CHAPTER IV

RESULTS AND DISCUSSION

The objective of this research was to investigate the possibility of combining fermentation and adsorption in one process that can enhance ethanol production. Adsorption capacities of water and ethanol from an ethanol-water mixture were determined in the vapor phase adsorption experiment. Also, the equilibrium adsorption capacity was evaluated in a batch liquid test. Additionally, from the dynamic adsorption experiment, the ethanol adsorption capacity from the breakthrough curve was studied.

4.1 Single Component Adsorption

This section shows the percent of ethanol and water adsorption capacities. Moreover, all data in this part can be used to calculate for ethanol selectivity. The experiments were divided into two sections, ethanol adsorption at 25°C and 40°C.

4.1.1 Moisture Adsorption

The results from water adsorption experiments are shown in Figure 4.1, which shows percent water adsorption capacities at equilibrium for each adsorbent at 25°C and 40°C.
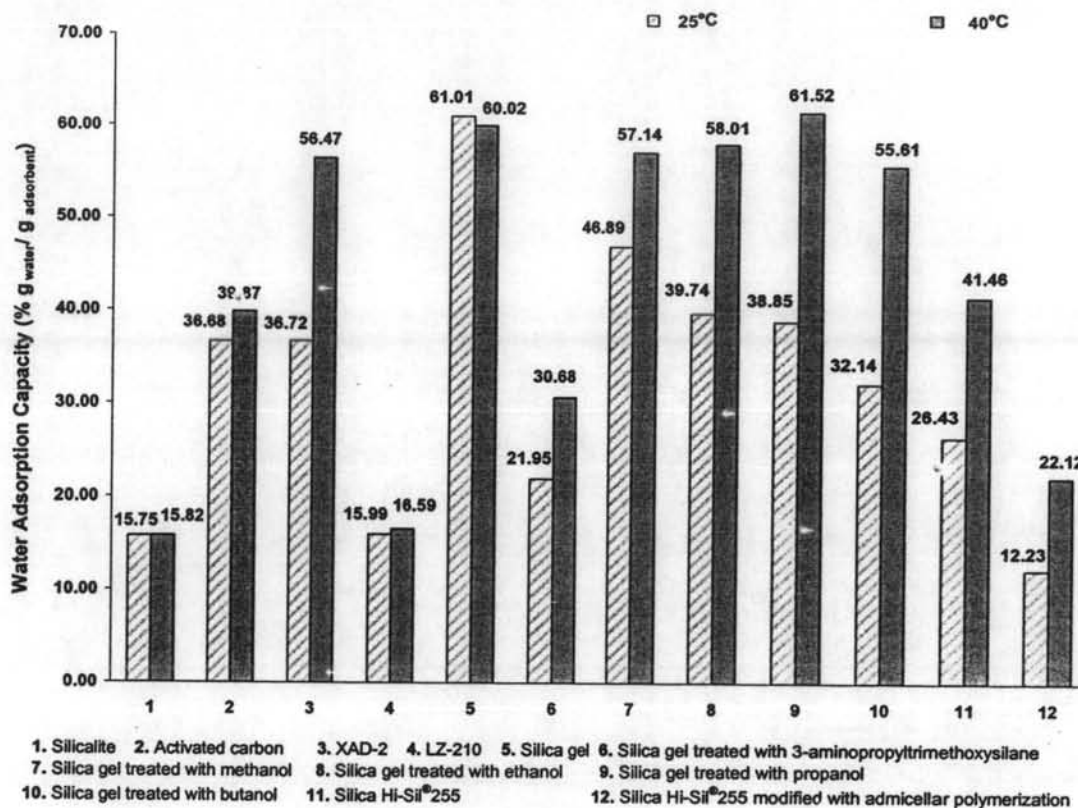
Figure 4.1 Water adsorption capacities at equilibrium for each adsorbent at 25°C and 40°C.

From the figure, silica gel has a higher water adsorption capacity than the others because it has the hydroxyl group on the surface that prefers to adsorb water. The treated silica gels are more hydrophobic than the untreated silica gel since the hydroxyl group on the surface decreases after the treatment. However, they still have high water adsorption capacities due to theirs polarity. Although the polarity decreases with the treatment, the treated silica gels still have more polarity than the other adsorbents, except the untreated one. Moreover, the water adsorption capacities are nearly the same for different temperatures for silicalite, LZ-210, and activated carbon. On the other hand, for XAD-2, silica Hi-Sil®255, and silica Hi-Sil®255 modified with admicellar polymerization, the water adsorption capacities are relatively higher at 40°C than that at 25°C.
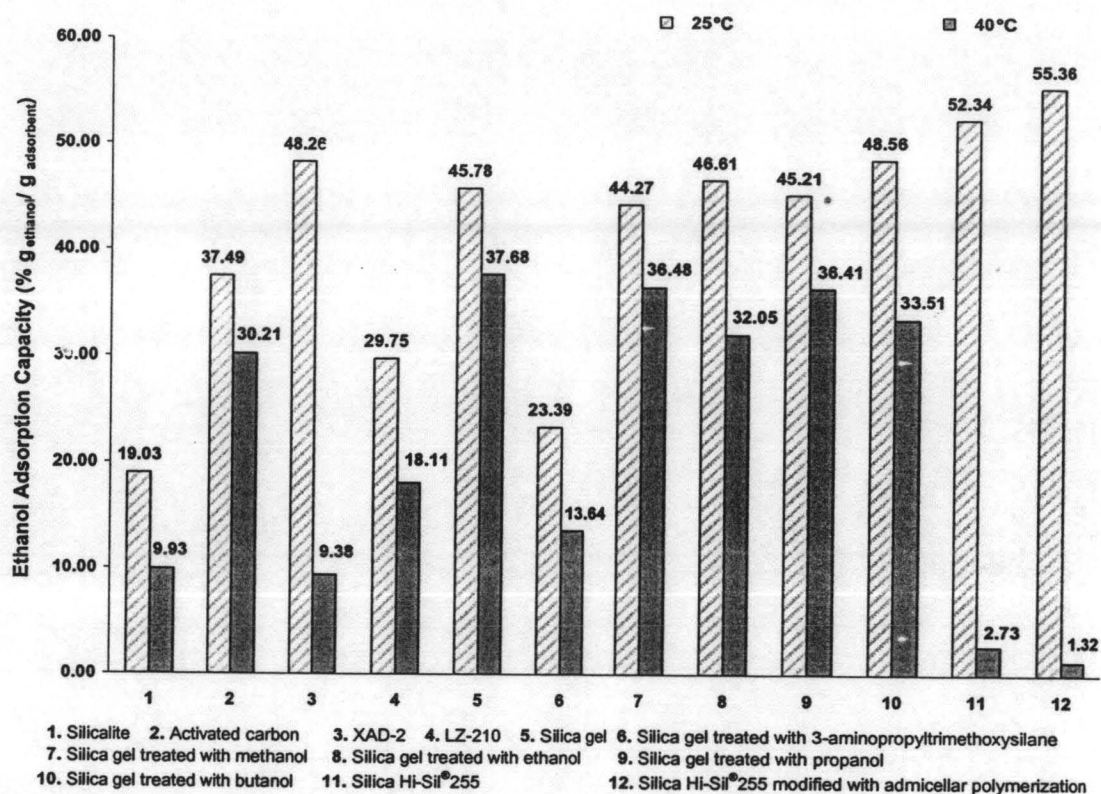
4.1.2 Ethanol Adsorption

Figure 4.2 Ethanol adsorption capacities at equilibrium for each adsorbent at 25°C and 40°C.

As can be seen in Figure 4.2, ethanol adsorption capacities of the adsorbents are higher at 25°C than 40°C because ethanol, a volatile component, easily vaporizes at the higher temperature. From the figure, the ethanol adsorption capacities of XAD-2, silica Hi-Sil®255, and silica Hi-Sil®255 modified with admicellar polymerization are significantly different between both temperatures. It implies that these adsorbents difficultly adsorb ethanol when temperature increases. The untreated silica gel and the treated silica gels also have high ethanol adsorption capacities. However, the lower ethanol adsorption capacities can be observed with silicalite, LZ-210, and activated carbon.

Figures 4.1 and 4.2 show the treated silica gels preferentially adsorb ethanol at 25°C. Among the treated silica gels, the one treated with 3-aminopropyltrimethoxysilane has the lowest ethanol adsorption capacity. Therefore, it is postulated that there must be significant changes in the surface properties of the silica gel treated with 3-aminopropyltrimethoxysilane.

4.1.3 Ethanol Selectivity

The definition of ethanol selectivity in this research is ethanol selectivity in only ethanol-water solution which calculated from ethanol adsorption capacity divided by water adsorption capacity.

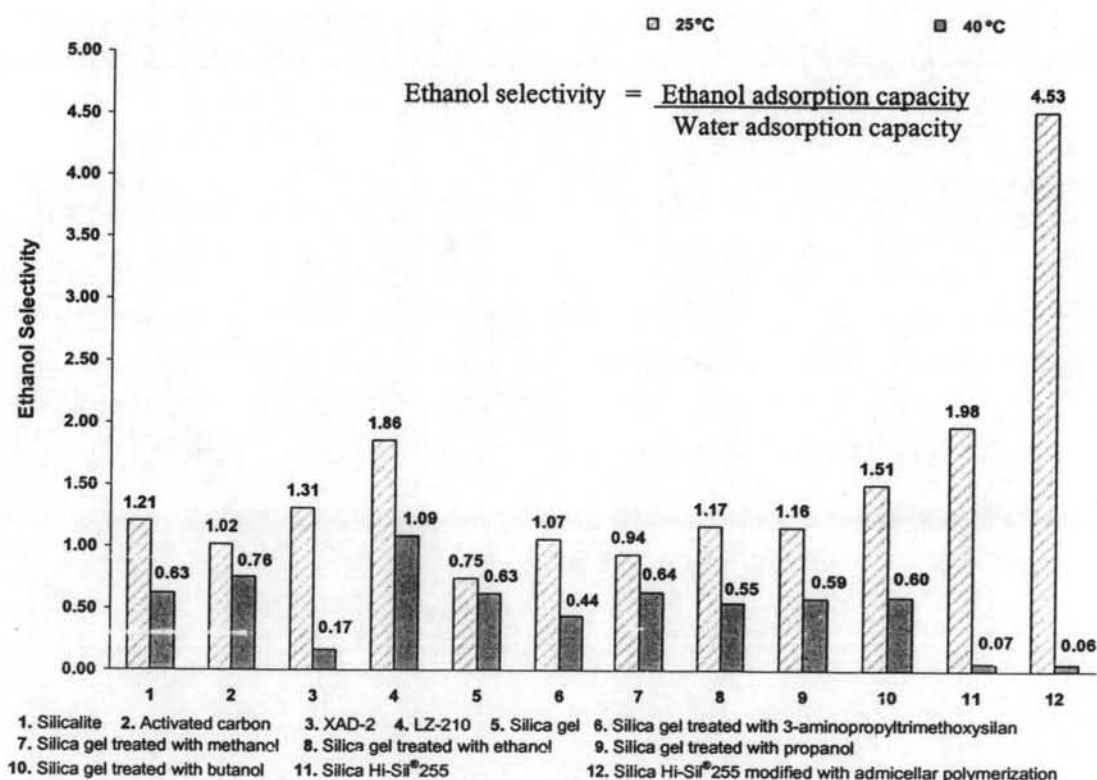Water adsorption and ethanol adsorption capacities for each adsorbent and temperature are shown in Figure 4.3.

$$\text{Ethanol selectivity} = \frac{\text{Ethanol adsorption capacity}}{\text{Water adsorption capacity}}$$

1. Silicalite   2. Activated carbon   3. XAD-2   4. LZ-210   5. Silica gel   6. Silica gel treated with 3-aminopropyltrimethoxysilan
7. Silica gel treated with methanol   8. Silica gel treated with ethanol   9. Silica gel treated with propanol
10. Silica gel treated with butanol   11. Silica Hi-Sil®255   12. Silica Hi-Sil®255 modified with admicellar polymerization

Figure 4.3 Ethanol selectivities at equilibrium for each adsorbent at 25°C and 40°C.

