Université de Monastir/Faculté des Sciences de Monastir
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Modeling of Water Vapor Adsorption on Foods by a Statistical Physics Treatment using the Grand Canonical Ensemble

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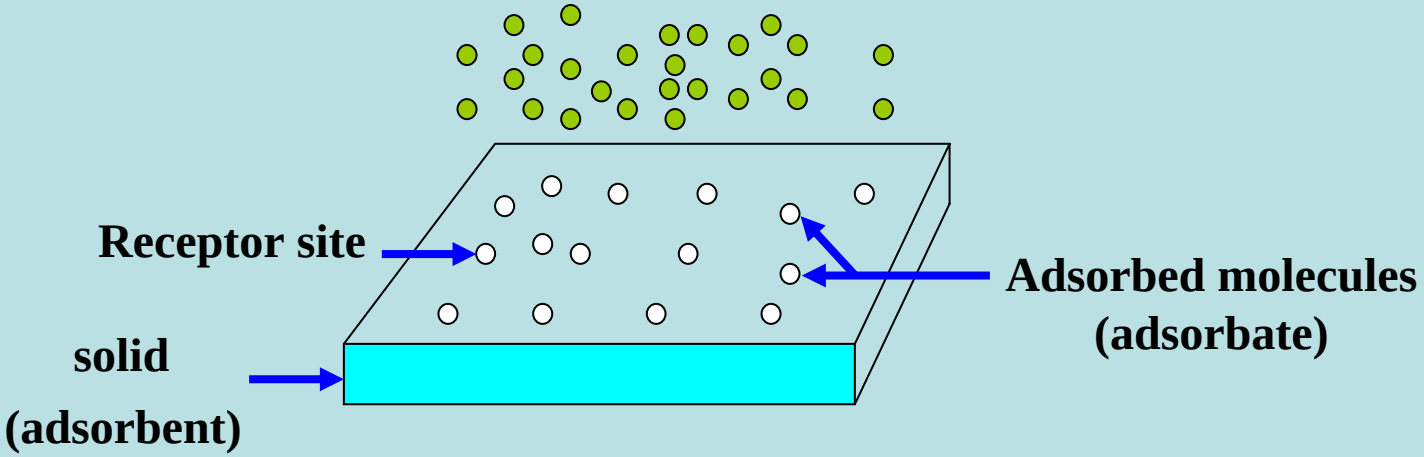
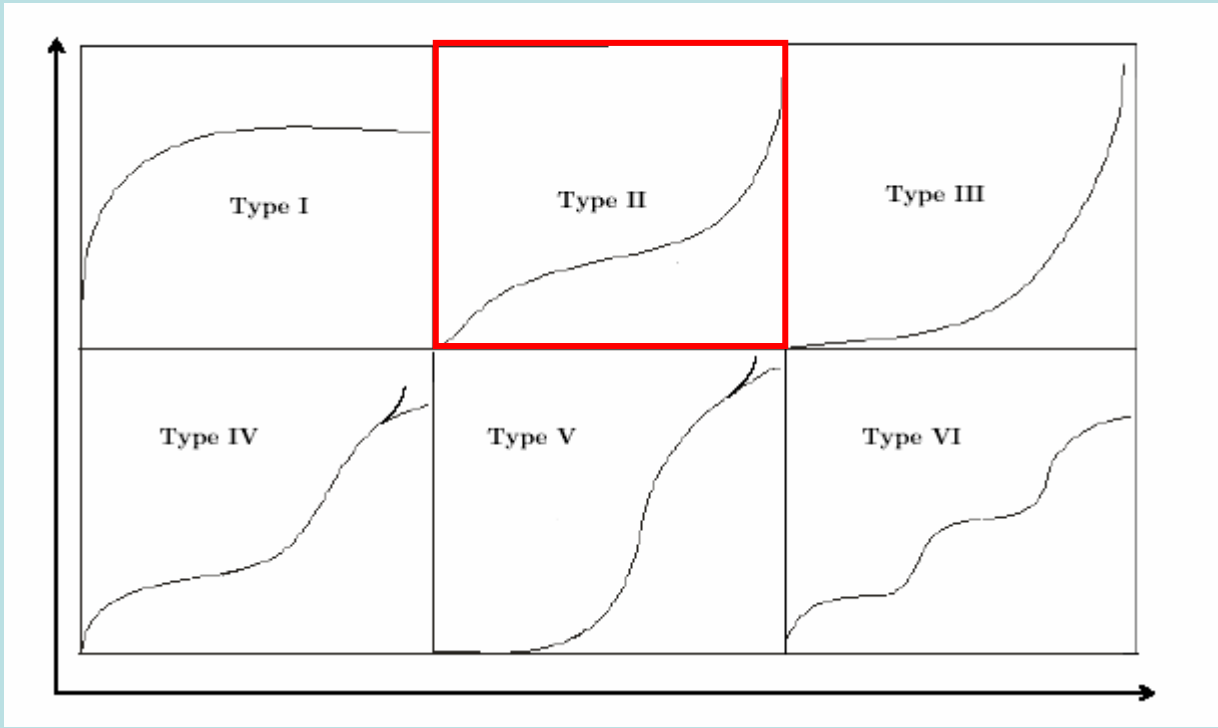
Summary

- Introduction
- **Part I: Treatment of the adsorption Model using Statistical physics**
- **Part II: Interpretation of adsorption isotherms**
- **Conclusion**

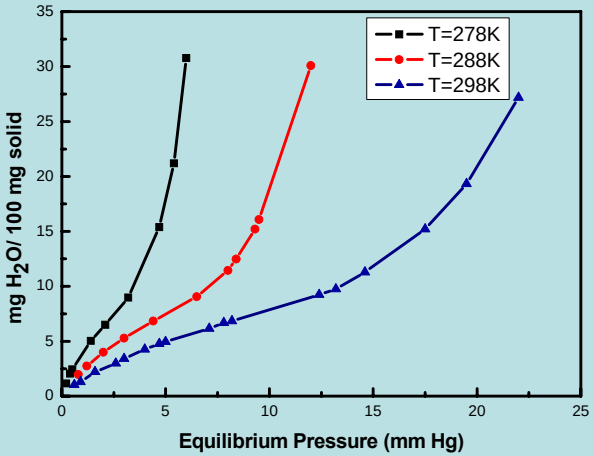
Adsorption


Receptor site
Adsorbed molecules
(adsorbate)
solid
(adsorbent)

