

Di-calcium phosphate; Thermodynamics and kinetics study

Sana JMAI, Mohamed BAGANE, Michèle QUENEUDEC_T'KINT

¹Applied thermodynamic laboratory, National School of Engineers of Gabes Tunisia, Medina Street 6029, University of Gabes.

²EPROAD IMAp Research Unit Materials and Processes Engineering 7 Moulin Neuf Street 80000 Amiens

Correspond author e-mail address: sanajmai1@gmail.com

Correspond author telephone number: +21624785147

Abstract— During the present work, the sorption isotherms of di-calcium phosphate were given using the gravimetric method at 50, 60, 70, 80°C. It has been found that GAB is the model which fit better the sorption curves. DCPs' convective drying kinetics modeling was carried by the experimental study of the aero-thermal condition's effects. The drying characteristic curves are then modeled using the nonlinear regression functions of MATLABR2013a. Midilli is considered the most suitable model for the experimental results.

Index Terms—Di-calcium phosphate, GAB, Thermodynamics, kinetics, modeling

1 INTRODUCTION

Di-calcium phosphate exists in two forms: the anhydrous form (CaHPO_4 , monetite) and the dihydrate form ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, brushite). Brushite, also commonly encountered in the literature under the abbreviation DCPD (for di-calcium phosphate dihydrate) and more rarely as CHPD (for calcium hydrogen phosphate dihydrate) is an acid calcium phosphate. The mineralogist GJ Brush [1] attributed his name to the di-calcium phosphates' dihydrate form to become "brushite". Jones and Smith [2] have confirmed that Brushite is a compound widely used on an industrial scale whether in fertilizers. Bohner and Gbureck [3] have said that it is also used as a bone substitute material, when Sainz-Diaz et al. [4] have assigned to brushite the role of additive food. Rabatin et al. [5] have found that monetite is obtained following calcinations of the brushite by losing its two molecules of water in two stages when heated. Tamimi et al. [6] have studied the effect of both brushite and monetite for bone regeneration by varying the physical forms.

Drying processes require a good knowledge of sorption isotherms. From these isotherms the final moisture content of the dried product and the energy required for drying can be estimated.

In this work we will study the physicochemical and thermal properties of di-calcium phosphate, in the second part, this work was devoted to study the DCP sorption isotherms for four temperatures (50, 60, 70, 80 °C) based on the static gravimetric method. In addition, to model the experimental data, several analytical models were used, and the net isosteric heat and differential entropy of the product at different humidities were determined. In the third part of this work DCP drying

kinetics will be studied by varying the aero-thermal conditions for the purpose to reach the characteristic drying curve and to model the DCPs' thin layer convective drying.

2 MATERIALS AND METHODS

2.1 Physicochemical and thermal characterization

The determination of the different chemical species constituting the di-calcium phosphate is carried out by fluorescence X. The morphology of di-calcium phosphate was examined using a scanning electron microscope of the FEI Quanta 200F type installed in the LRCS laboratory of the UPJV in Amiens France. The determination of the various mineralogical species is carried out by a Bruker D5000 X-ray diffractometer. The IR spectrum of di-calcium phosphate produced by a FTIR Spectrum 2 spectrometer by Perkin Elmer. The differential and gravimetric thermal analysis are carried out simultaneously using a device (ATD / ATG) of the SETARAM type. A heating rate of 10°C/min with nitrogen (inert gas) sweep was used, the protective gas was the argon. The thermal conductivity was studied by the Hot Disk method which is based on a probe composed of a thermal resistance and placed in a sandwich between two parts of the sample to be studied.

2.2 Study of di-calcium phosphates' sorption isotherms by the static gravimetric method

The static gravimetric technique was used to determine the desorption-adsorption isotherms. The basis of this method is the use of saturated salt solutions to achieve a constant relative humidity. We used in this work the following salts; LiBr, LiCl, KF, ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), K_2CO_3 , NaBr, KI, NaCl, KCl, ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$)

and K₂SO₄. These saturated solutions have a range of water activity between 0.05 and 0.96, as shown in **Table 1**.

Table 1: Water activities of saturated salt solutions [7],[8]

Salt	Activities			
	50	60	70	80
LiBr	5.5	5.3	5.2	5.2
LiCl	11.1	10.95	10.75	10.51
KF	20.8	20.77	21.74	22.85
MgCl ₂ ·6H ₂ O	30.54	29.26	27.77	26.05
K ₂ CO ₃	45.6	45	---	---
NaBr	50.93	49.66	49.7	51.43
KI	64.49	63.11	61.93	60.97
NaCl	74.43	74.5	75.06	76.29
KCl	81.2	80.25	79.49	78.9
BaCl ₂ ·2H ₂ O	88.23	87.28	---	---
K ₂ SO ₄	95.8	95.7	---	---

The samples (0.5 ± 0.01 g) were placed in hermetic enclosures (**Figure 1**) containing saline solutions saturated with salt, kept at a constant temperature in an oven.