The results show that the ethanol selectivities at 25°C are higher than that at 40°C. It implies that the adsorbents preferentially adsorb ethanol at low temperature. The explanation for this outcome is its surface properties (surface area, polarity, and hydrophobicity). Moreover, silica Hi-Sil®255 modified with admicellar polymerization has the highest ethanol selectivity, due to its high hydrophobicity. From the results, there is a possibility of using one of the adsorbents in the *in situ* ethanol removal from the fermentation process.
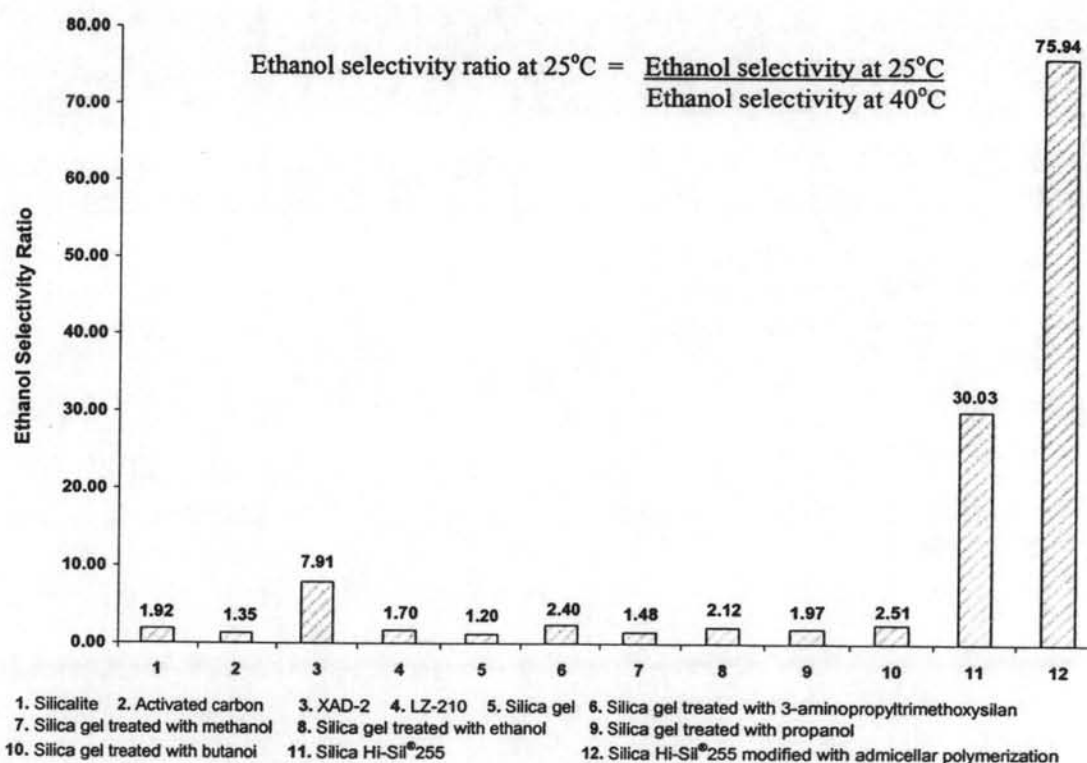
4.1.4 Ethanol Selectivity Ratio

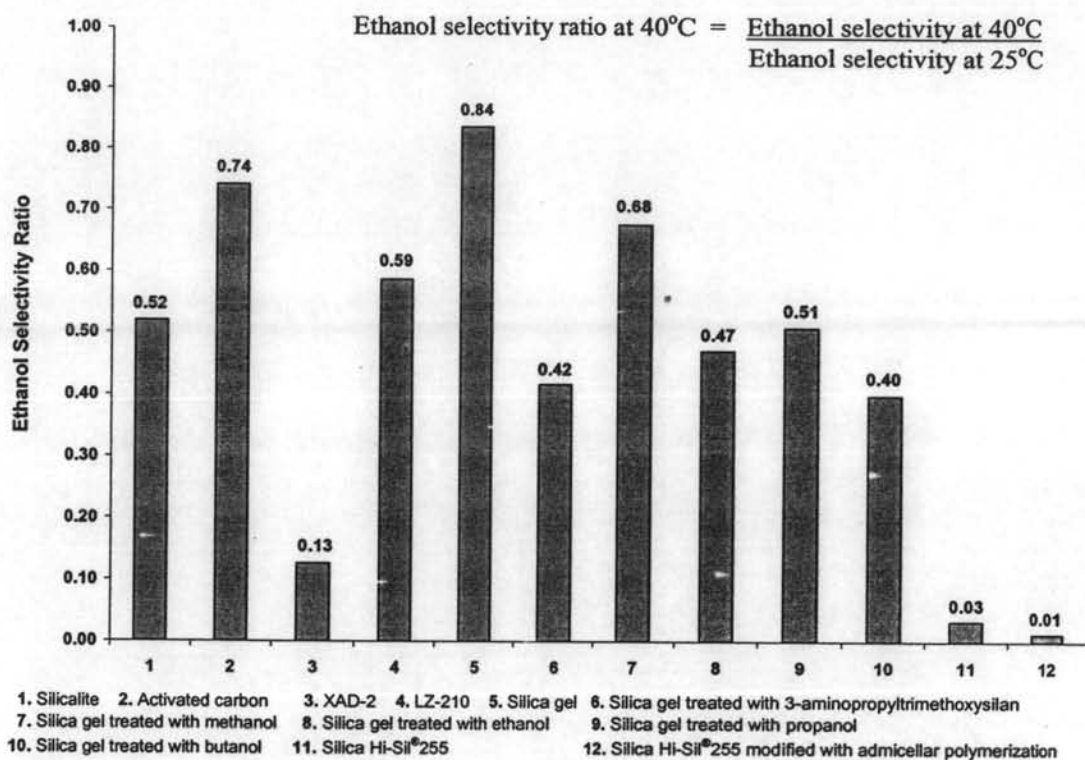Figure 4.4 Ethanol selectivity ratio at equilibrium for each adsorbent at 25°C.

Figure 4.5 Ethanol selectivity ratio at equilibrium for each adsorbent at 40°C.

The ethanol selectivity ratio was calculated from the ethanol selectivities at the two temperatures. Figures 4.4 and 4.5 show the ethanol selectivity ratios at equilibrium for each adsorbent at 25°C and 40°C, respectively. From the figure, the ethanol selectivity ratios of the adsorbents are lower at 40°C than those at 25°C. An interesting observation in this experiment is that the ethanol selectivity ratios for silica Hi-Sil®255 modified with admicellar polymerization, untreated silica Hi-Sil®255, and XAD-2 are relatively high at 25°C.

4.2 Competitive Component Adsorption

Competitive adsorption was conducted in a batch-wise fashion at 25°C. The adsorption capacity in gram of ethanol per gram of an adsorbent was determined.

The adsorption isotherms of the adsorbents are shown from Figures 4.6 to 4.17. The results indicate that the amount of ethanol adsorbed per unit mass of adsorbent increases from 1 to 12 wt% of ethanol concentration. This increase in the concentration gradient leads to a significantly higher driving force.

Figures 4.6 and 4.7 are the ethanol adsorption isotherms of silicalite and LZ-210, respectively. Silicalite and LZ-210 are zeolites, which have low amounts of aluminum in their frameworks. The LZ-210 zeolite is a dealuminated Y zeolite and the silicalite zeolite is an aluminum-free form of ZSM-5. Less aluminum in the framework gives a less hydrophilic zeolite, thus making both zeolites hydrophobic.
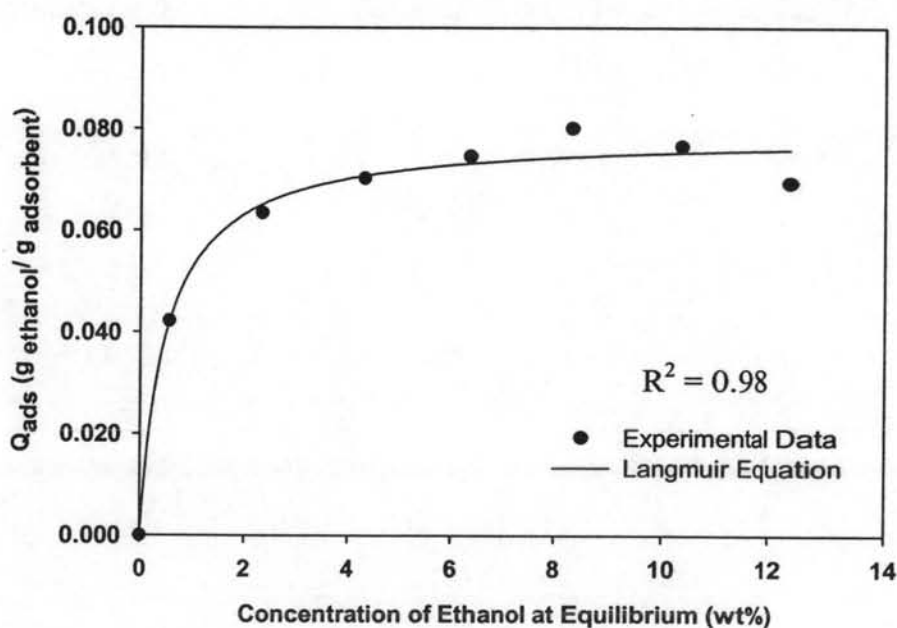

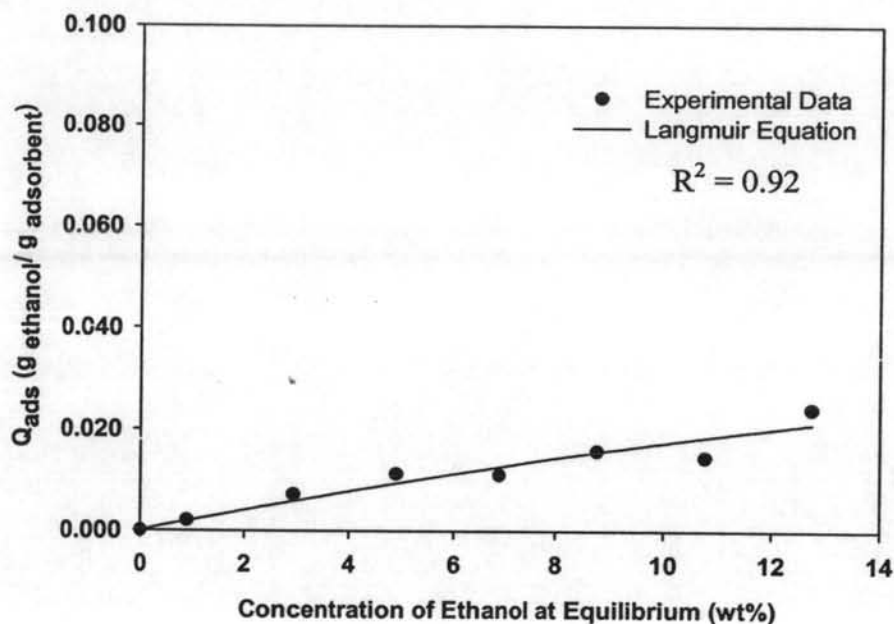**Figure 4.6** Ethanol adsorption isotherm of silicalite at 25°C.