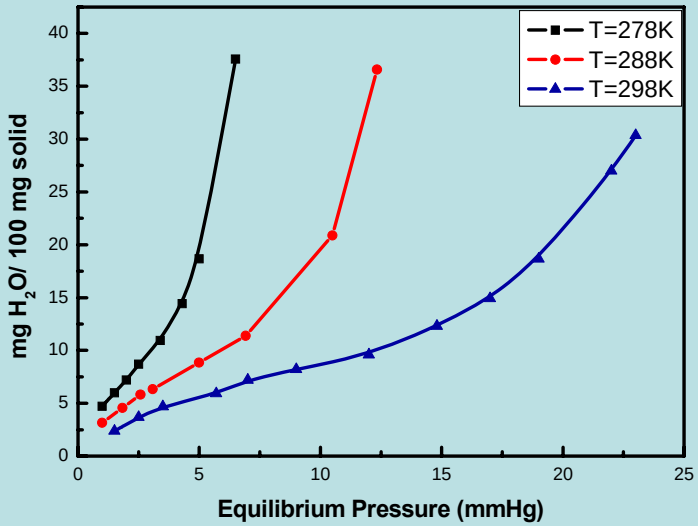

Type I
Type II
Type III
Type IV
Type V
Type VI
Adsorbed quantity
Pressure

Adsorption isotherms of water

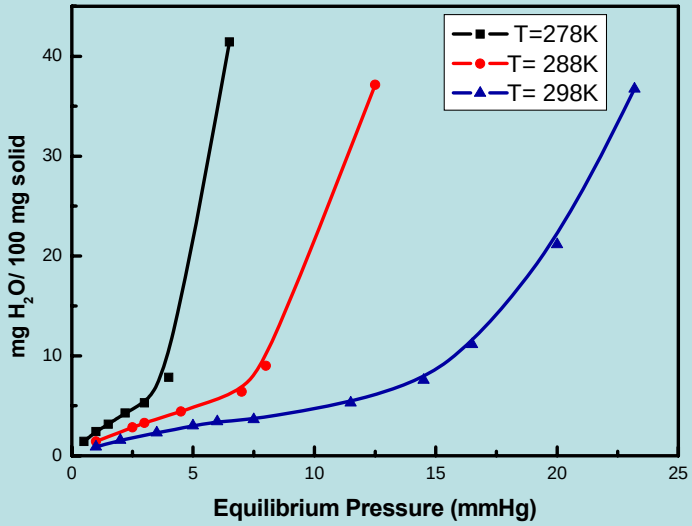
Isotherms of wheat bran



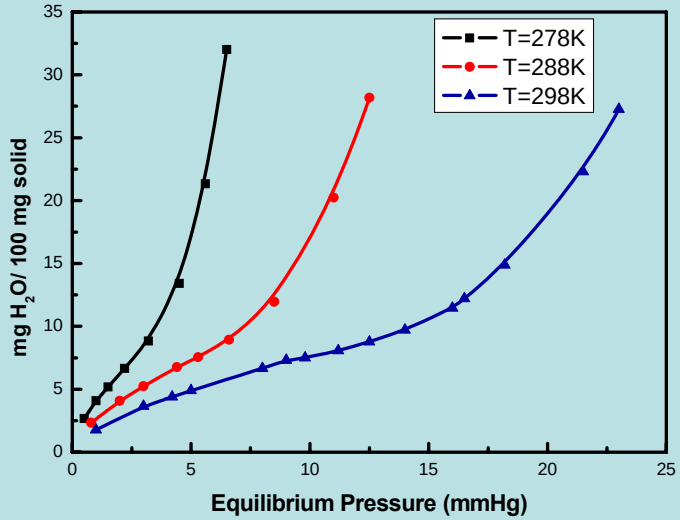
Isotherms of corn bran



Isotherms of rice fiber

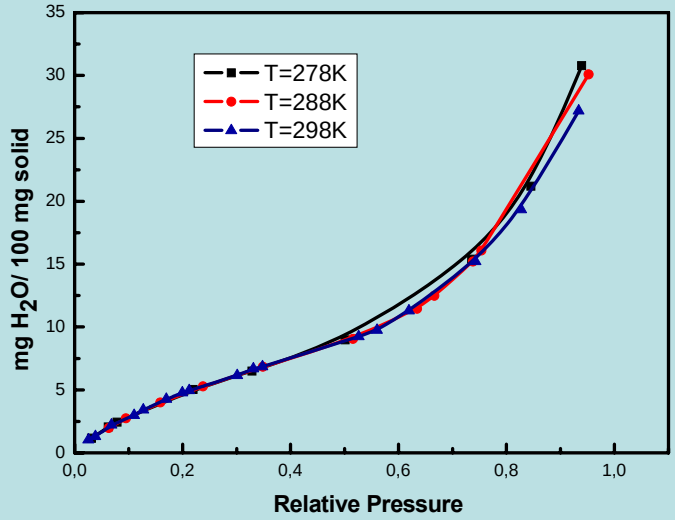


Isotherms of oat fiber

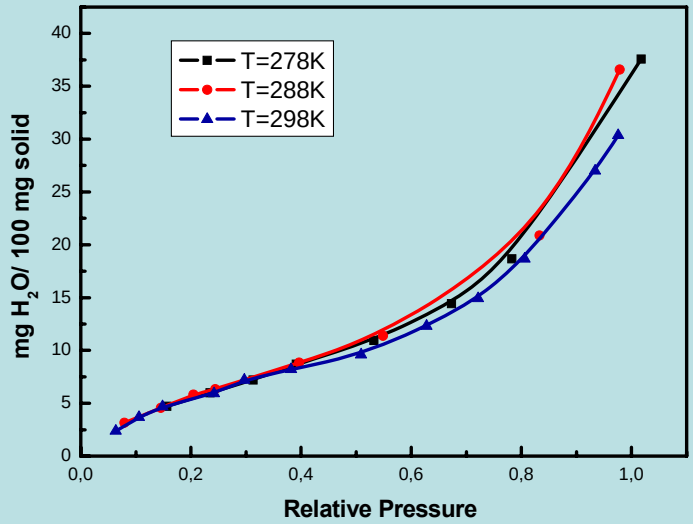


Nilufer H. Dual and Anthony L. Hines, Journal of Food Engineering 20 (1993) 17-43

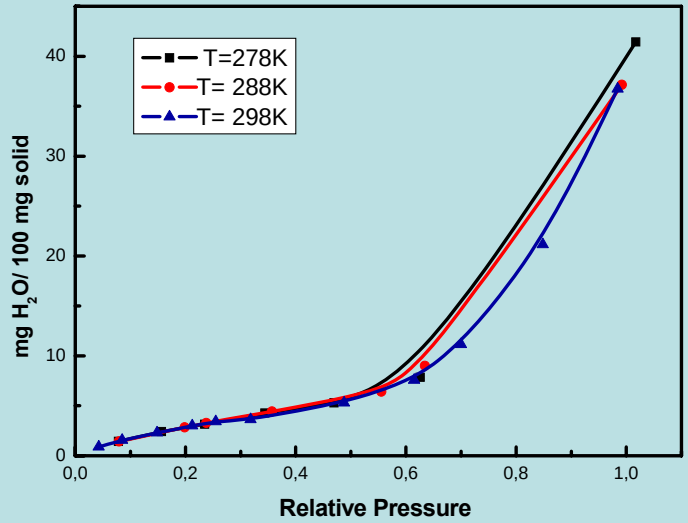
Isotherms of wheat bran



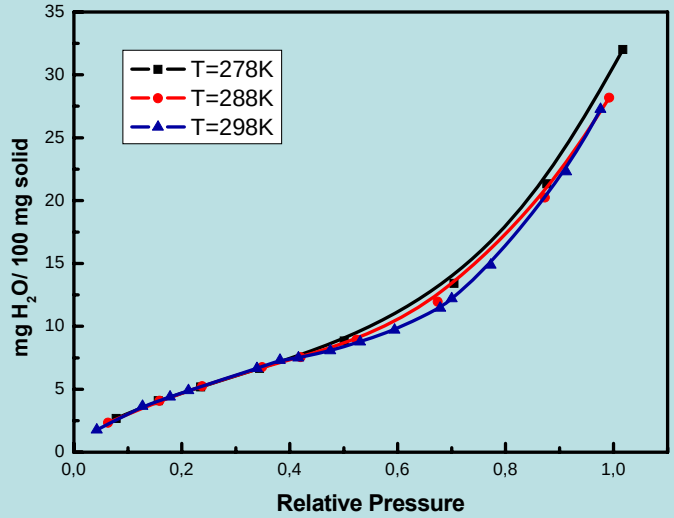
Isotherms of corn bran



Isotherms of rice fiber



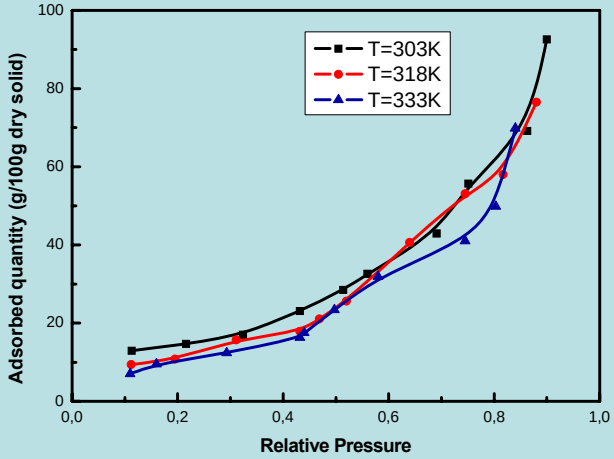
Isotherms of oat fiber



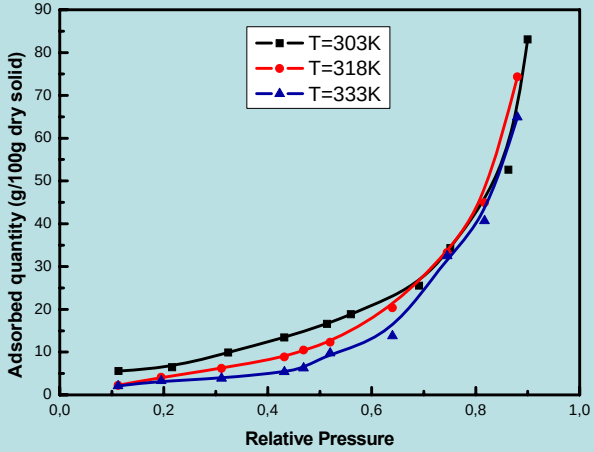
Nilufer H. Dual and Anthony L. Hines, Journal of Food Engineering 20 (1993) 17-43

