

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background

##### 2.1.1 Basics of Fermentation

Fermentation has long been an invaluable tool in the food industry. For centuries, human beings have utilized the natural process of fermentation as a means to increase nutritional value, change the taste, and most importantly, preserve many foods before the technological advances of modern times, such as refrigerators. This was a compelling motive for the production of wine, beer, cheeses, sauerkraut, and yogurt.

By definition, fermentation is the anaerobic process by which starches and sugars are converted to a number of end products such as ethyl alcohol, lactic acid, and other organic compounds. Many microorganisms, such as various types of yeast, bacteria, and filamentous fungi, utilize the fermentation process, allowing microorganisms to grow and thrive on certain food, resulting in preservation and a change in the taste of the food. The fermentation process determines the nutritional value and possibly the taste of the food. Given the wide variety of microorganisms capable of fermentation, it is no wonder that some fermented products employ more than one microorganism, either simultaneously or sequentially. Furthermore, fermentation (performed by yeast) is the exothermic process of converting sugars into alcohol and carbon dioxide gas or biogas. In addition to sugar, nitrogen and phosphorus are necessary for the growth and reproduction of new yeast tissue. Moreover, transformation of starch is under the influence of acids, or diastase, a principle existing in germinating grains, starch is changed first into gum (dextrin) and afterwards into sugar. Hence one of important sources of alcohol is to be found in the starch of barley, corn, wheat, potatoes, etc. Wood may be converted into sugar by the action of strong sulphuric acid which is afterwards neutralized. An attempt to produce alcohol in this way on a commercial scale was made in France.

For fermentation, temperature is important. A boiling heat instantly stops fermentation, by killing the ferment. To check fermentation we may remove

the yeast by filtration. Hops, oil of mustard, sulphurous acid (from burning sulphur), the sulphites, sulphuric acid, check the process by killing the ferment. Too much sugar is unfavorable to fermentation; the best strength for the syrup is ten parts of water to one of sugar. The following paragraphs are examples of fermentation.

#### *2.1.1.1 Alcoholic Fermentation*

The fermentation which saccharine bodies undergo when brought in contact with the yeast plant or *Torula*. The sugar is converted, either directly or indirectly, into alcohol and carbonic acid, the rate of action being dependent on the rapidity with which the *Torula* develop.

#### *2.1.1.2 Acetic Fermentation*

Weak fermented liquors will become sour on exposure to the air. This is owing to the conversion of their alcohol into acetic acid (Vinegar). This change is due to the absorption of the oxygen of the air and is much promoted by the presence of a peculiar plant, the mother of vinegar. It is sometimes called the acetous fermentation.

#### *2.1.1.3 Viscous Fermentation*

By the action of yeast on beet-sugar a peculiar fermentation is set up; but little alcohol is formed. The same gives ropiness to wines and beer. It is checked by vegetable astringents.

Most of the alcohols created during fermentation (including ethyl alcohol) have a boiling point of around 78.5° Celsius (173.3° F). Some higher alcohols boil at lower temperatures than others. Since this boiling point is much lower than that of water, when the fermented mass is heated, these alcohols are the first ones to evaporate. This allows the distillers to separate them from the undesirable byproducts and remnants from fermentation. The first alcohols to come out of the still are commonly referred to as the "heads" or "high wines" and contain a large amount of aldehydes and esters. These alcohols are responsible for some of the fruity aroma found on the distillate. Following a very small amount of "heads", the still begins extracting mainly ethyl alcohol (or ethanol), from the fermented liquid. The "tails" part of distillate contains fusel oils, which are the heaviest alcohols produced during fermentation. Today's formula, based on sugar-rich molasses, looks like this:

One ton molasses with 46% fermentable sugars = 920 pounds of sugar. Based on the Gay-Lussac equation for ethanol production from glucose by fermentation, this is equal to 470.21 pounds of ethanol, which is equal to 71.46 gallons of ethanol. Using the Pasteur Yield (which is a formula based on a statement by the notable scientific that it is impossible to get more than 95% of the maximum theoretical yield), we have an adjusted value of 67.89 gallons. This last number needs to be adjusted even further by a value which represents "plant efficiency," which denotes the extent to which the plant's equipment and processes can get close to the Pasteur Yield. The average plant efficiency is around 90%, giving as a final number of 61.10 gallons per ton of molasses. (Source: [www.rumuniversity.com](http://www.rumuniversity.com))

### 2.1.2 Reactive Separations

Reactive separations utilize close coupling of separation and chemical reactor systems, often in a single unit, to improve the yield of the reaction, the production of desired products, and/or to lower energy consumption and capital investment. Reactive separation systems may take many forms and may not resemble conventional chemical reactors and separations equipment. Reactors could be catalytic or homogeneous, continuous or batch. Any separation method could be used including adsorption, distillation, or extraction. A simple example of a reactive separation is a tubular reactor that utilizes a selective membrane tube filled with catalyst. The membrane selectively permeates a desired reaction product, and the removal of that product along the reactor length continuously shifts the chemical equilibrium among the potential products and reactants, increasing both the utilization of reactants and the production of the desired product. Improvements from combining separations and chemical reactor operations can be substantial. In conventional systems, the yields of desired products are often limited by the equilibrium constant, and a product's concentration is usually determined by a thermodynamic equilibrium distribution of products and reactants. By combining a reactor with a separation operation that removes the most desired product, as in the above example, the utilization of reactants can be improved, and the reaction can provide significantly higher yields of the most desired product according to Le-Schatelie principle, and irreversible reactions due to the law of mass action (as the

removal of reaction products results in the increase of reagents concentration in the reaction zone). Energy savings can also be realized when products from one reaction step can be separated and used as reactants in a second reaction step. When one reaction step is exothermic and the other reaction is endothermic, the energy from the exothermic reaction can be used to drive the endothermic reaction.

