of oxygen. Therefore, nitrogen and argon are injected into the vessel. Then, the temperature increases up to 1200°C, and the product is exposed to steam and oxygen for final pore formation [41-42].

3. Adsorption and regeneration processes

Adsorption process is a continuous operation consisting two main steps:
1. Adsorption cycle in which one or more components is adsorbed.
2. Regeneration cycle in which adsorbed components are separated from adsorbent [13].

3.1. Adsorption cycle
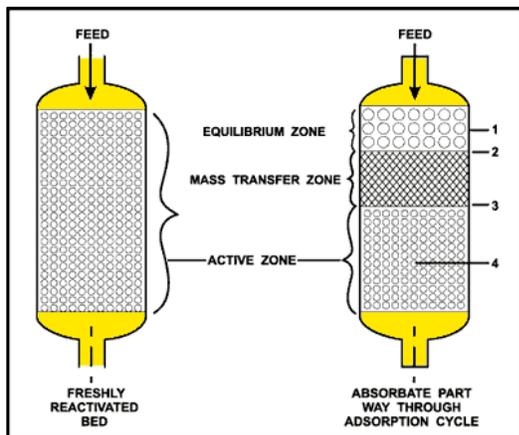
Figure 2. Three zones of an adsorption vessel during adsorption step

In this cycle, first of all, the vessel is filled with fresh adsorbents, and then the feed enters the vessel. Adsorption of molecules (adsorbate) on the adsorbents can be done due to various parameters such as size, polarity or charge of adsorbate. There are three zones in an adsorption tower including mass transfer zone (MTZ), saturated (equilibrium) and active zones (see Figure 2) [43]. The adsorption of adsorbate molecules is done in the MTZ. Length of that depends on some parameters such as fluid superficial velocity, inlet and outlet concentration, temperature etc. MTZ can be extended from few centimeters to several meters [44-45]. In the saturated zone, adsorbents are saturated with adsorbate and no more adsorption takes place whereas the adsorption is not yet occurred in the active zone.

3.2. Regeneration cycle

Regeneration can be done based on two different methods i.e. temperature swing adsorption (TSA) and pressure swing adsorption (PSA). In gas services, there are two main branches: bulk separation and impurity removal. When impurity content is more than 10%, the adsorption process is called bulk separation. When impurity content is less than this level, the process for separation is recognized as impurity removal. For the latter, TSA process is favored to remove impurities while PSA is utilized for bulk separation [46].

3.2.1. TSA regeneration

TSA is the most common method for regeneration of adsorption bed, and is used when a product with high purity is needed. In this method, at first, the gas stream is passed through a heater. The regeneration temperature is generally between 200°C and 300°C. This hot gas stream increases the vessel temperature, and separates adsorbate from adsorbent. The increase in gas stream temperature is done stepwise with an intermediate heating to prevent destructive effects such as reflux, coke formation and thermal damaging [13]. After this stage, the vessel is cooled by a stream having a temperature the same as the feed. In the adsorption process, a vessel adsorbs impurities, and simultaneously the other one is in the regeneration mode. Generally, heating time is around 60-65% of total regeneration step, and remaining time is used for valve switching, depressurizing and cooling [47].

3.2.2. PSA regeneration

PSA is primarily used for the bulk separation. In this method, adsorbents are regenerated by decreasing the vessel pressure. In the same condition and equal adsorption capacity, time of TSA process is longer than that of PSA one. Regeneration of adsorbent particles is not completely performed in PSA compared to TSA. This partially regeneration of adsorbents in PSA leads to sooner breakthrough in adsorption cycle and leads to shorter adsorption time [46-47].

4. Selection of adsorbents

Adsorption process can be applied into two main groups including gas and liquid services as follows:

4.1. Gas services

Adsorption process can be accomplished for separation and purification of gas streams in different services such as:

- Natural gas dehydration
- Olefin dehydration
- Mercury removal from natural gas
- Air drying

- Air purification
- Air separation
- Natural gas desulfurization
- Hydrogen separation and purification

4.1.1. Natural gas dehydration

Most of natural gas streams have water as an impurity at least in ppm value. But, the gas stream leaving amine or caustic wash units is saturated with water which should be removed from gas streams because of the following reasons [48]:

- Reducing corrosion and eliminate blockage by hydrate formation.
- Preventing water condensation in pipeline.
- Decreasing gas volume and increasing heating value.
- Controlling water content and dew point of gas stream.
- Preventing hydrate formation in the cryogenic units.

Commercial adsorbents such as SG, AA and MS can be used for gas dehydration process. The adsorbent selection for gas dehydration depends on various parameters. The most signify-cant ones are as follows:

- Water content and dew point of product stream.
- Feed composition.

- Temperature of regeneration gas.
- Cost.

4.1.2. Water content and dew point of product stream

The most important factor for choosing adsorbent in gas dehydration plant is water content and the required dew point of the product. Abilities of different adsorbents to provide minimum dew point and water content of product in gas dehydration plants are shown in Figure 3. As seen, MS can provide minimum dew point and water content compared to SG and AA which is attributed to crystalline structure of MS. Therefore, if the dehydration unit is designed to prepare a feed for cryogenic process, and a complete water removal is needed, MS is the best option for adsorbing purposes [49-50].
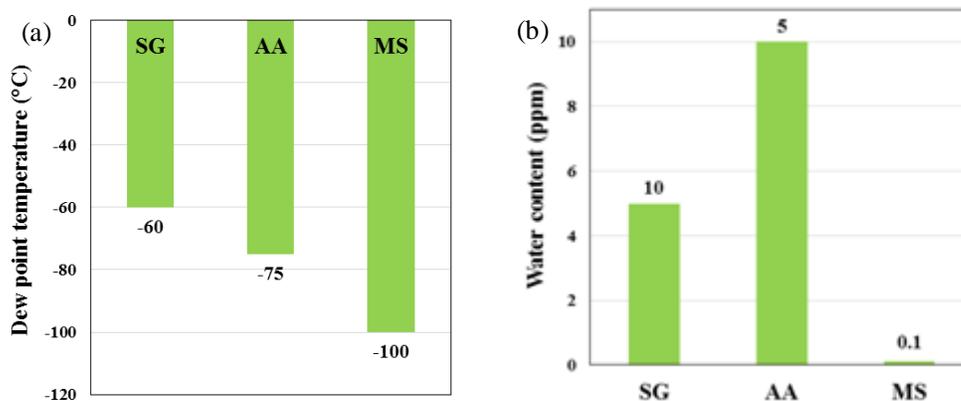
Figure 3. The abilities of SG, AA and MS adsorbents to decrease a) dew point temperature and b) water content of natural gas stream [19]

4.1.3. Feed composition

Another significant factor for adsorbent selection in a gas dehydration plant is the composition of feed. This factor is severely important for choosing different types of MS adsorbents. If the feed stream contains a lot of CO_2 and H_2S, 3A type should be selected for gas dehydration. In such streams, CO_2 can react with H_2S and produce COS which is called COS formation. 3A type has smaller pores, and consequently, CO_2 and H_2S molecules cannot enter to its micro

pores. Moreover, catalytic activity of MS can accelerate this phenomenon. Therefore, the modification of MS to reduce its catalytic activity creates more hindrance for COS formation. Some special grades of 3A type are recommended for cases in which COS formation may be a problem [16].