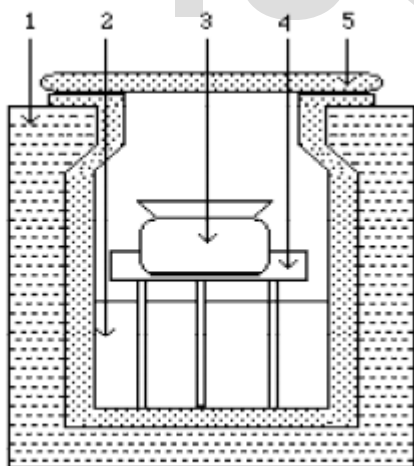


Figure 1: Diagram of a unit of the experimental device

(1): Bath thermostat; (2): Saline solution (3): Beaker containing the product; (4): Sample holder tripod;

(5): Jar with watertight closure.

The variation of the weight is controlled by successive weightings, by a precision balance ± 0.001 g at variable periods which can reach several days. Hygroscopic equilibrium is considered achieved when the weight of the sample does not vary between two successive weightings. Once the wet masses are known, the samples will be introduced into an oven at 105°C for 24 hours in order to determine their dry masses. To determine the products' water content at equilibrium X_{eq} , the difference between the mass of the sample before and after drying in the oven was calculated (Eq1).

$$X_{eq} = \frac{M_h - M_s}{M_s} \quad (1)$$

With: M_h = the samples' mass before drying; M_s = the samples' mass after drying; X_{eq} = the samples' water content at equilibrium.

The product undergoes pre-drying to undergo the adsorption phenomenon. The pre-drying is carried out in an oven carried at a temperature of 60°C in order to avoid degradation of the product, until maximum dehydration of the product.

2.3 Modeling of sorption isotherms

Different models (Table2) have been studied and tested in many works to correlate the equilibrium water content with relative humidity. Ten models were studied for adjustment of the experimental results of the DCP sorption isotherms at 50, 60, 70 and 80°C.

Table 2: The mathematical models used to fit DCPDs' sorption curves

Model	Equation of the model
Smith	$X_{eq} = A - B \ln(1 - a_w)$
Iglesias and chiriñe	$X_{eq} = A + B \frac{a_w}{1 - a_w^m}$
White and Eiring	$X_{eq} = \frac{A}{1 + B a_w^m}$
Peleg	$X_{eq} = A(a_w)^n + C(a_w)^p$
GAB	$X_{eq} = \frac{A C B a_w}{(1 - B a_w)(1 - B a_w + A B a_w)}$
Oswin	$X_{eq} = A \left(\frac{a_w}{1 - a_w} \right)^n$
Adam	$X_{eq} = A + B a_w + C a_w^2 + D a_w^3$
Caurie	$X_{eq} = \exp(A + B a_w)$
Halsey	$X_{eq} = \left(- \frac{A}{\ln(a_w)} \right)^{1/n}$
Langmuir	$X_{eq} = A \frac{a_w^n}{(1 + B a_w^n)}$
Henderson	$X_{eq} = \left(- \frac{\ln(1 - a_w)}{A} \right)^{1/n}$
Freundlich	$X_{eq} = A a_w^B$
Chung-Pfost	$X_{eq} = - \frac{1}{A} \ln \left[\frac{\ln(a_w)(T \times R)}{-B} \right]$

For the nonlinear regression analysis, we used the Curve Expert Professional 2.0.3 software to estimate the parameters of the model from the experimental results. The value of the adjustment was determined by standard error (ES) (Eq2) and the correlation coefficient (r^2) (Eq3).

$$ES = \sqrt{\frac{\sum_{j=1}^N (X_{jcal} - X_{jexp})^2}{N - n_p}} \quad (2)$$

$$r^2 = \sqrt{1 - \frac{\sum_{j=1}^N (X_{jcal} - X_{jexp})^2}{\sum_{j=1}^N (X_m - X_{jexp})^2}} \quad (3)$$

With

$$X_m = \frac{\sum_{j=1}^N X_{jexp}}{N} \quad (4)$$

When X_m : the value of the arithmetic mean of the reduced water contents' experimental values for drying kinetics and the equilibrium water content for of sorption isotherms; N : experimental points' number; N_p : the number of the models' constants. The models are compared according to the standard error (ES) and the correlation coefficient (r^2) at the average of studied temperatures. The lowest ES value and the highest r^2 value indicate the most suitable fit model.

2.3 Isostatic heat

Differential enthalpy or isosteric heat of sorption (ΔH_d) describes the phase of the water emerged in the solid. The net isosteric sorption heat (Δh_d) (Eq5) is the amount of energy above the heat of vaporization of the water (ΔH_{vap}) (Eq6) associated with the sorption process and this parameter was calculated based on the experimental data by the Clausius-Clapeyron equation the later was used by many authors. Abdenouri et al. [9] have used this equation in order to determine the isosteric heat of powdered milk. When Tsami et al. [10] have used the same method for the determination of isosteric heat of fruits.

$$\left[\frac{d(\ln(a_w))}{d\left(\frac{1}{T}\right)} \right]_{X_{eq}} = \frac{-\Delta h_d}{R} \quad (5)$$

$$\Delta h_d = \Delta H_d - \Delta H_{vap} \quad (6)$$

The study of the sorption isotherms at different temperatures is necessary to determine the logarithmic curve of variation of the water activity with the inverse of the temperature, to fixed water content.