Adsorption isotherms of water

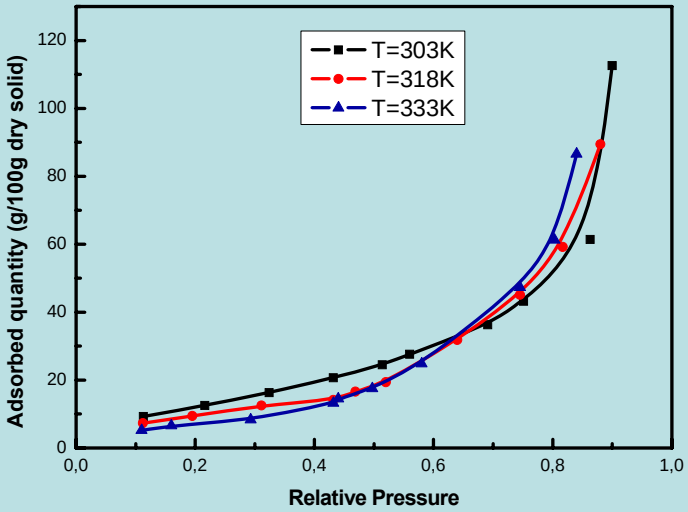
Isotherms of apples



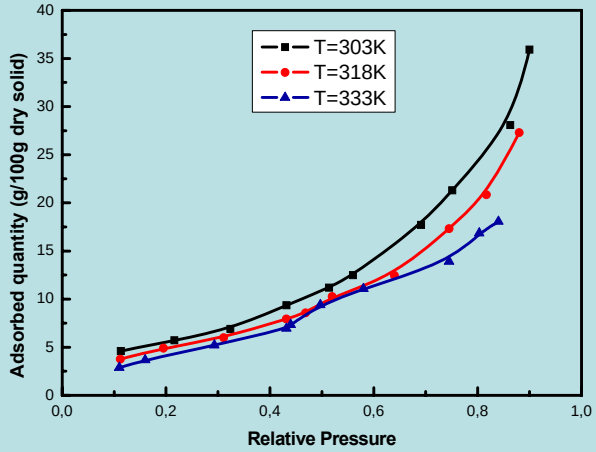
Isotherms of apricotes



Isotherms of grapes



Isotherms of potatoes



Figen Kaymak-Ertekin, Atl Gedik, Lebensm.-Wiss. u.-Technol. 37 (2004) 429–438

Proposed models to water adsorption

- Model 1(BET)

$$Q = \frac{Q_0}{\left[1+(1-\alpha)\left(\frac{P}{P_0}\right)\right]\left[1-\left(\frac{P}{P_0}\right)\right]}$$

P: Pressure

Q_0: Monolayer adsorbed quantity

P_0: Pressure of saturated vapor

α : constant

- Model 2

$$Q = \frac{Q_0}{\left[\left(\frac{P_1}{P}\right)^n - 1\right]}$$

P_1 : constant

n: number of molecules per site

- Model 3 (GAB)

$$Q = \frac{kcQ_0\left(\frac{P}{P_0}\right)}{\left[1-k\left(\frac{P}{P_0}\right)\right]\left[1-k\left(\frac{P}{P_0}\right)+kcQ_0\left(\frac{P}{P_0}\right)\right]}$$

P: Pressure

P_0: Pressure of saturated vapor

k, c: constants

Q_0: Monolayer adsorbed quantity

n: number of molecules per site

- Model 4

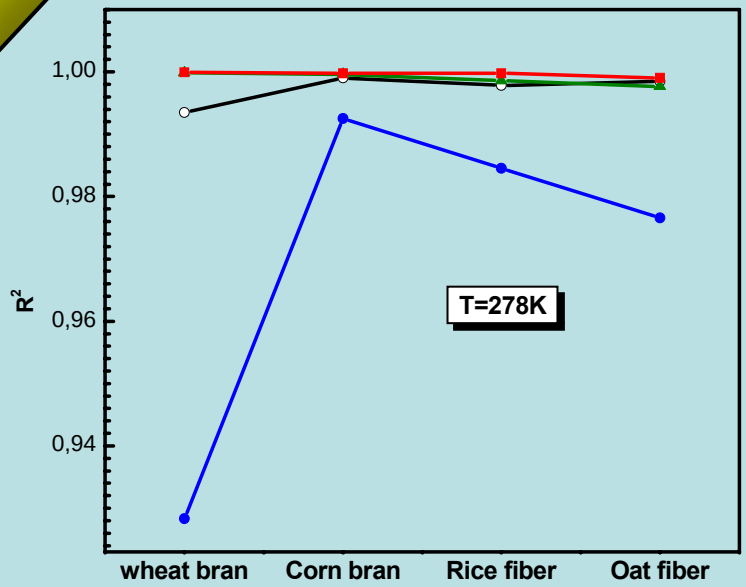
$$Q = \frac{Q_0}{\left[\left(\frac{P_1}{P}\right)^n - \left(\frac{P_1}{P_2}\right)^n + 1\right]\left[1-\left(\frac{P}{P_2}\right)^n\right]}$$