4.1.4. Temperature of the regeneration gas

Typical regeneration temperature for SG, AA and MS (3A and 4A type) are displayed in Table 5. The lower water content of the product needs the higher regeneration temperature. As seen in this table, the regeneration temperature for MS is higher than SG and also AA adsorbents [11]. Nowadays, MS manufacturers propose to use 3A type because of its lower regeneration temperature that reduces energy consumption. Of course, this lower temperature for regeneration needs more regeneration flowrate or regeneration time.

Table 5. Typical regeneration temperature of SG, AA and MS [16]

| SG | AA | MS | |
		3A	4A
190°C	160°C -220°C	220°C	290°C

4.1.5. Cost

Among common adsorbents i.e. SG, AA and MS, the latter is the most expensive one due to providing lowest dew point, working at higher operating temperature and having more adsorption capacity. AA is the least expensive adsorbent. However, it has lower adsorption capacity. Therefore, the capital cost due to requiring a larger vessel increases. 4A is cheaper than 3A due to additional process required for 3A production i.e. ion exchange process.

4.1.6. Olefin dehydration

Olefin dehydration is one of challenging adsorption processes in industrial plants. In an olefin stream, due to presence of unsaturated hydrocarbons, polymerization reactions are susceptible to be occurred. These reactions can be promoted on the surface of adsorbents, especially during the regeneration cycle where higher operation temperature is existed. The formed oligomer inside the pores of the molecular sieve is called green oil [51]. Therefore, in the dehydration of such streams, minimizing co-adsorption phenomenon is a crucial factor. To achieve this goal, some modifications are done on the produced MS. Some MS manufacturers have supplied special type of 3A MS which mostly prevents co-adsorption of unsaturated hydrocarbons such as cracked gas, ethylene and propylene. Also, modifying MS by using special type of binder minimizes the coke formation on the surface of adsorbents [52].

4.1.7. Mercury removal from natural gas

The presence of mercury in the gas stream causes many problems such as amalgam formation, environmental pollutions and catalyst poisoning. There are two major types of adsorbents that can be used in the mercury removal of natural gas units i.e. sulfur impregnated AC and silver impregnated MS. In sulfur impregnated AC, the mercury reacts with the sulfur to form a stable compound on the adsorbent surface. Hence, this adsorbent cannot be regenerated. Similarly, in MS with silver, chemisorption of mercury is occurred on the surface of adsorbents. In this type of adsorbents, both gas dehydration and mercury removal are carried out, simultaneously. The impregnated AC is preferred due to its lower cost [53].

4.1.8. Air separation

Air separation process is aimed for nitrogen or oxygen production. Nowadays, two methods are generally used for air separation i.e. adsorption and cryogenic distillation. Adsorption in air separation process includes vacuum pressure swing adsorption (VPSA) and PSA. The former is widely used for high volume pure oxygen production (300-10,000 Nm^3/h), and PSA is utilized for low volume pure oxygen (50-500 Nm^3/h). There are two types of adsorbent for air

separation i.e. 13X and carbon molecular sieve (CMS). The former adsorbs nitrogen and produces oxygen. In despite of 13X, CMS adsorbs oxygen and produce pure nitrogen [54].

4.1.9. Air purification

The main application of this process is pre-purification of air before cryogenic distillation columns in which oxygen and nitrogen are produced. Presence of impurities, especially H_2O and CO_2 can intensify freezing phenomenon at distillation column [55-56].

Different types of adsorbents can be used in an air purification. AA can be utilized for the production of instrument air with acceptable water content while for deep dehydration and high purification processes, MS should be used. 13X type is generally used for dehydration and purification, simultaneously. 4A and 5A types are just used for especial cases such as existing heavy component in air stream to decrease co-adsorption phenomenon.

4.1.10. Natural gas desulfurization

Different types of sulfur compounds such as H_2S, COS, CS_2 and mercaptans should be removed from natural gas in natural gas liquid (NGL) units. Burning of these sulfur compounds can cause air pollution and also create acidic rains. Consequently, deep sulfur removal with MS is favored in natural gas refineries because other sulfur removal methods do not have enough ability for deep removal of sulfur species [57]. Although, all A types of MSs can adsorb H_2S. But, 13X has more tendency to adsorb this compound from gas stream. For removing light and heavy mercaptans, 5A and 13X MSx can be used, respectively. Although, 13X type is also preferred for removing other organic sulfur components such as COS and CS_2, and it has higher capacity for adsorbing CO_2 in comparison to 5A type [58].

4.1.11. Hydrogen separation and purification

Hydrogen is one of the important feedstock in industries. Thus, the separation of hydrogen from other streams and purify this component is so important. Due to low polarity of hydrogen, PSA process is appreciably used with different types of adsorbents for hydrogen purification. For this purpose, different types of adsorbents have been recommended such as especial type of AC, SG and MS (5A type is the most common type and it has high selectivity for H_2 even at low temperatures [59]. In most cases, these adsorbents are simultaneously loaded in a multi-layer arrangement. AC generally consists of macropore and mesopore, and can adsorb large molecules. Therefore, it reduces the load of impurities on MS layer. Also, AC can be regenerated easier than MS. It can be concluded that multi-layer arrangement is the best design for hydrogen separation and purification.