Unfortunately, effective reactive separation systems usually are highly system-specific and particular combinations of separation and reactive systems are required for each potential application. For numerous low yield systems, no effective reactive separation systems are likely to be found. Part of the difficulty is that reactive separation systems not only must include both reactor and separation capabilities, but also both functions must take place at approximately the same temperature and pressure, at least if they are to be incorporated in the same equipment. Therefore, each grant application must identify a particular application one with the potential for large savings of energy and materials, and/or for significant reduction in waste products.

### 2.1.3 Selectivity

The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity, capacity, and life. The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium. In considering such processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B}, \quad (2.1)$$

where  $X_A$  and  $Y_A$  are, respectively, the mole fractions of component "A" in the adsorbed and fluid phases at equilibrium. The separation factor defined in this way is precisely analogous to the relative volatility, which measures the ease with which the components may be separated by distillation. The analogy is, however, purely formal and there is no quantitative relationship between the separation factor and

relative volatility. For two given components, the relative volatility is fixed whereas the separation factor varies widely depending on the adsorbent (Ruthven, 1984).

#### 2.1.4 Adsorption

Consider a heterogeneous system composed a fluid phase (liquid or gaseous) and a solid surface. Further assume that the fluid phase is a solution of several different chemical species and that the fluid and solid phases are under thermodynamic equilibrium. A species present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. Adsorption takes place because of the interaction between the species present in the fluid phase and solid surface.

It is obvious that adsorption is a surface phenomenon and that its definition rests upon concentration measurements and carries no implications of mechanisms. The species that is adsorbed is called adsorbate. There may be one or more adsorbates in a given adsorption situation. Adsorption-based separation processes, which are developed to separate or purify homogeneous mixtures, operate on the principle of difference in adsorption potential (Ruthven, 1984).

#### 2.1.5 Liquid Phase Adsorption Mechanisms

As some experiments in this work will be performed in liquid phase, information related to liquid phase adsorption mechanisms are provided here.

Liquid phase adsorption mechanisms are highly complex. This is due to the interaction of solid adsorbents, liquid adsorbates, and liquid desorbents during the separation process. By contrast, other conventional separation process mechanisms are based primarily on the differences in the physical properties of the components. In the liquid phase adsorption matrix, a virtually infinite variability in liquid separation can be achieved as a result of the number of ways available for adsorbent and desorbent modification. Adsorbent variables include the framework structure, the counter exchange ion, and water content. These variables are carefully modified to selectively adsorb one particular component over others. To desorb the adsorbed component, a suitable solvent functioning as a desorbent first needs to be



identified. To achieve the liquid phase adsorption separation, one has to balance two opposing forces: the adsorptive force of the adsorbent to a component and the desorption force of the desorbent (Kulprathipanja and Johnson, 2001).

Although there is complexity in the liquid phase adsorption mechanisms, they can be classified into five broad categories: equilibrium-selective adsorption, rate-selective adsorption, shape-selective adsorption, ion exchange, and reactive adsorption.

#### *2.1.5.1 Equilibrium-Selective Adsorption*

The foundation of equilibrium-adsorption is based on the differences in phase compositions at equilibrium. While all the adsorbates have access to adsorbent sites, the adsorbates are selectively adsorbed based on differences in the adsorbate-adsorbent interaction. Equilibrium-selective adsorption depends on the magnitude of the dispersion, repulsion, and electrostatic forces of adsorbate-adsorbent interactions. To achieve a meaningful separation, the adsorbent is manipulated to obtain a larger interaction, selectively, for one component of a mixture.

#### *2.1.5.2 Rate-Selective Adsorption*

In addition to being evaluated based on phase compositions at equilibrium, an adsorptive separation process may also be evaluated based on the diffusion rates through a permeable barrier. These evaluations are designated as “rate-selective adsorption” processes. In some instances, there may be true equilibrium selectivity as well as rate selectivity.

A rate-selective adsorption process will not yield a good separation unless the diffusion rates of the feed components differ by a wide margin. For example, the components that have smaller kinetic diameters, in turn, having a higher diffusion coefficient, usually yield better selectivity than bigger kinetic diameter components.

#### *2.1.5.3 Shape-Selective Adsorption*

Equilibrium- and rate-selective mechanisms deal with adsorbate-adsorbent interactions and molecular diffusion rates through adsorbent pores. Shape-selective adsorption is a process that separates molecules that can enter

the adsorbent pores from ones that are completely excluded. Thus, selectivity of the entered components with respect to the excluded components is infinite.

#### *2.1.5.4 Ion Exchange*

Ion exchange separation is defined as the reversible exchange of ions between a solid adsorbent and a liquid adsorbate, in which there is no substantial change in the structure of the solid adsorbent. The solid adsorbent is composed of a large number of ionic (or potentially ionic) sites such as zeolites and ion exchange resins. An ion exchange resin is elastic, three-dimensional hydrocarbon network attached by a large number of ionizable groups. For most zeolites, the aluminosilicate portion of the structure is a three-dimensional open framework consisting of a network of  $AlO_4$  and  $SiO_4$  tetrahedrons linked to each other by oxygen molecules. The framework contains channels and interconnected voids occupied by cations and water molecules. The cations are quite mobile and can usually be exchanged by other cations to varying degrees.

#### *2.1.5.5 Reactive Adsorption*

Reactive separation processes are unique in that they combine the normally unit operations of reaction and separation into a single, simultaneous operation. The advantages of such technology are principally in energy and capital cost reduction, as well as in increased reaction efficiency. Additionally, reactive separation is sometimes the only method by which effectively separate species when conventional means such as adsorption, distillation, or extraction are not applicable.

Reactive adsorption is characterized by simultaneous chemical reactions and separations. In a single reactor-separator vessel, it is possible to obtain high purity products directly from the reactor, with downstream purification requirements greatly reduced or even eliminated. These can result in reduced design complexity and capital costs.