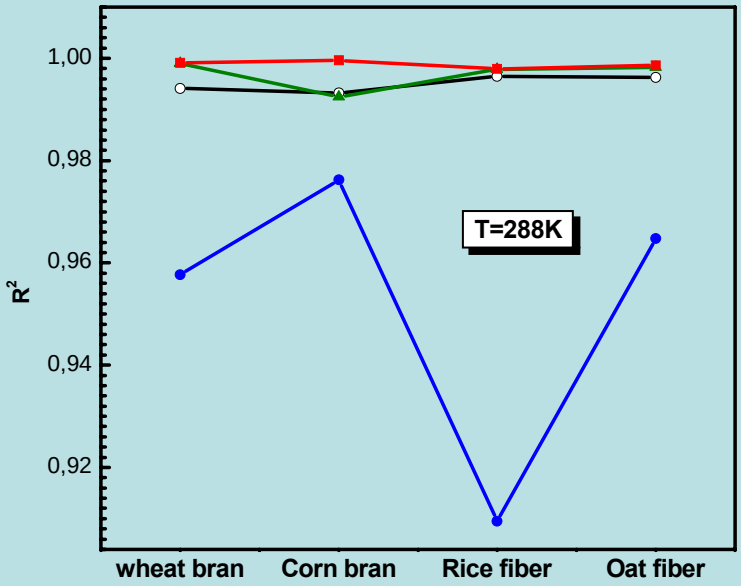
k, c, α, P_1, P_2 : constants

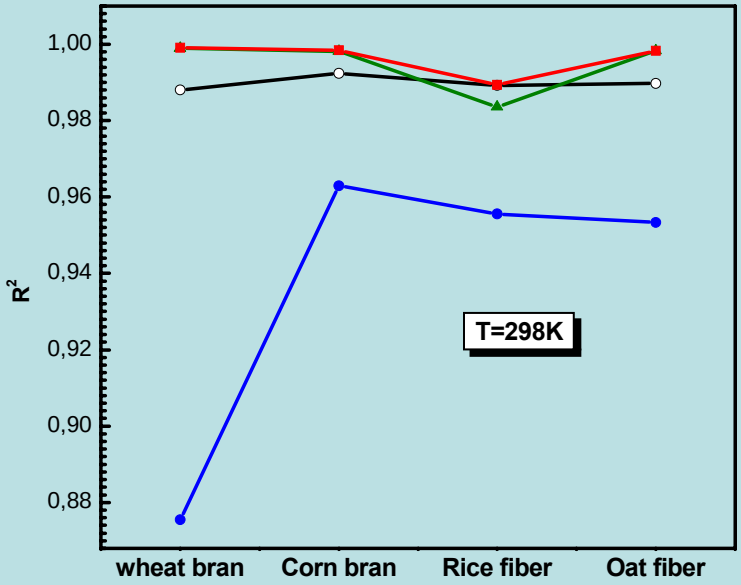
n: number of molecules per site

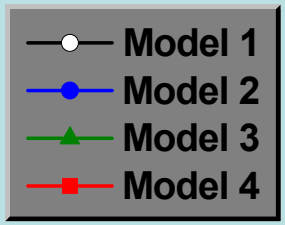
dietary cereals

Cœfficient of fitting R^2



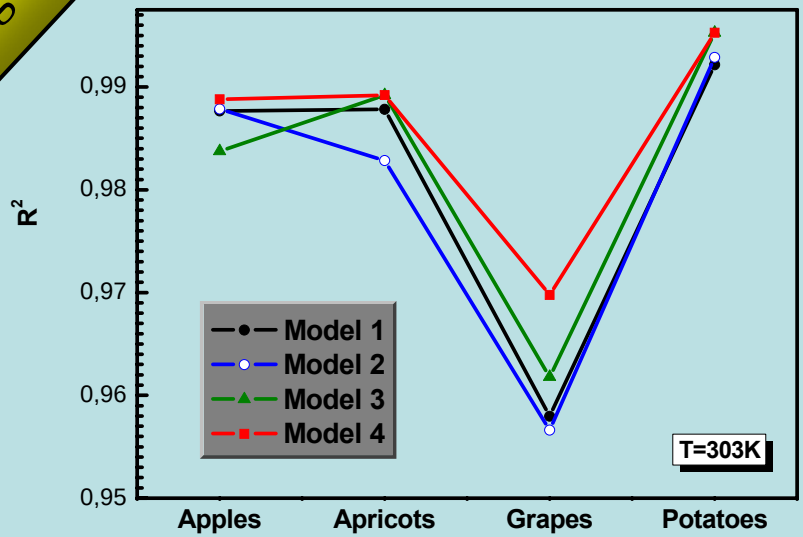


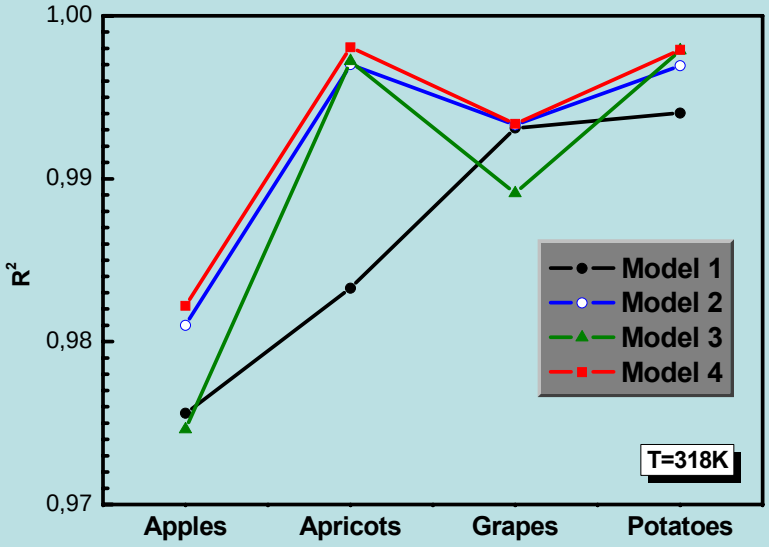


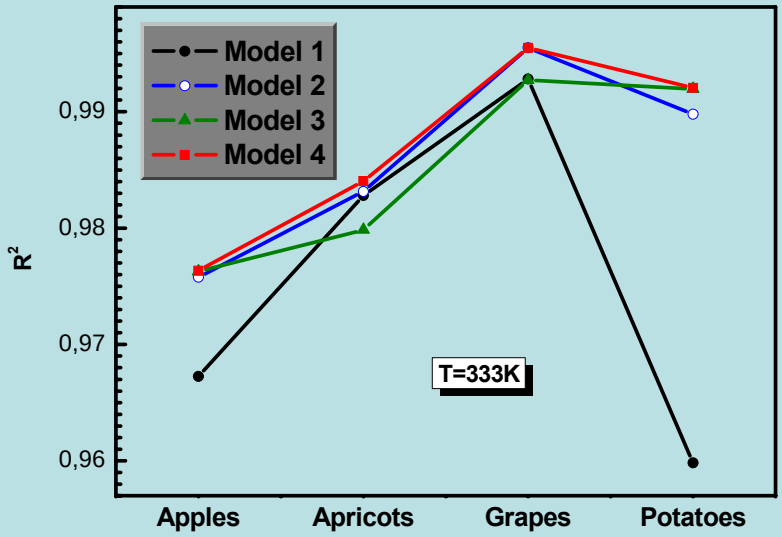


Vegetables

Cœfficient of fitting R^2







Objectives

- Obtain the expression of Model 4 (modified BET) in which we introduce four physico-chemical parameters by using statistical physics treatment

- Interpretation of parameters behavior according to the water isotherms of dietary cereals (wheat bran, corn bran, rice fiber and oat fiber) and vegetables (apples, apricots, grapes and potatoes)

Part I
Statistical Physics treatment

Statistical physics treatment

$$n\,A + R \rightleftharpoons A_nR$$

Equilibrium between free phase and adsorbed phase

- A: adsorbed water
- R: receptor site (ε: Energy , μ: chemical potential, N_M density of receptor sites)

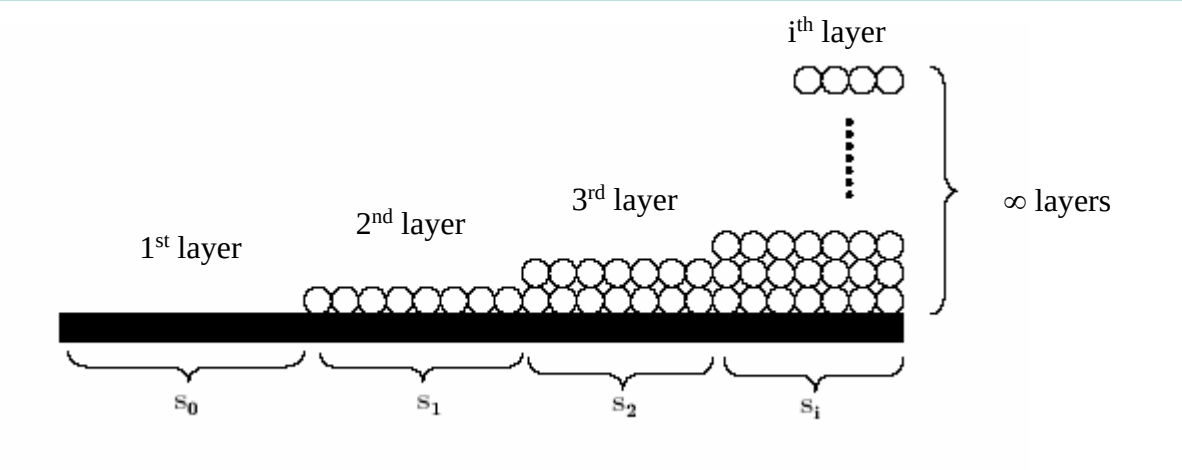
Hypotheses

- **We use the grand canonical ensemble**
- **We neglect the interaction between the adsorbed molecules**
- **We took account only of the freedom degree of translation**

Statistical physics treatment

- we suppose:

- **The N_M receptor sites are identical**
- **The receptor site can be empty or occupied by *n* molecules**



- **The molecules of the first layer are adsorbed with the energy ($-\varepsilon_1$)**
