Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Al-Asheh, Sameer , Banat, Fawzi and Fara, Ammar Abu(2009) 'Dehydration of Ethanol-Water Azeotropic Mixture by Adsorption Through Phillipsite Packed-Column', Separation Science and Technology, 44: 13, 3170 — 3188

To link to this Article: DOI: 10.1080/01496390903182479

URL: http://dx.doi.org/10.1080/01496390903182479

Separation Science and Technology, 44: 3170–3188, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903182479

Dehydration of Ethanol-Water Azeotropic Mixture by Adsorption Through Phillipsite Packed-Column

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Abstract: Phillipsite is a natural zeolite material available in several locations in Jordan. Phillipsite with and without treatment was used for dehydrating ethanol in the adsorptive distillation process. Molecular sieves 4A was taken as a reference material. According to the breakthrough curves phillipsite treated with 1 M calcium chloride solution gave the best performance. The water uptake using the 1 M-phillipsite was 0.1054 g H_2O/g adsorbent while the water uptake using the 4A molecular sieves was 0.1030 g H_2O/g adsorbent. The Guggenheim, Anderson, and De Boer (GAB) model and the Frenkel, Halsey, and Hill (FHH) model were used to represent the isotherms for water sorption on the adsorbents used. The GAB model fit the experimental data relatively better than the FHH model for all cases, except for the case of using 2 M-phillipsite. Using the Crank diffusion model the effective diffusivity of water vapor in raw phillipsite is $10.40 \times 10^{-8}\,mm^2s^{-1}$ while it is $6.9 \times 10^{-8}\,mm^2s^{-1}$ in the 1 M treated phillipsite.

Keywords: Asorption, azeotrope, $CaCl_2$, molecular sieves, phillipsite, water-ethanol

INTRODUCTION

Anhydrous ethanol is a very important renewable fuel, which can be produced by fermentation of biomass, and its use has been remarkably increased during the last decades. In ethanol production, water removal

Received 9 November 2008; accepted 4 May 2009.

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represents a serious problem due to the fact that ethanol forms an azeotropic mixture when present with water. This mixture is usually separated into its constituents by special techniques, such as azeotropic distillation, which requires a significant amount of energy. Another method for the separation of azeotropes is the membrane process. This method is called pervaporation; where a liquid mixture fed to one side of the membranes produces a vapor permeate on the other side of the membrane. The basic concept of this process is to make the vapor phase always depleted in one of the azeotrope components (1). Among other alternative techniques to dehydrate ethanol, adsorption processes appear particularly interesting, since water molecules are smaller than the ethanol ones, and furthermore have a slightly higher dipole moment. Therefore, it is possible to individuate adsorbing materials characterized by a high selectivity towards water, and achieving high separation factors.

The adsorption process is based on choosing adsorbents that are applicable to sorb the desired species, which is water in this case, with minimum cost and in the best performance manner. Desiccants showed good performance toward water sorption. They include molecular sieves, silica gel, lithium chloride, and biobased adsorbents (2). Ladisch and Dyck (1979) found that biobased adsorbents provide a positive energy balance compared to other adsorbents (3). They even showed better results compared to other separation methods such as extractive distillation (4). Corn is a known biobased adsorbent that has been frequently used to separate water-based azeotropic mixtures (3,5–9). Anderson et al (1996). proposed a new synthesized starch-based adsorbent, which is more efficient for dehumidification of air than corn grits (10). There are also other types of starch-based adsorbents that showed positive results in breaking water-based azeotropes, such as wheat and soy flour (11), maize (12,13) and potato granules (14).

Molecular sieves with their uniform pore size distribution were taken as reference materials to which the water sorption performance on biobased adsorbents can be compared with (15). Molecular sieves have also been used to separate water-based azeotropic mixtures, such as ethanol-water system (15–18). Another type of adsorbents which can be used in such application is natural zeolites. There are many natural zeolites of which a small number including clinoptilolite, chabazite, mordenite, erionite, ferrierite, and phillipsite offer the greatest promise for gas separation (19).

In this work, bentonite, natural phillipsite, and chemically treated-phillipsite were used as newly developed adsorbents to separate the ethanol-water azeotropic mixture. Zeolites in Jordan are mainly associated with the volcanic tuff pyroclastics. The largest volcanic eruptions occurred in the Badia region of northeast Jordan (Harrat Ash-Shaam).

Reshiedat (1991) recognized the presence of Chabazite, Faujasite, and Maszzite as subordinate minerals with phillipsite in Jabal El-Aritain (20). The locations of zeolite deposits are associated with volcanic cones in Tell Hassan, Tell Rimah (North and South), Jabal Aritain (North and South), and Jabal Hannoun. The highest phillipsite content in Jordan is at Jabal Hannoun, where it reaches 29% in one series of the beds (6 m thick). Phillipsite occurs in all the localities with the exception of Jabal Tarboush in northeast Jordan and in El-Ataita volcano and is considered the major zeolites phase in Jabal Artain, north and south (Rawajfih, 2008). Phillipsite occurs as a colorless radiating aggregate in the cement and growing at the vesicles wall. Phillipsite is also found as single prismatic crystals. The crystals are generally less than 50 µm in size (21).

The main objective of this work was to examine the potential use of the abundant and low cost phillipsite material in dehydrating ethanol. Raw phillipsite was treated with calcium chloride to enhance its sorption performance. The sorption data were analyzed using isotherm and dynamic models.

MATERIALS AND METHODS

Adsorbents

Molecular sieves 4Å was dried in an oven at temperatures of 190–210°C for 24 hours similar to Trent (1993). The dried molecular sieves were kept in bottles, which then were stored in a glass chamber. The glass chamber contained silica gel to make sure that no humidity would be sorbed onto the molecular sieves. Molecular sieves 4Å was also mixed with a bentonite powder (9 to 1) in an attempt to test the effect of bentonite presence on the sorption performance.