#### 2.1.6 Adsorbents

A practical adsorbent for liquid phase adsorptive separation has four primary requirements: selectivity, capacity, mass transfer rate, and long term stability. The requirement for adequate adsorptive capacity restricts the choice of adsorbents to microporous solids with pore diameters ranging from a few angstroms

to a few hundred angstroms. The following materials have properties as required for practical adsorbents:

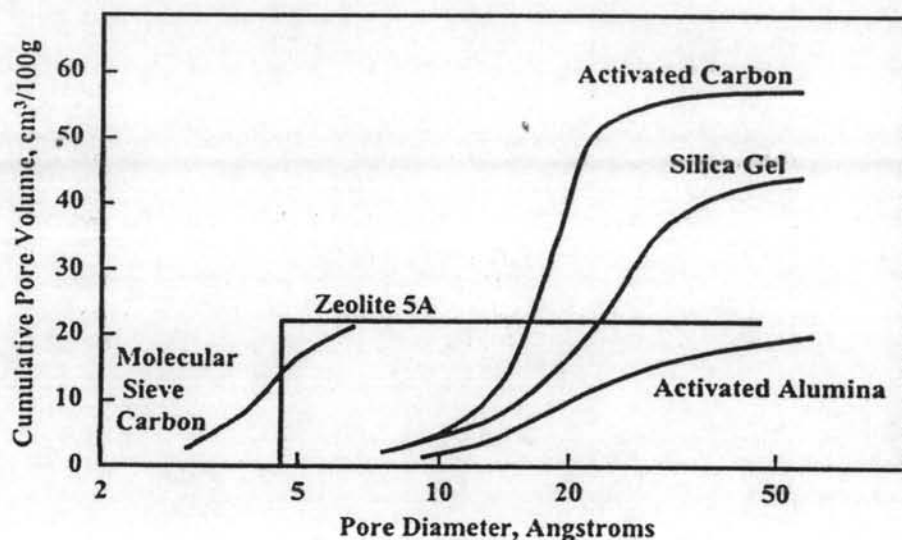
- Crystalline materials such as
  - Zeolites
  - AlPO-based molecular sieves
  - Metallosilicates
- Amorphous materials such as
  - Silica gel
  - Activated alumina
  - Transition metal oxides
  - Pillared clays
  - Carbon
- Polymeric resins such as
  - Cation exchange resin
  - Anion exchange resin
  - Neutral resin

Amorphous materials, such as silica gel, activated alumina, transition metal oxides, pillared clays, and activated carbon, exhibit large surface area and micropore volume. The surface chemical properties of these adsorbents make them potentially useful for separations by molecular class. However, the micropore size distribution is fairly broad for these materials (Figure 2.1). This characteristic makes such materials unsuitable for molecular size exclusion type separations.

In contrast to these adsorbents, crystalline materials such as zeolites, AlPO-based molecular sieves and metallosilicates offer increased possibilities for exploiting molecular level differences among adsorbates. Zeolites are crystalline aluminosilicates containing an assemblage of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons joined together by oxygen atoms to form a microporous solid, which has a precise pore structure. Nearly 40 distinct framework structures have been identified to date. The versatility of zeolites lies in the fact that widely different adsorptive properties may be realized by appropriate control of the framework structure, the  $\text{Si}/\text{Al}_2$  ratio, and the cation form. For example, zeolite A has a three-dimensional isotropic channel structure constructed by an eight-membered oxygen ring (Figure 2.2). The effective

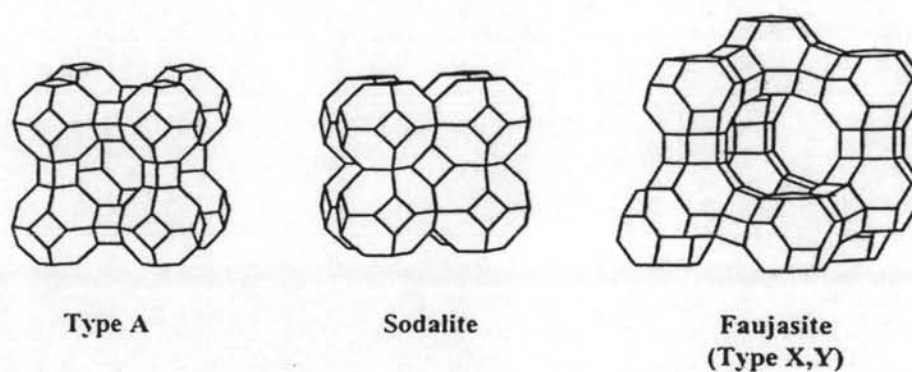


pore size can be controlled at about 3°A, 4°A, and 4.7°A by exchanging with potassium, sodium, and calcium, respectively.



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**Figure 2.1** Pore Size Distributions (Handbook of Porous Solids).



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**Figure 2.2** Three Zeolites with the Same Structural Polyhedron (Handbook of Porous Solids).

Large-pore zeolites, X and Y faujasites and mordenites, have pores defined by 12-membered oxygen rings with a free diameter of 7.4°A. The framework structure of X and Y faujasites (Figure 2.2) consists of a total of 192 SiO<sub>2</sub>

and  $AlO_2$  ratio for X is generally between 2 and 3. For Y, the  $SiO_2/AlO_2$  ratio is between 3 and 5. With suitable procedures, Y can be dealuminated to  $Si/Al_2$  ratios exceeding 50. Adsorption properties of faujasites are strongly dependent on not only the cation form but also the  $Si/Al_2$  ratio.