- **The molecules of the other layer are adsorbed with the energy ($-\varepsilon_2$)**

- Grand canonical function of partition (for one receptor site)

$$z_{gc} = \sum_{N_i=0}^{\infty} e^{-\beta(-\varepsilon_{N_i} - N_i\mu)} = 1 + e^{\beta(\varepsilon_1+\mu)} + e^{\beta(\varepsilon_1+\varepsilon_2+2\mu)} + \ldots$$

$\beta = 1/k_B T$

Boltzmann Factor

Statistical physics treatment

❑ Number of occupation

$$N_o = k_B T \frac{\partial Ln\left(z_{gc}\right)^{N_M}}{\partial \mu} = \frac{N_M e^{\beta(\varepsilon_1+\mu)}}{\left[1+e^{\beta\mu}\left(e^{\beta\varepsilon_1}-e^{\beta\varepsilon_2}\right)\right]\left[1-e^{\beta(\varepsilon_2+\mu)}\right]}$$

μ_m: Chemical potential of water vapor

N : Number of molecules

➢ Equilibrium Condition $\mu = n\mu_m$

$$\mu_m = k_B T Ln\left(\frac{N}{z}\right) \qquad z = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$: Partition function of translation

➢ Energetic conditions: $\varepsilon_{m1}=\varepsilon_1/n$ and $\varepsilon_{m2}=\varepsilon_2/n$

ε_m: energy of molecule water vapor

❑ Number of occupied sites

$$N_o = \frac{N_M}{\left[\left(\frac{P_1}{P}\right)^n - \left(\frac{P_1}{P_2}\right)^n + 1\right]\left[1-\left(\frac{P}{P_2}\right)^n\right]}$$

$$P_1 = ze^{-\frac{\Delta E_1^a}{RT}}$$

$$P_2 = ze^{-\frac{\Delta E_2^a}{RT}}$$

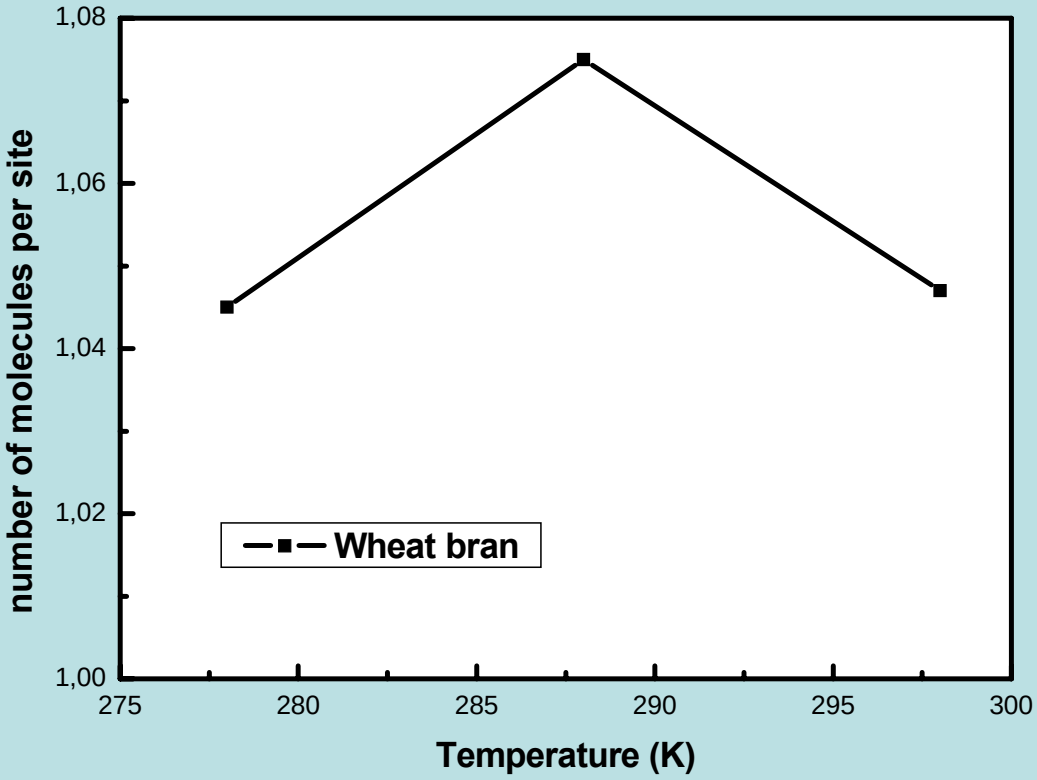
❑ Adsorbed quantity

$$Q = nN_o = \frac{Q_0}{\left[\left(\frac{P_1}{P}\right)^n - \left(\frac{P_1}{P_2}\right)^n + 1\right]\left[1-\left(\frac{P}{P_2}\right)^n\right]}$$