4.2 Liquid services

In addition to gas services, adsorption is also used in liquid services. In such a way, purification is carried out in different services such as:

- NGL sweetening and dehydration
- Ethanol dehydration
- Methanol guard bed in polypropylene services
- Separation of iso-normal butane
- Separation of xylenes
- Heavy hydrocarbon removal from amine streams

Liquid services differ in some aspects compared to gas services. The mass transfer resistance of liquid film is greater than that of gas film. To overcome higher mass transfer resistance, contact time in liquid services should be more than gas services which is obtained by increase in adsorption bed height or reduction in stream velocity. The typical liquid velocity in adsorption process is around 0.1-1 m/min which creates turbulent flow in the adsorption bed [60-61].

4.2.1. NGL sweetening and dehydration

MSs are suitable candidates for NGL services. In NGL dehydration, 4A is a proper choice as an adsorbent. While in simultaneous sweetening and dehydration of NGL, 5A and 13X are the most suitable adsorbents. In addition to water, there are other impurities such as methyl and

ethyl mercaptan, COS, CS$_2$, CO$_2$ and H$_2$S. 13X has a high adsorption capacity, and can uptake all mentioned impurities. Consequently, this type can be used in sweetening and dehydration of NGL units. Some MS manufacturers proposed a configuration composed of 13X and 5A MS layers to decrease loading on the 13X, and increase adsorbents lifetime.

4.2.2. Ethanol dehydration

MSs are currently used in many ethanol dehydration plants to produce purified alcohol from a mixture of ethanol/water. The purity of ethanol can be increased up to 95% by using a usual distillation column. Due to the azoetrope of water and methanol, distillation column cannot adequately purify ethanol. For higher purification of ethanol, two methods can be utilized i.e. azeotropic distillation (with additional benzene solvent) and adsorption. Ethanol dehydration by adsorption process is a particular process and can be used for especial applications such as pharmaceutical purposes [62-63].

Water and ethanol are highly polar compounds, and they can be adsorbed by MS. Therefore, this separation should be done based on difference in molecular size. The molecular diameters of water and ethanol are 2.8Å and 4.4Å, respectively. Thus, 3A is a good candidate for ethanol dehydration. Due to the pore size of 3A, water adsorption capacity of that is about 18-20 wt% in this process [64].

4.2.3. Methanol guard bed in polypropylene services

The feed of polymerization reactor contains trace of impurities such as water, methanol, COS, CO, CO$_2$ and mercaptanes which can poison the polymerization catalyst, and reduce the yield of polypropylene production. Consequently, MS is used as guard bed to remove impurities from propylene stream [65-66]. Physical properties of impurities existed in propylene stream are shown In Table 6.

Table 6. Physical properties of impurity in propylene stream [65]

Molecule	Polarity	Hydrogen bond	Diameter (Å)
Water	Polar	Applicable	Less than 3
CO	Medium polarity	Not applicable	Less than 4
CO$_2$	Medium polarity	Not applicable	Less than 4
Methanol	Polar	Applicable	Less than 4
COS	Weak polarity	Not applicable	Less than 5

With respect to the size and polarity of these impurities, a multi-layer bed composed of 5A and 13X MSs can be the best choice.

4.2.4. Separation of iso-normal paraffin

Isomerization reaction is carried out in a catalytic reactor converting normal paraffin, especially n-pentane to isomeric paraffin, preferably iso-pentane. This conversion increases octane number of product; but, the maximum conversion is about 85%. Therefore, normal paraffin should be separated from product stream and recycled to the isomerization reactor. For this purpose, PSA system with MS is used. In this process, 5A type is used to adsorb n-Pentane which enhances octane number of gasoline [67].

4.2.5. Separation of xylenes

Xylene is an aromatic compound with single ring and two methyl groups. According to different methyl positions, xylenes are categorized to three isomers i.e. o-xylene, m-xylene and p-xylene. Because of the similarity of chemical and physical properties of xylene isomers, xylene separation with high purity is difficult. P-xylene is the most useful xylene isomer. Hence, other xylene isomers are usually converted to p-xylene. In the next step, the separation of p-xylene from others is accomplished by using a special barium type MS which is called

BaX. In this adsorbent, sodium cations of zeolite adsorbents (NaX) are exchanged with barium cations [68]. The research showed that the diffusivity of xylene molecule is much higher in BaX than that of NaX. The para-isomer diffuses about three times faster than the meta-isomer in BaX [69].

4.2.6. Heavy hydrocarbon removal from amine streams

Amine package is one of the most practical systems in oil and gas industries used for sweetening applications. All amine packages consist of absorption and regeneration columns in which absorbed components in the absorption column should be removed at the regeneration step. Due to weak desorption of hydrocarbons from amine solvent, the regenerated amine (called rich amine) is passed through an AC bed to prevent accumulation of hydrocarbons.

5. Adsorbent selection diagram (ASD)

Despite of using various types of adsorbents in gas, oil and petrochemical plants, there is not any practical route for choosing suitable adsorbent. To solve this problem, based on wide investigations and real experiences, adsorption selection diagrams (ASD) are presented in Figures 4 to 7.

