CHAPTER IV

FIRST PHASE – FIXED BED ADSORBER

The ethanol derived from distillation process can achieve up to approximately 95 wt% since ethanol form azeotrope with water. In the process of making fuel grade ethanol further removal of water is needed. Older azeotropic distillation units often consumed almost as much energy as the fuel value of the ethanol produced (Gomis *et al*., 2007). Dyhydration by adsorption on a zeolite 3A has been suggested as a promising alternative to the conventional processes. This chapter aims to study the parameters that have an effect on the performance of the zeolite and to investigate the characteristic of the packed column.

4.1 Characteristic of the 3A zeolite

3A zeolite was used as adsorbent in the form of spheres with nominal diameters of 2.5-5 mm, as obtained from Zeochem® Molecular Sieve Z3-03. It has a controlled cubical structure with nominal pore diameter of 3 Ångstrom with bulk density of around 750 g/L and an equilibrium water capacity of around 18-21% of its own weight. General specification of Zeochem Z3-03 is shown in Table 4.1.

Table 4.1 Characteristic of Zeochem adsorbent (Source: Zeochem AG, Switzerland)

Subject	Unit	Value
Nominal pore diameter	Å	3.0
Tapped bulk density	g/L	750
Bead sizes nominal	Mm	2.5-5
Crush strength	N	70
Water loading	%wt	18-21
Specific heat	kJ/(kg.°C)	1.07
Residual water content at 550°C as shipped	%wt	1.5

Prior to the experiment the adsorbent, as obtained from Zeochem, was analyzed by Micromeritics Surface Area Analyzer model Flow Sorb II 2300. It was found that the adsorbent had a specific surface of 25.71 ± 0.02 m^2/g (Table 4.2).

Table 4.2 BET surface area analyzer testing condition for the 3A zeolite

Degas temperature	150°C
Degas time	60 minutes
Method	ISO 9277
Sample	Zeochem 3A
Specific Surface Area (m^2/g)	25.71 ± 0.02

4.2 Two-level factorial designed experiment

This experiment studied different parameters that had the effect on the breakthrough time of the packed column. Two-level factorial design experiment was used in this research work to preliminary screen the influence and interaction among each factor. In this work, the principal factors, which have an effect on the adsorption rate and the enrichment of the product from the fixed bed adsorber, are initial bed temperature, ethanol water mixture feed rate, and the concentration of the feeding mixture. Table 4.3 shows the conditions of each experimental run and their subsequent breakthrough time and water loading capacity.

Table 4.3 shows that at 100 °C, flow rate of 1 mL/min, and feed concentration of 95 wt% gave the longest breakthrough time at 3,600 seconds. It can be seen that an increase in the flow rate led to a significant decrease in breakthrough time, for all the operation temperature and feed concentration analyzed. In all cases the breakthrough time decreases by more than 35% when the flow rate is increased from 1 to 2 mL/min. The main reason for earlier breakthrough times with increasing water concentration is that the adsorbent is exposed to more adsorbate per unit time (Sowerby and Crittenden, 1988). Furthermore, Table 4.3 also shows that increasing the water concentration in the feed decreases the time for breakthrough to occur. For the same reason, the amount of water, which was put into the system per unit of time, was more leading to the bed to saturate more quickly.

From the experiment, it can be seen that increasing the initial bed temperature decreases the time for breakthrough to occur. There are two reasons for this. First, the capacity of the molecular sieve for water decreases with increasing temperature. Experimental capacities were computed from the breakthrough curve data and are shown in Table 4.3. Second, according to Chahbani and Tondeur (2000), increasing the bed temperature causes an increase in the rate of diffusion with the solid, thereby resulting in an increase in the adsorption rate.

As suggested by the literatures, higher initial bed temperature, higher flow rate and higher concentration of the adsorbate in the feed would lead to a shortest time to breakthrough, as shown in Run Number 8 in Table 4.3 where breakthrough time is 480 sec. However, it is shown that for comparable experimental conditions, the water adsorption capacity of the molecular sieve appears to be higher when the concentration of water is higher in the feed. This can be explained by the fact that feeding at higher water concentration resulting in a higher water partial pressure and hence corresponding to higher water loading capacity of the zeolite.

Table 4.3 2^k factorial designed experiment of the fixed bed adsorber

Run No.	Initial Bed Temp.(° C)	Flow rate (mL/min)	Feed Conc. (%wtEtOH)	Breakthrough time (sec)	q (g.H_2O/g.abs)
1	100	1	95	3,600	0.123
2	100	2	95	850	0.104
3	100	1	90	1,950	0.163
4	100	2	90	540	0.135
5	120	1	95	2,800	0.097
6	120	2	95	800	0.087
7	120	1	90	1,800	0.148
8	120	2	90	480	0.127

The experimental data shown in Table 4.3 was then analyzed by "Design Expert" software to perform the analysis of variance (ANOVA) to find significant effects on an answer of interest, in this case being breakthrough time. Figure 4.1 illustrates that flow rate and water concentration in the feed significantly affect the breakthrough time.