Part II
Interpretations

dietary cereals

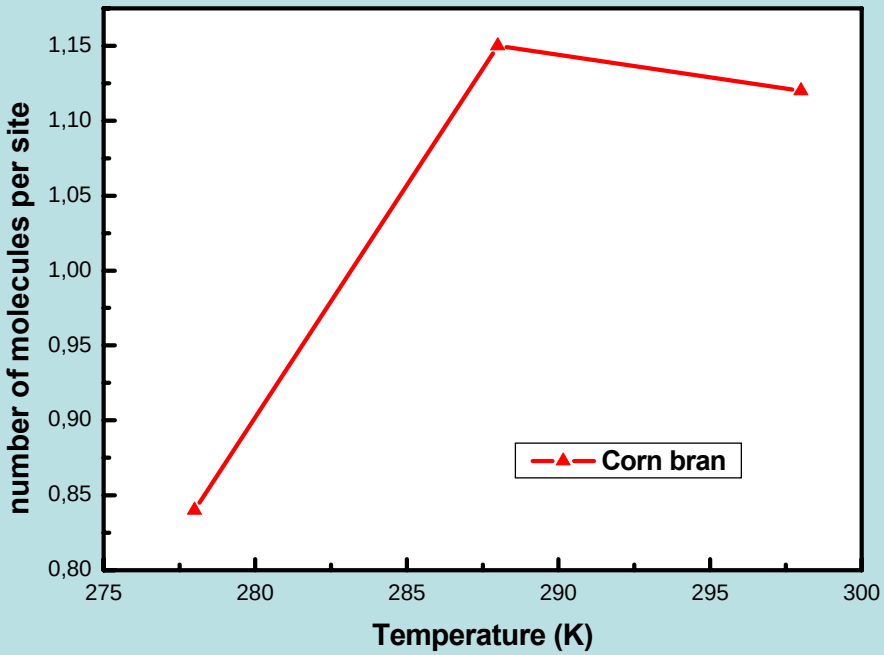
Parameter n

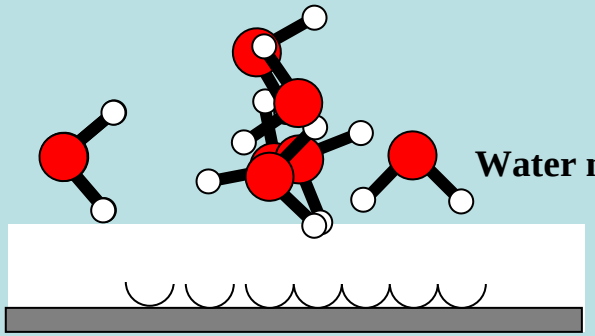


n ≈ 1→ The sites are monomolecular occupied

dietary cereals

Parameter n





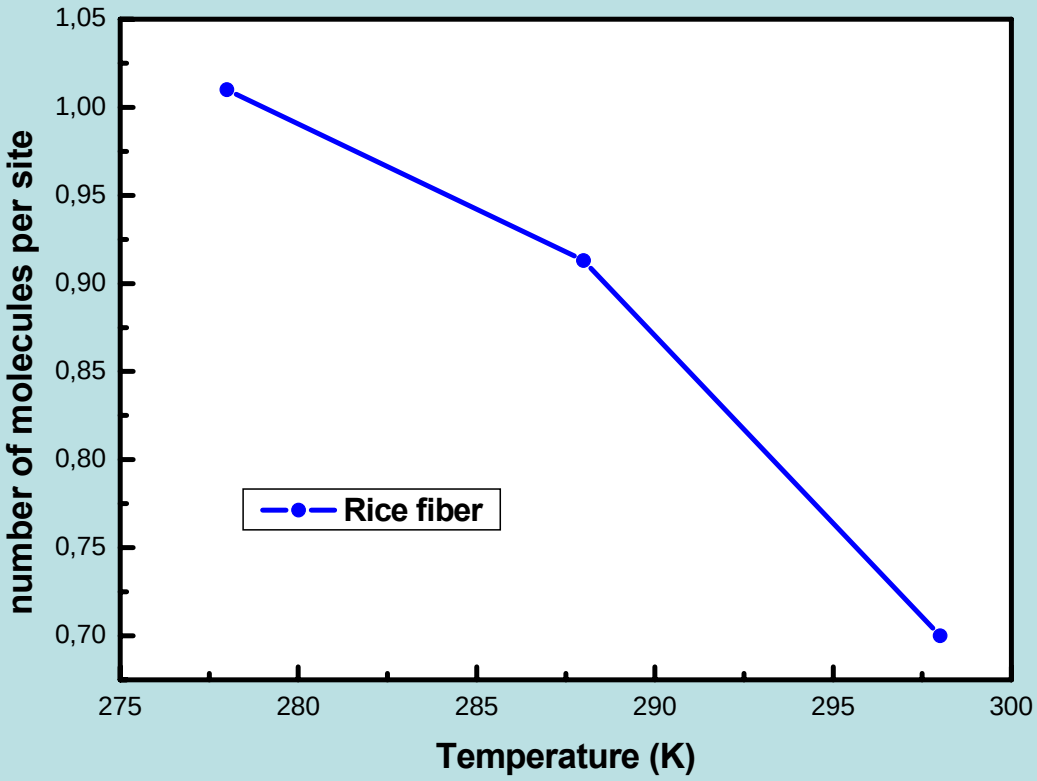
n>1 : multimolecular

n<1 : parallel anchorage

n increases → anchorage decreases ← thermal agitation

dietary cereals

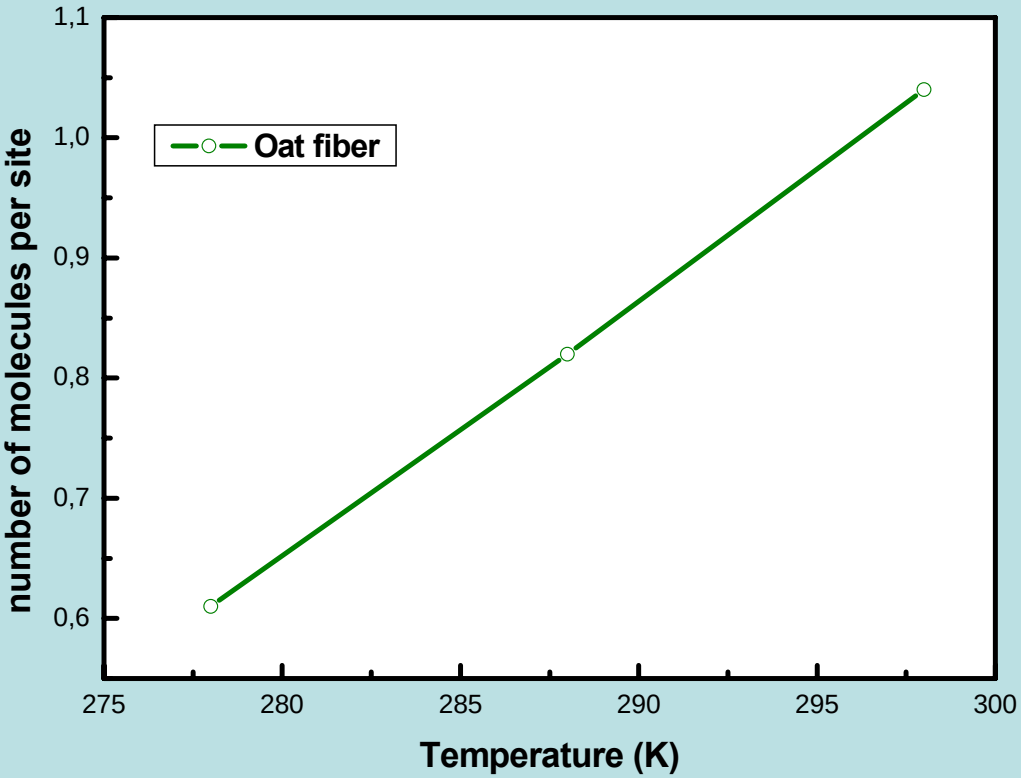
Parameter n



T increases → probability of parallel anchorage increases

dietary cereals

Parameter n

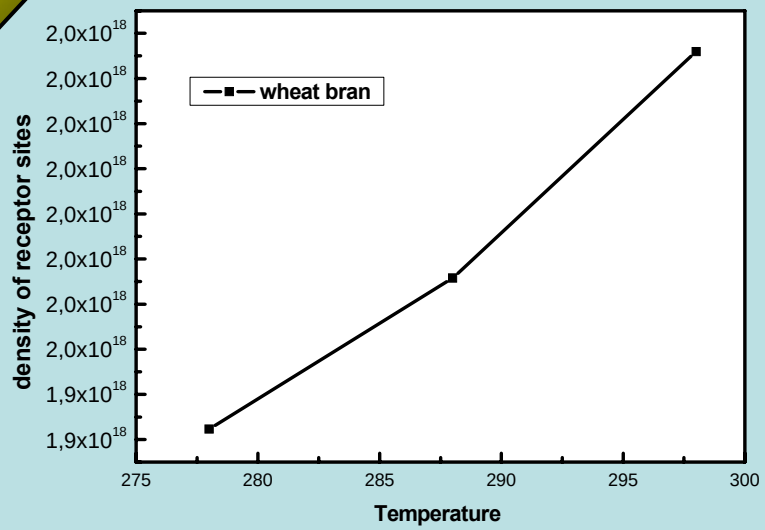


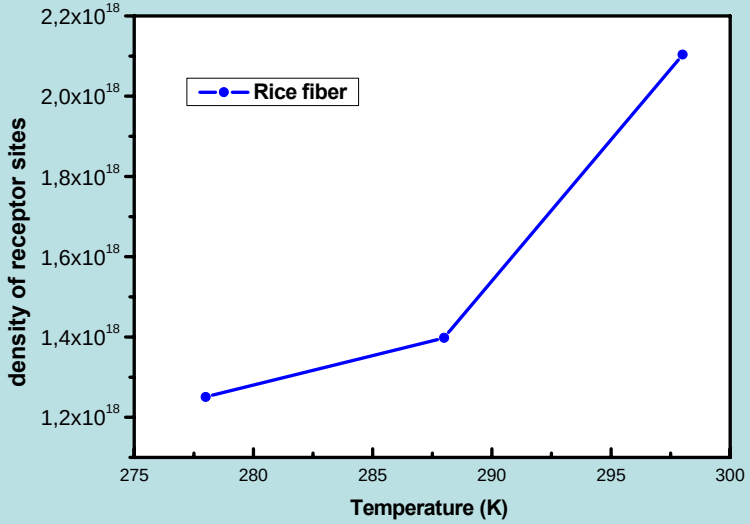
T increases → n increases

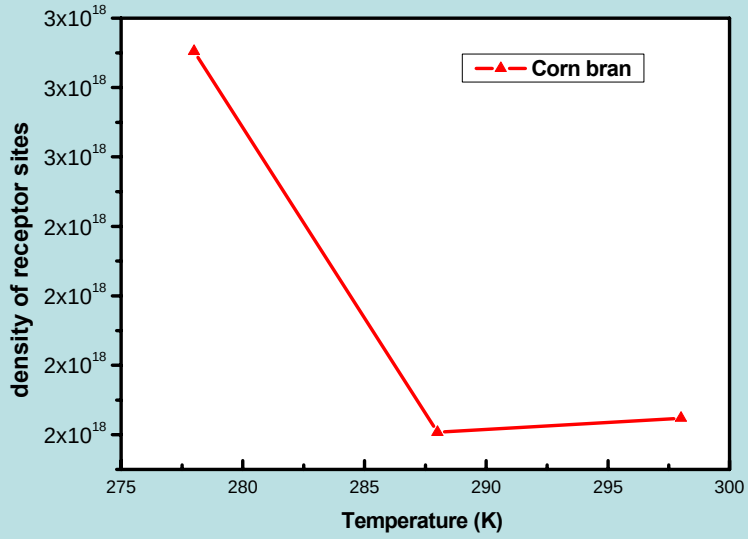
n increases → anchorage decreases ← thermal agitation