The obtaining of the analytical expression of the sorption heat Δh_d is possible from the modified equations. This approach shows that the temperature does not influence the isosteric heat ΔH_d . Everett [11] has created a relationship which relates the

net isosteric sorption heat Δh_d and the sorption differential entropy ΔS_d (7):

$$(7)$$

The sorption isotherms' experimental points were plotted as ($\ln(a_w)$) with the water content at equilibrium (X_{eq}). We have deduced Δh_d from the slope of the line ($-\ln(a_w)$) as a function of ($1/T$). Kechaou and Maalej [12] have deduced the values of ΔS_d from the intersection of this straight line with the ordinate axis.

A linear relation between Δh_d and ΔS_d has been proposed by The Theory of Compensation (8).

$$\Delta h_d = T_\beta \cdot \Delta S_d + \alpha \quad (8)$$

Arslan and Togrul [13] have confirmed that the iso-kinetic temperature T_β is the slope of the linear function connecting the differential entropy and the differential enthalpy of sorption.

2.5 Study of convective drying

To study the drying kinetics of di-calcium phosphate, drying was carried out by hot air with a closed loop. The unit used is a HILTON Air Conditioning Dryer (Figure 2). It was designed to demonstrate the basic principle of air conditioning; to show how heat and humidity can be added or subtracted from an air stream for environmental control and comfort conditions. The air flow is perpendicular to the products' surface to be dried, where the properties of the air (air temperature, relative humidity RH and air velocity) are controlled and the samples' mass is also calculated at each moment. This type of flow has the advantage of having optimum product-air contact conditions and a high heat transfer coefficient. The experimental device which is used to study the drying kinetics is installed in the Applied Thermodynamics Research Unit of the National School of Engineers of Gabes ENIG Tunisia.

Drying was carried out using hot air with a closed loop. The air flow is parallel to the product surface to be dried, where the properties of the air (air temperature, relative humidity RH and air velocity) are controlled and the sample mass is also calculate at each moment. The maximum temperature which can be supported by the installation is of the order of 92 ° C. in the test vein. The air flow can be changed by varying the speed of the fan via a variable speed drive. Before each test, the di-calcium phosphate powder was intruded in an oven at 60 ° C. for 24 hours for total desiccation. Is then weighed using a precision balance 0.0001g, an anhydrous mass m_0 , powder which is added the needed amount of water, m_e , to have a water content of sample denoted X_0 which is equal to 0.15 Kg of water / Kg db. The desired conditions (air temperature, relative humidity RH and air velocity) require about half an hour for each test to stabilize. Once the drying conditions set and the sample is prepared, the product is placed in thin layer on a metallic support and introduced into the test section in a horizontal position, parallel to the air flows' direction. With the aid of a digital scale connected to a computer, the reduction of the mass during drying processes was continuously monitored. The drying experiment is

$$(-\ln a_w)_{X_{eq}} = \frac{\Delta h_d}{RT} - \frac{\Delta S_d}{R}$$

stopped once the mass of the sample no longer varies. The sample after drying is then placed in a preheated oven at 105 °C for 24 hours in order to find the dry mass of the product, M_s . The curves of drying kinetics are obtained experimentally by following the progress of the water content of the product studied by measurements of successive masses throughout the drying process until the equilibrium water content previously determined at from the desorption isotherms. These curves are presented by equation (9).

$$X(t) = \frac{M(t) - M_s}{M_s} \quad (9)$$

Where X : Samples' water content at each instant (t) of drying (Kg of water / Kg db); $M(t)$: Samples' mass at instant (t); M_s : Samples' dry mass.

These curves characterize the materials' behavior to be dried along the drying process as a function of time. They vary according to the sample tested and contain one to three main phases of the drying kinetics, depending on the type of hygroscopic product studied. The drying curves are represented by the evolution of the humidity of the sample over time, the evolution of the drying rate (water mass evaporated per unit time and surface evaporation of the material (Kg of water / m².s)) with time and with water content. Several experimental conditions (air temperatures, drying air velocity, air humidity, etc.) are generally tested to obtain the curves of the kinetics. For various fixed operating conditions, the moisture transfer between the material to be dried and the air can be represented by the curve describing the evolution of the reduced water content as function of time.

Meel [14] has introduced the concept of drying characteristic curve CCS for the first time. Meel [14] has proposed to collect all the experimental drying curves obtained for different athermal conditions tested throughout the experimental process, a single curve called a drying characteristic curve. It is necessary to know the value of the initial water content and that of equilibrium, in order to be able to describe the kinetics of drying of a product whatever the aero-thermal condition of drying studied. The determination of the drying characteristic curve consists in normalizing the ratio of the drying speed at time t to the speed of the first drying phase with reduced water content. The drying kinetics can be represented in the form of equation (10).

$$X_r = \frac{X_t - X_{eq}}{X_0 - X_{eq}} \quad (10)$$

With: X_t represents the water content of the product at given time t (kg of water / kg db); X_{eq} represents the thermodynamic equilibrium water content determined by the sorption isotherms (kg of water / kg db) and X_0 represents the initial water content (kg water / kg db).

Table 3 presents the mathematical models used to choose the model that better describes the convection drying kinetics of di-calcium phosphate. These models give expression of the reduced water content (X_r) during the drying time.