These diagrams are divided into two main branches, i.e. gas and liquid services. Bulk separation for gas and liquid services are demonstrated in Figure 4. Then, Figure 5 illustrates impurity removal for gas services. Impurity removal for dehydration of paraffin and inert gases are shown in Figure 6. Additionally, Figure 7 shows the impurity removal for liquid services.
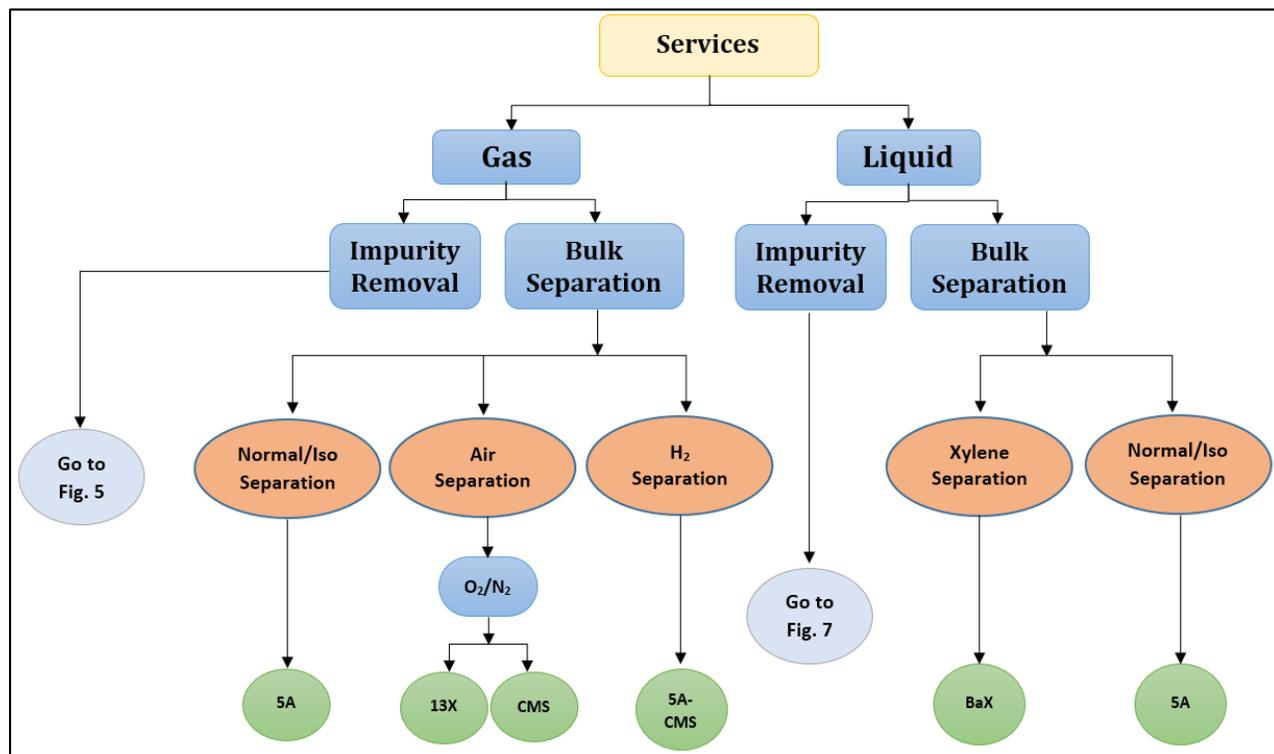
Figure 4. The adsorbent selection diagram (part 1)
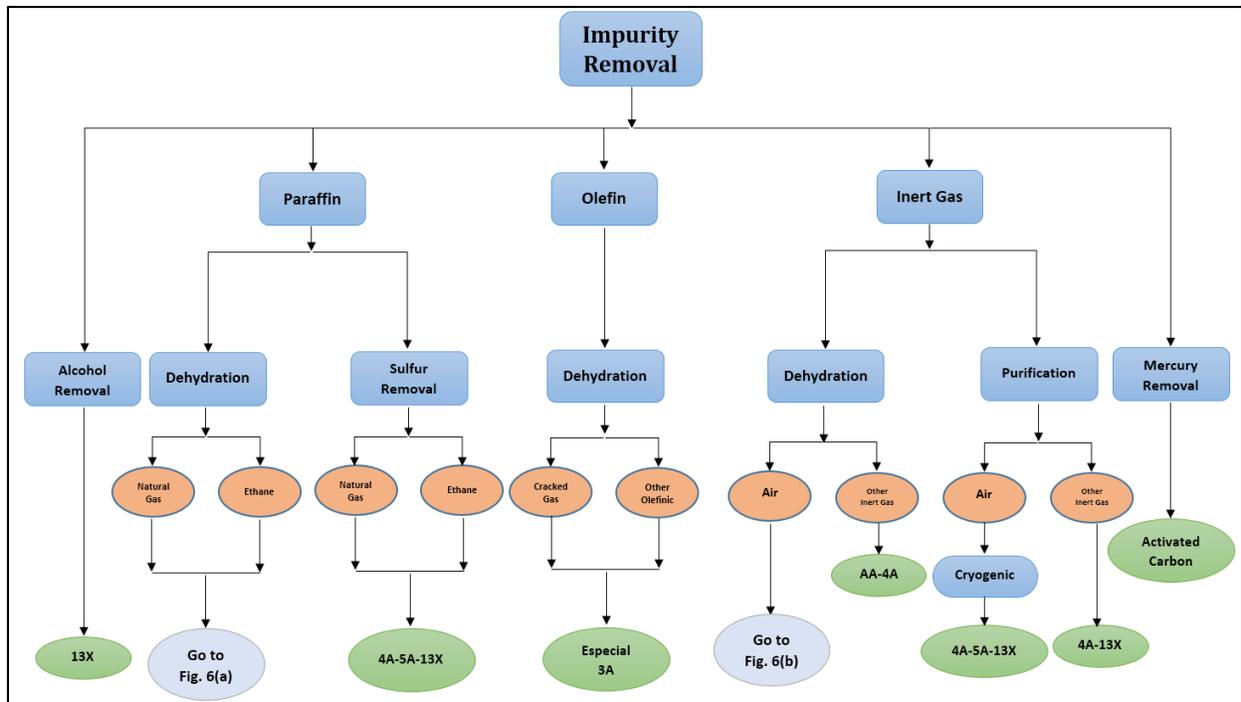
Figure 5. The adsorbent selection diagram (part 2)
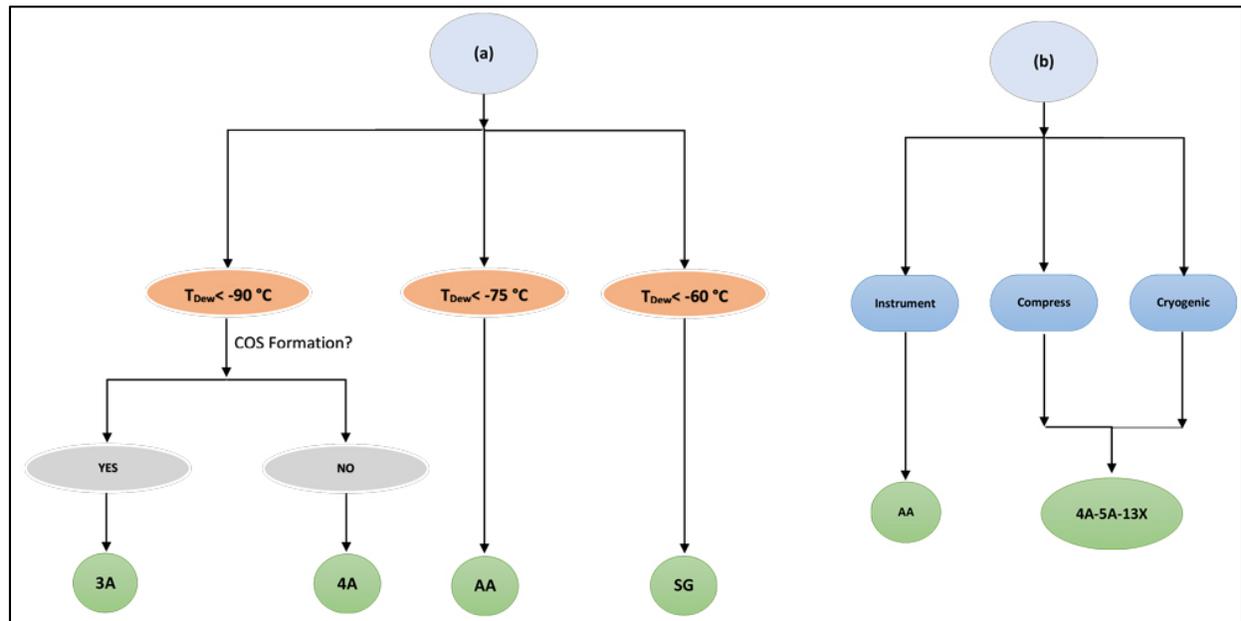
Figure 6. The adsorbent selection diagram (part 3)
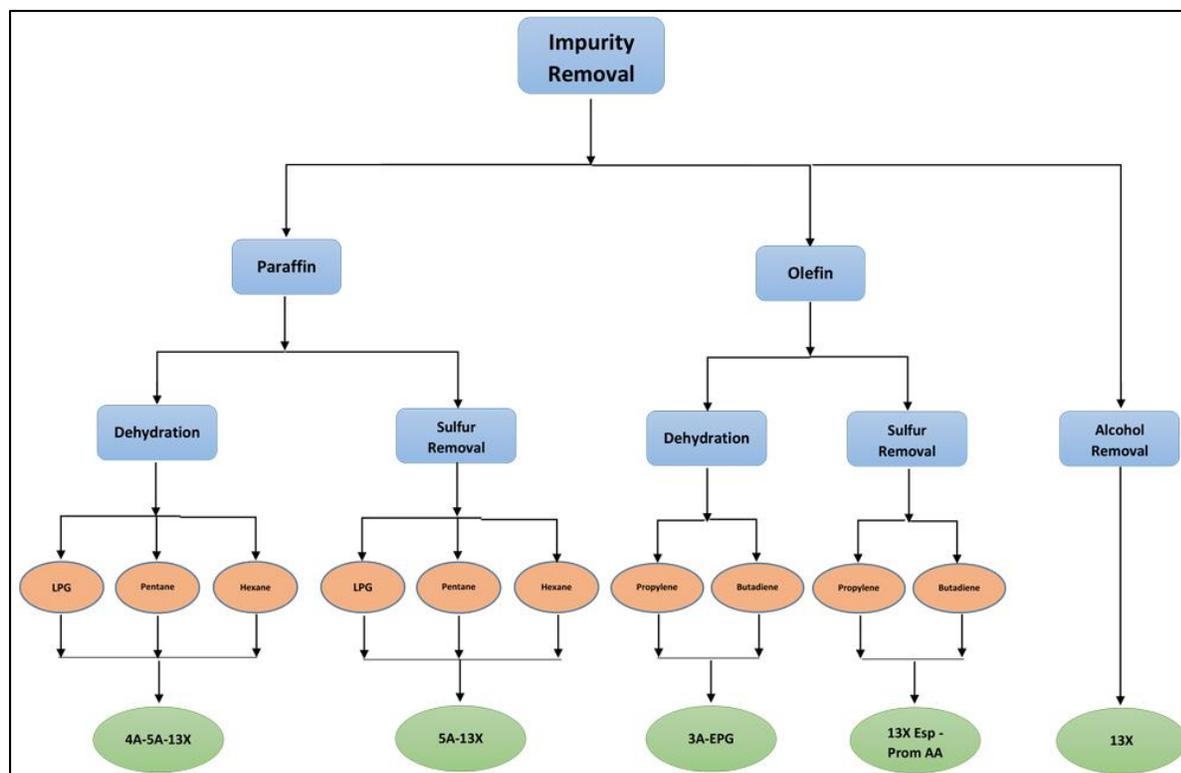
Figure 7. The adsorbent selection diagram (part 4)