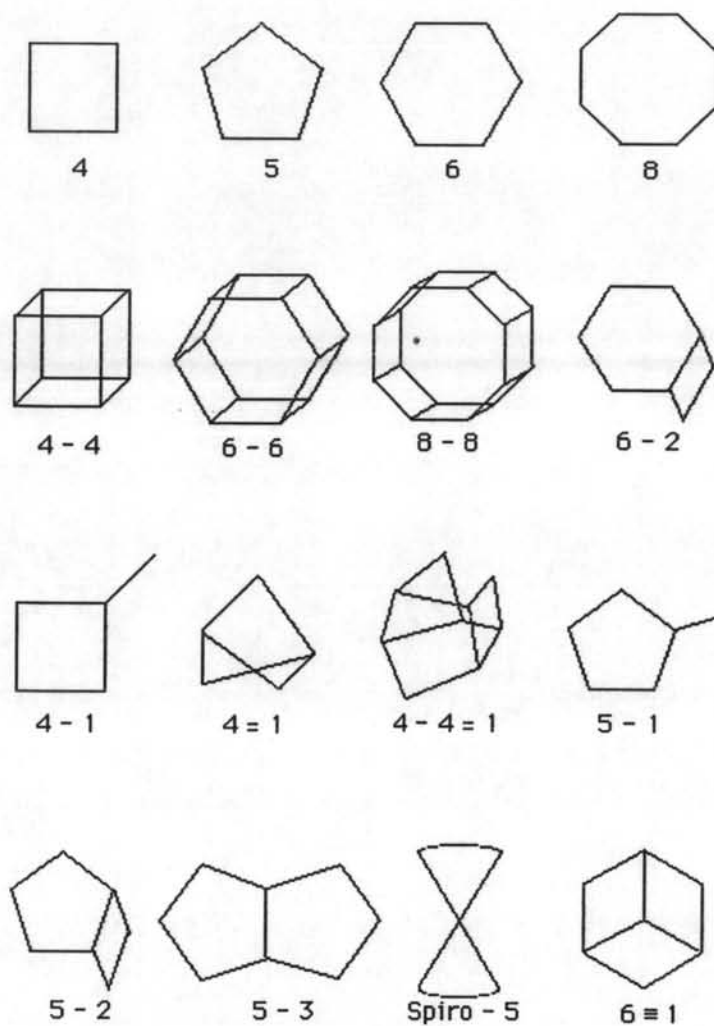
Polymeric resins, neutral or in ionic forms, are also widely used as adsorbents. A neutral polymeric resin can be visualized as an elastic, three-dimensional hydrocarbon network. The nature of the hydrocarbon network affects the adsorption behavior of the resin. The most ideal hydrocarbon network developed to date is that formed by the copolymerization of styrene-divinylbenzene. An ion exchange resin is a three-dimensional network, to which a large number of ionizable groups are attached.

#### 2.1.6.1 Zeolites

Zeolites are microporous inorganic compound with their crystal structures containing large pores and voids. Effective pore sizes in microporous solids range from 0.3 nm to over 1 nm, sufficient to permit the diffusion of organic molecules. This feature gives rise to many important applications of the materials.

The zeolite framework consists of an assemblage of  $SiO_4$  and  $AlO_4$  tetrahedral, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions, into which guest molecules can penetrate. Because the micropore structure is determined by the crystal lattice, it is precisely uniform with no distribution of pore size. This feature, which distinguishes the zeolites from traditional microporous adsorbents, is micropore structure.

In considering the zeolite framework, it is convenient to regard the structure as a built up from assemblages of secondary building units. The secondary building units and some of the commonly occurring polyhedral, which consists of several  $SiO_4$  and  $AlO_4$  tetrahedral, are shown schematically in Figure 2.3. In the diagrams, each vertex represents the location of a *Si* or *Al* atom while the lines represent, approximately, the diameters of the oxygen atoms ions, which are very much larger than the tetrahedral *Si* or *Al* atoms.

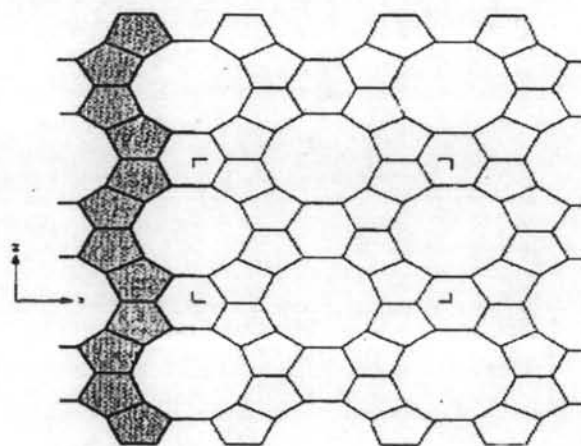


**Figure 2.3** Secondary building units and commonly occurring polyhedral units in zeolites framework structure (<http://chemmac1.usc.edu/bruno/zeodat/Intro.html>).

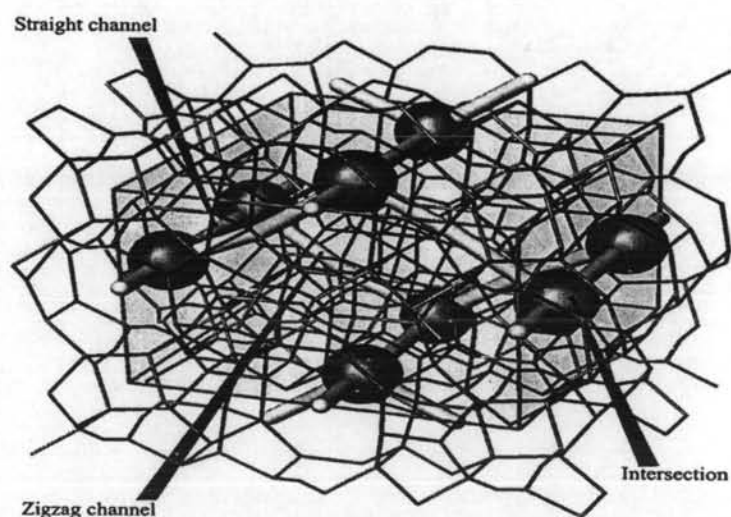
Each aluminum atom introduces one negative charge on the framework, which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties. Changing the exchangeable cation by ion exchange provides a useful means of modifying the adsorption properties.

The silicalite zeolite is an aluminum-free form of ZSM-5. The structure is based on the double five-ring unit (D5R). The structure of a characteristic layer of silicalite is shown schematically in Figure 2.4. By stacking such layers in different sequences, a variety of related structures may be obtained.