Table3: Mathematical models tested to fit the convective drying kinetics of di-calcium

Model	Model Equation
Newton	$X_r = \exp(-k.t)$
Page	$X_r = \exp(-k.t^n)$
Modified page	$X_r = \exp(-(k.t)^n)$
Two terms	$X_r = a \exp(-k_1.t) + b \exp(-k_2.t)$
Wang and Singh	$X_r = 1 + a.t + b.t^2$
Two exponential terms	$X_r = a \exp(-k.t) + (1-a) \exp(-k.a.t)$
Verma et al.	$X_r = a \exp(-k.t) + (1-a) \exp(-b.t)$
Henderson and Pabis	$X_r = a \exp(-k.t)$
Henderson and modified Pabis	$X_r = a \exp(-k.t) + b \exp(-g.t) + c \exp(-h.t)$
Logarithmic	$X_r = a \exp(-k.t) + b$
Diffusional Approach	$X_r = a \exp(-k.t) + (1-a) \exp(-k.b.t)$
Midilli-Kucuk	$X_r = a \exp(-k.t^n) + b.t$
Parabolic	$X_r = a + b.t + c.t^2$

X_r : reduced water content ; t : drying time; $a, b, c, g, h, k, k_0, k_1, n$: model settings

The statistical investigation of the curves of drying kinetics was carried out on the basis of the MATLAB R2013a calculation software. Nonlinear regression was used to estimate each constant of the selected models. The model fitting to the experimental kinetics drying data was tested by the statistical parameters; which are the correlation coefficient (R^2), the square root of the mean square error ($RMSE$), and the sum of square root of the quadratic error (SSE). The selection of the most suitable model was based on the comparison of the static parameters of the different models. Indeed, the higher value of the correlation coefficient (R^2) and the lower $RMSE$ values and the square root sum of the quadratic error (SSE) are the selection criteria that justify the choice of the most suitable model for the fitting of drying kinetics' curves. The correlation coefficient (R^2), the square root of the mean square error ($RMSE$) and the square root sum of the quadratic error (SSE) between the experimental and predicted data are given by the equations (11), (12) and (13):

$$R^2 = 1 - \frac{\sum_{i=1}^N (X_{ri,exp} - X_{ri,pre})^2}{\sum_{i=1}^N (X_{ri,exp} - \bar{X}_r)^2} \quad (12)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (X_{ri,exp} - X_{ri,pre})^2}{N}} \quad (13)$$

$$SSE = \frac{1}{N} \sum_{i=1}^N (X_{ri,exp} - X_{ri,pre})^2 \quad (14)$$

With: $X_{ri,exp}$ and $X_{ri,pre}$ represent respectively the experimental and predicted reduced water contents; \bar{X}_r represents the average reduced water content; N represents the experimental points' the number and n represents the number of constants.

3. RESULTS AND DISCUSSION

3.1 Sorption isotherm by gravimetric static method

In **Figure 2** the isotherms of adsorption and desorption of di-calcium phosphate at 50, 60, 70 and 80°C respectively are based on the gravimetric static method. It is noted that the general appearance of sorption isotherms of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is of type II following to the classification of the BDDT. Asymptotic behavior characterizes this type of isotherm in the range of high values of a_w where water is found as pure water. The influence of temperature on the sorption isotherms can be observed in a range of water activity varying from 0.052 to 0.958 (**Figure2**). These curves show that, at constant water activity, the equilibrium water content is inversely proportional to temperature; by increasing the temperature, the equilibrium water content decreases. On the other hand, by taking fixed water content, the water activity increases with temperature. It can be concluded that the di-calcium phosphate studied becomes less hygroscopic when the temperature increases. This decrease in hygroscopicity was explained by the decrease in the active sites' number due to chemical and / or physical modifications of the product. As a result, a decrease in desorbed amount occurred as the temperature increased. Still on the same figure (**Figure2**), the equilibrium water content increases with the activity of water for given temperatures. It can be seen that for values of water activity of less than 0.2 the equilibrium water contents are low. This implies that in the zone where the water is strongly bound in the form of the monomolecular layers, the di-calcium phosphate studied is stable. Whereas for very high water activity values the stability of the material becomes critical where water is retained in the microspores in its free form.

The adsorption and desorption isotherms of di-calcium phosphate for the four temperatures studied at 50, 60, 70 and 80°C are illustrated on the curves (**Figure2**).

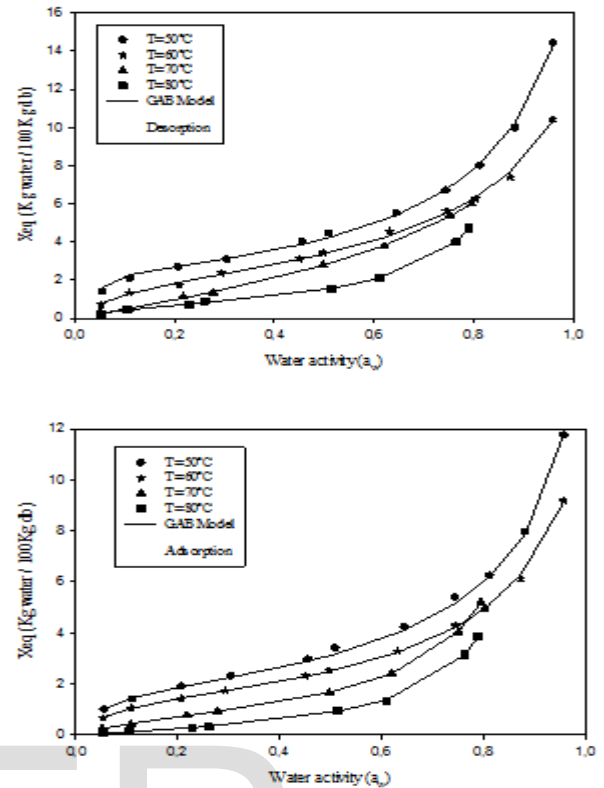


Figure 2: Experimental desorption-adsorption curves at 50, 60, 70 and 80 ° C of di-calcium phosphate