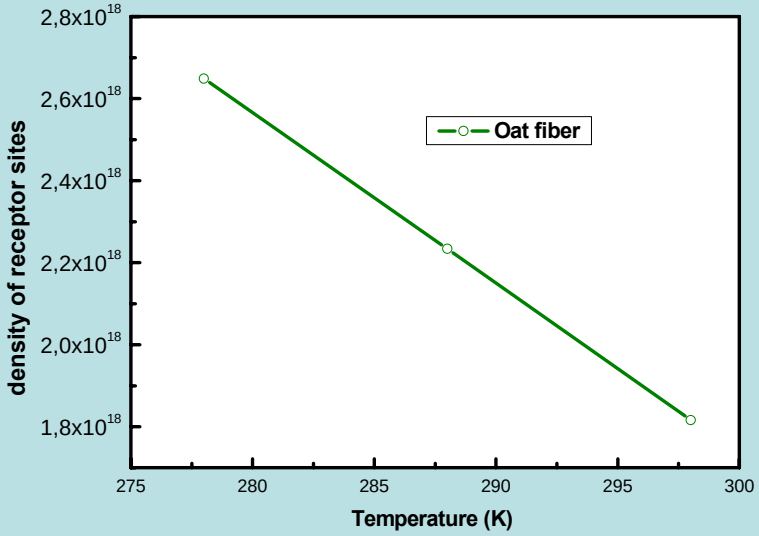
dietary cereals

Density of receptor sites N_M





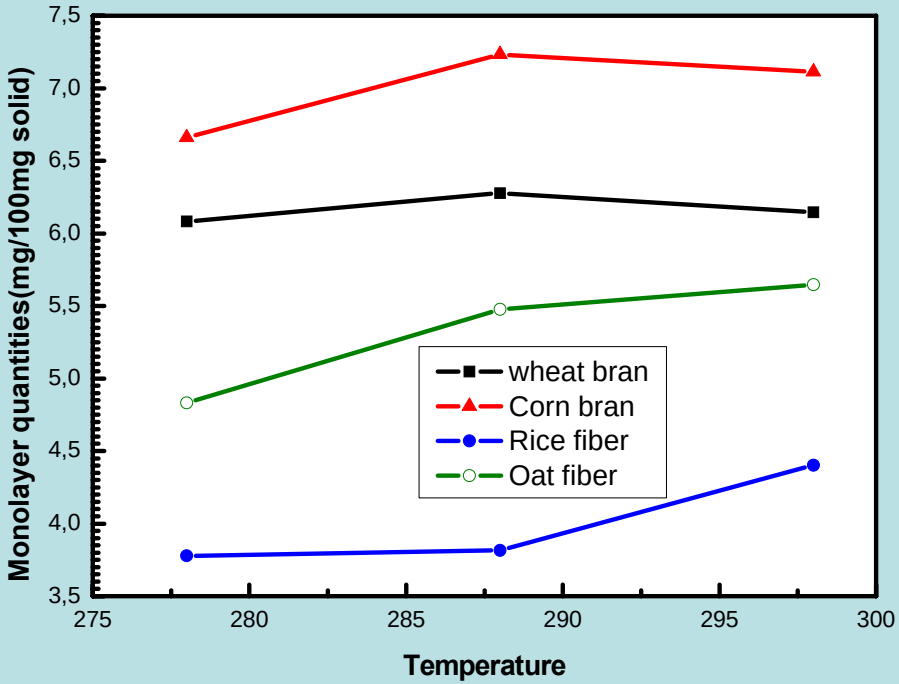




dietary cereals

Monolayer adsorbed quantity Q_0

$$Q_0 = nN_M$$



Ability of surface to retain water

Corn bran>Wheat bran>Oat fiber>Rice fiber

Relation with the porosity of cereal

dietary cereals

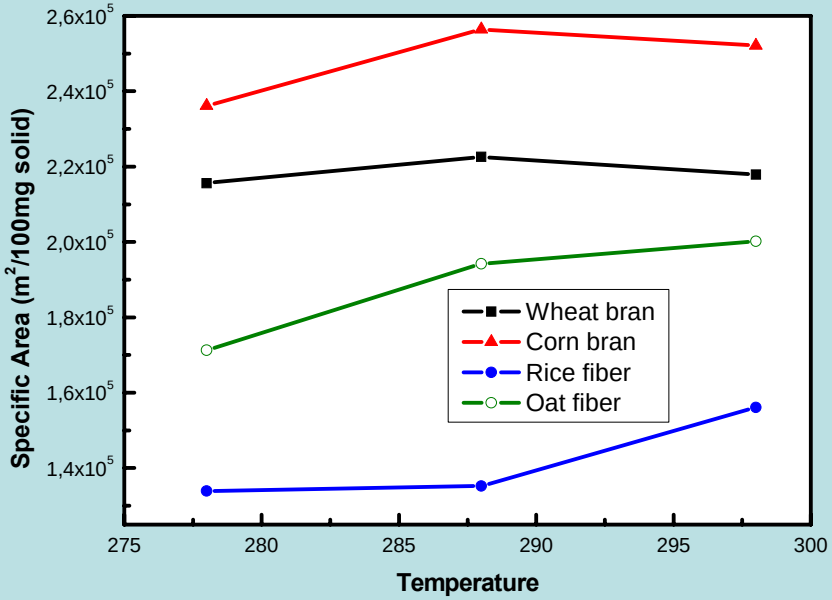
specific area

$$S = \frac{Q_0 N_A A_{H_2O}}{M}$$

N_A: Avogadro number

M: Molar mass

$A_{H_2O} = 10.6 \times 10^{-20} m^2$: molecule surface

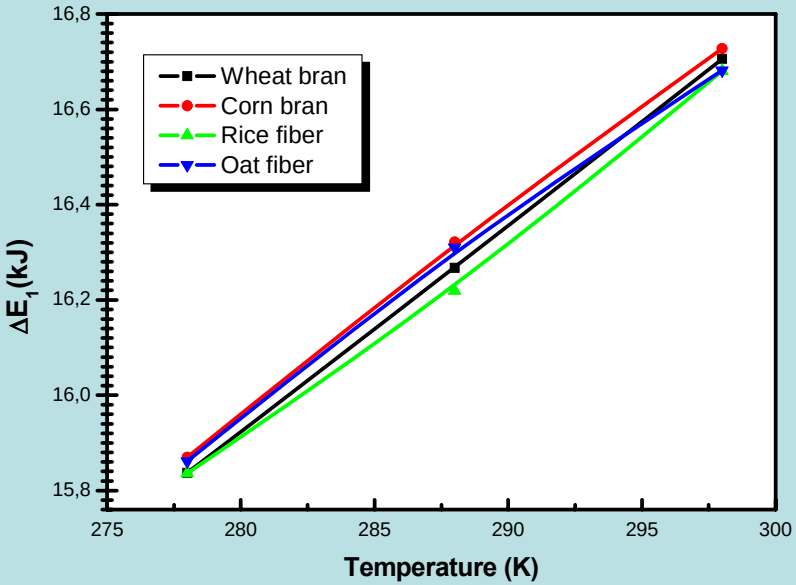


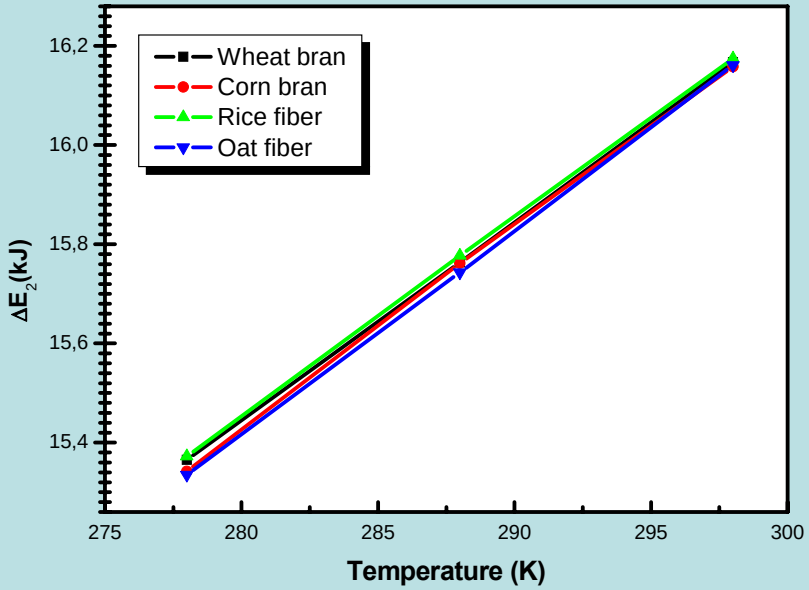
- Corn bran>Wheat bran>Oat fiber>Rice fiber
- S varies slightly versus temperature

dietary cereals

Energetic parameters P_1 and P_2

$$\Delta E_1 = RTLn\left(\frac{z}{P_1}\right) \quad \text{and} \quad \Delta E_2 = RTLn\left(\frac{z}{P_2}\right)$$





Energy of interaction water-surface

Energy of interaction water-water

Energies increases vs. temperature

Energy of Vaporization ΔE^V

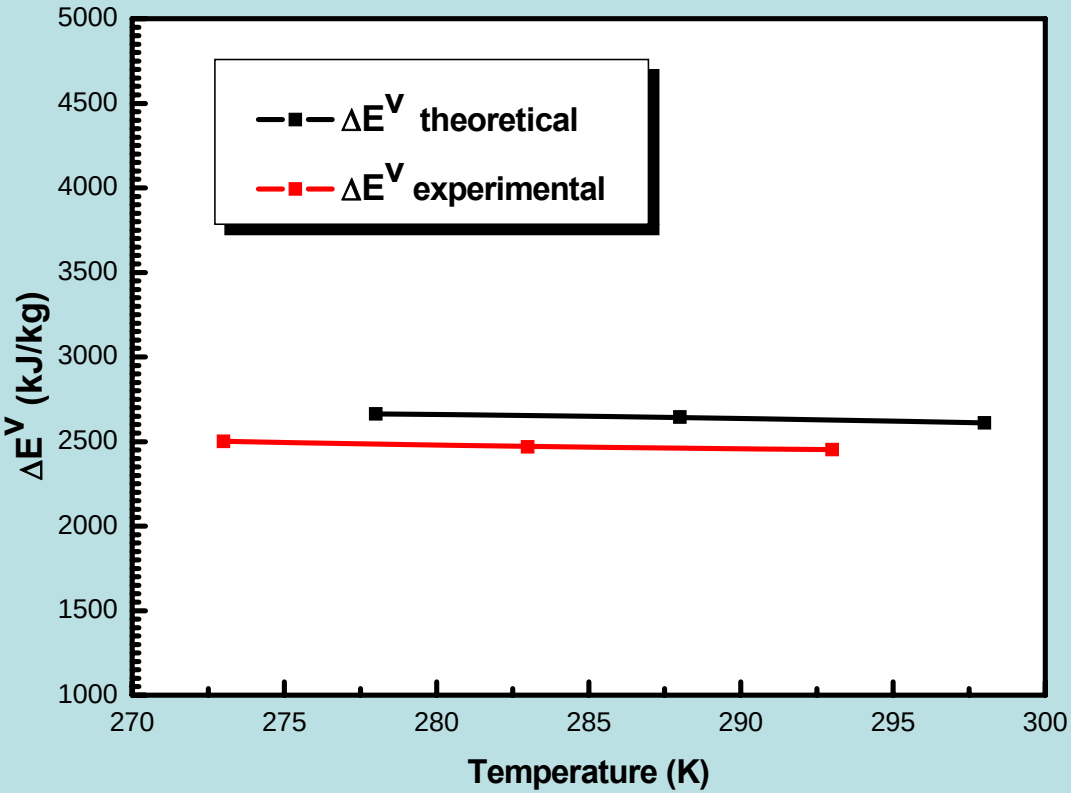
$$\Delta E^V = RTLn\left(\frac{z}{\beta Pvs}\right)$$

$$\log(Pvs) = A - \frac{B}{C+t}$$

A=7.9492, B=1657.5, C=227.02

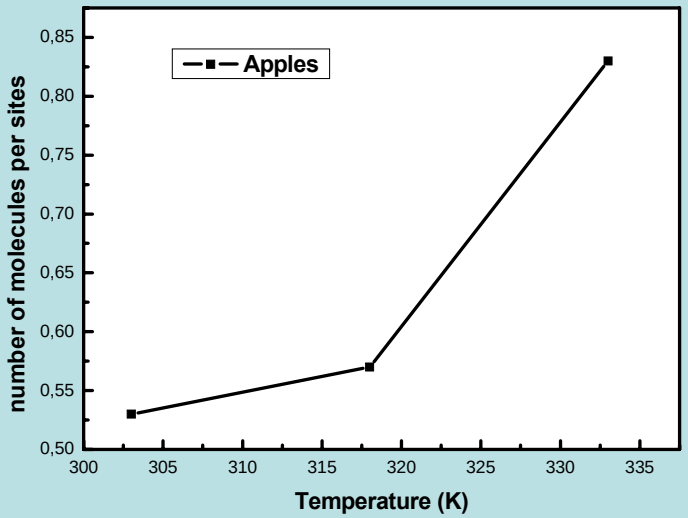
t : temperature (°C)