Figure 4.7 Ethanol adsorption isotherm of LZ-210 at 25°C.

From the experiments, it was determined that the ethanol adsorption capacities are 0.0759 gram ethanol per gram adsorbent for the silicalite and 0.0211 gram ethanol per gram adsorbent for the LZ-210 in ethanol-water mixtures. The results show that the ethanol adsorption capacity of silicalite is higher than the LZ-210. Because the silicalite has little aluminum in its framework, it has a highly hydrophobic surface, which is a reason for its high ethanol adsorption capacity. As for the isotherms, silicalite preferentially adsorbs ethanol molecules from ethanol-water mixtures, which can be seen from the shape of the isotherm. In contrast, the isotherm of the LZ-210 displays slightly favorable ethanol adsorption. The amount of aluminum in the LZ-210 justifies the observed capacity difference between silicalite and LZ-210.
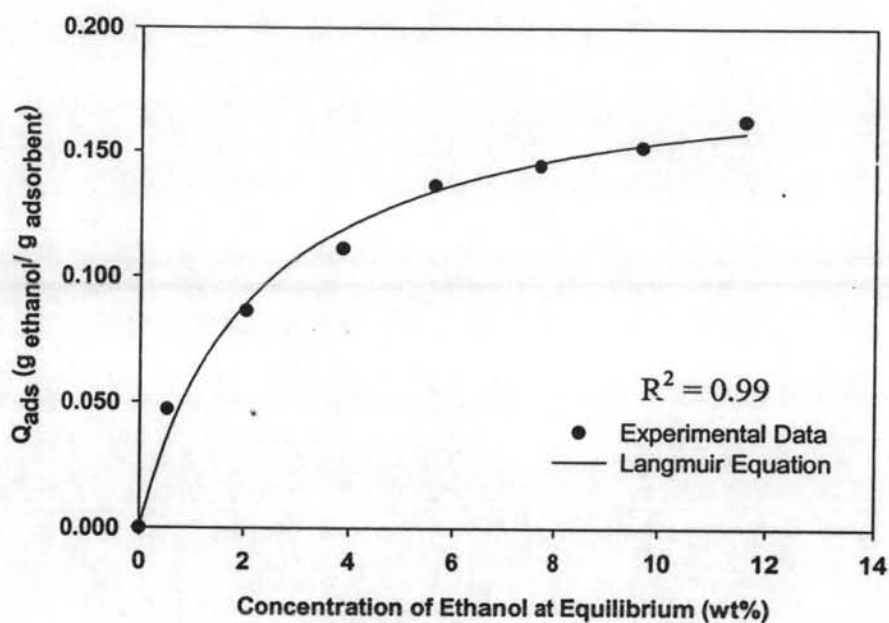
Figure 4.8 Ethanol adsorption isotherm of activated carbon at $25^{\circ}C$.

The ethanol adsorption isotherm of activated carbon is shown in Figure 4.8. Its ethanol adsorption capacity is 0.1577 gram ethanol per gram adsorbent. Activated carbon is an adsorbent, which has a high surface area and preferentially adsorbs organic molecules. These properties are the reasons why activated carbon has a higher ethanol adsorption capacity than the others. Moreover, its ethanol adsorption isotherm shows that it selectively adsorbs ethanol molecules. The shape of the isotherm demonstrates the favorable adsorption type.

Figure 4.9 shows that in the ethanol adsorption isotherm of XAD-2, ethanol adsorption capacity is 0.0664 gram ethanol per gram adsorbent. XAD-2 is a polystyrene-divinylbenzene resin that is nonpolar and hydrophobic. Normally, it is used in the removal of organic compounds. Therefore, XAD-2 has quite a high ethanol adsorption capacity in the experiments.
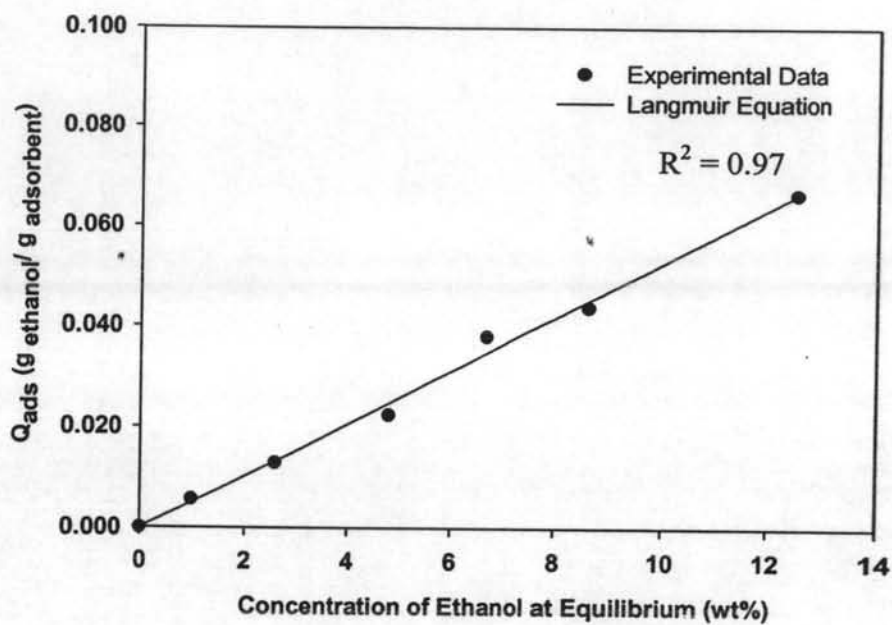
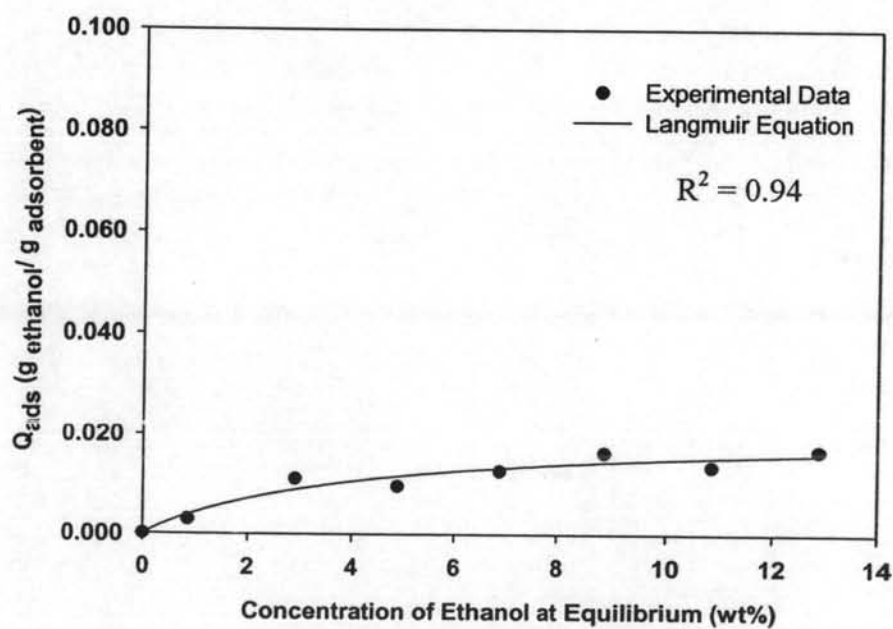**Figure 4.9** Ethanol adsorption isotherm of XAD-2 at 25°C.

Figure 4.10 Ethanol adsorption isotherm of silica gel at 25°C.

Figure 4.10 is the ethanol adsorption isotherm of silica gel. It has a hydrophilic surface that shows favorable water adsorption. The shape of the isotherm acts unfavorably for ethanol adsorption because its surface provides the hydroxyl group needed to adsorb water over ethanol molecules. The ethanol adsorption capacity of silica gel is 0.0168 gram ethanol per gram adsorbent, which is quite a low capacity.
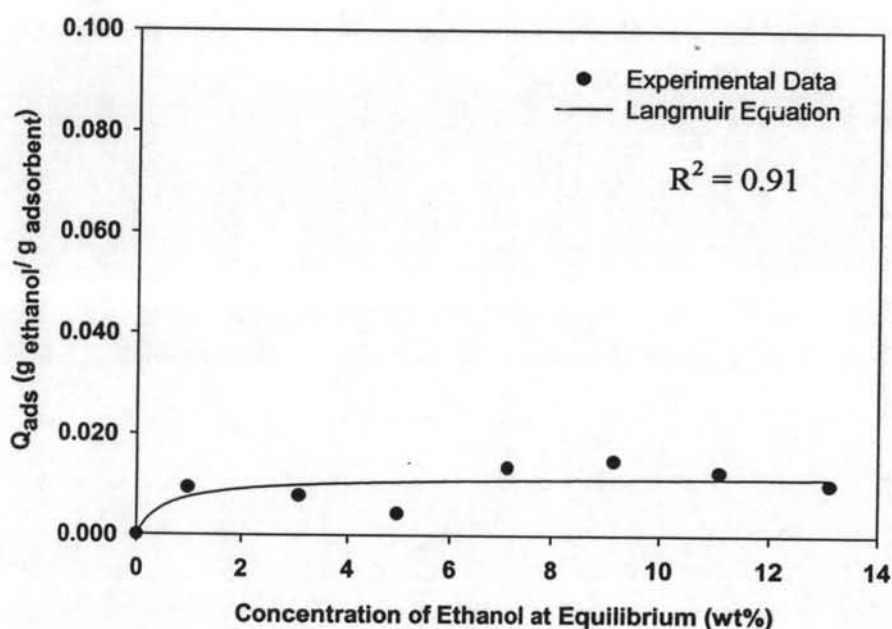

Figure 4.11 Ethanol adsorption isotherm of silica gel treated with 3-aminopropyl trimethoxysilane at 25°C.

