Influence of temperature and Thermodynamic Analysis on Adsorption/Desorption Isothermss for green menth.

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ABSTRACT

The objective of this study is to experimentally determine the sorption isotherms and thermodynamic properties of green mint after undergoing thermal and biochemical treatment. The method employed is the gravimetric method using saturated saline solutions at various temperatures. In order to model and predict the hygroscopic behavior during drying and storage, we have utilized developed mathematical models (such as the Langmuir, GAB, modified BET, Peleg models, etc.). The adjustment and optimization of these models will be conducted using statistical techniques to analyze the obtained data. The isosteric desorption heats of green mint will be calculated using the Clausius-Clapeyron equation. This study will provide an expression to predict the thermodynamic properties of green mint.

I. Introduction

Renewable energies are derived from natural resources such as the sun, wind, water, tides, and geothermal heat, and are considered the future of energy. However, they are still underutilized, covering only 20% of global electricity consumption. The use of these energies has numerous advantages, such as reducing greenhouse gas emissions. Among the five main families of renewable energies, solar energy is abundant in desert regions like the Adrar province in southwestern Algeria [1]. This free solar energy can be utilized for various daily activities.

Solar drying, which involves removing water from food using solar energy, is an important process in the agri-food industry. Determining sorption isotherms, which reveal the hygroscopic equilibrium properties of products [2], is crucial for optimizing drying conditions and should be established through experiments. These sorption isotherm curves provide valuable information about the distribution and intensity of water molecule binding [3], as well as their functional availability in biochemical and biological substances. They also provide reliable data on the product's water balance, enabling the determination of its stability range after drying [4]. Sorption isotherm curves also offer insights to ensure better storage preservation by determining the optimal moisture content to reach, approaching an equilibrium state. Studies on sorption isotherms rely on mathematical models, including eight empirical and semi-empirical models (mentioned in the literature) that are more or less based on physical principles [5]. These models describe the correlation between water content and water activity in the products. Among these models, the modified BET model [6], GAB model [7], modified Halsey model [8], Peleg model [9], Henderson-Thompson model [9], and modified Oswin model [11] can be found.

Experimental sorption curves allow for the determination of maximum temperatures and final water contents. This information is crucial for optimizing drying conditions of various products to ensure their physicochemical and microbiological stability during storage. Mediani et al. [12] conducted a study to identify physicochemical elements and establish desorption isotherm curves for different date varieties found in the Algerian Sahara.

In this context, the objective of this study is to valorize green mint, a plant cultivated in large quantities in southwestern Algeria, by examining its drying properties. This will be accomplished through experimental determination of sorption isotherms and thermodynamic properties using the gravimetric method with saturated saline solutions at different temperatures to model and understand its hygroscopic behavior.

II. Materials And methods for Preparation of product

In the context of this study, samples of green mint from the Adrar region were collected. These samples were transported in a fresh and healthy state to the URER/MS laboratory. For the desorption process of green mint, small pieces of approximately the same mass (1 g) were accurately cut using a digital balance. Each sample was then placed in a jar previously equipped with a perforated grid, positioned above an acidic solution. The samples were kept in an environment where temperature and humidity were maintained constant.

Figure 1. The green mint.

III. Experimental Procedure

This study employs the static gravimetric method in conjunction with saturated salt solutions to investigate the phenomena of desorption and adsorption. The selected salts include NaOH, LiCl, KF, MgCl2, (Mg(NO3)2, 6H2O), NaNO2, NaCl, KCl, and (BaCl2, 2H2O). The sample is positioned above the salts in a controlled environment, ensuring stable temperature and humidity.

Mass variations are measured at three different temperatures (30, 40, and 50 °C) using a precision balance. After determining the wet masses, the samples undergo a drying process in a 105 °C oven. Prior to that, a pre-treatment at 60 °C is performed to ensure complete dehydration of the product. This approach enables the acquisition of accurate information regarding hygroscopic equilibria and adsorption properties of the studied material.