By analyzing the sorption isotherms (**Figure 3**) at a given temperature, it can be seen that the two adsorption and desorption curves do not overlap and a gap between the humidification curve and the dehydration curve can be observed. In other words, for the same value of water activity, two values of different equilibrium water contents X_{eq} are observed; for a given temperature, the desorption equilibrium water content is higher than that of adsorption. This non-coincidence is attributed to the phenomenon of hysteresis which was the subject of different hypotheses in the literature such as; Thony [15] who has studied the hysteresis phenomenon into a non saturated porous media when Agroba [16] has studied this phenomenon in this paper effect of temperature on the moisture sorption isotherm of a biscuit containing processed mango. This phenomenon is clearly observed in the **Figure 3**.

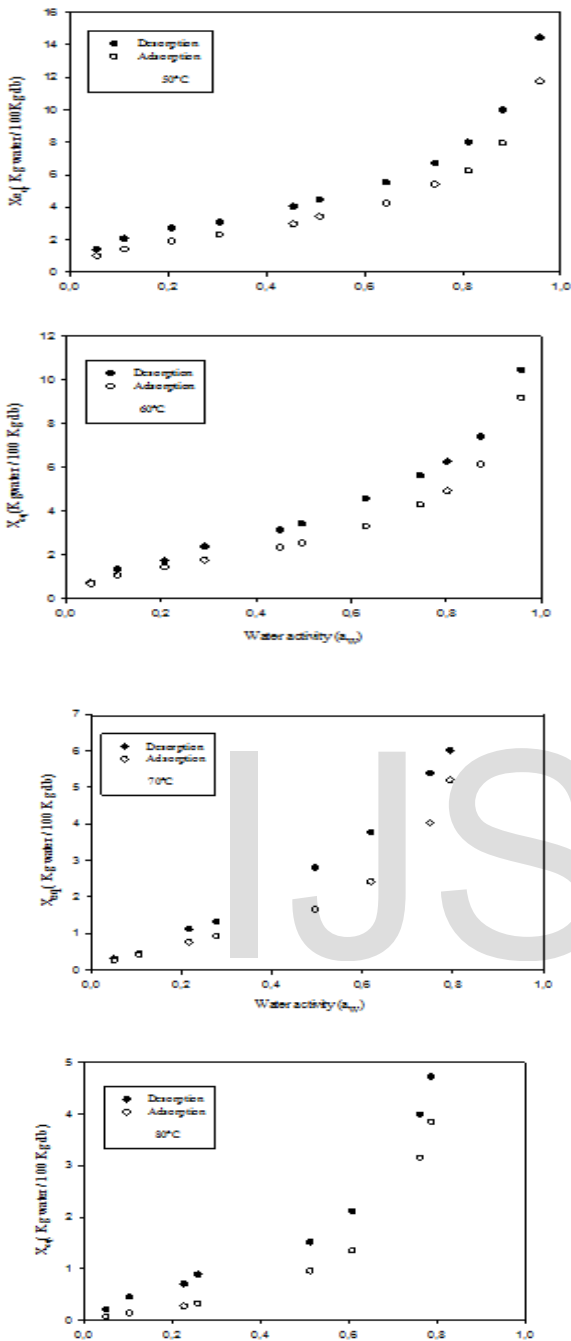


Figure 3: Isotherm adsorption-desorption of di-calcium phosphate at 50, 60, 70 and 80°C

Crausse et al. [17] have attributed the phenomenon of hysteresis to the physical changes of the product caused by the loss of water many others authors did the same attribution when studding porous media. Many empirical, semi-empirical and theoretical models have been developed to describe the equilibrium water content as a function of the temperature of the material and the relative humidity of the air. In this study, thirteen mathematical models were chosen to describe the adsorption and desorption isotherms of di-calcium phosphate.

The nonlinear regression functions of Curve Expert Professional version 2.0.3 were used to estimate each constant of the selected models. The model fitting to the experimental data of the sorption isotherms was evaluated with the correlation coefficient (r^2) and the mean square error (RMSE). The model with the highest value of r^2 (near 1) and the lowest value of RMSE was considered the most suitable model for smoothing the experimental sorption curves of DCP. The constants as well as the statistical parameters of the models used for the smoothing of the sorption isotherms are grouped in Table 4.