The channel systems of the silicalite are sketched in Figure 2.5. This zeolite has a two-dimensional pore structure consisting of straight channels (pore size, 0.51x 0.54 nm) with intersecting sinusoidal channels (pore size, 0.54 x 0.56 nm), composed of 10-membered oxygen rings. Each unit cell is constructed from four segments of linear channel, four segments of sinusoidal channel, and four channel intersections (Olson *et al.*, 1981).



**Figure 2.4** Characteristic layer of silicalite (Olson *et al.*, 1981).



**Figure 2.5** 3-Dimension of the pore structure of silicalite (UOP LLC).

LZ-210 is a second type of modified Y zeolite which depends on chemical treatment in order to increase the silica to alumina framework ratio in the zeolite by selectively replacing alumina tetrahedral units with silica tetrahedral units via so called secondary synthesis technology. The LZ-210 has framework silica to alumina ratio greater than 8:1. Zeolite LZ-210 having, in the dehydrated state, a chemical composition expressed in terms of mole ratios of oxides as  $(0.85-1.1) M_{.2/n} O : Al_{.2} O_{.3} : xSiO_{.2}$  wherein "M" is a cation having the valence "n" and "x" is a value greater than 8, preferably greater than 9 more preferably and within the range of 9 to 60. The zeolite is thus the type of hydrophobic, ultra-stable, zeolitic material.

#### 2.1.6.2 Activated Carbon

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1100°C). The activation process involves essentially the removal of tarry carbonization products formed during the pyrolysis, thereby opening the pores.

The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The surface of carbon is essentially nonpolar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. They are therefore widely used for the adsorption of organics in decolorizing sugar, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and as a general purpose adsorbent in range hoods and other air purification systems. In order to decrease the mass transfer resistance, the activated carbons used for adsorption from the liquid phase generally have somewhat larger pore diameters than those used for adsorption from the gas phase.

#### 2.1.6.3 Silica Gels

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. The chemical composition can be expressed as  $SiO_2 \cdot n H_2O$ . The water content, which is present mainly in the form of chemical bound hydroxyl groups,



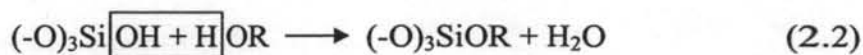
amounts typically to about 5 wt%. The material appears first to have been developed during the First World War for use in gas masks although in this service it proved inferior to activated carbon.

The presence of hydroxyl groups imparts a degree of polarity to the surface so that molecules such as water, alcohols, phenols, and amines (which can form hydrogen bonds) and unsaturated hydrocarbons (which can form  $\pi$ -complexes) are adsorbed in preference to nonpolar molecules such as saturated hydrocarbons. Because of its selectivity for aromatics silica gel was used as the adsorbent in the Arosorb process for separation of aromatics from paraffins and naphthenes but by far the most important current application is as a desiccant.

#### *a) Chemical Modification of Silica Surface*

Surface silanol groups of silica can be involved in chemical reactions with various organic and inorganic compounds which make it possible to graft to the silica surface different functional groups and by this method to change adsorption properties of surfaces of silica adsorbents. Many reactions are presented, by means of which on hydroxylated silica surfaces it is possible to create relatively high concentrations of new functional groups. The most promising chemical modification reactions of silica surfaces are those with chlorosilanes, silanols, disilazanes, and esters of silicic acid. Also other types of chemical reactions are used for preparation of adsorbents for immobilization of enzymes (Papirer, 2000).

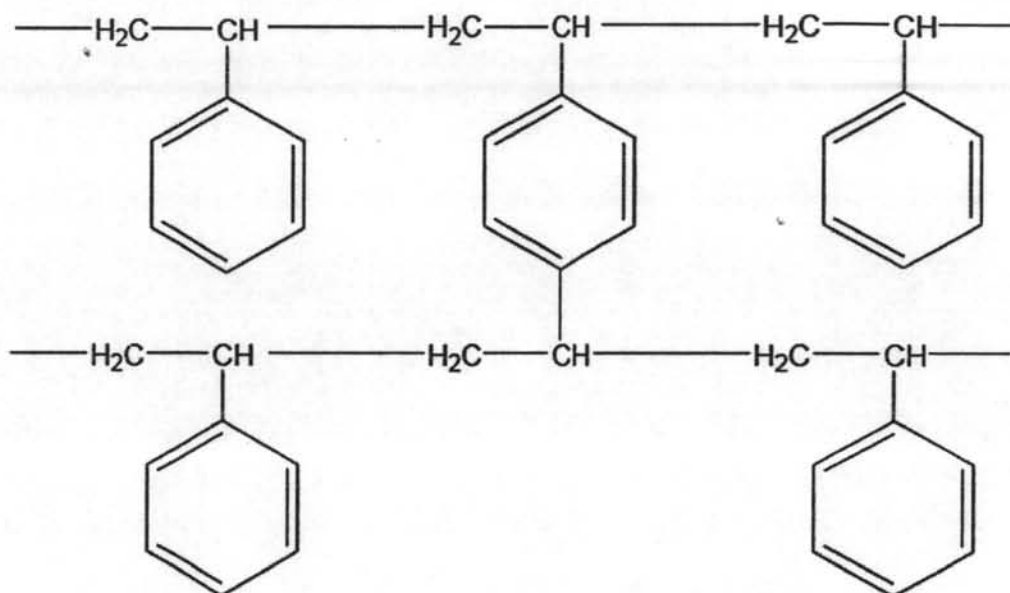
The reaction of chemicals with surface silanol groups of silica occurs at a high rate at high temperatures. Silanol groups act as "Trojan horses" to impart wanted properties to the silica by grafting suitable groups. For instance, the surface of silica gels (which has a hydrophilic character because of the silanols it hosts) may become hydrophobic after reaction with alcohols ROH (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc.):



#### *2.1.6.4 Polymeric Resins (XAD-2)*

XAD-2 is a polystyrene-divinylbenzene polymeric resins which are nonpolar and thus hydrophobic, whereas polyacrylate-divinylbenzene resins are

relatively polar and hydrophilic. XAD-2 is useful in sensitive analytical procedures for the detection and identification of narcotics and environmental organic contaminants. As compared to activated carbon, which has a typical life of 10-20 cycles of regeneration, resin adsorbents are highly durable.