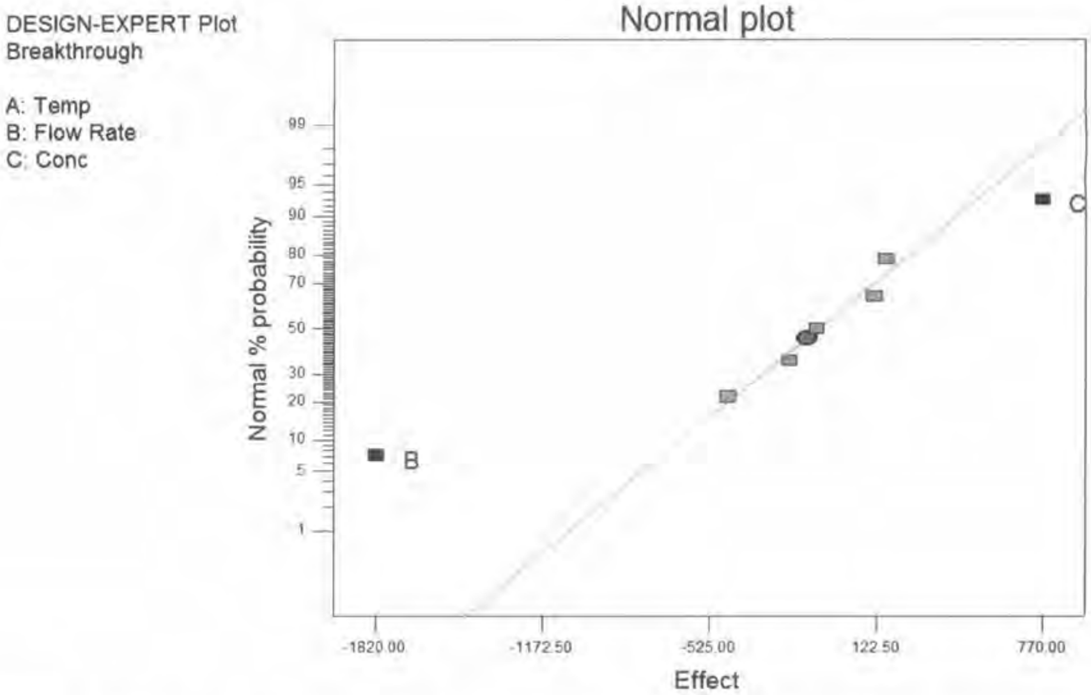

Figure 4.1 Design Expert normal plot of significant effects on breakthrough time.

Table 4.4 Analysis of variance of significant effects on breakthrough time

Source	Sum of Square	DoF	Mean Square	F Value	Prob > F
Model	7.811E+06	2	3.905E+006	32.1	0.0014
B	6.625E+06	1	6.625E+006	54.45	0.0007
C	1.186E+06	1	1.186E+006	9.75	0.0262
Residual	6.083E+05	5	1.217E+005		
Cor Total	8.419E+06	7			

From Table 4.4, the Moldel F-value of 32.1 implies the model is significant. There is only a 0.14% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant. In this case it is confirmed that flow rate and concentration of water in the feed are significant model terms. Furthermore, the regression model was given as following:

$$\text{Breakthrough time (sec)} = -9{,}937.5 - (1{,}820 \times \text{Flow Rate (mL/min)}) + (154 \times \text{Concentration (wt \%)}) \qquad (4.1)$$

It must be noted that the initial temperature of the adsorption column was accurately set at different values. However, due to heat of adsorption, the temperature inside the column may vary and affect the experimental results.

4.3 Effects of different parameters

The previous section showed that there were two significant effects on the breakthrough time which were flow rate and feed concentration. Hence further studies were made to thoroughly examine the effects of each parameter.

4.3.1 Effect of flow rate

The experiment was performed to study the effect of flow rate on time to breakthrough. Hence, the adsorption in the packed bed was carried out at initial bed temperature of 100 °C, packing weight of 30 g, and ethanol feed concentration of 95 wt%. It can be seen from Figure 4.2 that an increase in the flow rate led to a significant decrease in breakthrough time, for all the operation temperature and feed concentration analyzed. This happened due to a shorter retention time of the mixture ethanol-water in contact with adsorbent bed for the larger flow rates, which caused a decrease in the amount of adsorbed water, at the same operating conditions. Moreover, the main reason for decrease breakthrough time with increasing flow rate is that the adsorbent is exposed to more water per unit time, and so becomes saturated more quickly (Sowerby and Crittenden, 1988). As can be predicted, Table 4.5 shows the longest breakthrough time of 3,600 seconds at the lowest flow rate of 1 mL/min.

Likewise, the shortest breakthrough time of 420 seconds happened when the adsorption column was fed with the highest flow rate of 2.5 mL/min.