Calcium chloride was used as a drying agent. Calcium chloride is a chemical compound that is crystalline and is highly soluble in water. The anhydrous compound is hygroscopic; it rapidly absorbs water and is used to dry gases by passing them through it (22).

Phillipsite is a natural local zeolite with chemical formula $(Na,K)_5\{Al_{15}Si_{11}O_{32}\} \cdot 20\,H_2O$, typically found in cavities in basalt, or in deep-sea sediments (23). Crystals of natural phillipsite are often found in spherical radiating aggregates, and the Si/Al-framework of this zeolite is built up by 4- and 8-membered rings. Some of the selected physical and chemical properties of natural phillipsite are shown in Table 1 (24).

Different forms of phillipsite were prepared by soaking a fixed amount of natural phillipsite (150 g) in an aqueous solution of calcium

Table 1. Physical and chemical properties of natural phillipsite

Zeolite	Void volume (%)	Channel dimensions (nm)	Si/Al Ratio	Density ($\mathrm{mg\,m^{-3}}$)	Cation exchange capacity ($\mathrm{Cmol\,kg^{-1}}$)*
Phillipsite	31	0.33	1.7–2.4	2.15	380

*Centimol positive charge per kg.

chloride at different concentrations, namely 0.5, 0.75, 1.0, and 2 M for three hours. These were then dried at 220°C for 3 hours. The resulted materials are denoted as impregnated phillipsite or 0.5 M-phillipsite, 0.75 M-phillipsite 1.0 M-phillipsite, and 2 M-phillipsite, respectively.

Bench-Scale Fixed Bed Adsorber

A bench-scale fixed bed adsorber apparatus has been constructed and is shown schematically in Fig. 1. The adsorbent was packed in the fixed bed (14.6 mm ID; 25 cm depth). The column wall temperature was maintained at the initial bed temperature during the experiment by circulating hot water through the jacket. The jacket was insulated using heating tape. In a typical experiment, vapor was boiled up from a 500 ml flask surrounded by an electric heating mantle. The atmospheric pressure was assumed constant at 760 mmHg. The temperature of the jacket was controlled and kept constant during the runs. The exit stream was condensed using water as a cooling medium. A Karl Fischer titrator was used to measure the water content of the condensate. The error in the water content analysis was within ±0.1-wt%. The aqueous ethanol mixtures were prepared at the azeotropic concentration, i.e., 5-wt% water content. They were prepared by weighing the desired amounts of distilled water and ethanol to make about 250 ml solution. The temperature of the mixture in the boiling flask was measured by a thermocouple. This corresponds to the azeotrope temperature of the ethanol-water mixture at 5-wt% water content, which was about 78.1°C. During the experimental runs, the condensate was removed every five minutes and a sample of about 8 ml was collected. Thus, the average flow of the condensate was about 1.6 ml $\mathrm{min^{-1}}$. This was achieved by controlling the heat input via manipulating the power supply.

To calculate water uptake at every feed composition, which changes with time, it is necessary to know the condensate as well as the feed compositions. From the difference between the number of moles of water in

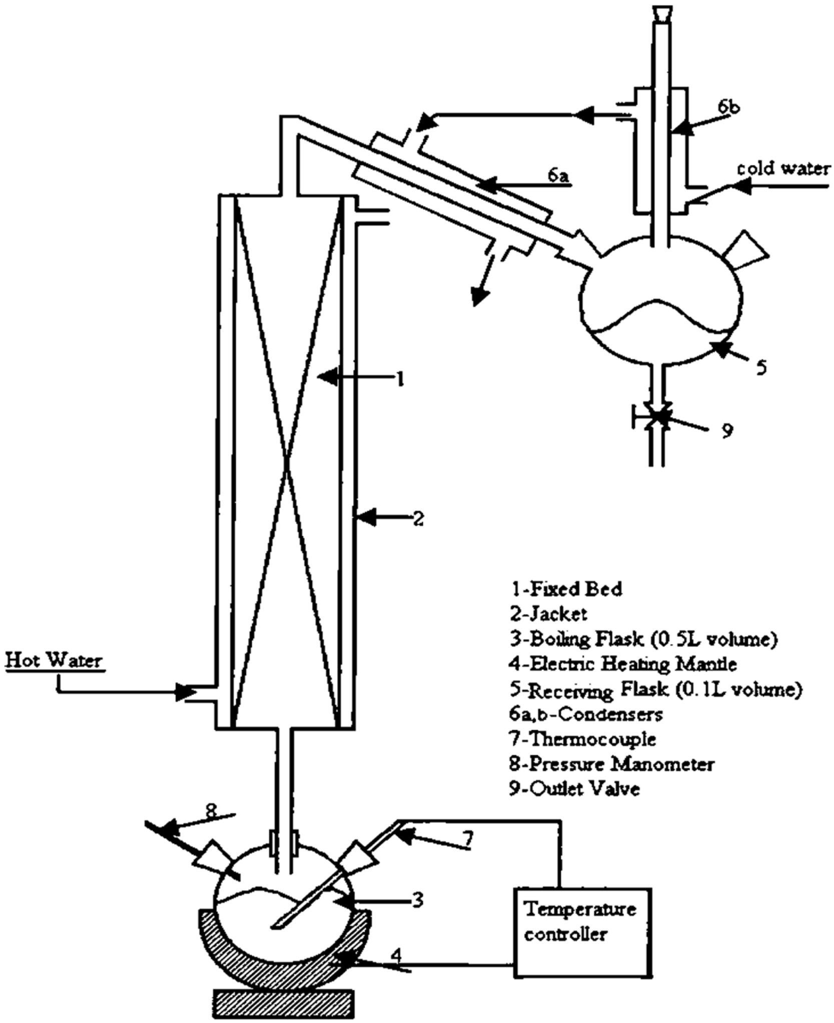


Figure 1. Schematic diagram of bench-scale fixed bed adsorber.