Table 1. Standard values of relative humidity given by different salts as a function of temperature [13]

Salts	**T=30°C**	**T=40°C**	**T=50°C**
NaOH	7	7	6
LiCl	11	11	10
KF	27	22	20
$MgCl_2$	32	32	31
$Mg(NO_3)_2$, $6H_2O$	51	48	45
$NaNO_2$	63	62	59
NaCl	75	75	75
KCl	84	82	81
$BaCl_2$, $2H_2O$	90	89	88

The experimental setup used to investigate the phenomena of desorption and adsorption consists of nine hermetically sealed jars (Figure 2). Each jar contains 140 ml of a saturated salt solution and is equipped with a grid that supports a fresh green mint sample weighing approximately 1 g for desorption.

For adsorption, the green mint samples are pre-dried in an oven set at 60 °C. A second grid containing approximately 0.1 gram of the dried sample is placed next to the first grid with the fresh sample. Prior to introducing the study product, the jars are kept in a thermostatic bath at a fixed temperature of 30 °C for 24 hours.

Figure 2. System for the preparation of sorption isotherms.

Adsorption and desorption experiments are then conducted at three different temperatures: 30 °C, 40 °C, and finally 50 °C, with nine relative humidity values. The wet masses (Mh) of the product in each jar are measured daily until hygroscopic equilibrium is reached.

$$\mathbf{X_{eq}} = \frac{\mathbf{M_h - M_s}}{\mathbf{M_s}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (\mathbf{1})$$

Once the sample masses become nearly constant, the experiment is stopped, and the samples are weighed and placed in an oven set at approximately 105 °C until their masses no longer vary over time. The difference in mass before and after drying in the oven allows for the calculation of the equilibrium water content (equation 1). The temperature of the thermostatic bath is then changed, and the same experiment is repeated for working temperatures of 30 °C, 40 °C, and 50 °C.

VI. Results And Discussion

Influence of temperature on the sorption isotherms of green mint:

After several days of sorption experiments, Figure 3 presents the experimental results of adsorption and desorption of green mint at different temperatures. The adsorption and desorption curves do not overlap, revealing a hysteresis phenomenon. The sorption isotherms exhibit a sigmoidal shape according to the BET classification. The equilibrium water content increases with water activity at a constant temperature. The sorption isotherms of green mint can be divided into three zones, each corresponding to a specific behavior in terms of the amount of bound water.

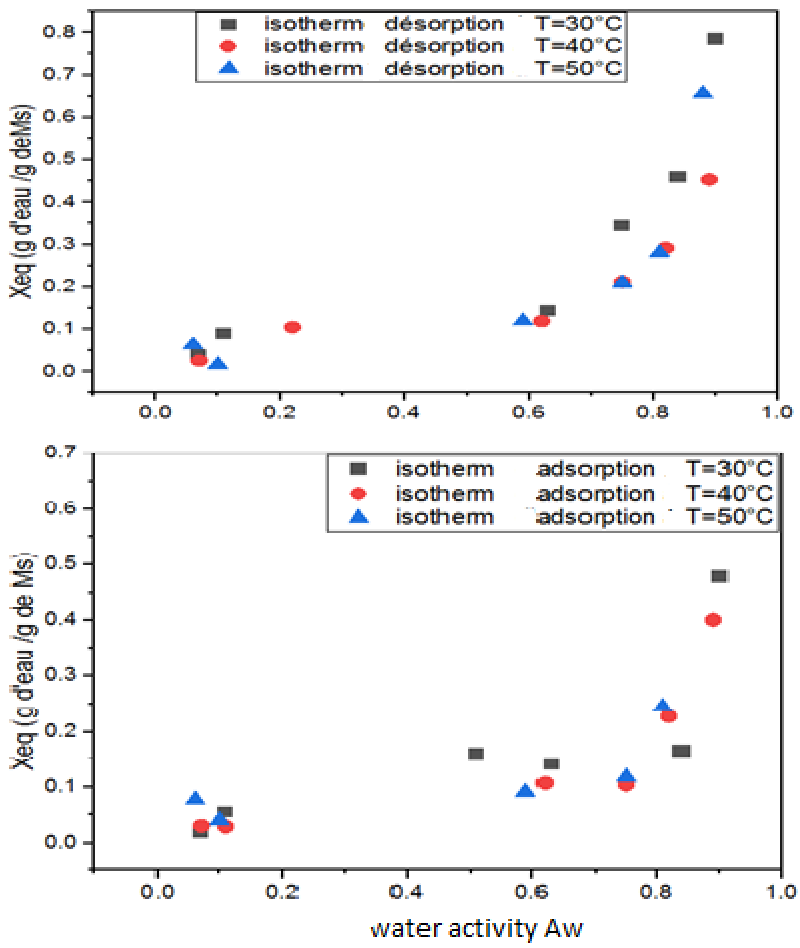


Figure 3. Influence of temperature on the sorption isotherms of green mint.