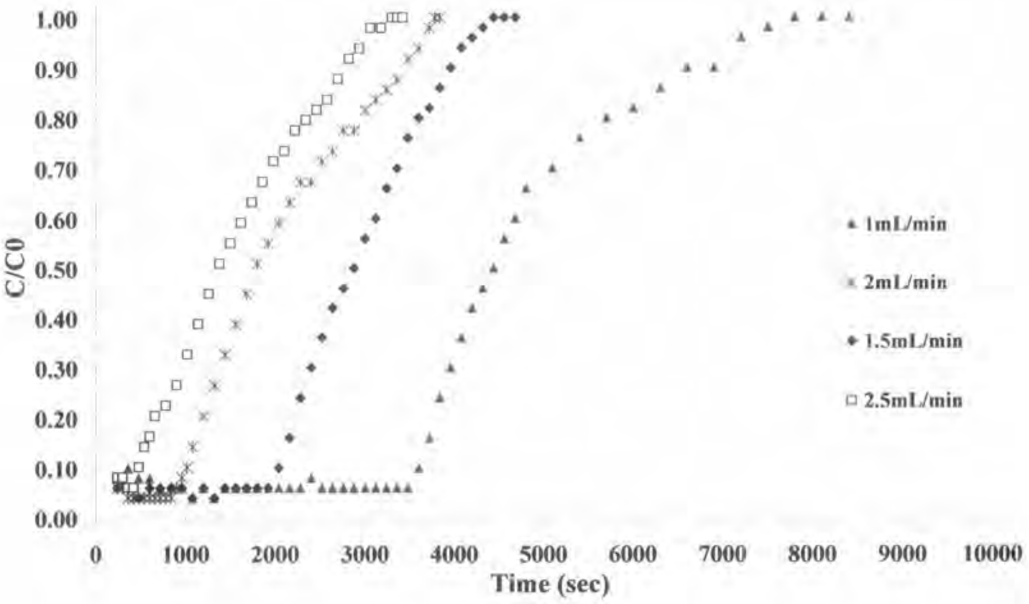

Figure 4.2 Effect of flow rate on breakthrough time (Initial bed temperature 100 °C, 30 g of zeolite, and ethanol feed concentration of 95 wt%).

Table 4.5 Breakthrough time of the fixed bed adsorber at different flow rate

Flow rate (mL/min)	Breakthrough time (sec)
1.0	3,600
1.5	1,920
2.0	850
2.5	420

4.3.2 Effect of feed concentration

The analysis from Design Expert software showed that there were two parameters that significantly affected the time to breakthrough of a packed bed adsorption. Hence, this section was carried out to further illustrate the effect of feed concentration on the breakthrough time. All experiments were conducted at initial bed temperature of 100 °C, packing weight of 30 g, and ethanol-water mixture flow rate of 1 mL/min.

It is shown in Figure 4.3 that for comparable experimental conditions, the time to breakthrough of the adsorption column appears to be lower when the concentration of water is higher in the feed even if there is an increase in the amount of water adsorption and a slight decrease in the adsorption amount of ethanol with the increasing mole fraction of water in the feed stream (Lu *et al.*, 2007). This can again be explained by the fact that the molecular sieve is exposed to more amount of water per unit time when feeding at higher water concentration. Table 4.6 and Figure 4.3 illustrates that the longest time to breakthrough of 3,600 seconds can be achieved by feeding the ethanol-water mixture was at 95 wt%, whereas the shortest breakthrough time was found to be 1,320 seconds when the feed concentration was at 85 wt%.

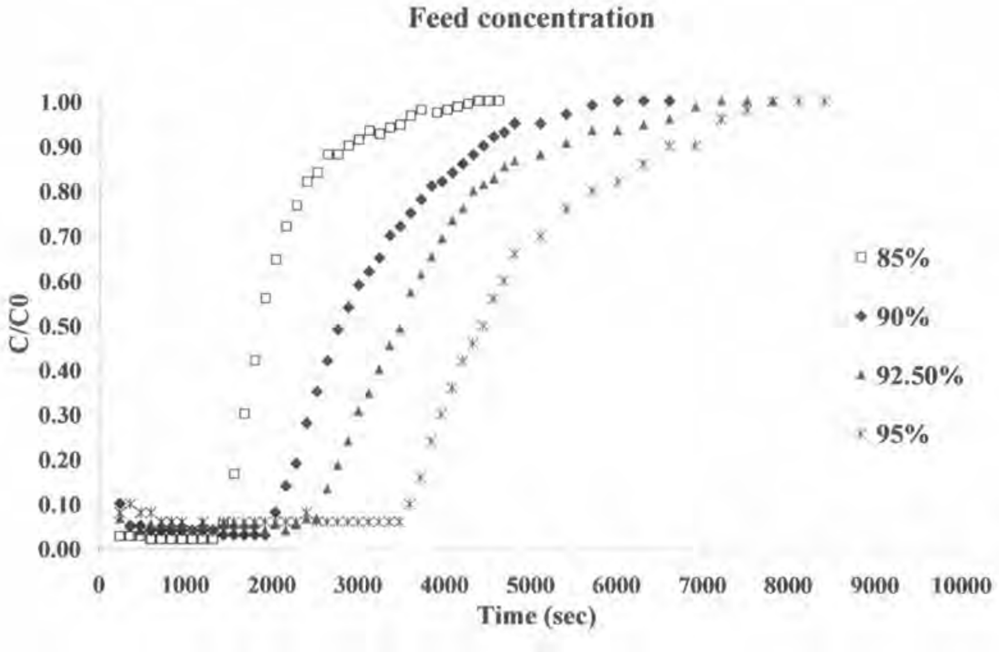

Figure 4.3 Effect of feed concentration on breakthrough time (Initial bed temperature 100 °C, 30 g of zeolite, and feed rate of 1 mL/min).