the feed flask and the number of moles of water in the condensate stream the uptake of water can be calculated at each value of the feed composition (25). The calculation procedure was as follows. Knowing the initial feed composition allows the determination of vapor composition fed to the adsorption column from the equilibrium relationship:

$$x_w \gamma_w P_w^{sat} = y_w P \tag{1}$$

where P_w^{sat} is the saturation pressure of water at the isotherm temperature, x_w is the water feed mole fraction, and γ_w is the activity coefficient of water that was calculated from Wilson's activity coefficient model. The saturation pressure was calculated using the Antoine equation:

$$lnP^{sat} = A - \frac{B}{T - C} \tag{2}$$

where A, B, and C are constants. The values of these constants for water vapor are 16.29, 3816.44, and 46.13 (26). The saturation pressure in this equation is in kPa and the temperature is in Kelvin. Since y_w equals the number of moles of water in the vapor phase divided by the number of moles of water and ethanol, knowing the number of moles of ethanol allows the determination of the number of moles of water fed to the column. As ethanol was assumed not to be sorbed by the sorbents, the amount of ethanol collected in the first outlet sample is the same amount of ethanol that was initially introduced to the column as vapor. Knowing the number of moles of ethanol in the vapor phase, the number of moles of water can thus be calculated. Since the number of moles of water introduced to the column and in the condensate is now known, then water adsorbed on the sorbent can be calculated from the difference. The water uptake can simply be calculated by dividing the mass of water adsorbed by the mass of the sorbent in the column.

The new feed composition in the boiling flask can be calculated by subtracting the moles of ethanol and water vaporized from the moles initially present in the flask. As such the new value of x_w was calculated and the same calculation procedure was repeated for this new value. Water activity was calculated from

$$aw = \frac{p_w}{P_w^{sat}} \tag{3}$$

The water activity coefficient, γw, was determined using Wilson's equation (27):

$$\begin{aligned} ln\gamma_1 &= -ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \\ ln\gamma_2 &= -ln(x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \end{aligned} \tag{4}$$

where x_1 and x_2 are the mole fraction of the two components forming the system; Λ_{12} and Λ_{21} are the parameters of Wilson's equation.

The first sample was collected after five minutes and its water content was determined using the Fischer technique. It is assumed here that no sorption of ethanol took place on the adsorbent and the only water is sorbed on the adsorbents (6,7,25). Based on this assumption, the difference between the amounts of water in vapor introduced to the fixed-bed adsorber and that in the outlet sample would be the amount of water sorbed on the adsorbents.

Since y_w equals the number of moles of water in the vapor phase divided by the number of moles of water and ethanol, then knowing the number of moles of ethanol allows determination of the number of moles of water fed to the column. As ethanol was assumed not to be sorbed by the adsorbents, the amount of ethanol collected in the first outlet sample is the same amount of ethanol that was initially introduced to the column as vapor. Knowing the number of moles of ethanol in the vapor phase, the number of moles of water can thus be calculated. Since the number of moles of water introduced to the column and in the condensate is now known, then water adsorbed on the adsorbent can be calculated from the difference. The water uptake can simply be calculated by dividing the mass of water adsorbed by the mass of the adsorbent in the column. The new feed composition in the boiling flask can be calculated by subtracting the moles of ethanol and water vaporized from the moles initially present in the flask. As such, the new value of x_w was calculated and the same calculation procedure was repeated for this new value.

RESULTS AND DISCUSSION

Breakthrough Curves Using Impregnated Adsorbents

Molecular sieves 4Å was used as a reference adsorbent. Data for the breakthrough curves were obtained and represented as C/C_0 versus time. The objective was to search for an abundant and cheaper adsorbent than molecular sieves. To achieve this, several materials were tested for ethanol dehydration.

A mixture of molecular sieves and bentonite in nine to one ratio was used in the bed. As shown (Fig. 2) the adsorption capacity of the mixture was lower than that of the molecular sieves alone; the breakthrough time was 57 min in the case of 4A molecular sieves, while it was 4 min in the case of the mixture. The breakthrough time was selected as the time required to reach 2-wt% of water content in the outlet condensed sample (i.e., $C/C_0 = 0.4$). It is not only that bentonite presence decreased the breakthrough time but also it increased the resistance for vapor flow. In other words, it increased the pressure drop in the column because. Natural zeolite (Mordenite) was used as another material. However, the results were not better than the mixed adsorbent of bentonite and

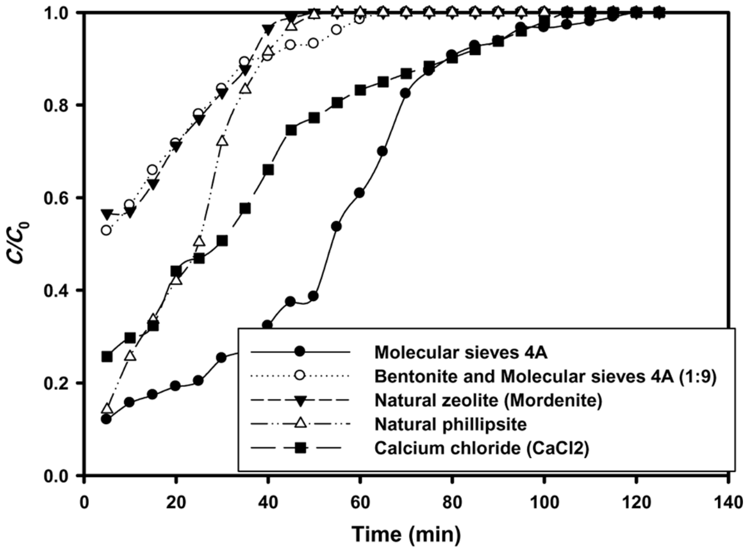


Figure 2. Breakthrough curves for ethanol-water system during water sorption on different adsorbents using 5-wt% inlet water content.

molecular sieves (Fig. 2). This could be also attributed to poor sorption capacity; breakthrough time was short (5 minutes), and the time required to reach the plateau level was 65 minutes. As shown in Fig. 2, natural phillipsite gave relatively acceptable results compared with the other adsorbents mentioned above; however, the sorption performance is still not superior compared to that of molecular sieves 4 Å. The breakthrough time for the case of natural phillipsite was 20 minutes and the time required to reach the plateau value was 55 minutes.