6. Some case studies for adsorption units

6.1. Case study 1: Dehydration of isomerization feed

In the isomerization unit, there are two main feed streams including naphtha and hydrogen. In Table 7, specifications of these streams are shown. In this plant, an adsorption process is utilized to dehydrate both streams.

Table 7. Specifications of isomerization feed

Feed	Property		Unit	Value
Naphtha	Flow Rate		kg/h	233 854
	Pressure		bar	11
	Temperature		°C	38
	Composition	Paraffin	Mole fraction	0.99
		H_2O	ppm	276
Hydrogen	Flow Rate		kg/h	4 200
	Pressure		bar	38
	Temperature		°C	38
	Composition	H_2	Mole fraction	0.9
		Light hydro-carbons	Mole fraction	0.1
		H_2O	ppm	1 700

Because water is the poison for isomerization catalyst, feed dehydration should be completely accomplished. Therefore, a MS bed is used to dehydrate the normal paraffin stream. According to ASD (Figure 7), 4A, 5A and 13X types can be selected. But, 4A type is the best choice due to preventing co-adsorption of heavier hydrocarbons.

Hydrogen is the other feed of isomerization unit. According to ASD (Figure 5), for dehydration of an inert gas stream both of 4A MS and AA can be used. Due to the sensitivity of catalyst

to water, deep dehydration is necessary. Thus, 4A type should be selected as the main adsorbent. Moreover, a thin layer of AA (guard bed) is used to prevent liquid carry over to the MS layer.

6.2. Case study 2: C_2^+ polishing unit

In polishing unit, impurities such as sulfur and water should be removed from feed stream. The product specifications assigned for C_2^+ polishing unit are as follows:
- Total organic sulfur content is less than 20 ppm.
- Total hydrogen sulfide and carbonyl sulfide content is less than 7ppm.
- Total C_1 and C_2 mercaptan contents are less than 1 ppm.
  The adsorption unit is used to remove sulfur compounds from C_2^+ stream. Table 8 shows specifications of C_2^+ polishing feed.