Modeling of sorption isotherms (desorption/adsorption) of green mint:

Once the experimental data regarding sorption isotherms have been obtained in the previous sections, it is crucial to establish the correlation between the water activity of the product and the equilibrium water content in order to control and manage this phenomenon through modeling.

Given the complexity of biological products and the phenomena involved in water sorption, numerous researchers have proposed mathematical models formulated as empirical and semi-empirical relationships to describe equilibrium curves. In this study, the GAB model was selected due to its renown and relevance for medicinal and agri-food products [14].

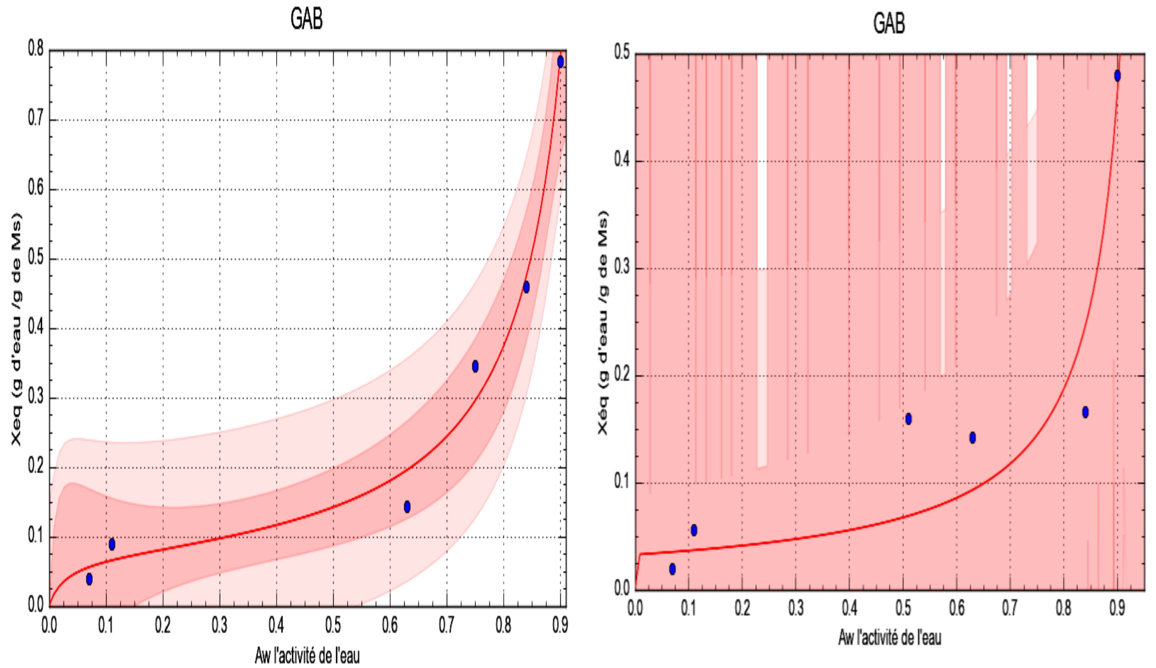


Figure 4. Desorption/adsorption isotherms of green mint adjusted by GAB models at a temperature of 30°C.