As an inorganic salt, calcium chloride ($CaCl_2$) has a greater hygroscopic capacity than the organic adsorbents, such as phillipsite. However, the deliquescence phenomenon, which depresses the performance, often occurs outside the calcium chloride granules and results in the formation of solid crystalline hydrate $CaCl_2 \cdot H_2O$; this phenomenon is considered as a defect for this type of adsorption system (Zhang and Qiu, 2006) (22). Compared with molecular sieves 4 Å, calcium chloride gave a relatively better water vapor sorption than that of phillipsite (Fig. 2). In the case of calcium chloride, the breakthrough time was 20 minutes and the time required to reach the plateau value was 120 minutes; values that are longer than the case of natural phillipsite.

Impregnated adsorbents obtained by soaking natural phillipsite in 0.5–2 M calcium chloride solutions were tested in this work. These

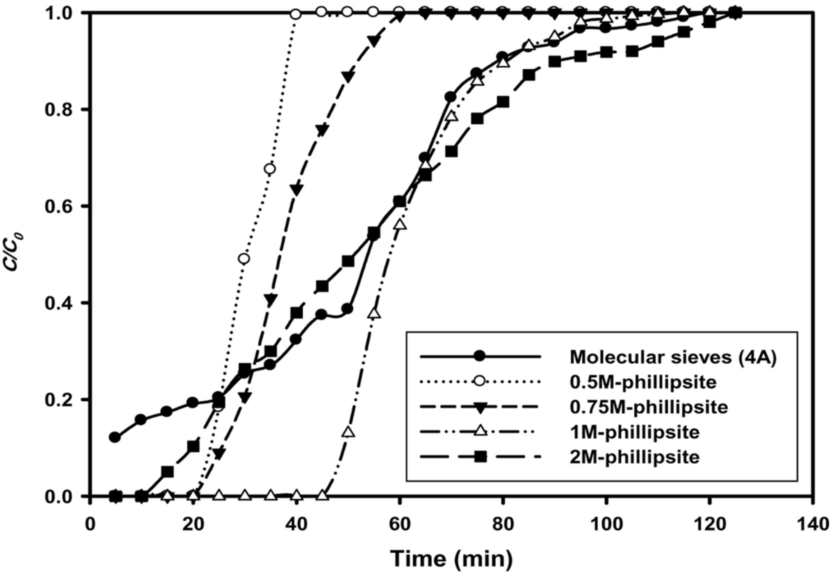


Figure 3. Breakthrough curves for ethanol-water system during water sorption on different impregnated adsorbents using 5-wt% inlet water content.

adsorbents were used for dehydrating ethanol at the azeotropic point (5-wt% H_2O). The performance of each adsorbent was compared to the permformance of 4 Å molecular sieves. As seen in Fig. 3, the breakthrough time and the plateau are not the same for all cases. The time needed to reach the plateau in the case of 1.0 M-phillipsite was about 130 minutes, which is longer than that in the case of molecular sieves 4Å while the breakthrough time is about 55 mins which is almost similar to that for molecular sieves. Anyhow, the sorption performance of 1.0 M-phillipsite was the best and better than that of 4Å molecular sieves. The 1.0 M-phillipsite as such is a promising material for ethanol dehydration.

Results for breakthrough and plateau times are summarized in Table 2 for phillipsite materials used in this work. According to the values displayed in this table, the 1.0 M-phillipsite has the best sorption performance followed by the 2.0 M-phillipsite.

As seen in Fig. 3, when the calcium chloride concentration increased above 1.0 M, the phillipsite treated material became less effective. High content of calcium chloride would occupy more void volume in the micropores of phillipsite. This would leave less space for water vapor and the vapor sorption would be due to solution sorption only. In other

Table 2. Breakthrough time and plateau time for the sorption of water vapor on different adsorbents using 5-wt% inlet water content

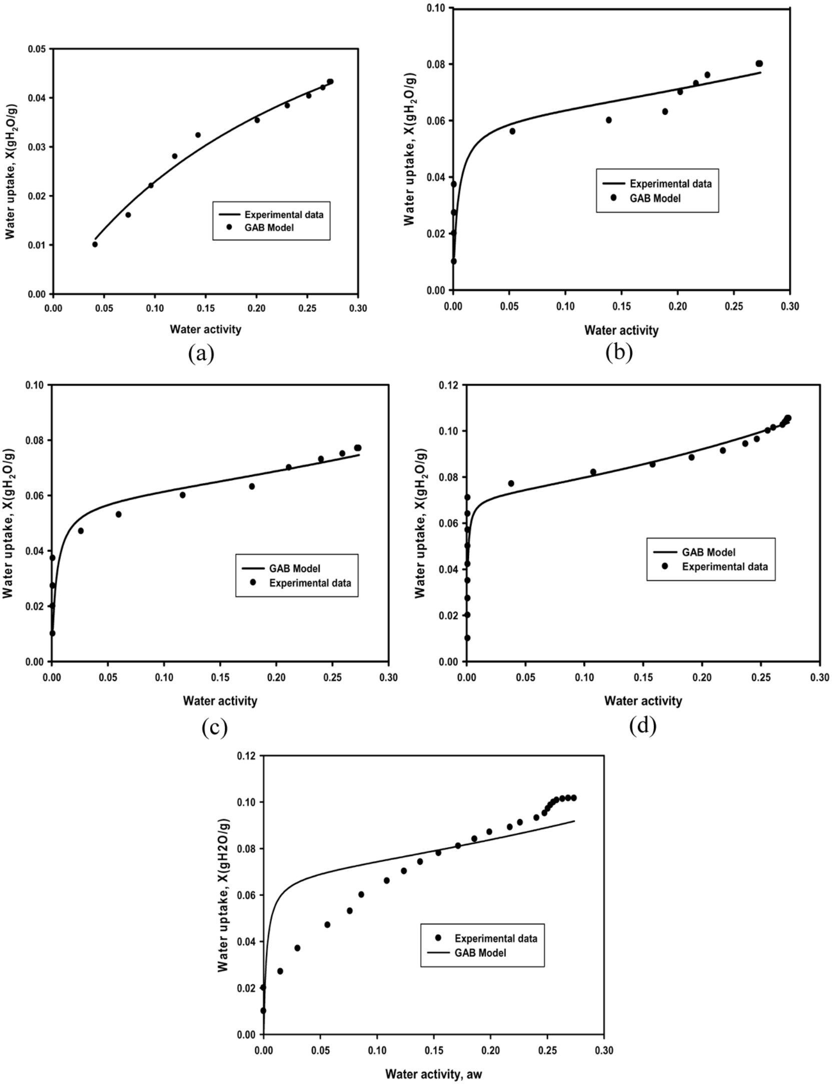
Adsorbent	Breakthrough time (min)	Plateau time (min)
Molecular sieves (4A)	57	120
0.5 M-phillipsite	34	75
0.75 M-phillipsite	35	75
1.0 M-phillipsite	55	130
2 M-phillipsite	41	120