Figures 4.11 through 4.15 are the ethanol adsorption isotherms of treated silica gels with 3-aminopropyltrimethoxysilane (4.11), methanol (4.12), ethanol (4.13), n-propanol (4.14), and n-butanol (4.15) whose ethanol adsorption capacities are 0.0113, 0.0158, 0.0195, 0.0174, and 0.0269 in gram ethanol per gram adsorbent, respectively.
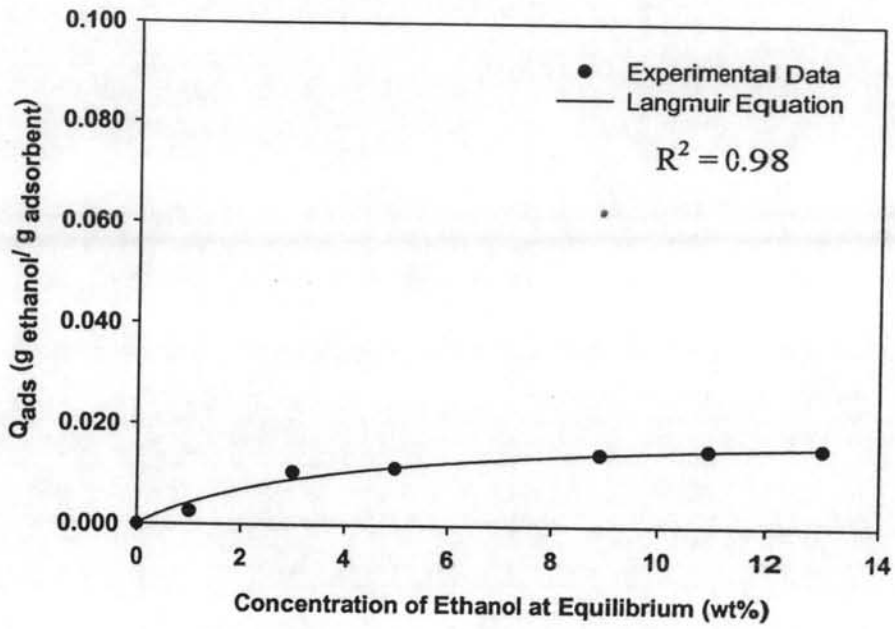
Figure 4.12 Ethanol adsorption isotherm of silica gel treated with methanol at 25°C.
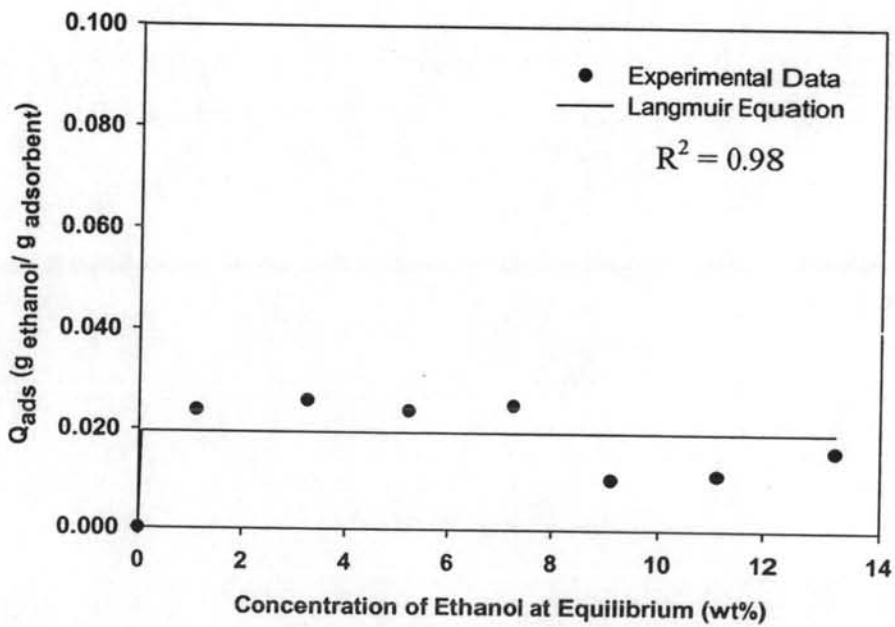

Figure 4.13 Ethanol adsorption isotherm of silica gel treated with ethanol at 25°C.
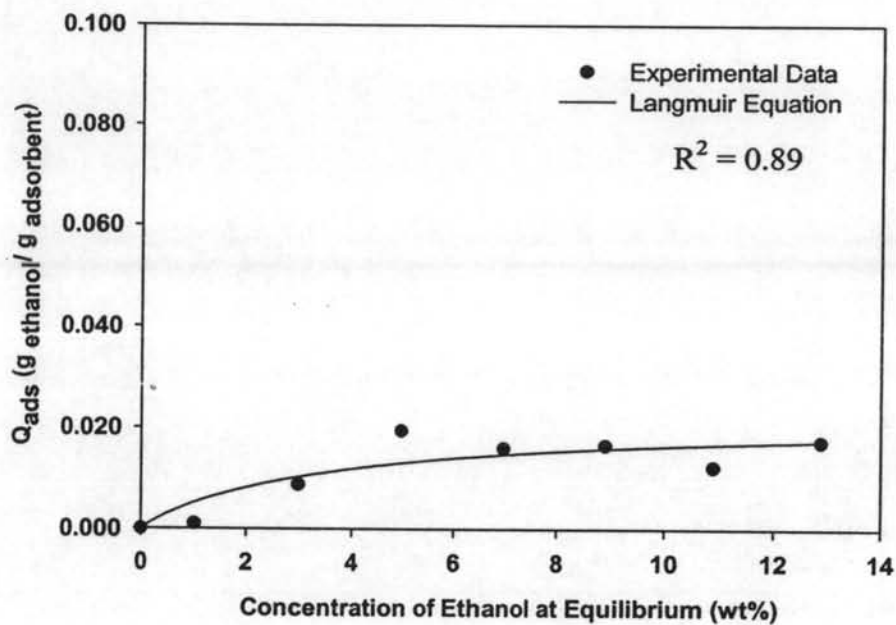
Figure 4.14 Ethanol adsorption isotherm of silica gel treated with propanol at 25°C.
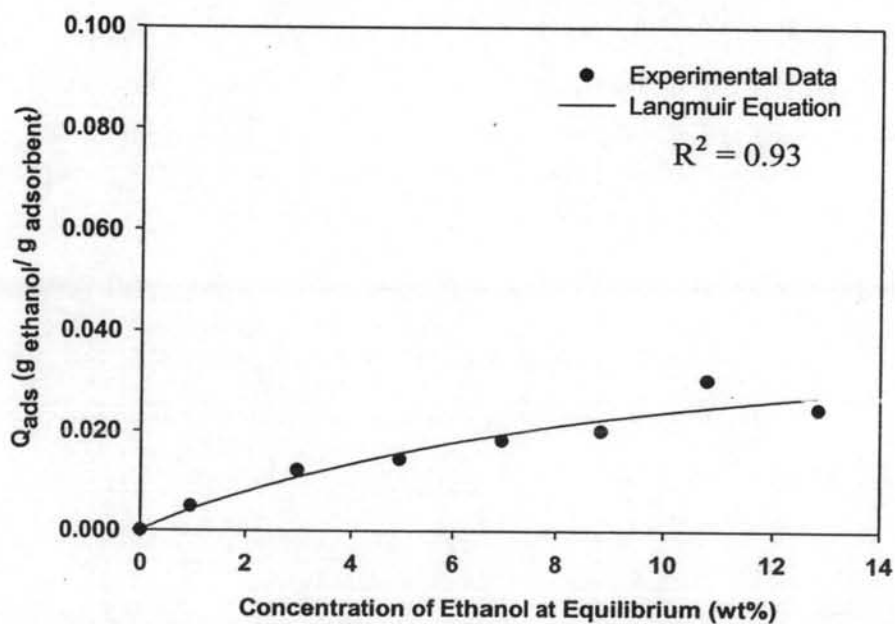

Figure 4.15 Ethanol adsorption isotherm of silica gel treated with butanol at 25°C.

The results indicate that the ethanol adsorption capacities of the untreated and treated silica gels are not significantly different. Even though in the treated silica gels their polarities are adjusted by chemicals, they still preferentially adsorb water over ethanol molecules.

As can be seen in these figures, the isotherms tend to be flat demonstrating that ethanol adsorption is unfavorable. It is obvious that the silica gels treated with these chemicals are not enough to selectively adsorb ethanol.
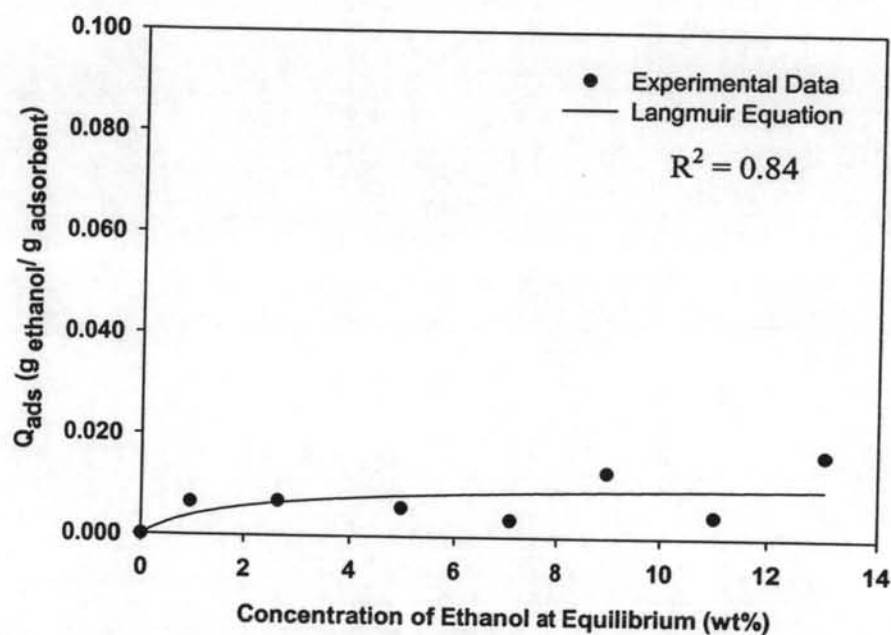

Figure 4.16 Ethanol adsorption isotherm of silica Hi-Sil®255 at 25°C.

Silica Hi-Sil®255 is a silica whose surface is modified to obtain hydrophobicity. Its ethanol adsorption isotherm can be seen in Figure 4.16. The shape of the isotherm displays the unfavorable ethanol adsorption and the ethanol adsorption capacity is 0.0096 gram ethanol per gram adsorbent.
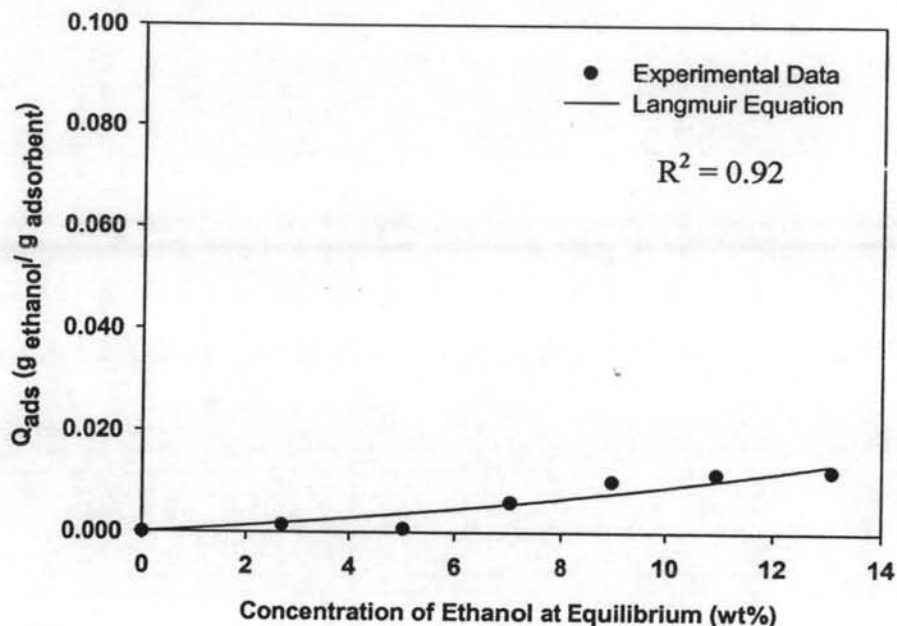
Figure 4.17 Ethanol adsorption isotherm of silica Hi-Sil®255 modified with admicellar polymerization at 25°C.