Table 4.6 Breakthrough time of the fixed bed adsorber at different feed concentration

Feed concentration (wt% ethanol)	Breakthrough time (sec)
85	1,320
90	1,920
92.5	2,520
95	3,600

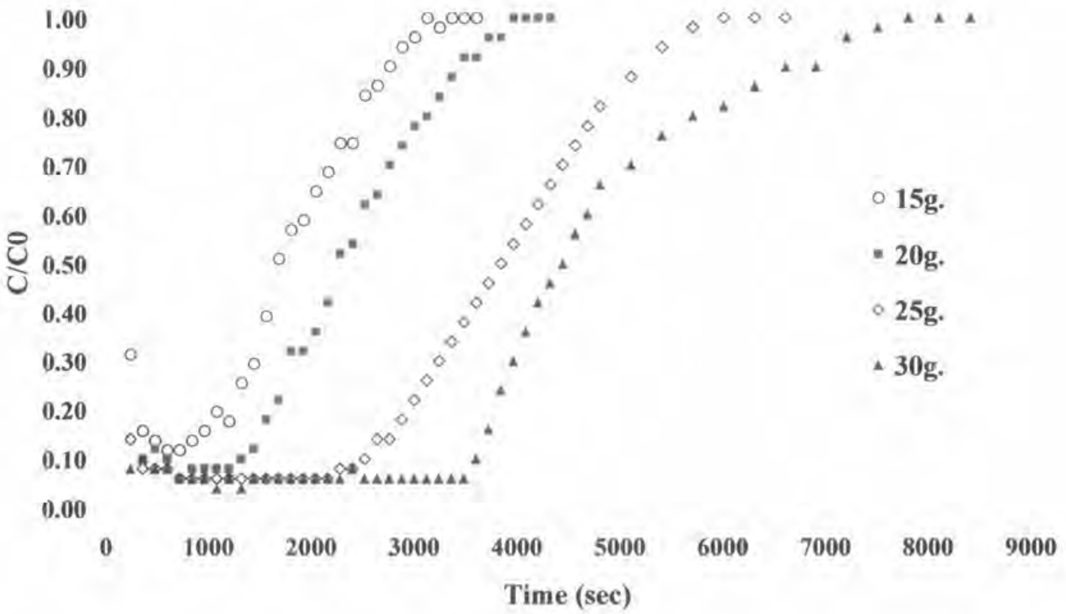

Figure 4.4 Effect of zeolite packing weight on breakthrough time (Initial bed temperature 100 °C, feed rate of 1 mL/min, and ethanol feed concentration of 95 wt%).

4.3.3 Effect of packing weight

To study the mass transfer zone (MTZ) length or the length of equilibrium section (LES) it is necessary to see how the adsorption could perform with different bed height. Figure 4.4 and Table 4.7 show the time to breakthrough that was achieved by different packing zeolite weights at a flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95 wt%. It can be seen that decreasing the zeolite packing weight in the adsorber decreases the time for breakthrough to occur, this event occurring almost immediately with packing weight of 20 g or less. This implies that the LES is almost the same or longer than the packed bed length of 16 cm which corresponds to the weight of 20 g. When the column was packed with 30 g of zeolite, which corresponded to the bed height of 24 cm, the packed bed was able to produce high concentration ethanol until breakthrough occurred at 3,600 seconds.

Figure 4.5 also illustrates that in case of the same operating condition, water adsorption capacity is a direct proportion of the loading of the zeolite in the adsorber. Likewise, Figure 4.4 shows that breakthrough time is highly dependable on the weight of the zeolite, given a particular adsorption condition.

Table 4.7 Breakthrough time of the fixed bed adsorber of different zeolite packing weights

Packing weight of zeolite (g)	Breakthrough time (sec)
15	720
20	1,320
25	2,520
30	3,600

It can be seen in all experiment that the value of C/C_0 was not equal to zero because pure ethanol ($C=0$) could not be achieved. The highest ethanol concentration of 99.8 wt% in the product stream was obtained in a few experimental conditions. The reason there was a small amount of water in the product might be explained by the fact that the ethanol was not analyzed directly after adsorption process but instead was condensed in the condenser and collected in a small container which may allow re-adsorption of water into the product.

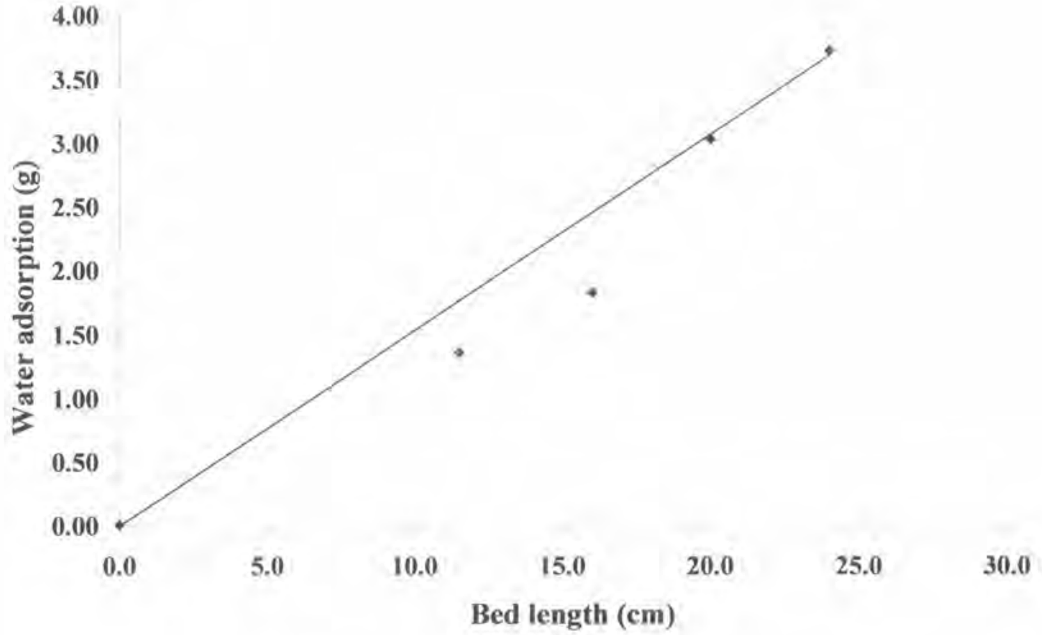

Figure 4.5 Relationship between bed length and water adsorption capacity.