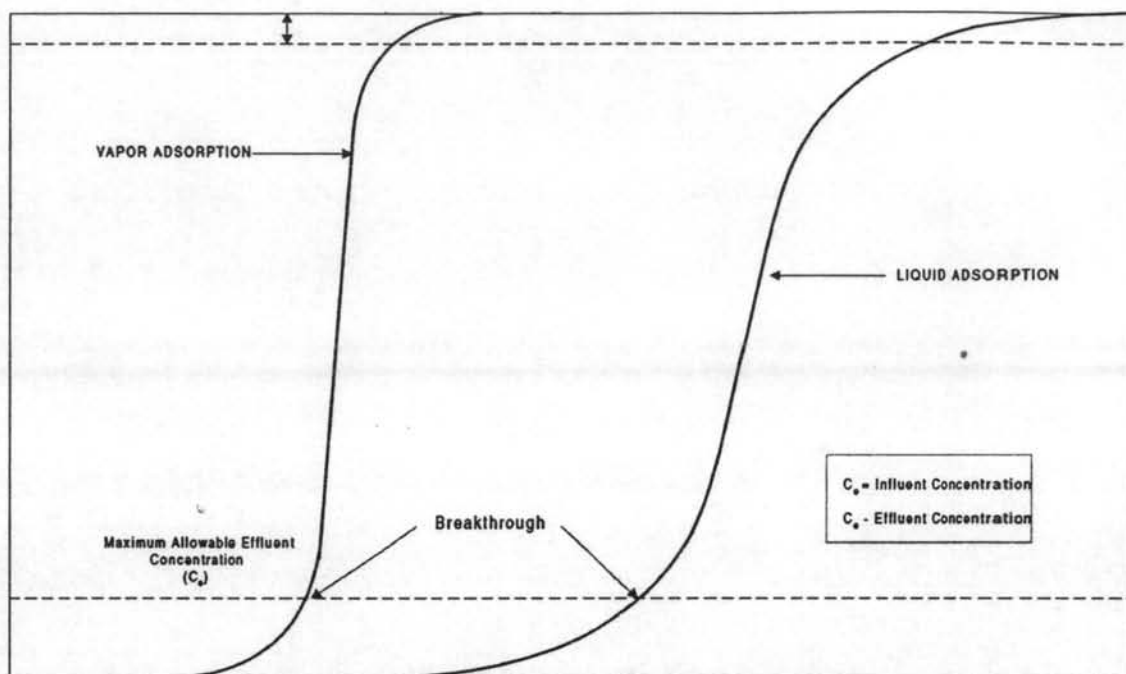
**Figure 2.6** Structure of polystyrene-divinylbenzene resins, such as Amberlite XAD-2 and XAD-4 (Kunin, 1976).

### 2.1.7 Dynamic Operation Testing

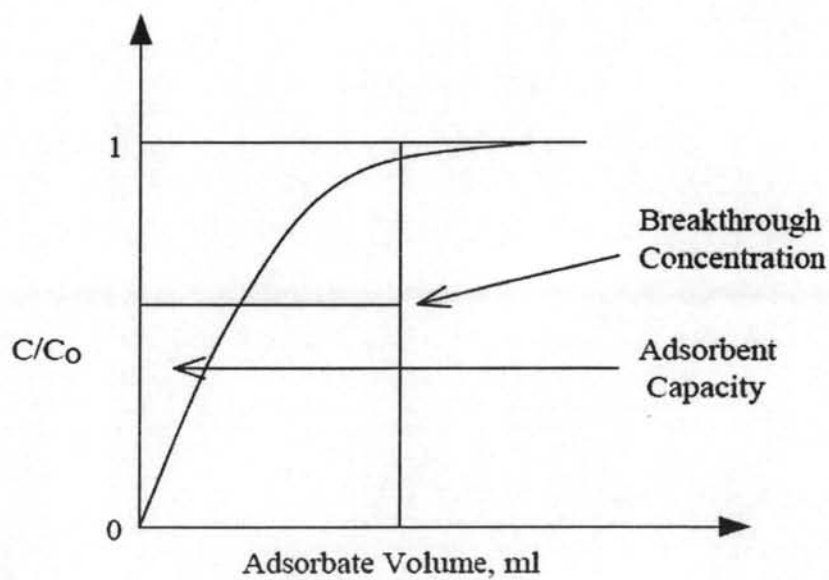
The following parameters must be considered when designing a pilot scale evaluation.

#### 2.1.7.1 *Breakthrough Curves*

The breakthrough curve can be defined as the "S" shaped curve that typically results when the effluent adsorbate concentration is plotted against time or volume. Breakthrough curves can be constructed for full scale, dynamic, or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal. The treatment goal is usually based on regulatory or risk based numbers (see Figure 2.7).