Figure 4.17 is the ethanol adsorption isotherm of silica Hi-Sil®255 modified with admicellar polymerization. The surface modification process with admicellar polymerization is to reduce its polarity. Its ethanol adsorption capacity is 0.0121 gram ethanol per gram adsorbent. The shape of the isotherm is flat, similar to the unmodified silica Hi-Sil®255. Although the modified and unmodified silica Hi-Sil®255 are arranged in a hydrophobicly adsorbent manner, their ethanol adsorption capacities are quite low.

The discrepancy might be due to the use of powder adsorbents in the liquid phase, which diminishes the surface area by the presence of the agglomeration. Therefore, both adsorbents are unsuitable to pack into a column in continuous process experiments because they can agglomerate and plug the column, causing a pressure drop in the column.

The shape of the isotherms displays the adsorption characteristic. Therefore, a langmuir-type equation was used to represent equilibrium adsorption. The sigmaplot scientific graphing system was used to determine the values of the model parameters by fitting the experimental data to the proposed equation (equation 4.1):

$$Q_a = \frac{Q_{max} \, KaC_a}{(1 + KaC_a)}, \qquad (4.1)$$

where C_a refers to the equilibrium concentration, Q_a is the adsorption uptake, Q_{max} is the maximum capacity, and Ka is the equilibrium constant. The subscripts "a" in this equation refer to the ethanol component. Saturation capacity is defined as the maximum capacity that molecules can pack in the pores of the adsorbent and is obtained from the plateau regions in the isotherms.

The equilibrium adsorption capacities obtained by equation 4.1 for each of the adsorbents are listed in Table 4.1, which shows the individual adsorption capacities as a function of ethanol concentration for each adsorbent tested. This verifies the theory that the adsorption capacity also increases until enough ethanol molecules are present to saturate the adsorbent material when the concentration of ethanol increases.

Table 4.1 Ethanol adsorption capacities (gram ethanol per gram adsorbent) from the batch experiments

| Adsorbent	Adsorption Capacity (Q_a)	Predicted Adsorption Capacity (Q_{max})
Silicalite	0.0759	0.0790
Activated carbon	0.1577	0.1885
XAD-2	0.0664	0.0686
LZ-210	0.0211	0.0336
Silica gel	0.0168	0.0208
Silica gel treated with 3-aminopropyltrimethoxysilane	0.0113	0.0118
Silica gel treated with methanol	0.0158	0.0205
Silica gel treated with ethanol	0.0195	0.0195
Silica gel treated with propanol	0.0174	0.0220
Silica gel treated with butanol	0.0269	0.0491
Silica Hi-Sil®255	0.0096	0.0110
Silica Hi-Sil®255 modified with admicellar polymerization	0.0121	0.0214
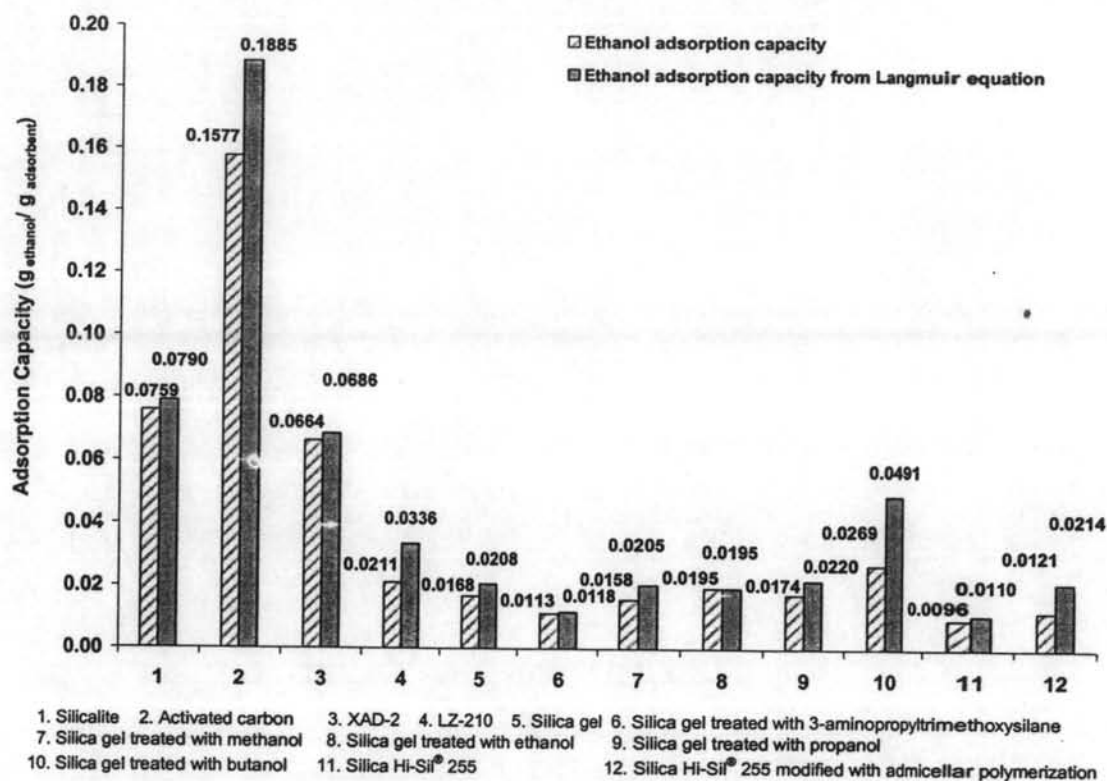
Figure 4.18 Equilibrium ethanol adsorption capacities of the adsorbents at 25°C.

The batch liquid experiment indicates that the ability of activated carbon to preferentially adsorb ethanol over water molecules is significantly greater than the other adsorbents. Its capacity is 0.1577 gram ethanol per gram adsorbent. In literature reviews, Lee and Wang (1982) found an adsorption capacity of 0.13 gram ethanol per gram adsorbent for the adsorption of ethanol on to conventional activated carbon. This is because activated carbon selectively adsorbs organic molecules and has a high surface area. This is a reasonable outcome. In addition, the results show that the adsorption capacities for silicalite and XAD-2 are very close and both also provide good ethanol adsorption capacities.

4.3 Dynamic Adsorption: Breakthrough Curves

4.3.1 Breakthrough Curves

A batch operated adsorption still is used to investigate the liquid phase adsorption of ethanol onto the adsorbents from an ethanol-water solution. For these experiments, the breakthrough curves from ethanol adsorption were obtained. The Y-axis of the graphs represent the concentration of ethanol, which is the value when the concentration of a sample taken at a particular time, t, is divided by the initial concentration of the mixture fed to the adsorber column, and the X-axis gives the volume (mL) throughout the experiment run. For the column, which had an inside diameter of 0.78 cm and a column length of 114 cm, a volumetric flow rate of 12 wt% ethanol in the fed mixture is 1.20 mL/min.

The adsorbents, which are silicalite, activated carbon, LZ-210, XAD-2, silica gel, silica gel treated with 3-aminopropyltrimethoxysilane, silica gel treated with methanol, silica gel treated with ethanol, silica gel treated with propanol, and silica gel treated with butanol, were used. Silica Hi-Sil®255 and silica Hi-Sil®255 modified with admicellar polymerization were not used. The reason for this is that both adsorbents are fine dust particles, which creates a clogging effect within the column. This produces a large pressure drop across the adsorbent bed causing column flooding.

The breakthrough curves of each adsorbent demonstrate the ethanol adsorption characteristic, where the ethanol adsorption capacity can be calculated. A graphical representation of data can be made, in which the concentration of ethanol is plotted versus the total adsorbate volume of the experiment. The total amount adsorbed is the area that exists above the curve. This area is estimated by creating a triangle from the linear portion of the curve up to the point of breakthrough. Theoretically, adsorption capacity is used up in the initial mass transfer zone (MTZ), the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration gradually increases until it equals the influent concentration.
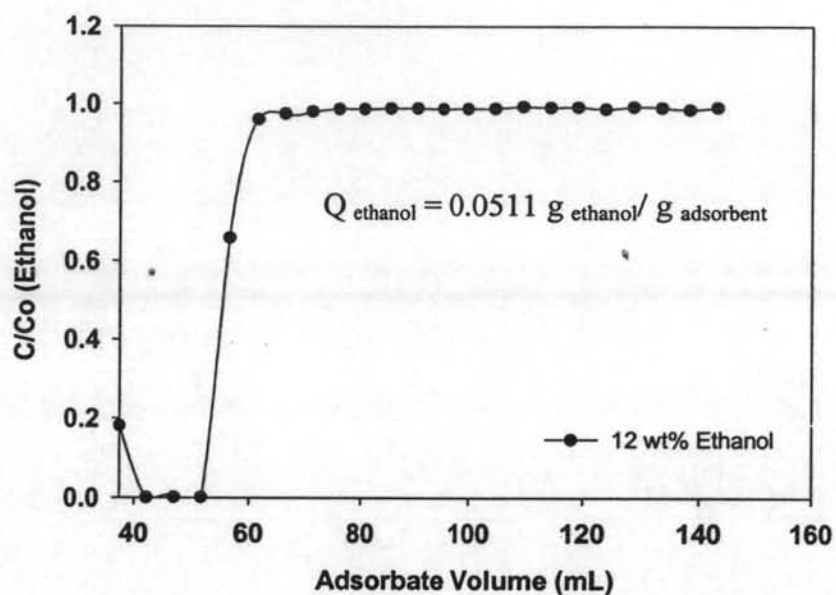
Figure 4.19 Breakthrough curves demonstrating adsorption characteristics for silicalite at 30°C.
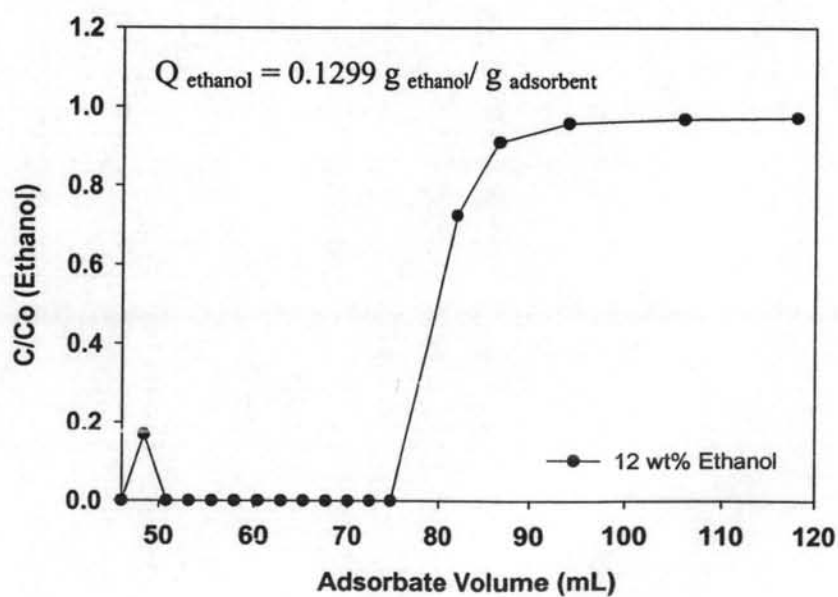

Figure 4.20 Breakthrough curves demonstrating adsorption characteristics for activated carbon at 30°C.