4.4 Mass transfer zone (MTZ) and length of equilibrium section (LES)

The mass transfer zone (MTZ) is the region in the bed where adsorption takes place. The MTZ has a leading edge where the adsorbent is still unused (the gas phase has the composition of the product) and trailing edge where the adsorbent is already equilibrated (the gas phase) has the composition of the feed. The distance between the leading edge and the trailing edge is the length of equilibrium section. One way to maximize the use of the molecular sieve in the adsorber is by minimizing the MTZ (Serbenov, 2001).

Dry ethanol can be produced only when the length of equilibrium section (LES) is less than the bed length. Increasing the initial bed temperature decreases the time for breakthrough to occur. There are two main explanations for this. First, Tanaka and Otten (1987) suggested that the apparent decrease in adsorbent capacity with an increase in bed temperature is consistent with adsorption theory. The region of favorable uptake in an adsorption isotherm decreases as temperature increases, making adsorption reaction less probable. It was noted that the LES elongated marginally under higher temperature, which in some cases caused premature breakthrough and therefore decreased capacity. Secondly, as explained earlier in this chapter, increasing the bed temperature causes an increase in the rate of diffusion within the solid, thereby resulting in an increase in the adsorption rate.

Table 4.8 shows that increasing the feed flow rate also decreases time for breakthrough to occur. The main reason is that the zeolite is exposed to more adsorbate per unit time, and becomes saturated quicker. A second effect is the reduction in LES as the flow rate is increased, given similar initial bed temperature and feed concentration. This observation indicates that the rate of adsorption is influenced by a fluid-side mass transfer resistance. As suggested by Schweitzer (1979), the LES zone is proportional to the length of equilibrium section velocity raised to the power of 0.72 for adsorption of water onto 3A molecular sieves. Furthermore, it can be observed that by increasing the water concentration in the feed, the LES also decreases slightly due to greater water capacity resulting from adsorption at higher water partial pressure.

Table 4.8 Length of equilibrium section of the adsorber at different operating conditions

Run No.	Initial Bed Temp. (°C)	Flow rate (mL/min)	Conc. (%wt EtOH)	Breakthrough time (sec)	q ($g.H_2O$/ g.ads)	LES (cm)	LUB (cm)
1	100	1	95	3,600	0.123	14.67	9.33
2	100	2	95	850	0.104	9.72	14.28
3	100	1	90	1,950	0.163	12.18	11.82
4	100	2	90	540	0.135	7.27	16.73
5	120	1	95	2,800	0.097	12.35	11.65
6	120	2	95	800	0.087	9.60	14.40
7	120	1	90	1,800	0.148	11.08	12.92
8	120	2	90	480	0.127	6.19	17.81

4.5 Adsorption equilibrium

Equilibrium behavior of adsorbents is usually determined as constant temperature isotherms. At low concentration or partial pressures isotherms are often linear. As the partial pressure of the gas increases the isotherms becomes nonlinear. Equilibrium data for adsorption of single gases is often fit with the Langmuir isotherm. This section aims to fit the experimental data into one of the isotherms (linear, Freundlich, and Langmuir) to best predict the behavior of the adsorption of water from ethanol onto 3A molecular sieves. The experiments was performed at initial bed temperature of 100 °C, flow rate of 1 mL/min and the ethanol feed concentration of 85, 90, 92.5, and 95 wt%, respectively. Table 4.9 demonstrates the molecular sieves' water adsorption capacity at equilibrium under different feed concentration.

Table 4.9 Water adsorption capacity at different feed concentration

Run	Initial bed temperature (°C)	c Mass fraction of water in the feed	q (g/g_{ads}) Water adsorption capacity at equilibrium	log c	log q	c/q
1	100	0.15	0.1624	-0.7895	-0.8239	0.9239
2	100	0.1	0.1616	-0.7916	-1	0.6189
3	100	0.075	0.1484	-0.8286	-1.1249	0.5054
4	100	0.05	0.1235	-0.9085	-1.3010	0.4050

4.5.1 Linear isotherm

The simplest expression of equilibrium adsorption is the linear isotherm, which is valid for dissolved species that is present at concentration less than one-half of its solubility (Seader and Henley, 1998). In this experiment, the linear isotherm would represent the molecular sieve water adsorption capacity which depends directly on the water concentration in the feed. The linear isotherm can be expressed as the following equation:

$$q = K c \tag{4.2}$$

where q is the water adsorption capacity at equilibrium, K is the rate constant, and c is the water concentration in the ethanol-water mixture. The rate constant can be found by fitting a plot of the water adsorption capacity versus water concentration in the mixture from the data given in Table 4.9. From Figure 4.6, the rate constant is found to be 1.4231 and Equation (4.2) can be rewrite into:

$$q = 1.4231 c \tag{4.3}$$

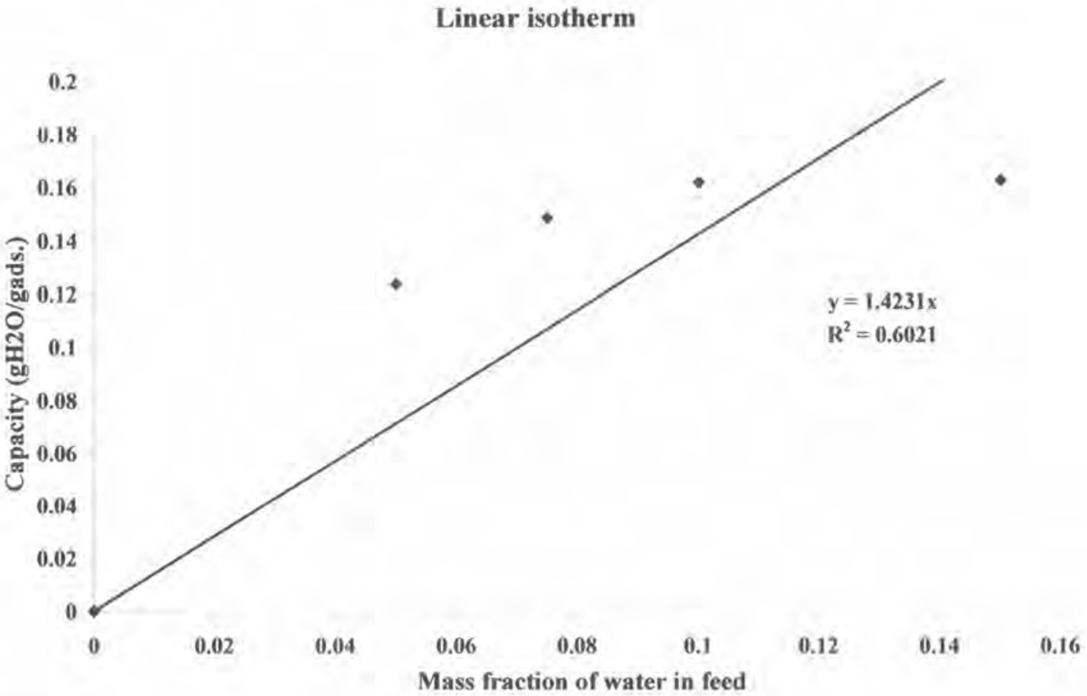

Figure 4.6 Fitting of experimental adsorption capacity and water concentration to linear isotherm.

4.5.2 Freundlich isotherm

The equation attributed to Freundlich is empirical and nonlinear in pressure.

$$q = K_f c^{1/n} \tag{4.4}$$

where K_f and n are temperature-dependent constants. Generally, n lies in the range of 1 to 5. With n = 1, Equation (4.4) reduces to the Henry's law equation (linear isotherm). Experimental isothermal data can be fitted to Equation (4.4) by a nonlinear curve-fitting program or by converting Equation (4.4) to a linear form as follows, and using a graphical method or a linear regression program:

$$\log q = \log K_f + (1/n) \log c \tag{4.5}$$

In this case the graphical method is employed. The data from the experiment are plotted as log q versus log c. The best straight line through the data has a slope of (1/n) and the intercept of log K_f. According to Ruthven (1984), in general, K decreases with increasing temperature, while n increases with increasing temperature and approaches a value of 1 at high temperatures. Equation (4.4) is derived by assuming a heterogeneous surface with a nonuniform distribution of the heat of adsorption over the surface. From Figure 4.7, the slope (1/n) is 0.2523 and the intercept is -0.5615 which makes K_f = 0.2745. Hence, the Freundlich isotherm could be given as:

$$q = 0.2745\, c^{0.2523} \tag{4.6}$$

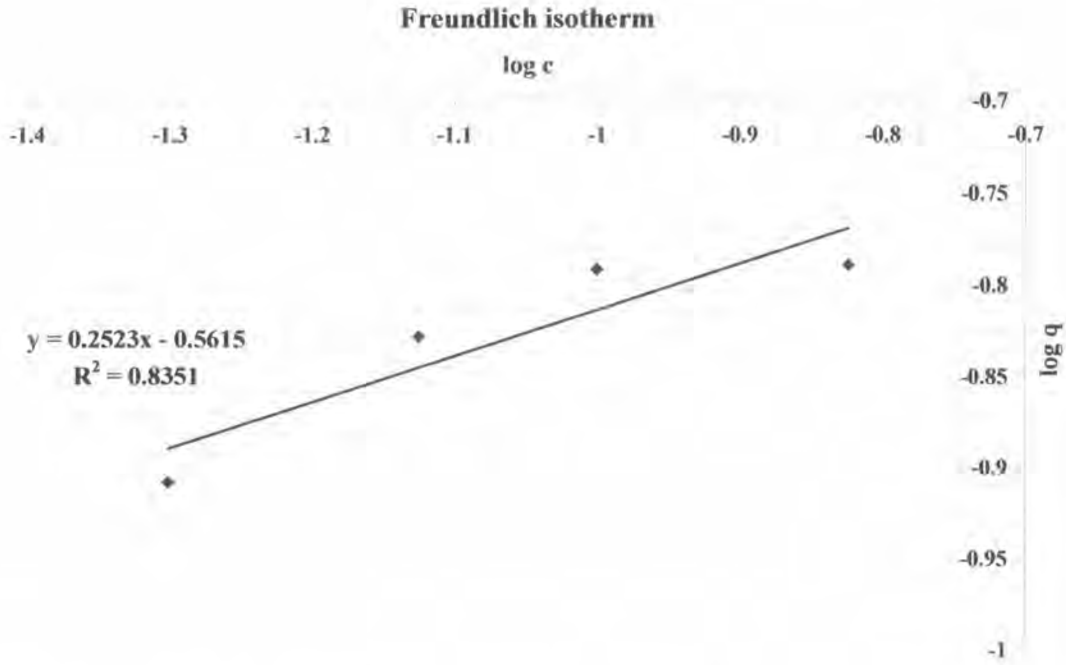

Figure 4.7 Fitting of experimental adsorption capacity and water concentration to Freundlich isotherm.