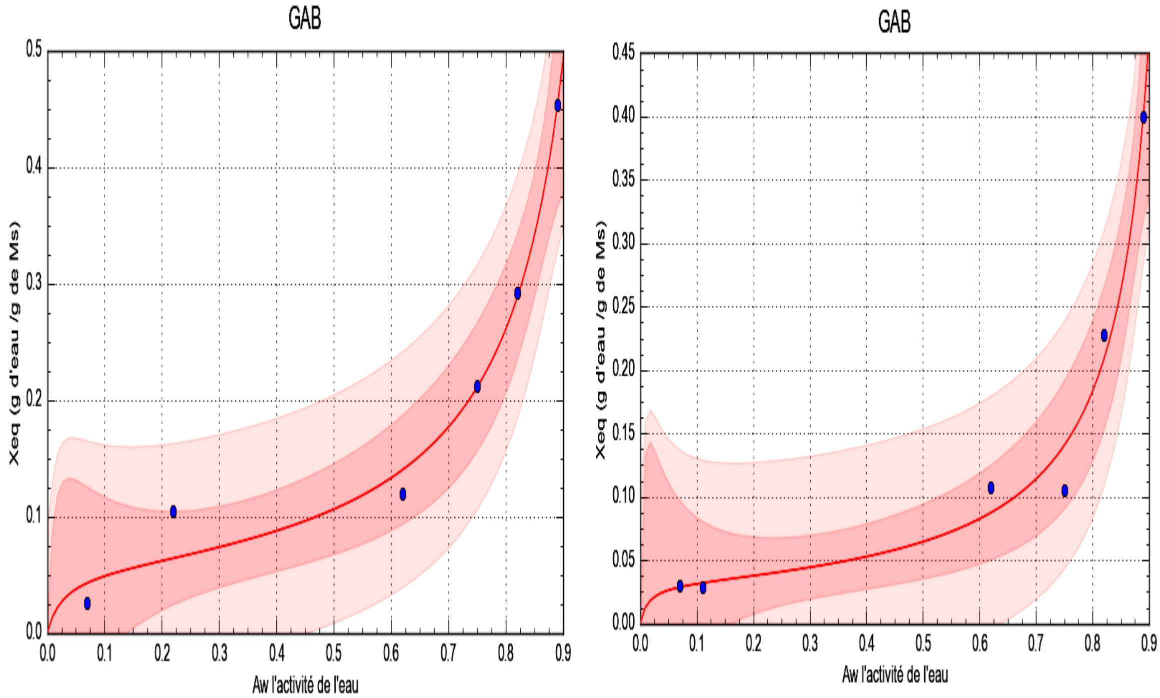
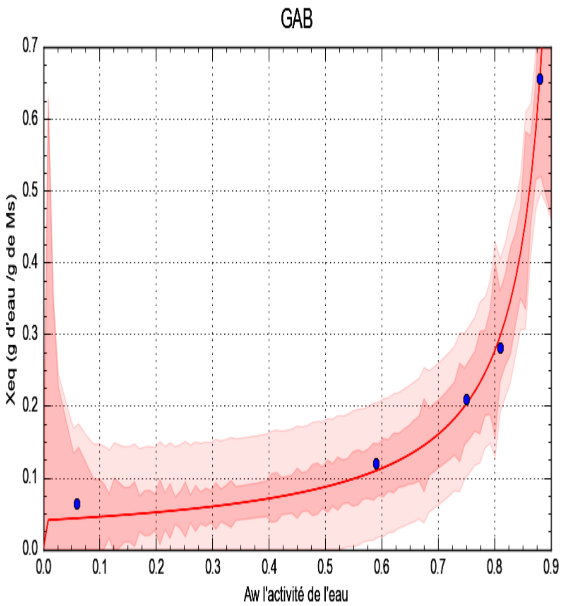


Figure 5. Desorption/adsorption isotherms of green mint adjusted by GAB models at a temperature of 40°C.



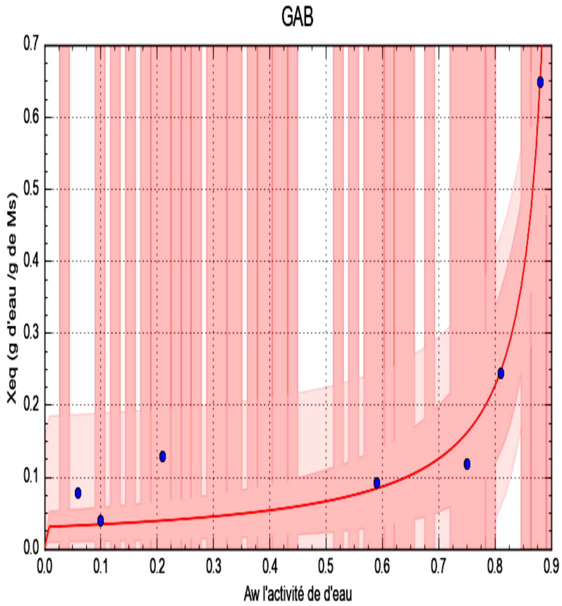


Figure 6. Desorption/adsorption isotherms of green mint adjusted by GAB models at a temperature of 50°C