The chart shows C/Co (Ethanol) on the y-axis (from 0.0 to 1.2) versus Adsorbate Volume (mL) on the x-axis (from 40 to 120), with a legend marked "12 wt% Ethanol" and annotation:

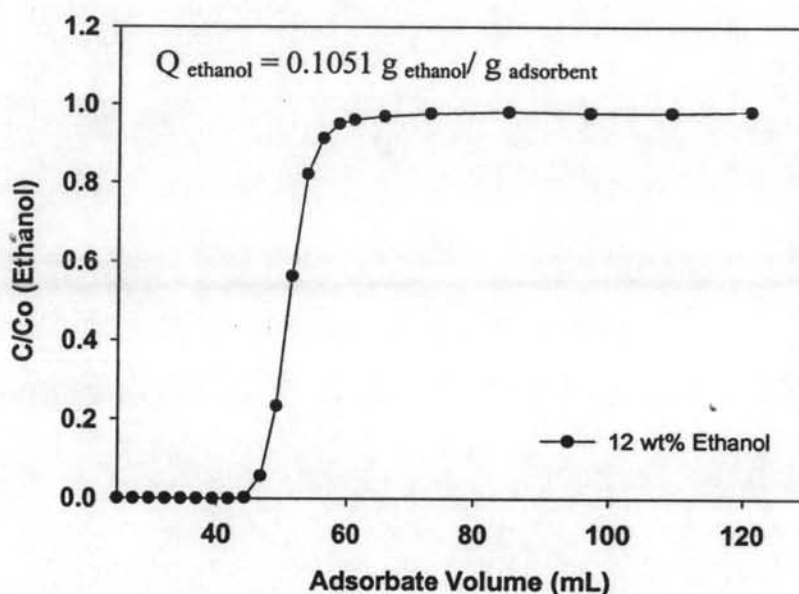$$Q_{ethanol} = 0.1051 \text{ g}_{ethanol}/\text{ g}_{adsorbent}$$

Figure 4.21 Breakthrough curves demonstrating adsorption characteristics for XAD-2 at 30°C.

Figures 4.19 to 4.21 illustrate the breakthrough curves of silicalite, activated carbon, and XAD-2. These three have longer breakthrough times than the others. The longer breakthrough times of each adsorbent show a good ability to selectively adsorb ethanol. Their ethanol adsorption capacities calculated from the breakthrough curve of silicalite, activated carbon, and XAD-2 are 0.0511, 0.1299, 0.1051 gram ethanol per gram adsorbent, respectively. XAD-2 has higher swelling factors in ethanol than water. Resin XAD-2 has a macroreticular structure with a high divinyl benzene content (polystyrene-DVB) and 300 m^2 surface area/ g of resin. In literature reviews, Marik *et al.* (1983) inferred that the macroreticular structures can be a hopeful possibility of preferentially adsorbing ethanol. Moreover, they found an ethanol adsorption capacity of 0.108 gram ethanol per gram adsorbent for the adsorption of ethanol onto XAD-2 (Rohm and Haas Co.) and 0.1800 gram ethanol per gram adsorbent for activated carbon (Sarabhai Chemicals, India). These adsorbents are a highly hydrophobic group, which gives good results.
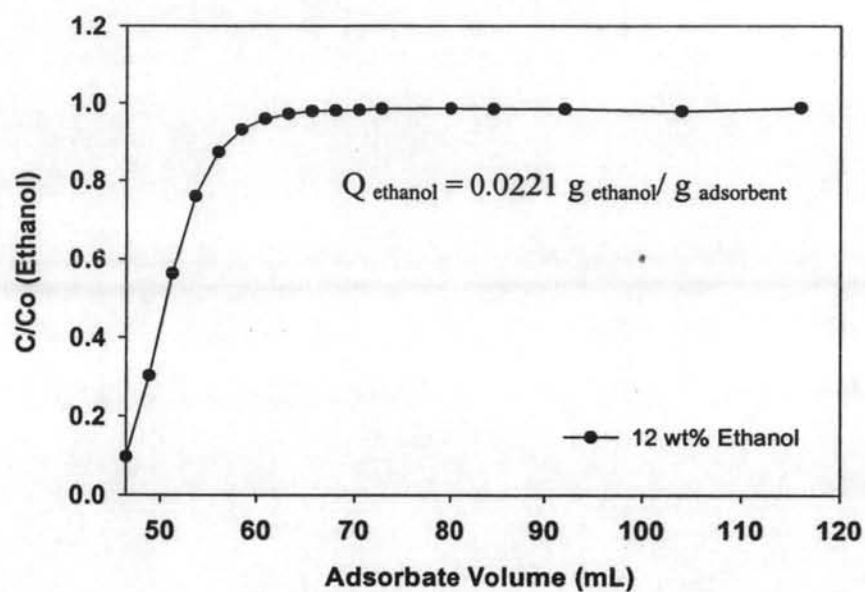
Figure 4.22 Breakthrough curves demonstrating adsorption characteristics for LZ-210 at 30°C.
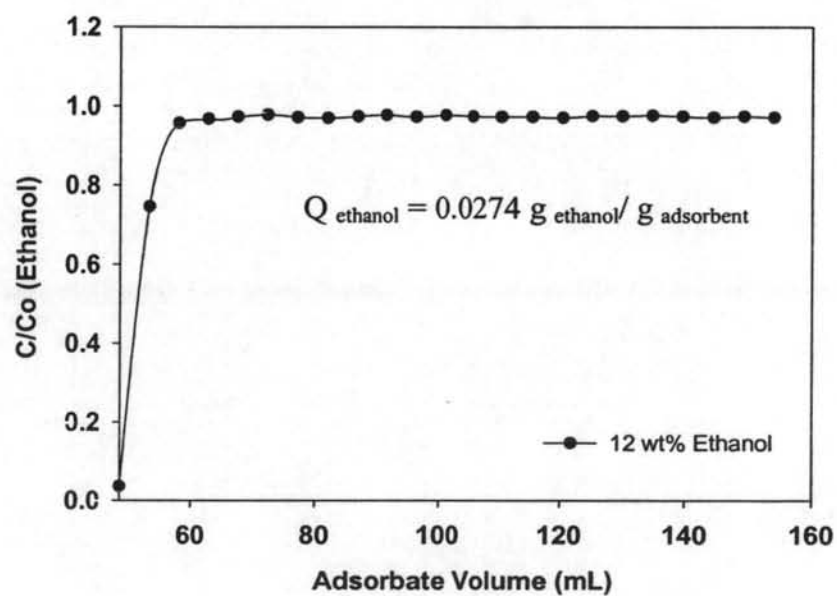

Figure 4.23 Breakthrough curves demonstrating adsorption characteristics for silica gel at 30°C.

Figure 4.24 Breakthrough curves demonstrating adsorption characteristics for silica gel treated with 3-aminopropyltrimethoxysilane at 30°C.

Figure 4.25 Breakthrough curves demonstrating adsorption characteristics for silica gel treated with methanol at 30°C.

Figure 4.26 Breakthrough curves demonstrating adsorption characteristics for silica gel treated with ethanol at 30°C.

Figure 4.27 Breakthrough curves demonstrating adsorption characteristics for silica gel treated with propanol at 30°C.