Table 8. Feed specifications of C_2^+ polishing unit

Property		Unit	Value
Flow rate		kg/h	2106
Pressure		bar	35
Temperature		°C	36.6
Impurities composition	COS	ppm	14.2
	MeSH	ppm	613.2
	EtSH	ppm	525.9
	Heavier mercaptans	ppm	73.6
	CS_2	ppm	51.7

According to the ASD (Figure 7), 4A, 5A and 13X can be selected. But, the designer is recommended 13X type because of existing heavy mercaptans and other organic sulfur components. Generally:
- 4A type can be used to remove H_2S and CO_2 besides water.
- 5A type can be used to remove H_2S, CO_2 and light mercaptans such as ethyl and methyl mercaptans besides water.
- 13X type can be used to remove H_2S, CO_2, light and heavy mercaptans with organic sulfur components and water.
  Therefore, for this case, all unwelcome impurities are removed due to high adsorption capacity of 13 X.

6.3. Case study 3: Methanol guard for high density polyethylene (HDPE) unit

Table 9 shows the feed specifications of HDPE unit consists more than 99.95% of ethylene in the liquid phase. Due to increasing the life of catalyst, contaminants such as methanol and sometimes water should be removed from the feed stream, and their concentration should be decreased to less than 0.5 ppm. According to ASD, HDPE plants are equipped with methanol guard bed i.e. 13X MS due to its high adsorption capacity for alcohols in comparison to other types.

Table 9. Specifications of HDPE feed

Property		Unit	Value
Flow rate		kg/h	50 000
Pressure		bar	29
Temperature		°C	40-55
Composition	Ethylene	wt %	99.95
	Methanol	ppm	100

6.4. Case study 4: Oxygenate guard for polypropylene (PP) plant

Table 10 shows properties and composition of feed stream for a PP unit containing more than 99.98 % of propylene.

Table 10. Physical properties of feed stream of PP unit

Property		Unit	Value
Flow Rate		kg/h	40 000
Pressure		bar	25
Temperature		C	35
Composition	Propylene	wt%	99.98
	H_2O	ppm wt.	50
	CO & CO_2	ppm wt.	63
	COS	ppm wt.	5
	Methanol	ppm wt.	50

Impurities should be removed at upstream of PP reactor due to the sensitivity of catalyst. Therefore, a guard bed is provided to decrease these impurities to less than 13 ppm. According to ASD (Figure 5), both 5A and 13X can be individually used for this special case. Though, to decrease loading of each layer and increase the life time of adsorbent, a multi-layer design consists of above MSs are recommended.

6.5. Case study 5: Propane and butane drying and polishing unit

In this unit (Table 11), water (main impurity), and also sulfur compounds such as carbonyl sulfide, mercaptans and disulfide should be removed.

In other design approaches, caustic wash process is used to remove mercaptans. Due to high fixed capital costs and operating charges, this process is not feasible for LPG treatments when low amount of impurities in the feed, and a high purity product (water content<0.1 ppm wt. and total sulfur content< 10 ppm wt.) are expected.

According to ASD (Figure 7), for liquid impurity removal, two options are practical for sulfur removal and dehydration processes, simultaneously i.e. 5A and 13X MSs. The presence of heavy mercaptans and disulfides in feed stream make designer choose 13X type due to its high adsorption capacity for such impurities. The former is suitable for light mercaptans, and it cannot be a proper selection in the presence of heavy mercaptans and disulfides.

Table 11. Physical properties of propane and butane feed streams

Feed	Property		Unit	Value
Propane	Flow rate		kg/h	20 652
	Pressure		bar	25.3
	Temperature		°C	60
	Composition	Water	ppm	200
		Carbonyl sulfide	ppm	20
		Methyl mercaptan	ppm	4.2
		Ethyl mercaptan	ppm	1.5
		Alkyl disulfide	ppm	25
Butane	Flow rate		kg/h	20 729
	Pressure		bar	12.4
	Temperature		°C	60
	Composition	Water	ppm	200
		Methyl mercaptan	ppm	4.9
		Ethyl mercaptan	ppm	21
		Iso-propyl mercaptan	ppm	0.6
		Alkyl disulfide	ppm	36

7. Conclusions

Adsorbents such as activated alumina, silica gel, activated carbon and molecular sieves are conventionally used in oil, gas and petrochemical facilities for many years. The key variables to choose a suitable adsorbent are feed composition, operating conditions and product requirement. In this paper, main issues related to the features, properties and selection of industrial adsorbents, and their applications in liquid and gas services were described. Moreover, the adsorption and regeneration cycles, and routes for the regeneration of an adsorption bed i.e. temperature swing adsorption (TSA) and pressure swing adsorption (PSA) were introduced. Then, based on both wide investigations and industrial scale experiences, an adsorption selection diagram (ASD) was introduced. By choosing adsorbents for industrial scenarios (i.e. dehydrating isomerization feed, polishing C_2^+, removing methanol and oxygenated compounds from HDPE and PP feeds, and drying propane and butane), the validity and accuracy of ASD were confirmed.

References

[1] Sadeghzadeh Ahari J, Shafiee Z, Mohammadbeigy K, Pakseresht S, Kakavand M, Kolivand M. 2016. Modeling and Investigation of the Operational parameters in the Process of Mercaptan and Water Removal from Natural Gas by Adsorption on Zeolite 13X. Pet Coal, 2016; 58 (3): 307-320.

[2] Ackley MW, Rege SU, and Saxena H. Application of natural zeolites in the purification and separation of gases. Micropor. Mesopor. Mat., 2003; 61: 25-42.

[3] Dabrowski A. Adsorption-from theory to practice. Adv. Colloid. Interfac., 2001; 93: 135-224.

[4] Otten W, Kast W. Development of Design Charts for Fixed-bed Adsorption. Chem. Eng. Technol., 1988; 11:289-297.

[5] Saleem M, Afzal A, Naeem TM, Mahmood F. Adsorption characteristics of organic dyes on alumina powder from aqueous solutions. Adsorpt. Sci. Technol., 1994; 11(2): 95-104.

[6] Farooq S, Ruthven DM. A comparison of linear driving force and pore diffusion models for a pressure swing adsorption bulk separation process. Chem. Eng. Sci., 1990; 45(1): 107-115.

[7] Doong SJ, Yang RT. Bulk separation of multicomponent gas mixtures by pressure swing adsorption: Pore/surface diffusion and equilibrium models. AIChE J., 1986; 32(3): 397–410.

[8] Sircar S. Applications of Gas Separation by Adsorption for the Future. Adsorpt. Sci. Technol., 2001; 19(5): 347-366.

[9] Sadighi S, Asgari M, Mohammadi H, Noorbakhsh F. Increasing the efficiency of a temperature swing adsorption (TSA) natural gas dehydration plant. Pet Coal, 2016; 58(2): 260-269.