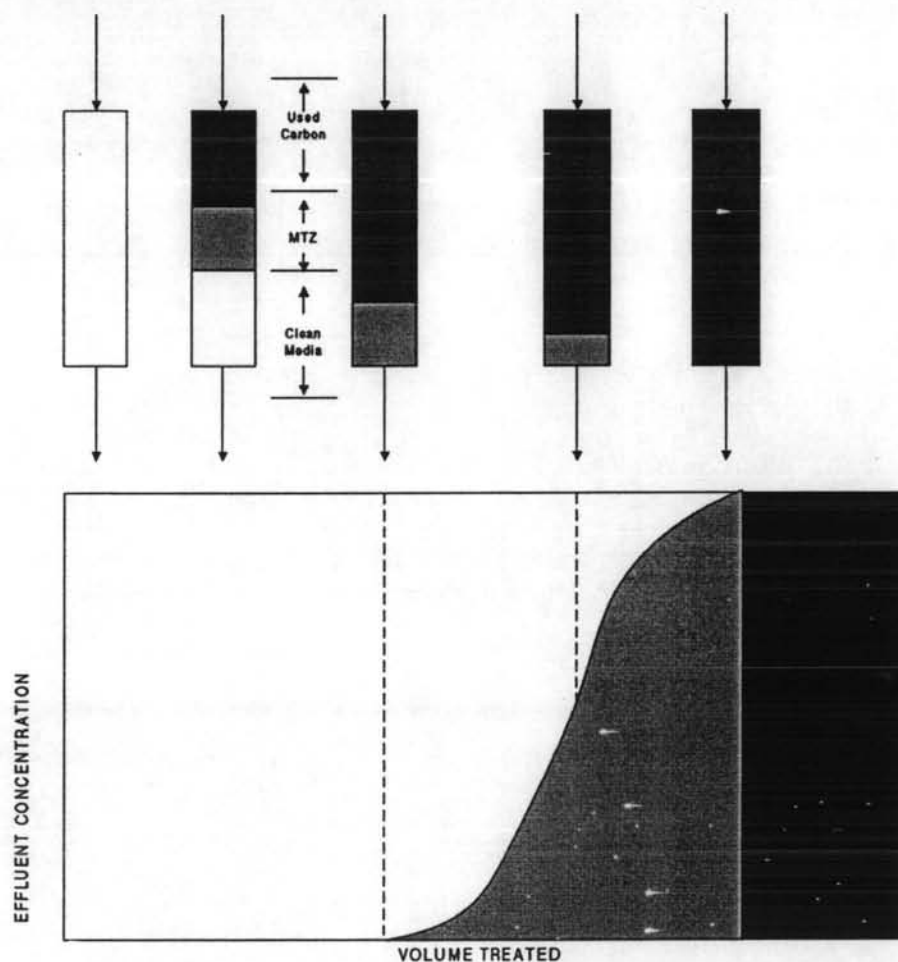
**Figure 2.7** Comparison of idealized vapor and liquid breakthrough curves (<http://www.usace.army.mil/usace-docs/design-guides/dg1110-1-2/chap2.pdf>).



**Figure 2.8** Graphical method for determining adsorption capacity (Benson, 2003).

### 2.1.7.2 Mass Transfer Zone

The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is sometimes called the adsorption zone or critical bed depth. The MTZ is generally a band, between the spent carbon and the fresh carbon, where adsorbate is removed and the dissolved adsorbate concentration ranges from  $C_0$  to  $C_e$ .



**Figure 2.9** Adsorption column mass transfer zone and idealized breakthrough zone (<http://www.usace.army.mil/usace-docs/design-guides/dg1110-1-2/chap2.pdf>).

## 2.2 Literature Review

One of commonly used methods in separating water from ethanol (or ethanol from water) is adsorptive separation. The adsorbents for water adsorptive separation are called desiccants, which include molecular sieves (3A, 4A and 5A), chloride salts, silica gel, and bio-based desiccants. However, dehydration of ethanol via adsorption using molecular sieves has recently been suggested as a promising alternative to the conventional separation methods for ethanol-water mixtures. 3A zeolites are typical molecular sieves possessing selective micropores whereon, due to the small size of their pores, enabling them to adsorb the water molecules but exclude the ethanol molecules. The thermodynamic results showed that the spherical and cylindrical zeolites had the same adsorbing capacity at the studied temperatures and that this capacity decreased with temperature increase (Carmo and Gubulin, 1997).

Beery and Ladisch (2001) studied the removal of water by liquid-phase contacting of water-ethanol mixtures with limiting starch-based materials. The mass of water adsorbed per gram of dry adsorbent increased with increasing water content by forming hydrogen bonds between the hydroxyl groups on the surface of the adsorbent and the water molecules. In 2004, Al-Asheh *et al.* found that adsorptive distillation could be used for separation of an ethanol-water system. The potential use of new bio-based adsorbents and different types of molecular sieve was assessed in the separation of the ethanol-water azeotrope. The breakthrough results of water sorption on molecular sieves indicated that type 3A molecular sieves had the largest surface area and the highest of water uptake compared with molecular sieves type 4A and 5A. Type 5A molecular sieves were found suitable for sorption of ethanol molecules. However, for the bio-based adsorbents, activated palm stone had the largest surface area and the highest value of water uptake compared to natural corncobs and oak.

Since water is a major component in the ethanol-water mixture after fermentation processes, water adsorptive separation requires much quantity and capacity of adsorbents entailing with a high cost. Therefore, separation of ethanol from water is much more attractive. The adsorbents of using ethanol adsorptive



separation are activated carbon, silicalite and silanized silica, which are of interest in this study.

For activated carbon adsorbent, the commonly known amorphous form of carbon is treated to obtain a large surface area (300-2,000 m<sup>2</sup>/g). The adsorbent comprised hard granules of from 20 to 48 mesh size (Kulprathipanja, 1983). In 1995, Aranovich and Donohue developed a new equation for isotherms of gas adsorption on microporous adsorbents. They found that adsorption capacity for ethanol on activated carbon is about 6.9 mmol/g at 303 K and used  $E/kT \sim -5$  that corresponds to the energy of the H-bond in a liquid phase. In 2001, Nakai measured the adsorption isotherms of ethanol and water vapor mixtures by active carbon fiber. The adsorption data clearly showed that ethanol molecules are preferentially adsorbed into the micropores of active carbon fiber with a pore width of 0.67 nm. The ethanol isotherm is a Type I isotherm. The initial shape rise in the isotherm ( $P/P_s = 0-0.05$ ) is due to micropore filling of ethanol molecule, which arises from the lyophilic interaction of the ethyl group with graphite surface of the ACF micropores. The ethanol isotherm rises almost vertically along the ordinate, indicating that most of the dosing ethanol molecules are adsorbed on the coverage of ethanol is estimated to be 0.5%, assuming the cross-sectional area of an ethanol molecule to be 0.22 nm<sup>2</sup>. Adsorption capacity of ethanol vapor on active carbon fiber at 300 K is 5.6 mmol/g. The present adsorption result suggests the possibility of the energy-saving separation of ethanol from the mixed vapors of ethanol and water.