4.5.3 Langmuir isotherm

In the Langmuir model adsorption increases linearly with increasing solute concentration at low c values and approaches a constant value at high concentrations. The adsorbed concentration approaches a constant value because there are limited numbers of adsorption sites in the molecular sieve. The Langmuir equation is derived from simple mass-action kinetics assuming chemisorption. Assume that the surface of the pores of the adsorbent is homogeneous and that the forces of interaction between adsorbed molecules are negligible. The Langmuir adsorption isotherm is restricted to a monomolecular layer and can be written as:

$$q = \frac{K_L q_m c}{1 + K_L c} \tag{4.7}$$

The values K_L and q_m in Equation (4.7) are treated as empirical constants, obtained by fitting the nonlinear equation directly to experimental data or by employing the following linearized form:

$$\frac{c}{q} = \frac{1}{q_m K} + \frac{c}{q_m} \tag{4.8}$$

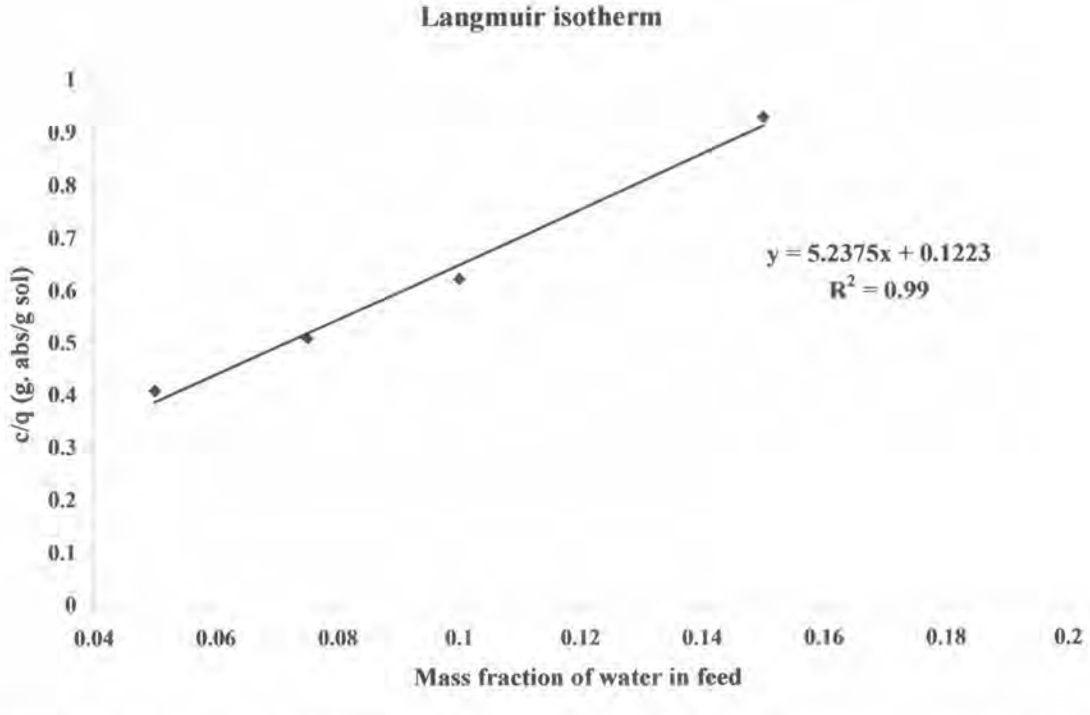

Figure 4.8 Fitting of experimental adsorption capacity and water concentration to Langmuir isotherm.

Using (4.8), the best straight line is drawn through a plot of points c/q versus c, giving the slope of $(1/q_m)$ and the intercept of $1/(q_mK_L)$ in Figure 4.8. Hence, the Langmuir isotherm of this experiment can be written as:

$$q = \frac{8.18c}{1 + 42.83c} \tag{4.9}$$

Table 4.10 compares the values of R^2 from the different methods of fitting the experimental data into 3 types of isotherms. It can be seen that Langmuir isotherm, with R^2 equals to 0.99, could most accurately represent the actual equilibrium behavior. Figure 4.9 illustrates fittings of experimental results with different adsorption isotherms. In this case Langmuir isotherms could best predict the adsorption capacity of the 3A zeolite. Hence monolayer adsorption of water from ethanol/water mixture on 3A zeolite can be expected.