Models	Desorption				Adsorption			
	T=50°C	T=60°C	T=70°C	T=80°C	T=50°C	T=60°C	T=70°C	T=80°C
$GAB: X_d = \frac{X_m \cdot A \cdot Baw}{(1 - Baw)(1 - Baw + A \cdot Baw)}$								
Models	Desorption				Adsorption			
	T=50°C	T=60°C	T=70°C	T=80°C	T=50°C	T=60°C	T=70°C	T=80°C
$GAB: X_d = \frac{X_m \cdot A \cdot Baw}{(1 - Baw)(1 - Baw + A \cdot Baw)}$								
X_m	2.412	0.0226	0.0316	0.00786	0.0187	0.0153	0.00933	0.0060
A	54.451	10.645	1.947	7.677	21.461	15.304	5.7484	1.7009
B	0.868	0.8215	0.762	1.060	0.8769	0.8718	1.0397	1.0872
r^2	0.99890	0.9989	0.99973	0.9996	0.99927	0.9997	0.99995	0.99993
RMSE	0.002013	0.001544	0.0007	0.00052	0.001385	0.000667	0.000269	0.00019

The results show that the most suitable model for the fitting of experimental sorption curves is the Guggenheim Anderson Boer (GAB) model in temperature ranges from 50 to 80°C and water activity ranging from 0.052 to 0.958, followed by the models of Adam, Oswin and Henderson. It can be observed that among all models, the GAB model had the highest correlation coefficient r^2 value and the lowest RMSE squared error value. The values of r^2 and RMSE for the sorption isotherms range from 0.9989 to 0.99995 and from 0.00019 to 0.002, respectively. Therefore, the GAB model was most suitable for predicting experimental data.

3.2 Isothermic heat

These results (Figure 4) show that, by increasing the water content, net isosteric heats decrease, indicating that at low water content the maximum energy is used to eliminate the water emerged in the solid. Tsami [18] has suggested that this could be attributed to the presence of highly active polar sites on the surface of the product, which are surrounded by water molecules, constituting a monomolecular layer. Iglesias and Chirifie [19] have given another assignment for this phenomenon may be the progress of isosteric low-moisture sorption heat due to the bigger resistance to water movement from the heart of the sample to his surface. Isothermic heats of sorption are high at small moisture contents (<20%) and the next isosteric heats of adsorption and desorption of the DCP decrease strongly with a growth of the products' moisture content. The heat of desorption is higher than that of the adsorption with small val-

ues of the moisture content. This means that the energy required during the desorption process is higher than that of the adsorption process. The net isosteric heats as well as the differential entropy of adsorption and desorption of water in di-calcium phosphate are mathematically expressed by a second-order exponential function of the water content for adsorption and desorption.

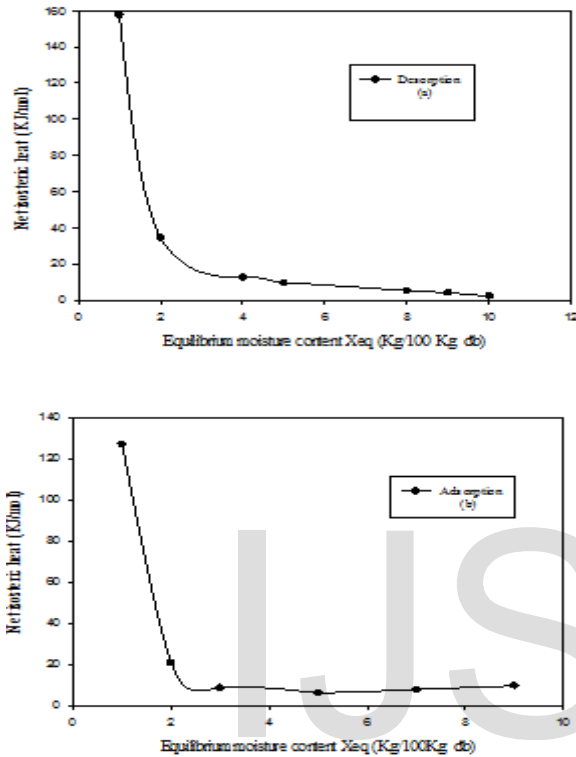


Figure 4: Variation of net isosteric heat of desorption (a) and adsorption (b) with moisture content for DCP.

For desorption

$$\Delta h_d = 1206 \cdot \exp(-2.209 \cdot X_{eq}) + 32.209 \cdot \exp(-0.241 \cdot X_{eq})$$

R=0.999 ; SSE=0.9109

For adsorption

$$\Delta h_d = 956.8 \cdot \exp(-2.059 \cdot X_{eq}) + 4.527 \cdot \exp(0.080 \cdot X_{eq})$$

R=0.999 ; SSE=1.271

3.3 Kinetics study

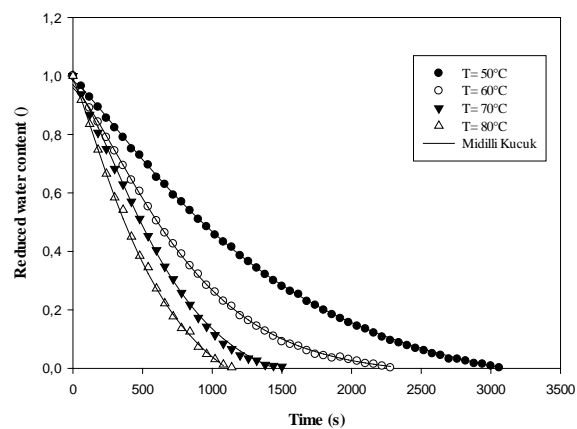
In this section, we test the thermal-hydric behavior of di-calcium phosphate by measuring the kinetics of drying under different conditions and the study of the influence of the operating variables on drying. Aero-thermal conditions, such as temperature, relative humidity and air velocity, were varied with each experiment. On the Table 7 are presented the different operating conditions of the tests carried out during the study of the drying kinetics.