[10] Audeh CA, Hoffman BE. Simultaneous dehydration and removal of residual impurities from gaseous hydrocarbons. US patent no. 5120515 A, 1992.

[11] Gandhidasan P, Al-Farayedhi AA, Al-Mubarak, AA. Dehydration of natural gas using solid desiccants. Energy, 2001; 26(9): 855–868.

[12] Zhang H, Luo YB, Yu P, Yuan Z. Removal of colored impurities from caprolactam solution by adsorption onto activated carbon: Equilibrium and thermodynamic studies. Adsorpt. Sci. & Technol., 2006; 24(1): 41-53.

[13] Asgari M, Anisi H, Mohammadi H, Sadighi S. Designing a commercial scale pressure swing absorber for hydrogen purification. Pet. Coal, 2014: 56(5): 552-561.

[14] Girimonte R, FormisaniB, Testa F. Adsorption of CO_2 on a confined fluidized bed of pelletized 13X zeolite. Pow. Technol., 2017; 311: 9-17.

[15] Sun H, Zhao S, Ma Y, Wu J, Liang P, Yang D, Zhang H. Effective and regenerable Ag/4A zeolite nanocomposite for $Hg0$ removal from natural gas. J. Alloy. Compd., 2018; 762: 520-527.

[16] Kohl AL, Nielsen RB. Gas purification, 5th ed.; Gulf Professional Publishing, 1997.

[17] Sing KSW. Characterization of adsorbents. Adsorpt. Sci. Technol., 1989; 158: 3-14.

[18] Bergna HE, Roberts WO. Colloidal Silica, Fundamentals and applications, CRC Press, 2005.

[19] Kidnay AJ, Parrish WR, McCartney D.G. Fundamentals of natural gas processing, 2nd ed.; CRC Press, 2005.

[20] Planda M, Staszczuk P, Pekalska J. Correlation between adsorption and porosity properties of alumina samples as obtained from classical adsorption and thermal analysis methods. Adsorpt. Sci. Technol., 2001; 19(5): 367-380.

[21]   Campbell, JM. Gas conditioning and processing, 7th ed.; Campbell Petroleum Series, 1992; Vol. 2: The Equipment Modules.

[22]   Kasprzyk-Hordern B. Chemistry of alumina, reactions in aqueous solution and its application in water treatment. Adv. Colloid Interfac., 2004; 110:19-48.

[23]   Striolo A. From Interfacial Water to Macroscopic Observables: A Review. Adsorpt. Sci. Technol., 2011; 29(3): 211-258.

[24]   Choi JG, Do DD, Do HD. Surface diffusion of adsorbed molecules in porous media: monolayer, multilayer, and capillary condensation regimes. Ind. Eng. Chem,. 2001; 40: 4005-4031.

[25]   Mustafa S, Dilara B, Naeem A, Rehana N, Nargis K. Temperature and pH Effect on the Sorption of Divalent Metal Ions by Silica Gel. Adsorpt. Sci. Technol., 2003; 21(4):297-307.

[26]   Chua HT, Ng KC, Wang W, Yap C, Wang XL. Transient Modeling of a Two-Bed Silica Gel–Water Adsorption Chiller. Int. J. Heat Mass Tran., 2004; 47: 659-669.

[27]   Wang DC, Xia ZZ, Wu JY, Wang RZ, Zhai H, Dou WD. Study of a Novel Silica Gel–Water Adsorption Chiller. Part I. Design and Performance Prediction. Int. J. Refrig., 2005; 28: 1073-1083.

[28]   Gervasini A, Marzo M. Study of the Influence of the Nature of the Support on the Properties of Ferric Oxide in Relation to its Activity in the Decomposition of N_2O. Adsorpt. Sci. Technol., 2011; 29(4): 365-379.

[29]   Appleby WG, Gibson JW, Good GM. Coke Formation in Catalytic Cracking. Ind. Eng. Chem. Process Des. Dev., 1962; 1(2): 102-110.

[30]   Maddox RN. Gas Conditioning and processing: gas and liquid sweetening, 4th ed.; Campbell Petroleum Series, 1998.

[31]   Lu GQ, Zhao XS. Nanoporous Materials: Science and Engineering, World Scientific, 2004; Volume 4 of Series on Chemical Engineering.

[32]   Banerjee R, Furukawa H, Britt D, Knobler C, O'Keeffe M, Yaghi O.M. Control of pore size and functionality in isoreticular zeolitic imidazolate frameworks and their carbon dioxide selective capture properties. J. Am. Chem. Soc. 2009; 131: 3875-3877.

[33]   Lin R, Ladshaw A, Nan Y, Liu J, Yiacoumi S, Tsouris C, DePaoli DW, Tavlarides LL. Isotherms for water adsorption on molecular sieve 3A: Influence of cation composition. Ind. Eng. Chem. Res., 2015; 54(42):10442-10448.

[34]   Mondale KD, Carland RM, Aplan FF. The comparative ion exchange capacities of natural sedimentary and synthetic zeolites. Mine. Eng. 1995; 8(4): 535-548.

[35]   Hayashi H, Cote AP, Furukawa H, O'Keeffe M, Yaghi OM. Zeolite A Imidazolate Frameworks. Nat. Mater., 2007; 6: 501-506.

[36]   Karge HG, Hatada K, Zhang Y, Fiedorow R. conversion of alkylbenzenes over zeolite catalysts II. Disproportionation of ethylbenzene over faujasite-type zeolites. Zeolites, 1983; 3: 13-21.

[37]   Wender A, Barreau A, Lefebvre C, Lella AD, Boutin A, Ungerer P, Fuchs AH. Adsorption of n-alkanes in faujasite zeolites: Molecular simulation study and experimental measurements. Adsorp. Sci. Technol., 2006; 24(8): 713-736.

[38]   Ahmedna M, Marshall WE, Rao RM. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresource Technol., 2000; 71:113-123.

[39]   López-Velandia C, Moreno-Barbosa JJ, Sierra-Ramirez R, Giraldo L, Moreno-Piraján JC. Adsorption of volatile carboxylic acids on activated carbon synthesized from watermelon shells. Adsorp. Sci. Technol., 2014; 32(2&3): 227-242.

[40]   Kadirvelu K, Kanmani P, Senthilkumar P, Subburam V. Separation of mercury (II) from aqueous solution by adsorption onto an activated carbon prepared from Eichhornia Crassipes. Adsorpt. Sci. Technol., 2004; 22(3):207-222.