words, the water vapor adsorption is due to inorganic salt ($CaCl_2$) only. Thus, the contribution of solid sorption (micropores of phillipsite) is lowered and so does its capacity toward water vapor. In this work, 1.0 M-phillipsite is considered as the most effective adsorbent for separation of ethanol-water system.

Lee et al. (6) studied the sorption of the ethanol-water system on starch, a biobased adsorbent, and found that the rate of ethanol sorption can be assumed to be negligible, compared to the rate of water sorption. This assumption was also applied in this work. This is because the size of the ethanol molecule, 4.4 Å, is larger than the size of the water molecule, 2.8 Å (15); thus, ethanol will be excluded and only water molecules would be admitted to the available sorption sites. In addition, the water molecules have a larger dipole moment than ethanol molecules which make the former more accessible for the sorption process.

Equilibrium Isotherms for Water Sorption on Impregnated Adsorbents

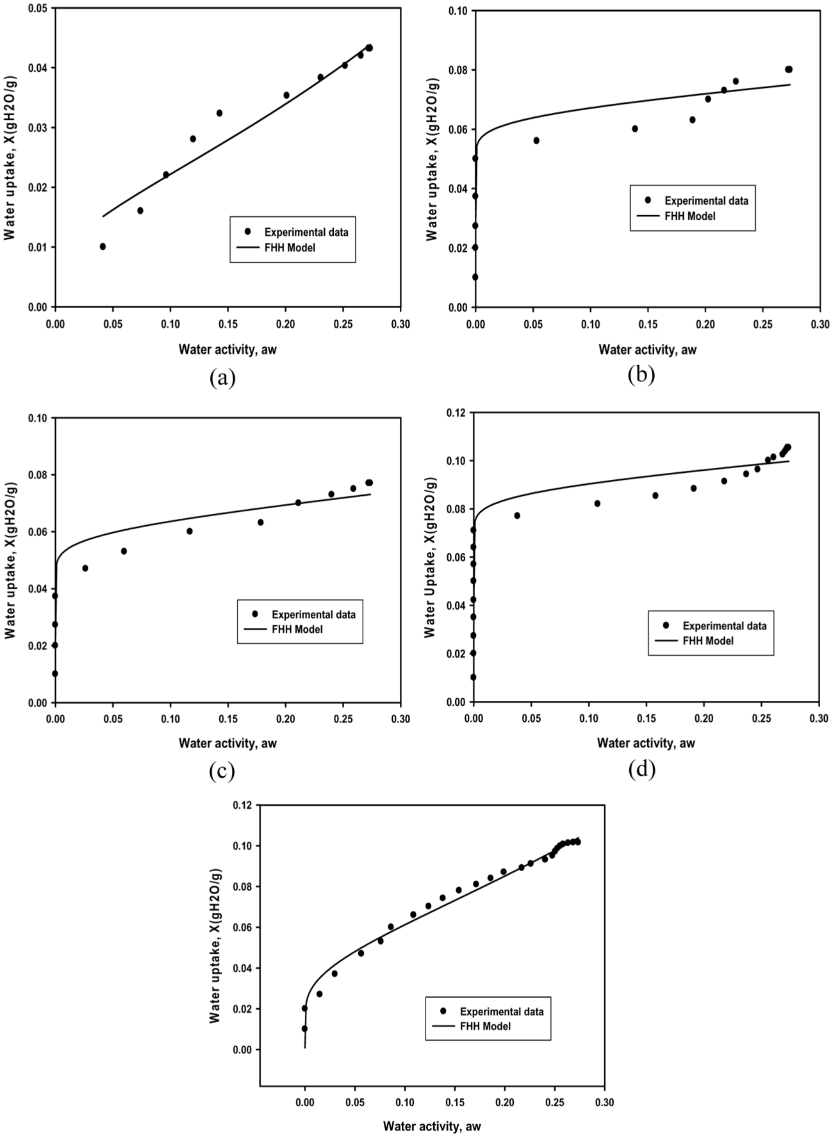
The assumption of partial equilibrium of water vapor introduced to the fixed bed and the water uptake on the composite adsorbents allow the determination of equilibrium isotherms for such system. The experimental data for water vapor uptake versus water activity using different types of impregnated phillipsites, depending on the concentration of $CaCl_2$, are shown in Fig. 4 (or Fig. 5). There are many isotherm models that can be applied for the results of water vapor sorption process. The Brunauer, Emmelt, and Teller (BET) a two-parameter isotherm, the Guggenheim, Anderson, and de Boer (GAB), a three-parameter isotherm and the Frenkel, Halsey, and Hill (FHH model) are the most common models. It is reported that the GAB model covers a wider range of water activity up to 0.9, while the BET model covers only up to 0.4 of water activity



(a) (b) (c) (d) (e)

Figure 4. GAB isotherm of water sorption on Natural Phillipsite (a), 0.5 M-phillipsite (b), 0.75 M-phillipsite (c), 1 M-phillipsite (d), and 2 M-phillipsite (e) using 5-wt% inlet water content for ethanol-water system.