The graph shows C/Co (Ethanol) on the y-axis (0.0 to 1.2) versus Adsorbate Volume (mL) on the x-axis (60 to 120), with the annotation $Q_{ethanol} = 0.0231\ g_{ethanol}/\ g_{adsorbent}$ and legend "12 wt% Ethanol".
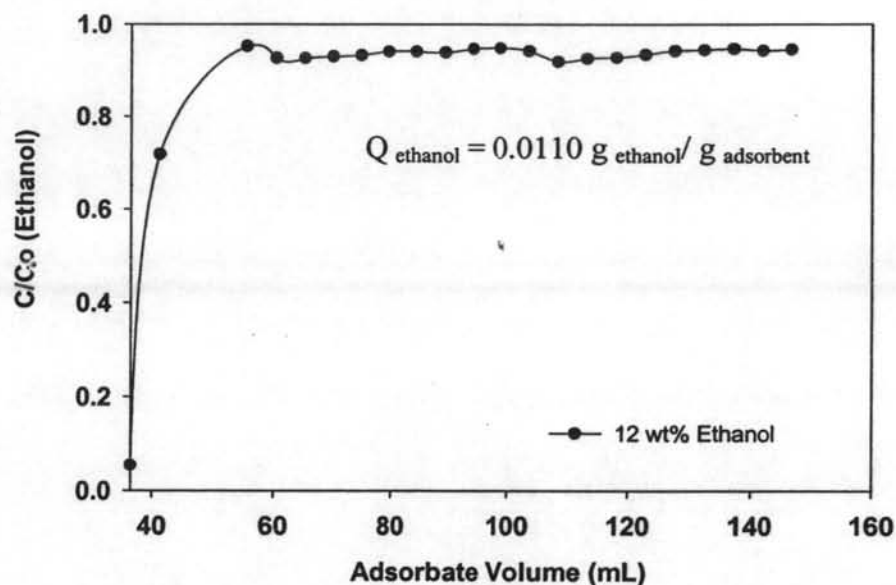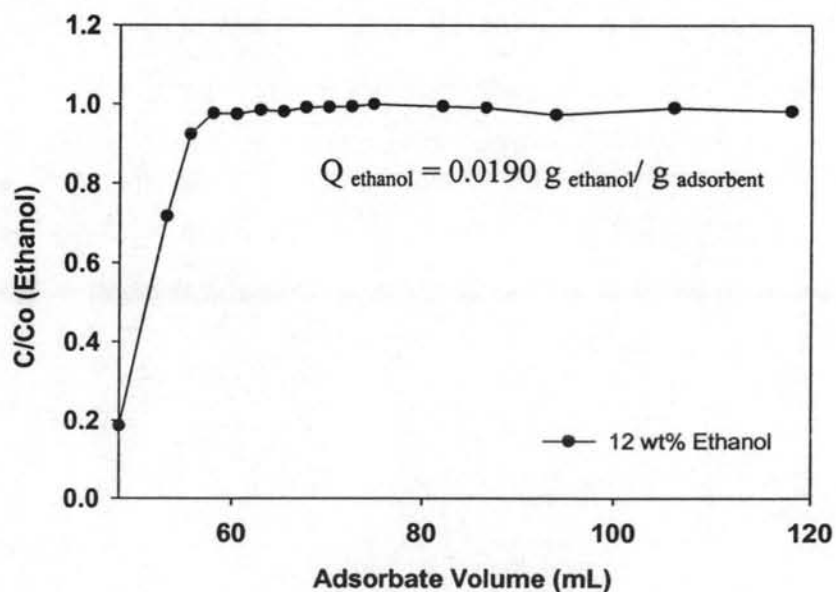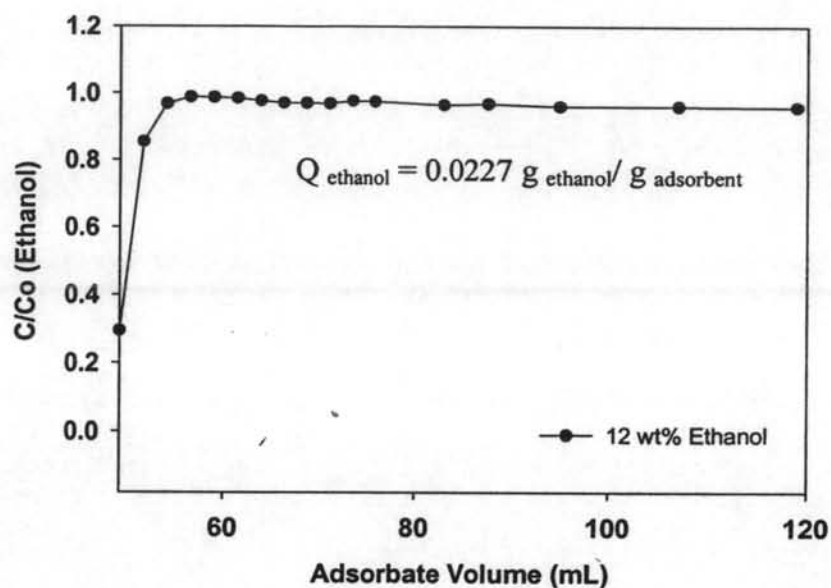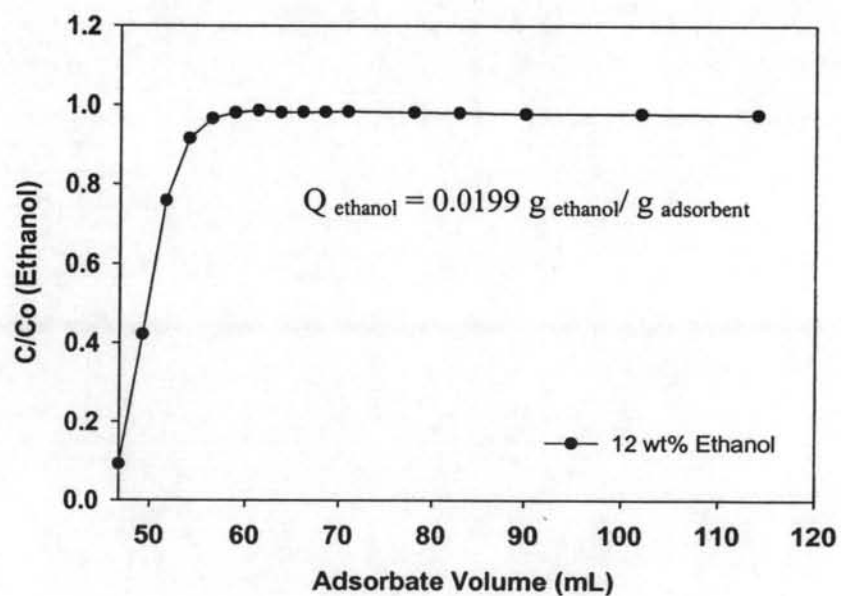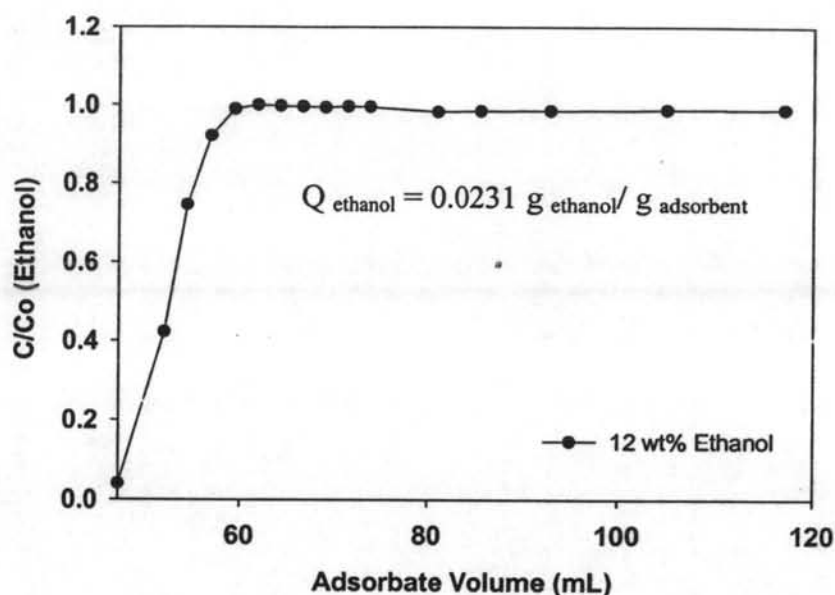
Figure 4.28 Breakthrough curves demonstrating adsorption characteristics for silica gel treated with butanol at 30°C.

Figures 4.22 through 4.28 are the breakthrough curves of LZ-210 (4.22), silica gel (4.23), silica gels treated with 3-aminopropyltrimethoxysilane (4.24), methanol (4.25), ethanol (4.26), n-propanol (4.27), and n-butanol (4.28), whose ethanol adsorption capacities are 0.0221, 0.0274, 0.0110, 0.0190, 0.0227, 0.0199, and 0.0231 in gram ethanol per gram adsorbent, respectively. From the breakthrough curves, the adsorbents of this group have a short breakthrough time. In other words, they show very low ethanol adsorption capacities in that their breakthrough curves reach equilibrium rapidly. Equilibrium is characterized as the time when the breakthrough curves develop a plateau, indicating that no more ethanol is adsorbed. There are several reasons for this. First, the properties of the adsorbents (such as hydrophobicity, surface area, and selective pores) are not suitable for selectively adsorbing ethanol. Although LZ-210 is a modified Y zeolite by chemical treatment to become a hydrophobic adsorbent, it still prefers to adsorb water in an ethanol-water mixture. The reason of LZ-210's results is that the nature of Y zeolite is hydrophilic. When it is modified, the ratio of the silica to alumina

framework is increased from 5:1 to 8:1. This very low ratio indicates that LZ-210 is not acceptable to use for adsorbing ethanol from the mixture because it still has an electrostatic field to react with high polar molecules (water). In the case of untreated and treated silica gels, the untreated silica gel shows that there are hydroxyl groups on the surface, which are needed to adsorb water molecules. The decrease of adsorption of the polar component is connected with the decrease of the concentration of surfaces of the silanol group (Goworek, 1990). Although the silica gels are treated with chemicals to decrease polarity on the surface, their ethanol adsorption capacities are not significantly different between untreated silica gel and treated silica gels, except silica gel treated with 3-aminoproplytrimethoxysilane. The ethanol adsorption capacity of the treated silica gel with 3-aminoproplytrimethoxy silane is the lowest, which reflects its poor ability to adsorb ethanol. Secondly, the mixture flow rate might be fast, resulting in a poor mass transfer of ethanol from the fluid to the adsorbents.
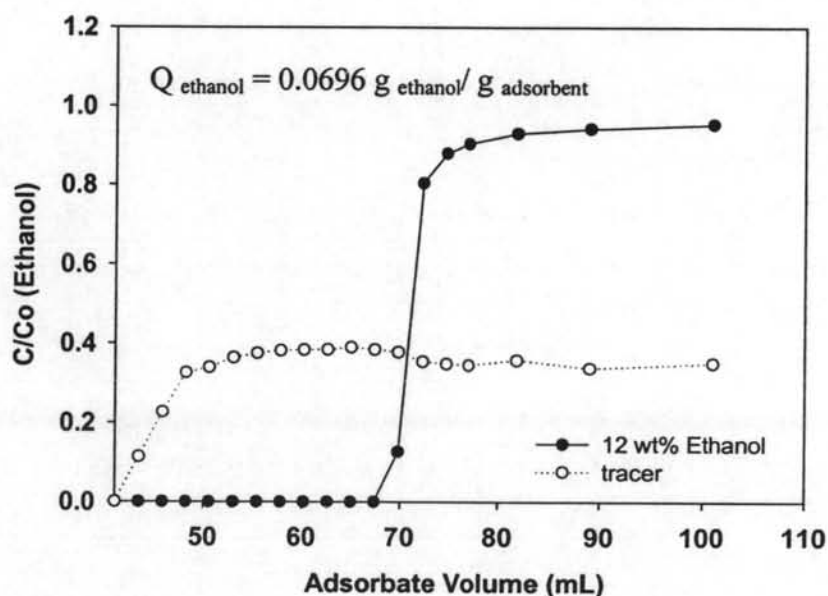

Figure 4.29 Breakthrough curves demonstrating adsorption characteristics for silicalite at 30°C.
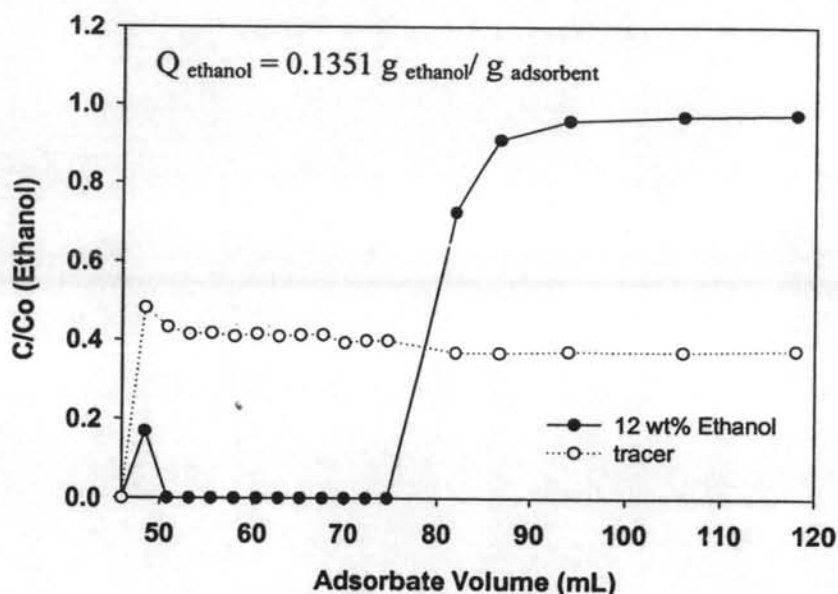
Figure 4.30 Breakthrough curves demonstrating adsorption characteristics for activated carbon at 30°C.