Silicalite (a zeolite composed of ion-free silicon oxide) has been proposed as an adsorbent for recovery of dilute solutes. Non-polar molecules are strongly adsorbed due to hydrophobic nature of silicon oxide. Silicalite as manufactured by Union Carbide and UOP is a fine powder with a consistency much like flour. For ethanol molecules adsorbed on pure silicalite powder at equilibrium is 0.089 g/gads (Holtzapple *et al.*, 1994).

In fermentation process, Chung and Lee (1985) studied on ethanol inhibition of growth and fermentation in *S. cerevisiae*. Ethanol causes inhibition of cell metabolism and viability in D-glucose fermentation by yeast. The effect of inhibition is quite significant in that the fermentation is adversely affected by ethanol when it is present in quantities as low as 19 g/l. However, adsorption by the

hydrophobic silicalite was convenient and effective in that silicalite-broth contact did not create any ill effects on the fermentation. In 1994, Sivaraman *et al.* showed silicalite as an acceleration of fermentation of sugarcane molasses to ethanol product by *Saccharomyces cerevisiae*. The immobilization of yeast cells within the silicalite had also been suggested by them as a possible cause for the increase in fermentation rates. Among other possible modes of action of silicalite are the removals of inhibitory substances or a lowering of product levels in the beer through adsorption by the additive. The effect of the silicalite is partially due to the removal or abatement in the level of inhibitory components from the molasses medium.

The active silicalite crystals, which do not contain alumina or cations, exhibit hydrophobic and organophilic surface characteristics. The organophilic nature of silicalite is manifested in the selective adsorption of organic molecules, so water is slightly adsorbed whereas ethanol is strongly adsorbed due to ethanol is small an organic molecule. The ethanol capacity is 0.13 kg/kg crystals (Farhadpour and Bono, 1996).

Carton *et al.* (1998) showed that the shape of the isotherms displays the adsorption type favorable in all cases. Therefore, a Langmuir-type equation was used to represent equilibrium adsorption. The asymptotic uptakes at ethanol adsorption equilibrium increase in the order: 0.068 (ZSM-5, R=50) < 0.084 (silicalite, R=300) < 0.126 (CMS-5A). For the same systems at similar temperatures: 0.131g ethanol/g microcrystalline silicalite and 0.12 g ethanol/g microcrystalline ZMS-5. The discrepancy might be due to the use of pelletized adsorbents, which diminishes the hydrophobicity by the presence of the agglomerate. The content of  $Al_2O_3$  in the adsorbent ZSM-5, even while low, could justify the observed capacity difference between ZSM-5 and silicalite. CMS-5A, an activated carbon molecular sieve, is the highest adsorbed ethanol molecules and type 5A is suitable ethanol adsorptive separation (Al-Asheh *et al.*, 2004).

Silanized silica is produced by spraying a silica under intensive mixing, optionally with water or dilute acid at first and then with a surface-modifying reagent or a mixture of several surface-modifying reagents, then mixing, tempering, and subsequently destructuring/compressing and grinding. The modification of the silica surface by dimethylsilane resulted in the strong adsorption of the polar component on

the surface silanols by hydrogen bonding and markedly higher amount of the non-polar component is adsorbed between chains of the non-polar phase. The functional group is adsorbed specifically on the silanol group. However, the hydrocarbon chain of the same molecule is adsorbed on the hydrophobic center (the methyl group). One can say that on a no modified silica gel hydrocarbon chains of alcohols or esters are oriented towards the bulk solution, whereas in the case of silanized silica the radical is oriented parallel to the surface. The results presented confirm the possibility of a change in the surface character of the adsorbent of physically adsorbed molecules (Goworek, 1990).

In terms of the surface adsorbent properties, Kim *et al.* (2000) investigated the effect of surface silanization. The results showed that the attachment of chelating agents can be accomplished via hydrophobic attraction between the methyl groups on the silanized surface and the carbon chains of the chelating agents. This type of adsorption through van der Waals interactions or hydrophobic attractions. In 2001, Park *et al.* studied water adsorption on the silylation with trimethylsilane and triethylsilane, which was used to enhance hydrothermal stability and hydrophobicity of the MCM-48 membrane. The silyl-group was substituted for the Si-OH group on the pore surface of MCM-48. The pore sizes of the nonsilylated and the silylated MCM-48 were 2.4 (nonsilylated), 1.9 (trimethylsilylated), and 1.8 nm (triethylsilylated). The water adsorption study showed that the pore surface of MCM-48 significantly changed to hydrophobic by silylation, used for the separation of an ethanol/water mixture. The report indicated that the separation factor  $\alpha_{EtOH}$  of the nonsilylated, the trimethyl- and triethylsilylated MCM-48 membranes were 0.3, 16 and 24, respectively, and these silylated MCM-48 membranes were 53 and 80 times larger than that of the nonsilylated MCM-48 membrane. This clearly showed that the silylation effectively changed the properties of pore surfaces and affected the ethanol/water adsorption properties.

Park *et al.* (2003) found that adsorbed amount of ethanol vapors on silylated MCM-48 powders is 0.224 g/gads at 303 K,  $p/p_0 \sim 1$ . This selectivity of adsorption is due to the hydrophobic character of the sily-MCM-48 membranes. The adsorbed organic molecules must have blocked the membrane's pores, an effect resulting in the obstruction of diffusion of water molecules in pores. The high selectivity in the

separation of the organic/water mixtures is attributable not only to the hydrophobic nature of the pore surface but also to the uniform mesopores of the sily-MCM-48. Furthermore, the thermal stability of sily-MCM-48 membrane is much higher than polymeric organic membranes.