(28). Thus, the GAB and the FHH model have been applied to the experimental results of this work for water sorption on impregnated phillipsite adsorbents.



(a) (b) (c) (d) (e)

Figure 5. FHH isotherm of water sorption on Natural Phillipsite (a), 0.5 M-phillipsite (b), 0.75 M-phillipsite (c), 1 M-phillipsite (d), and 2 M-phillipsite (e) using 5-wt% inlet water content for ethanol-water system.

GAB Model

The GAB model is based on the same theory as that of the BET model. As the BET model postulated that the states of sorbate molecules in the liquid state, the GAB model introduced a second well-differentiated sorption stage for sorbate molecules. This assumption introduced an additional degree of freedom, an additional constant K by which the GAB model gains its greater versatility. The GAB model can be represented by the following equation:

$$X = \frac{X_m C K a_w}{[(1 - K a_w)(1 + (C - 1) K a_w)]} \tag{5}$$

where X is the water uptake on adsorbent (g H_2O/g), a_w is the water activity, X_m is the monolayer capacity (g H_2O/g), C is the energy constant related to the difference between the chemical potential of sorbate in the upper layers and that in the monolayer, K is also another energy constant related to the difference in the sorbate's liquid states and in the upper states. The products of both C and K represent an energy constant equivalent to the energy constant of BET model, C_{BET} (28). The GAB model has some advantages over the BET model. It covers a wide range of water activity up to 0.9, while the BET model covers only up to 0.3–0.4. The parameters of the GAB model X_m and K were predicted by using nonlinear regression software (Sigmaplot 10.0.1, version 10). Figure 4 shows predicted data using GAB model for water sorption on different impregnated adsorbents, namely 0.5 M-, 0.75 M-, 1.0 M-, and 2.0 M-phillipsite, in addition to the natural phillipsite at azeotropic composition for the ethanol-water system. It is seen that this model fit the experimental data reasonably well for all cases except the 2.0 M-phillipsite.

The GAB parameters are shown in Table 3 for different types of adsorbents. Theoretically, the monolayer capacity X_m is supposed to be constant for each type of adsorbent. The monolayer capacity X_m, can be used to determine the available surface area for water sorption on the adsorbent. It is observed (Table 3) that the monolayer capacity increases with the increase in the $CaCl_2$ content up to 1.0 M and then slightly decreases when using phillipsite treated with 2.0 M. This could be due to the same reason mentioned above for such increase in $CaCl_2$ concentration. Also the high content of calcium chloride may create a strong resistance to water vapor sorption on the internal pores of the adsorbent which makes water sorption more difficult and limited. Large magnitude values of the parameter C indicate high amount of heat of adsorption (29); this is useful for the regeneration process of adsorbents. The constant C in the case of 1 M-phillipsite adsorbent is always higher

Table 3. The GAB parameters for water vapor adsorption on different impregnated adsorbent using 5-wt% inlet water content from ethanol-water system

Adsorbent	Monolayer capacity, X_m (g H_2O/ gadsorbent)	Energy constant, C	Energy constant, K	R^2	Experimental Maximum water uptake, g H_2O/g adsorbent
Natural Phillipsite	0.0843	109	0.76	0.99	0.0432
0.5 M-phillipsite	0.0918	306	0.81	0.86	0.0800
0.75 M-phillipsite	0.0950	372	0.83	0.86	0.0770
1.0 M-phillipsite	0.1200	1240	1.2	0.84	0.1054
2.0 M-phillipsite	0.0978	705	0.93	0.70	0.1016

than that of the other adsorbents (Table 3). The isotherms of water sorption on the impregnated adsorbents, particularly for the case of 1.0 M, indicate that there is a high increase in water uptake in narrow range of water activity (Fig. 4). The experimental values of the maximum uptake of water adsorbed on impregnated adsorbents as well as natural phillipsite are also displayed in Table 3. In general, the case of 2.0 M-phillipsite shows poor results; this could be due to the poor fitting of the GAB model for the experimental data for this adsorbent. On the other hand, natural phillipsite, 0.5 M, 0.75 M, and 1.0 M-phillipsite impregnated adsorbents showed better results; again this could be due to the good fitting of the experimental data for such types of adsorbents. It is seen that for the cases 0.5 M-, 0.75 M-, and 1.0 M-phillipsite impregnated adsorbents, Fig. 4, the increase in water uptake at low values of water activity was sharp and more noticeable than for the other adsorbents. This also could be related to the fact that the heat of adsorption of water on the 0.5 M-, 0.75 M- and 1.0 M-phillipsite impregnated adsorbents are higher than that of the other impregnated adsorbents. The high value of C indicates more heat generation during the sorption process which would result in temperature rise along the bed, thus enhancing the sorption process.

FHH Model

The FHH model has been used in this work in order to find good understanding of the water sorption in terms of the combination of solid adsorption and liquid absorption of classical heterogeneous adsorption. It is described by the following equation (22),

$$X = X_m[-\ln a_w]^{-1/r} \tag{6}$$

where the exponent $1/r$ is related to the nature of the gas solid interaction, and other variables are similar to the above. According to this model, if r is very large, then the attraction between solid and vapor is very close and does not extend far from the surfaces; but when r is smaller, then the forces are more typically Van der Waals and are able to act at a greater distance (30). Generally, $r = 3$ for Van der Waals forces, and the deviations of r from this value can be attributed to energy or geometric heterogeneity effects. For the impregnated adsorbent used in this work, the adsorption process comprises of classical heterogeneous adsorption on the pore surface; solid sorption resulting in the formation of salt crystalline hydrates (due to the structure of phillipsite) and liquid absorption resulting in salt solution (due to $CaCl_2$).