[41]   Ioannidou O, Zabaniotou A. 2007. Agricultural residues as precursors for activated carbon production—A review. Renew Sust. Energy Rev., 11:1966-2005.

[42]   Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos E. Production of Activated Carbon from Bagasse and Rice Husk by a Single-Stage Chemical Activation Method at Low Retention Times. Bioresource Technol., 2008; 99: 6809-6816.

[43]   Taty-Costodes VC, Fauduet H, Porte C, Ho YS. Removal of Lead (II) Ions from Synthetic and Real Effluents Using Immobilized Pinus Sylvestris Sawdust: Adsorption on a Fixed-Bed Column. J. Hazard. Mater., 2005; 123: 135-144.

[44]   Jichang L, Benxian S, Hui S. Adsorption Behavior of Normal Paraffins in a Fixed Bed Adsorber Containing 5 Å Molecular Sieves. Adsorpt. Sci. Technol., 2006; 24(4):311-320.

[45]   Moreno-Castilla C. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon, 2004; 42: 83-94.

[46] Li JR, Kuppler RJ, Zhou HC. Selective Gas Adsorption and Separation in Metal-Organic Frameworks. Chemical Society Reviews, 2009; 38: 1477-1504.

[47] Menard D, Py X, Mazet N. Activated Carbon Monolith of High Thermal Conductivity for Adsorption Processes Improvement Part B. Thermal Regeneration. Chem. Eng. Process, 2007; 46: 565-572.

[48] Mokhatab S, Poe WA, Speight JG. Handbook of Natural Gas Transmission and Processing, Gulf Professional Publishing, 2015.

[49] Defu L, Jinqu W. The Adsorption and Separation of Ethylene. Oxygen and Carbon Dioxide Gases on Molecular Sieves. Adsorpt. Sci. Technol., 2002; 20(1): 83-90.

[50] Watson G, May EF, Graham BF, Trebble MA, Trengove RD, Chan KI. Equilibrium Adsorption Measurements of Pure Nitrogen, Carbon Dioxide, and Methane on a Carbon Molecular Sieve at Cryogenic Temperatures and High Pressures. J. Chem. Eng. Data, 2009; 54: 2701-2707.

[51] Lee DK. Green-oil formation a selectivity change in selective hydrogenation on titania- supported and unsupported palladium catalyst for acetylene removal from ethylene-rich stream. Korean J. Chem. Eng., 1990; 7(3):233-235.

[52] Norton CJ. Olefin Polymerization over Synthetic Molecular Sieves. Ind. Eng. Chem., 1964; 3(3): 230-236.

[53] Liu W, Vidica RD, Brown TD. Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal. Environ. Sci. Technol., 1998; 32: 531-538.

[54] Smith AR, Klosek J. A Review of Air Separation Technologies and their Integration with Energy Conversion Processes. Fuel Process. Technol., 2001; 70: 115-134.

[55] Hassan MM, Ruthven DM, Raghavan NS. 1986. Air Separation by Pressure Swing Adsorption on a Carbon Molecular Sieve. Chem. Eng. Sci., 41(5): 1333-1343.

[56] Khaleel A, Kapoor PN, Klabunde KJ. Nanocrystalline Metal Oxides as New Adsorbents for Air Purification. Nanostruct. Mater., 1999; 11(4): 459–468.

[57] Cao B, Shen, W, Liu Y. Adsorption Desulphurization of Gasoline by Silver Loaded onto Modified Activated Carbons. Adsorpt. Sci. Technol., 2008; 26(4): 225-231.

[58] Abdul Kareem FA, Shariff AM, Ullah S, Dreisbach F, Keong LK, Mellon N, Garg S. Experimental measurements and modeling of supercritical CO_2 adsorption on 13X and 5A zeolites. J. Nat. Gas Sci. Eng. Micropor. Mesopor. Mat., 2018; 50:115-127.

[59] Xiong R, Xicohténcatl RB, Zhang L, Li P, Yao Y, Sang G, Chen C, Tang T, Luo D, Hirscher, M. Thermodynamics, kinetics and selectivity of H_2 and D_2 on zeolite 5A below 77K. Microporous and Mesoporous Materials, 2018; 264: 22-27.

[60] McKay G. Two-Resistance Mass Transfer Models for the Adsorption of Dyestuffs from Aqueous Solutions Using Activated Carbon. J. Chem. Technol. Biot., 1984; 34A: 294-310.

[61] Garcia-Ochoa F, Gomez E. Prediction of Gas-Liquid Mass Transfer Coefficient in Sparged Stirred Tank Bioreactors. Biotechnol. Bioeng., 2005; 92(6): 761-772.

[62] Benson TJ, George CE. Cellulose Based Adsorbent Materials for the Dehydration of Ethanol Using Thermal Swing Adsorption. Adsorption, 2005; 11: 697-701.

[63] Quintero JA, Cardona CA. Ethanol Dehydration by Adsorption with Starchy and Cellulosic Materials. Ind. Eng. Chem., 2009; 48: 6783-6788.

[64] Al-Asheh, S., Banat, F., Al-Lagtah, N. Separation of Ethanol–Water Mixtures Using Molecular Sieves and Biobased Adsorbents. Chem. Eng. Res. Des., 2004; 82(A7): 855-864.

[65] Ali B, Karrer L. Increase polypropylene production via ultra-low levels of carbon monoxide-Case study. Hydrocarbon Process, Oct; 2014: 78-81.

[66] Slaugh LH, Willis CL. 1984. CO_2 Removal from gaseous streams. US patent no. 4433981 A.

[67] Hidalgo JM, Zbuzek M, Černý R, Jíša P. Current Uses and Trends in Catalytic Isomerization, Alkylation and Etherification Processes to Improve Gasoline Quality. Cent. Eur. J. Chem., 2014; 12(1): 1-13.

[68] Tournier H, Barreau A, Tavitian B, Roux DL. Adsorption equilibrium of xylene isomers and p-diethylbenzene on a prehydrated BaX zeolite. Ind. Eng. Chem., 2001; 40: 5983-5990.

[69] Jobic H, Methivier A, Ehlers G. Different diffusivities of xylene isomers in BaX zeolite measured by the neutron spin echo technique. Micropor. Mesopor. Mat., 2004; 56: 27-32.

To whom correspondence should be addressed: Dr. Sepehr Sadighi, Research Institute of Petroleum Industry (RIPI), Catalysis Technologies Development Division, P.O. Box 14665137, Tehran, Iran