Figures 4.29 through 4.31 show the breakthrough curves of silicalite, activated carbon, and XAD-2 when the feed of the experiments is composed of 12 wt% ethanol in ethanol-water mixture, and tracer (salt). The results show that there are no significant differences when the tracer is used or not used. But in the experiments conducted with the tracer, they can show an amount of void in the column packed with the adsorbents. The ethanol adsorption capacities of these adsorbents are 0.0696 (silicalite), 0.1351 (activated carbon), and 0.1144 (XAD-2) in gram ethanol per gram adsorbent. These adsorbents have much higher ethanol adsorption capacities than the others. The reasons for using them to adsorb ethanol, with mixing the tracer in the feed, are that they are organophilic, thermally stable, selective to ethanol, and have good capacities, which means they would be good to use in the combining process. Therefore, silicalite, activated carbon, and XAD-2 were used in the adsorption-desorption process to study the effect of temperature on ethanol removal.
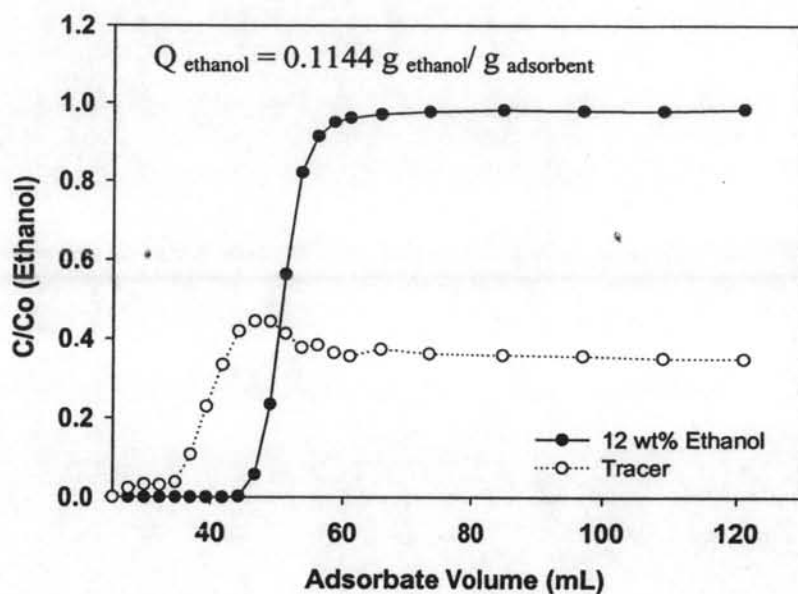
Figure 4.31 Breakthrough curves demonstrating adsorption characteristics for XAD-2 at 30°C.

The actual amounts of material placed inside the column with a bed volume of 54 cm³ are 45.12, 28.06, and 22.73 grams of silicalite, activated carbon, and XAD-2, respectively. The relative amounts placed in the column were chosen to offer the best adsorption results with the optimal column operating parameters. This included careful consideration of column flooding caused by too large of a pressure drop across the adsorbent material, especially as the XAD-2 adsorbent swells. Therefore, XAD-2 should be swelled with water at 25°C overnight before packing in the column to prevent clogging of the adsorbent during the running of the experiments.

4.3.2 Ethanol Removal

There are several methods of regeneration (such as thermal swing, pressure swing, purge gas stripping, and displacement desorption). The choice between the possible modes of regeneration depends on economic factors as well as on technical considerations. For example, the availability of a cheap source of steam or waste heat tends to favor the thermal swing operation over the other alternatives. Nevertheless, there are a number of general considerations which provide initial guidance. In this work, heated nitrogen gas purge was used in the desorption step. In terms of regeneration, thermal swing is regenerated by heating to a temperature at which the adsorbed species are desorbed and removed from the bed in the fluid stream. Purge gas stripping is regenerated at essentially constant pressure or temperature by purging with a non-adsorbing inert gas. This method is applicable only when the adsorbed species are weakly held. More commonly a combination of purge gas stripping with a modest thermal swing is used. This permits desorption of somewhat more strongly held species while at the same time the temperature change is small enough to avoid most of the disadvantages associated with a standard thermal swing process (Ruthven, 1984).

Desorption is accomplished by heating the bed with either an *in situ* steam coil or, more commonly, by heating with a hot purge gas stream. The regeneration temperature and purge gas flow rate during generation are related since any defined degree of regeneration may be achieved either by a relatively low temperature rise coupled with a high purge flow rate or by a higher temperature with a smaller purge. The optimal combination for any particular system depends on the cost, quality, and availability of steam relative to the cost of purge gas.

Regeneration with hot feed is also common where product purity requirements are not too stringent. For systems in which the desorbate is to be recovered, a relatively high desorption temperature is desirable in order to increase the desorbate concentration in the effluent and thus reduce downstream recovery costs. These experiments were conducted with the flow rate of nitrogen gas at 200 mL/min and heated at various temperatures. The results for ethanol removal in wt% are shown in table 4.2.

Table 4.2 Ethanol concentration in wt% desorp at various temperatures

	Silicalite (wt% ethanol)	Activated Carbon (wt% ethanol)	XAD-2 (wt% ethanol)
Inlet Feed Composition	11.882	11.982	11.874
Outlet Effluent Composition at 25°C	11.497	11.857	11.759
Outlet Effluent Composition at 40°C	15.285	14.541	14.700
Outlet Effluent Composition at 120°C	23.519	25.251	14.569

From the table, the results indicate that ethanol concentration from desorption at 120°C of silicalite and activated carbon are 23.519 wt% and 25.251 wt%, respectively, which are significantly higher than inlet feed (11.882 wt% of silicalite and 11.982 wt% of activated carbon). In contrast, XAD-2's ethanol concentration at 120°C (14.569 wt%) is not significantly different from inlet feed (11.874 wt%). Though, 25°C and 40°C for desorbed temperatures are not enough to get a high ethanol concentration for these three adsorbents. The explanations for this outcome are that the interaction between ethanol molecules and selective pores on the surface of the adsorbents is a physical adsorption (van der waal force) and that the boiling point of ethanol is 78.4°C. This infers that the bond between ethanol molecules and the surface is easily broken when the temperature is increased. Although the desorption step which is run at 120°C would be enough to desorb the ethanol molecules from selective pores of silicalite and activated carbon, this temperature cannot be used to desorb ethanol for XAD-2. The reason for this is that it has the complicated structure of polystyrene-divinylbenzene resin. When ethanol molecules are adsorbed, they are strongly held on the surface due to the characteristics of this structure. Therefore, 120°C for the desorption experiment for XAD-2 is insufficient for ethanol removal. Severe conditions would be required in this case.
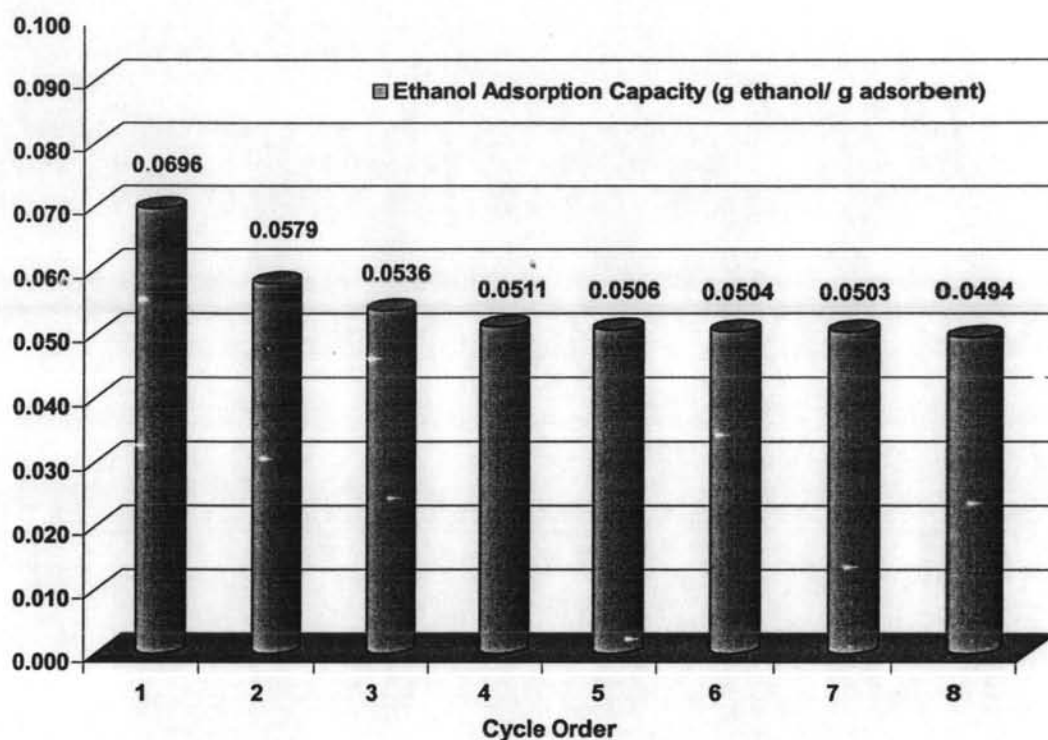
Figure 4.32 Ethanol adsorption capacities of silicalite in several cycles of regeneration.

Figure 4.32 illustrates the ethanol adsorption capacities of silicalite in each cycle of regeneration. The graph indicates that silicalite appears to be stable as an adsorbent when it was run several times. Why is silicalite chosen to study regeneration? In literature surveys, adsorption by hydrophobic silicalite as a means of ethanol separation was convenient and effective in that the silicalite-broth contact did not create any ill effects on the fermentation (Chung *et al.*, 1985). Even though, from the results of all experiments, activated carbon is shown to be the best adsorbent for the ethanol adsorption-desorption process, it is not convenient to use in the fermentation process. Therefore, silicalite would be suitable as an adsorbent to use for combining the processes (fermentation and separation).

4.3.3 Adsorbent Properties

From the liquid phase adsorption experiments, which were conducted on an equilibrium basis, it was reported that activated carbon would offer the highest ability to adsorb ethanol, followed by the silicalite and then the XAD-2. This, however, was not the case in the column adsorption experiments, in which the ethanol adsorption capacity of XAD-2 was higher than those of silicalite.

Adsorption is a surface phenomenon, and the binding of ethanol to an adsorbent therefore occurs at the surface. This means that the surface properties of the adsorbents may be an explaination for the results.

Activated carbon may adsorb more ethanol on a per weight basis because its surface area is much larger than silicalite and XAD-2, as shown in table 4.3. The surface areas of activated carbon, silicalite, and XAD-2 are 1,100, 478.2, and 300 $m^2/$ g, respectively. The activated carbon has the highest surface area and an organophilic surface which is why it can adsorb more than the others. XAD-2 and silicalite have a predominantly hydrophobic surface, which means they prefer to adsorb ethanol more than water in an ethanol-water mixture, especially XAD-2, which rarely adsorbs water on the surface, which is shown from its contact angle (119.3°).

For treated and untreated silica gels, their surface areas and the contact angles are not significantly different, except silica gel treated with 3-aminopropyltrimethoxysilane. This supports the results of the adsorption experiments where the ethanol adsorption capacities of the silica gels are not appreciably changed. In the case of silica gel treated with 3-aminopropyltrimethoxysilane, it has the lowest surface area after treating the silica gel resulting in its low ethanol adsorption capacity.

All the contact angles of the adsorbents cannot be used for comparing hydrophobicity among all adsorbents because the characteristic surfaces of the adsorbents are different. The surface of silicalite is smooth, whereas the surface of silica gel is rough. Therefore, the value of the contact angle alone would not be sufficient to explain the hydrophobicities of each adsorbent.

Table 4.3 Physical properties of adsorbents

Adsorbent	Surface Area (m²/g)	Contact Angle Theta (θ)
Silicalite	478.2	16.8
Activated carbon	1,100.0	43.2
XAD-2	300.0	119.3
LZ-210	524.8	28.9
Silica gel	480.0	20.9
Silica gel treated with 3-aminopropyltrimethoxysilane	6.9	13.0
Silica gel treated with methanol	504.5	22.1
Silica gel treated with ethanol	500.9	19.0
Silica gel treated with propanol	536.7	24.8
Silica gel treated with butanol	516.7	28.7
Silica Hi-Sil®255	117.0	34.5
Silica Hi-Sil®255 modified with admicellar polymerization	129.8	63.5