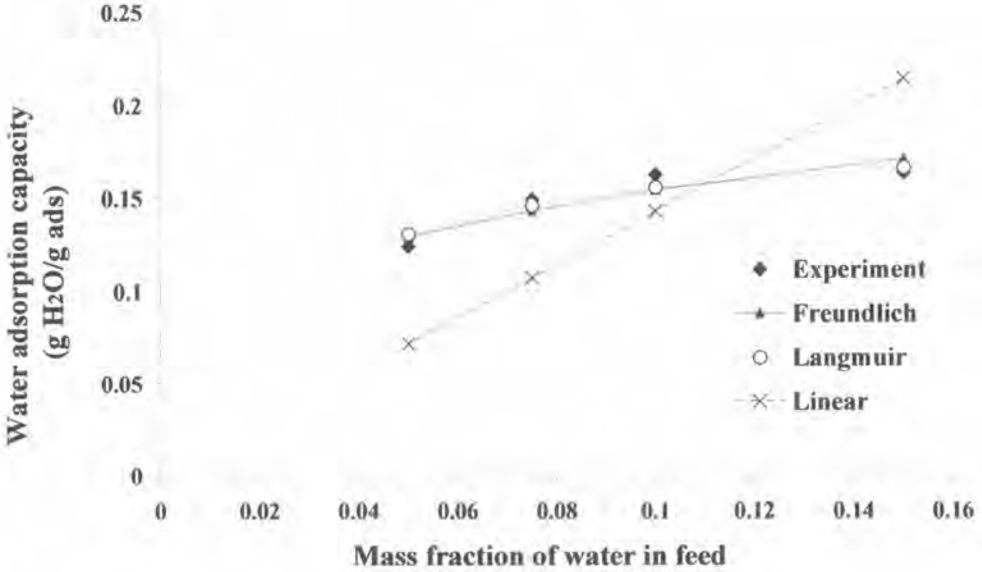

Figure 4.9 Comparison of water adsorption capacity by different isotherms to the experimental data.

It must be noted that in some findings Freundlich isotherm would be the most accurate model to predict the adsorption of water on 3A zeolite. In this study all the experiment was setup at desired initial temperature but in some cases the temperature rose significantly due to heat of adsorption and hence violating the isothermal assumption. However, the experiments show that Langmuir isotherm gave the closest prediction.

Table 4.10 Comparison of the R^2 of different isotherms

Isotherm	R^2
Linear	0.6021
Freundlich	0.8351
Langmuir	0.99

4.6 Coke formation on zeolite surface

The process of regeneration of the 3A molecular sieve involves high temperature. In the early stage of the experiment, the adsorption column was heated by the jacket heating furnace up to 300 °C to allow the zeolite to desorp water and use nitrogen gas as a purge stream. However, with this method, it appeared that there was a carbon deposit onto the surface of the molecular sieve (Figure 4.10). There was a high possibility of coking, with absence of oxygen, from the ethanol that was also trapped inside the adsorption column. This would significantly decrease the performance of the adsorbent due to a decrease in the surface area. Table 4.11 shows that after coking occurred, the surface area of the Zeochem 3A adsorbent was reduced from 25.71 ± 0.02 to 20.63 ± 0.01 m^2.

As a result, the adsorbent had to be removed after each experimental run. It was then placed into a muffle at 220 °C for 4 hours to remove as much as possible the ethanol and water that were trapped in the pore and on the surface. Only then the zeolite was repacked into the adsorption column and preheated under Nitrogen gas flow through to 300 °C to ensure that all water was removed prior to the next experimental run.

The zeolite was also analyzed in a Thermal gravimetric analysis to study a presence of these undesired products. The TG/DTA (Thermal Gravimetric/Differential Thermal Analysis) model 851^e from Mettler Toledo was used to analyze the weight lost of the zeolite, which was found to be approximately 4%, with changing temperature under a period of time. This corresponded with the result from CHN

Element Analysis which showed carbon deposition of around 3.72 wt% of the total weight of the zeolite.

Table 4.11 BET surface area analyzer testing condition for the 3A zeolite with coking

Degas temperature	150°C
Degas time	60 minutes
Method	ISO 9277
Sample	Zeochem 3A (coke)
Specific Surface Area (m^2/g)	20.63 ± 0.01

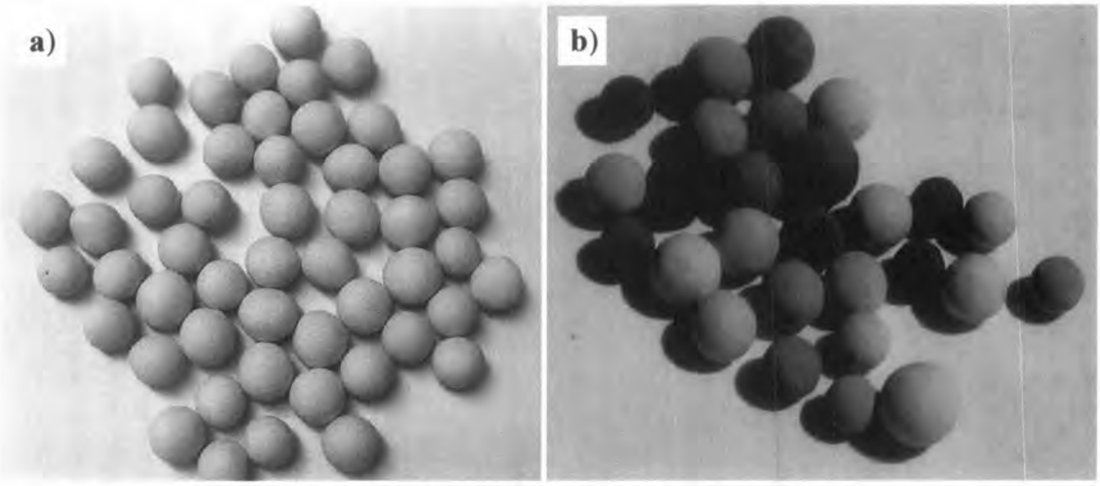

Figure 4.10 Zeochem 3A a) as obtained from the manufacturer and b) with coking on the surface after experimental runs and regeneration under high temperature.