Thus, the water sorption mechanism is not the same on the impregnated as on the organic salt or on the inorganic solid surface. Representations of isothermal data for water sorption on different types of impregnated phillipsite using FHH model are shown in Fig. 5 for different types of impregnated phillipsite. It can be seen that this model fits the experimental data poorer than that of the GAB model for all cases, except 2.0 M-phillipsite. The parameters for the FHH model were obtained using non-linear regression and are displayed in Table 4 along with the R^2 value for the different adsorbents used in this work. According to Table 4, it is noted that for the cases of 0.5 M-, 0.75 M-, and 1.0 M-phillipsite impregnated adsorbents the r values are greater than 3 for Van der Waals forces. This means the attraction between the solid and the water vapor is very close and does not extend far from the surface. On the other hand, for the case of natural phillipsite and 2.0 M-phillipsite, the r values are smaller and deviate significantly from $r = 3$ value. This means that the attraction between the solid and the water vapor is more typically van der Waals and are able to act at a greater distance.

Table 4. Parameter values and goodness of fit R^2 for the FHH model

Adsorbent	r	X_m	R^2
Natural phillipsite	0.84	0.0596	0.95
0.5 M-phillipste	5.21	0.0788	0.84
0.75 M-phillipsite	4.14	0.0778	0.90
1.0 M-phillipsite	5.82	0.1042	0.82
2.0 M-phillipsite	1.09	0.0901	0.97

It can be said that the mechanism of water sorption on the impregnated adsorbent is determined by the two steps; solid sorption and solution sorption. In an impregnated particle, as $CaCl_2$ content increases above a certain limit, 1.0 M of $CaCl_2$ in this work, some of the volume of micropore volumes are occupied by $CaCl_2$ granules. Thus, according to the theory of micropore volume filling, there will be less pore space to adsorb water which results in a decrease in water loading.

The values listed in Table 4 indicated that as $CaCl_2$ content increases in the impregnated adsorbent the X_m values increases. This indicates that the equivalent monolayer capacity increase until 1.0 M concentration. This is due to the fact that the solution sorption improves the hygroscopic capacity. After 1.0 M concentration, the equivalent monolayer capacity decreased (Table 4). It can be concluded that the content of $CaCl_2$ impregnated in the pores of phillipsite is the most dominant factor influencing the water vapor sorption on the impregnated adsorbent. These results ensure that the FHH theory can be used to predict the water sorption phenomena and gives an interpretation for the collected data.

Adsorption Kinetics and Diffusion Analysis

Effective diffusivities can be used to study quantitative analysis of moisture transport in the composite adsorbent pores. In the following analysis, the effective diffusion coefficient was obtained by fitting the experimental data of uptake rate to a certain kinetics model. To apply this model, the time variation of the water loading was represented in a dimensionless form (η). In this work, the effective total diffusion coefficient is determined using the Crank diffusion models described by the following equation (Zhang and Qiu, 2007):

$$\eta = 1 - 6\sum_{n=1}^{\infty} \frac{exp(-n^2\pi^2 De\tau/R^2)}{n^2\pi^2} \tag{7}$$

where τ is the time in minutes, η is a dimensionless variable given by $\eta = \frac{\overline{w}-w_i}{w_{\max}-w_i}$, $\overline{w}$ is the transient average water uptake of a particle at each outlet collected sample, $w_{\max}$ is the average water uptake as $\tau \rightarrow \propto$, R is the radius of the phillipsite particle (0.05 mm), and D_e is the effective diffusivity. This model was used to determine D_e values for the different sorbents used in this work. This was done using curve fitting and the values of D_e are displayed in Table 5 for the different adsorbents. It was found that the exponential term in Eq. (7) does not affect the value of η for $n > 3$. Thus, only the first three terms were used for the determination of De.

Table 5. Effective diffusivities for impregnated adsorbents

Adsorbent	Effective diffusivity, $D_e \times 10^8$ ($mm^2 s^{-1}$)	R^2
Molecular sieves	10.09	0.95
Natural phillipsite	10.40	0.83
0.5 M-phillipsite	9.750	0.80
0.75 M-phillipsite	9.485	0.85
1.0 M-phillipsite	6.900	0.93
2.0 M-phillipsite	6.663	0.88

It is noted (Table 5) that natural phillipsite seems to adsorb water faster than adsorbents obtained by impregnating the phillipsite with $CaCl_2$. As a result, the presence of salt inside the pores slows down the rate of water vapor mass transfer. It is also seen that as the $CaCl_2$ content increases, the rate of water adsorption decreases. Thus, it would be reasonable to conclude that the sorption rate is mostly determined by the solution film (salt solution), which creates a stronger mass transfer resistance in the impregnated adsorbents for vapor to penetrate into the internal part of the pellet than that in the pure adsorbent. In conclusion, the mass diffusivity in the impregnated adsorbents drastically decreases due to the presence of salt inside the pores.

CONCLUSIONS

The impregnated adsorbents examined in this work were capable of breaking the azeotrope point of the ethanol-water system. The breakthrough curves of water sorption showed that the 1.0 M-treated phillipsite gave the best separation of the ethanol–water azeotropic mixture. The 1.0 M-phillipsite was found to have the highest value of water uptake compared to the 4A molecular sieves and to the other used adsorbents. The GAB model fit the experimental data better than the FHH model for all cases, except 2.0 M-phillipsite. The content of $CaCl_2$ impregnated in the pores of phillipsite is the most dominant factor influencing the vapor adsorption on the impregnated adsorbent. With an increase in $CaCl_2$ content, the water uptake increases until 1.0 M. However, the presence of salt inside the pores slowed down the rate of water vapor transport and thus decreased the effective diffusivity. Impregnated material is considered cheaper than molecular sieves; hence using it as an alternative adsorbent for drying of water from the ethanol-water system is promising.