The modeling and fitting results for the three temperatures are presented in Figures 3, 4, and 5. The parameters of each equation (refer to Table 2) were adjusted to the experimental data using the Marquardt-Levenberg nonlinear optimization method. The software "CurveExpertPro-2.6.3" and "OriginPro 2021b" were employed to calculate the coefficients of the models describing the equilibrium sorption curves of green mint and to obtain their statistical parameters, including the coefficient of determination (R2), the mean relative error (MRE), and the standard error (SE) of the equilibrium water content.

Tableau 2. Table Parameters adjusted by the GAB model of the Desorption/Adsorption isotherms at T=30, 40 and 50°C.

Model	Parameter	Temperature		
		30°C	**40°C**	**50°C**
Désorption	A	0.072	0.055	0.040728
	B	1.009	0.987	1.065582
	C	32.422	34.725	17859.242757
	R^2	0.984	0.979	0.996
	EST	0.045	0.028	0.020
	EMR	0.992	0.989	0.996
Adsorption	A	0.032	0.031	0.030
	B	1.033	1.035	1.083
	C	26149026.386	68.703	162421752.488
	R^2	0.865	0.979	0.955
	EST	0.077	0.026	0.055
	EMR	0.930	0.989	0.977

Isosteric Heat of Sorption for Green Mint:

Figure 7 displays the isosteric sorption curves derived from the Clausius-Clapeyron equation for green mint. As the moisture content of green mint increases, the slopes progressively decrease until they reach absolute zero values.

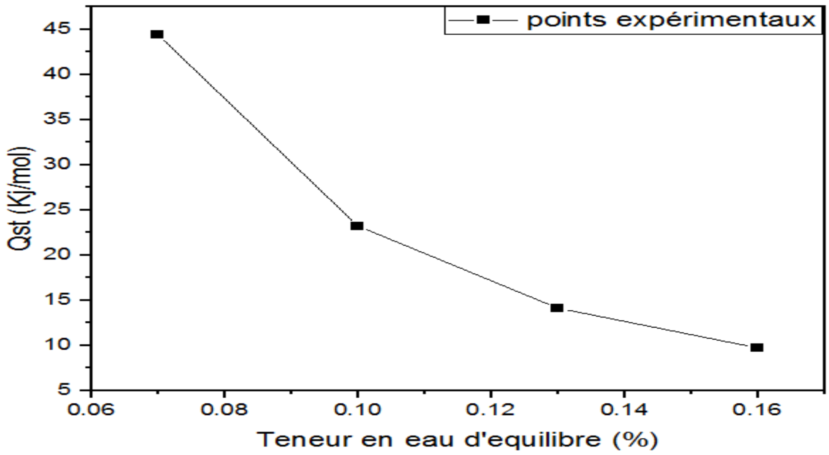


Figure 7. Isosteric heat of adsorption for green mint

By employing the GAB model in conjunction with the Clausius-Clapeyron equation, the net quantities of isosteric adsorption heat were determined for various equilibrium water contents. The changes in green mint desorption relative to water content are illustrated in Figure 7. These findings emphasize that at low water content, the isosteric heat is more pronounced, indicating a strong interaction between water and the substrate. However, it becomes negligible in the presence of latent heat under high humidity conditions.

VII. Conclusion

The experimental sorption curves have enabled the determination of optimal drying conditions for green mint by identifying maximum temperature thresholds and final water content levels. This ensures the preservation of its physicochemical and microbiological stability during storage.

The sorption isotherms of green mint were obtained through experimental application of the static gravimetric method. The experimental findings for green mint are depicted by the sorption isotherms at three different temperatures (30, 40, and 50 °C). These sorption curves are adjusted using the GAB statistical model, which has been found to be the most suitable for accurately describing the complete set of sorption isotherms and effectively representing the relationship between the three influential parameters. The net isosteric adsorption heat is subsequently calculated.

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