Table 5: Operating conditions of the experiments data

Temperature (°C)	Relative humidity (%)	Speed (m / s)
50		0.5
60	35	1
70	55	1.44
80	75	

The variations of the water content of the product studied with time in a temperature range of the drying air varying from 50 to 80 ° C. are shown in Figure 5. The experimentals were carried out at a relative humidity of 55% and a speed of 1 m/s. The effect of temperature on the variation of the water content of the product is clearly observed, it is noted that the water content decreases with the increase in temperature at a given time of drying. By analyzing on the other hand, it is observed that at constant water content the drying time increases by decreasing the temperature. Zagrouba [20] agrees these resultants on convective drying of porous media. Citing the example where the water content is equal to 0.08 Kg of water/ Kg db, the drying time passes respectively from 1140 seconds to 470 seconds for temperature values varying from 50 to 80 ° C. The influence of the drying air temperature on the water content and the drying time is explained by the increase in the heat supplied to the product with the air temperature. This increase leads to a dilation of the bonds of the water molecules, which promotes the evaporation of the contained water. The increase in temperature results in a partial pressure difference of the water vapor between the surface of the product and the drying air. A drop in evaporation flow characterizes the end of the drying process, this fall being due to passage of the surface of the DCP in the hygroscopic domain. This evaporation is compensated by the diffusion of the water content from the center to the surface. As the drying process evolves, the water content in the material decreases until it reaches the state of hygroscopic equilibrium.

In order to test the influence of the drying air velocity on the drying kinetics of di-calcium phosphate, the speed of the drying air entering the drying chamber via d a variator responsible for properly adjusting the air velocity while fixing the temperature of the drying air at 60°C. and the relative humidity at 50%.



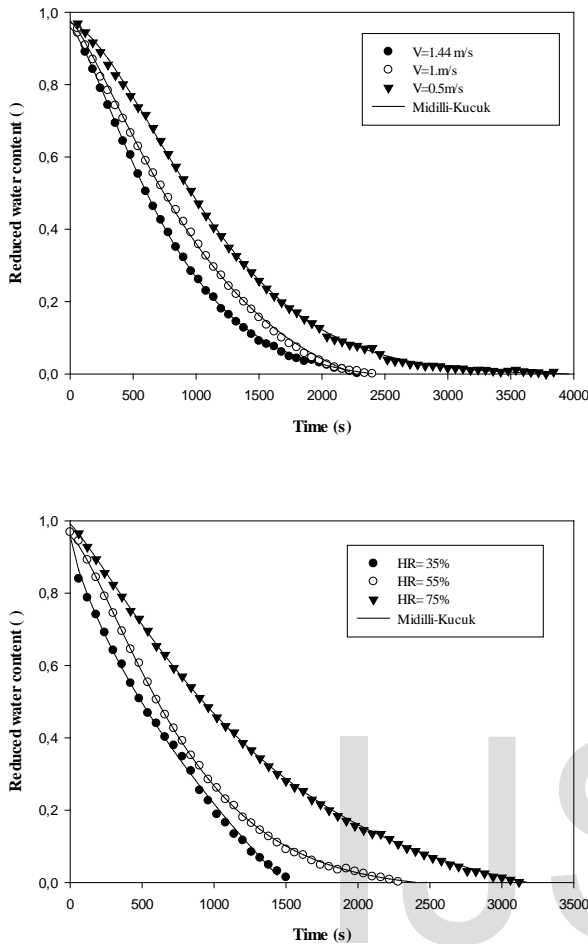


Figure 5: Variation of water content with time

The first observation detected is that the influence of temperature on the drying time is more important than the effect of the speed of drying air. Madamba et al. [21] have attributed this to the fact that increasing the rate of drying air results in a drop in the temperature of the product resulting in a decrease in the pressure of the water vapor, which implies a decrease in the evaporation some water. From these curves an observation can be clearly deduced, when the speed of the drying air increases the water content of the product decreases at a fixed time. For example, at time $t = 1020$ seconds the variation of the water content is of 0.0934 Kg of water/ Kg db at 0.0628 Kg of water/ Kg db for a passage from the drying air velocity of 0.5 m/s to the maximum blower speed (1.44 m/s). By increasing the speed of the drying air, the latter undergoes a rapid change of state, favoring a good transfer of mass and heat, which is manifested by a very rapid drying speed.

By observing the variation in the water content with the moisture content of the drying air (Figure 5), it is evident that the drying speed of the material and the drying time depend on the relative humidity of the air drying; by increasing the rela-

tive humidity, the drying speed slows down so the drying time increases. This observation can be verified for example at time $t = 540$ seconds the water content equal to 0.0891 Kg of water / Kg db, 0.0995 Kg of water / Kg db and 0.1152 Kg of water / Kg db for relative humidity of air of 35%, 55% and 75% respectively. These results can be explained by the fact the implication of these results is that when the relative humidity of the air increases, the difference between the concentrations of water in the drying air and the product thus decreases the exchange between the surface of the product and the product, the air will be more difficult. Kaya and Aydin [22] have developed similar results on some herbal leaves. And Andriazafimahazo et al.[23] have developed similar results on corn.