REFERENCE

1. Cussler, E.L. (1997) *Diffusion: Mass Transfer in Fluid Systems*, 2nd Ed.; Cambridge University Press: New York, 428–440.
2. Beery, K.E.; Ladisch, M.R. (2001) Chemistry and properties of starch based desiccants. *Enzyme and Microbial Technologys*, *28*: 573–581.
3. Ladisch, M.R.; Dyck, K. (1979) Dehydration of ethanol: New approach gives positive energy balance. *Science*, *205*: 898–900.
4. Lee, J.Y.; Ladisch, M.R. (1987) Polysacchraides as adsorbents: An update on fundamental properties and commercial prospects. *Biochemical Engineering*, *506*: 492–498.
5. Neuman, R.; Voloch, M.; Bienkowski, P.; Ladisch, M.R. (1986) Water sorption properties of a polysaccharide adsorbent. *Industrial & Engineering Chemistry Process Design and Development*, *25*: 422–426; Al-Mohammad, H. Z. (2008). Adsorption of Pyridine Derivatives by Jordanian Zeolites: Phillipsite and Faujasite. Master's. Thesis, Jordan University of Science and Technology.
6. Lee, J.Y.; Wesstagate, P.J.; Ladisch, M.R. (1991) Water and ethanol sorption phenomena on starch. *American Institute of Chemical Engineers Journal*, *37*: 1187–1195; Lee, W.H.; Reucroft, P.J. (1999). Vapor adsorption on coal- and wood-based chemically activated carbons (I) surface oxidation states and adsorption of H2O. *Carbon*, *37*: 7–14.
7. Westgate, P.J.; Ladisch, M.R. (1993) Sorption of organics and water on starch. *Industrial & Engineering Chemistry Research*, *32*: 1676–1680.
8. Ladisch, M.R. (1997) Biobased adsorbents for drying of gases. *Enzyme and Microbial Technology*, *20*: 162–164.
9. Hu, X.; Xie, W. (2001) Fixed-bed adsorption and fluidized-bed regeneration for breaking the azeotrope of ethanol and water. *Separation Science and Technology*, *36*: 125–136.
10. Anderson, L.E.; Gulati, M.; Westgate, P.J.; Kvam, E.P.; Bowman, K.; Ladisch, M.R. (1996) Synthesis and optimization of a new starch-based adsorbent for dehumidification of air in a pressure-swing dryer. *Industrial & Engineering Chemistry Research*, *35*: 1180–1187.
11. Riganakos, K.A.; Demertzis, P.G.; Kontominas, M.G. (1994) Water sorption by wheat and soy flour: Comparison of three methods. *Journal of Cereal Science*, *20*: 101–106.
12. Crawshaw, J.P.; Hills, J.H. (1990) Sorption of ethanol and water by starchy materials. *Industrial & Engineering Chemistry Research*, *29*: 307–309.
13. Crawshaw, J.P.; Hills, J.H. (1992) Experimental determination of binary sorption and desorption for the system ethanol, water, and maize at 90°C. *Industrial & Engineering Chemistry Research*, *31*: 887–892.
14. Czepirski, L.; Komorowska-Czepirrska, E.; Szymonska, J. (2002) Fitting of different models for water vapor sorption on potato starch granules. *Applied Surface Science*, *196*: 150–153.
15. Trent, R.E. (1993) Fundamentals and applications to ethanol drying. Presented at the Codistil-Dedini International Worshop, Ribeirao Preto, SP, Brazil. September 2–3.

16. Teo, W.K.; Ruthven, D.M. (1986) Adsorption of water from aqueous ethanol using 3-°A molecular sieves. *Industrial & Engineering Chemistry Process Design and Development*, *25*: 17–21.
17. Sowerby, B.; Crittenden, B.D. (1988) An experimental comparison of type A molecular sieves for drying the ethanol-water azeotrope. *Gas Separation and Purification*, *2*: 77–83.
18. Al-Asheh, S.; Banat, F.; Al-Lagtah, N. (2003) Separation of ethanol-water mixtures using molecular sieves and biobased adsorbents. *Chemical Engineering Research and Design*, *82*: 855–864.
19. Ackley, M.W.; Rege, S.U.; Saxena, H. (2002) Application of natural zeolites in the purification and separation of gases. *Microporous and Mesoporous Materials*, *61*: 25–42.
20. Reshiedat, R. (1991) Evaluation of Jordanian Phillipsite Tuff "Aritain Area" For agricultural Applications. Master's Thesis, Yarmouk University.
21. Ibrahim, K. (1997) The geology of Al-Bishriyya (Al-Aritain) area. *Natural Resources Authority*, *39*: 918–922.
22. Gatta, G.D.; Lee, Y. (2007) Anisotropic elastic behavior and structural evolution of zeolite phillipsite at high pressure: A synchrotron powder diffraction study. *Microporous and Mesoporous Materials*, *105*: 239–250.
23. Ladisch, M.R.; Voloch, M.; Hong, J.; Bienkowski, P.; Tsao, G.T. (1984) Cornmeal adsorber for dehydrating ethanol vapors. *Industrial & Engineering Chemistry Process Design and Development*, *23*: 437–443.
24. Smith, J.M.; Van Ness, H.C. (1987) *Introduction to Chemical Engineering Thermodynamics,* 7th Ed.; McGraw-Hill Book Company: Singapore, 358–363.
25. Walas, S.M. (1985) *Phase Equilbria in Chemical Engineering,* 2nd Ed.; Butterworth Publishers: Stoneham, MA.
26. Timmermann, E.O.; Chirife, J.; Iglesias, H.A. (2001) Water sorption isotherms of food and foodstuffs: BET or GAB parameters. *Journal of Food Engineering*, *48*: 19–31.
27. Iglesias, O.; Bueno, J.L. (1999) Water agar–agar equilibrium: determination and correlation of sorption isotherms. *International Journal of Food Science and Technology*, *34*: 209–216.
28. Zhang, X.J.; Qiu, L.M. (2007) Moisture transport and adsorption on silica gel–calcium chloride composite adsorbents. *Energy Conversion and Management*, *48*: 320–326.