The sample changes to a water content of 3% for 1500 seconds for relative humidity of 35%, 2280 seconds for relative humidity of 55%, and 2120 seconds relative humidity of 75% air. Therefore, in order to accelerate the drying process, it is necessary to lower the relative humidity of the air for a constant temperature and air drying rate.

The regression method nonlinear function of MATLABR2013a was used for smoothing the experimental points and we used thirteen mathematical models of the literature. The Table 8 preserves the parameters and the constants of the studied models.

Table 6: Statistical constants and parameters of the Midilli model used for the smoothing of the experimental curves of drying kinetics.

Models	Temperature ($V=1.44\text{m/s}, HR=55\%$)				Speed ($T=60^\circ\text{C}, HR=55\%$)		Humidity ($V=1.44\text{m/s}, T=60^\circ\text{C}$)	
	50°C	60°C	70°C	80°C	0.5m/s	1m/s	35%	75%
Midilli-Kucuk	$X_w = a \cdot \exp(-k \cdot t^n) + b \cdot t$							
A	0.9844	0.959	0.970	0.9915	0.9713	0.9802	0.9571	0.9918
K	0.0245	0.0288	0.0326	0.0687	0.0088	0.0336	0.0882	0.0266
N	1.1910	1.3410	1.4140	1.2120	1.556	1.288	0.7672	1.168
B	-0.0013	-0.0004	-0.0021	-0.0051	-3.51 ^{***}	-0.0006	-0.0137	-0.0012
r ²	1	0.9999	0.9987	0.9989	0.9996	0.9996	0.9982	0.9999
RMSE	0.0017	0.00346	0.0122	0.0114	0.0068	0.00641	0.0125	0.0037
SSE	0.00014	0.00041	0.00330	0.0021	0.0027	0.0014	0.0034	0.0006

Thirteen mathematical models were tested in order to select the most suitable model to describe and to smooth the experimental curves of drying of calcium phosphate in the temperature ranges from 50 to 80 ° C., with a velocity ranging from 0.5 to 1.44 m/s and relative humidity ranging from 35 to 75%. The high values of R^2 and the low values of RMSE indicate a good fit of all these models to the experimental results. Under the experimental conditions studied, these values vary from 1 to 0.9217 and from 0.0930 to 0.0017.

Analysis of the results shows that the Midilli-Kucuk model is the most appropriate model for describing the kinetics of drying of the calcium phosphate followed by the Prabolic model and then the model of Wang Singh.

The figure 5 illustrates the experimental data of the kinetics curves and various conditions and their description by the

Midilli-kucuk model. Indeed, the curves predicted by the model coincide well with the majority of the experimental points.

Figure 6 shows the characteristic drying curve of the DCP. The different experimental drying tests under different operating conditions, enabled us to establish a correlation expressed as the rate of drying of a 3 order polynomial function of the reduced water content Xr (15).

$$Rr = -0,517x^3 + 0,665x^2 + 0,777x + 0,062 \quad (15)$$

With $R^2 = 0.936$

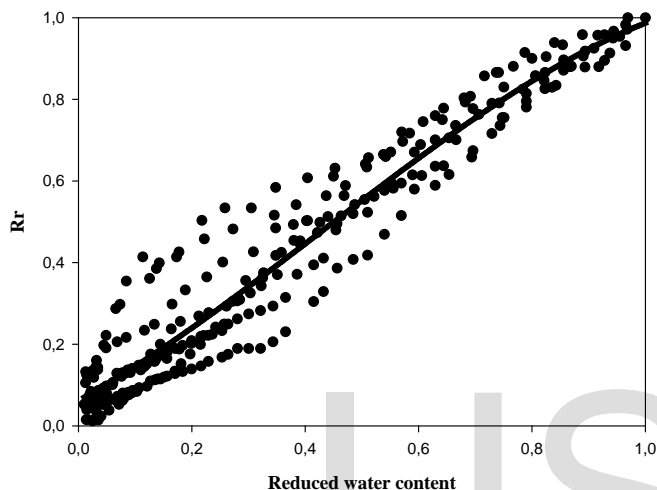


Figure 6: Drying characteristic curve of DCP

4. CONCLUSION

The sorption isotherms were determined with the gravimetric method then the modeling of sorption isotherms shows that the GAB model is the appropriate model for adsorption and desorption with both the highest (r^2) coefficient values and the most basic standard error values for the temperature range between 50° and 80° C. The net isosteric heats and the differential entropy of sorption were determined for DCP by combining the GAB model with the Clausius-Clapeyron equation. The heat of sorption and the differential entropy were inversely proportional to the amount of moisture and are found to be an exponential function of moisture content. The study of the convective drying kinetics of the di-calcium phosphate studied was carried out under different aero-thermal conditions. The results show that the kinetics of drying of the product has only one drying phase, the drying phase at decreasing speed. The experimental data of the drying kinetics of DCP were adjusted by thirteen mathematical models. The Midilli model was the most suitable model to describe the experimental data of drying kinetics in temperature ranges $50-80^\circ$ C, velocity $0.5-1.44$ m / s and relative humidity 35-75%. The performance of the model chosen for the description of the drying kinetics at different operating conditions was confirmed by a statistical analysis of the experimental data (highest correlation coefficient and lowest mean squared error).

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