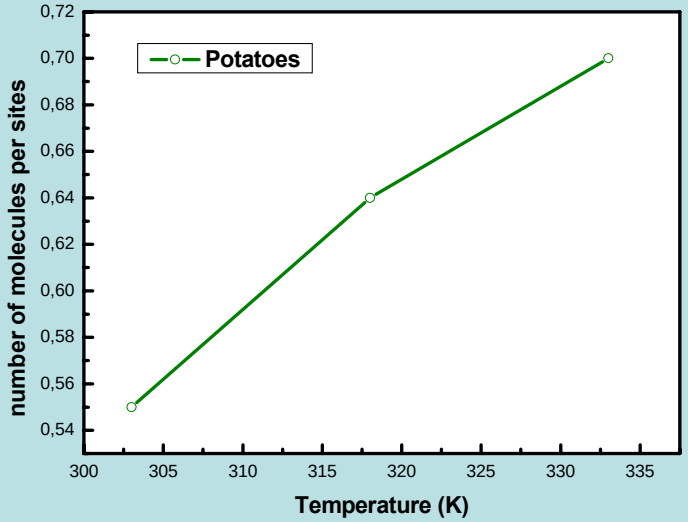
P_{vs}: pressure of saturated vapor (mm Hg)

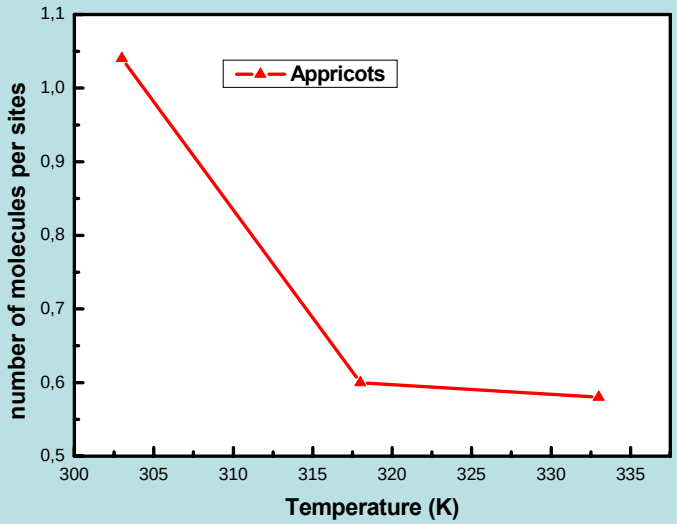


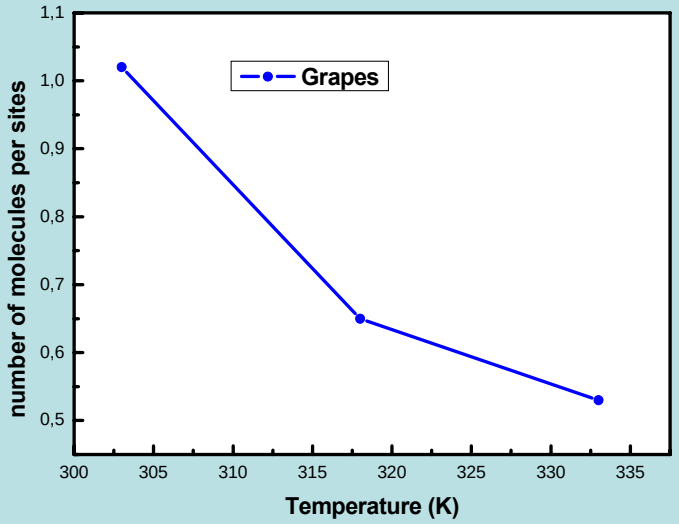
vegetables

Parameter n



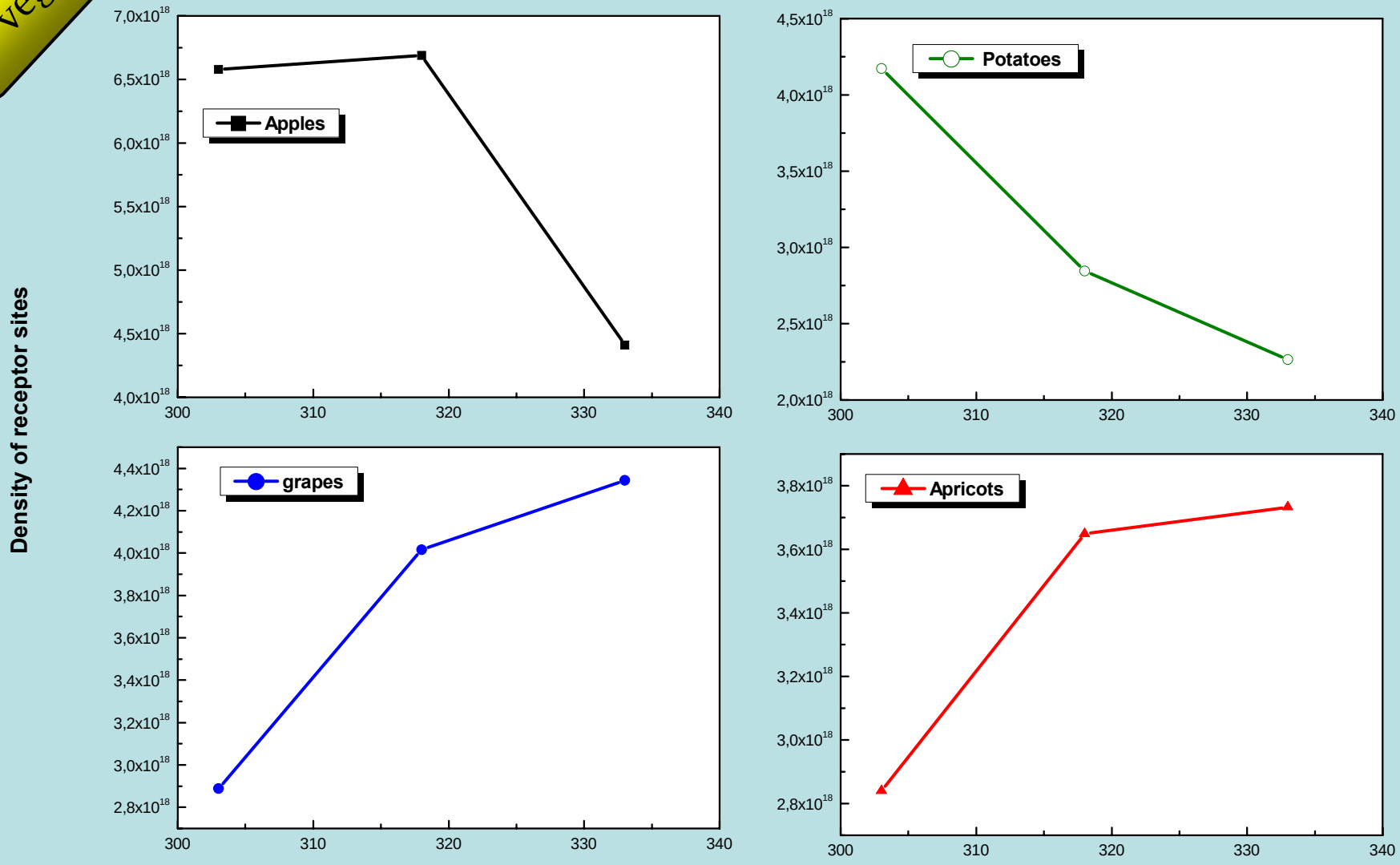






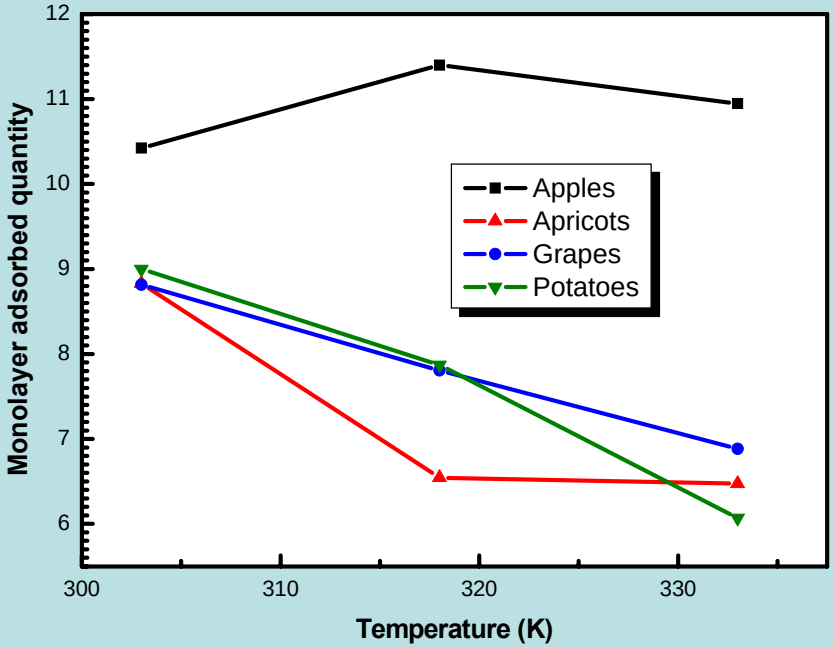
Vegetables

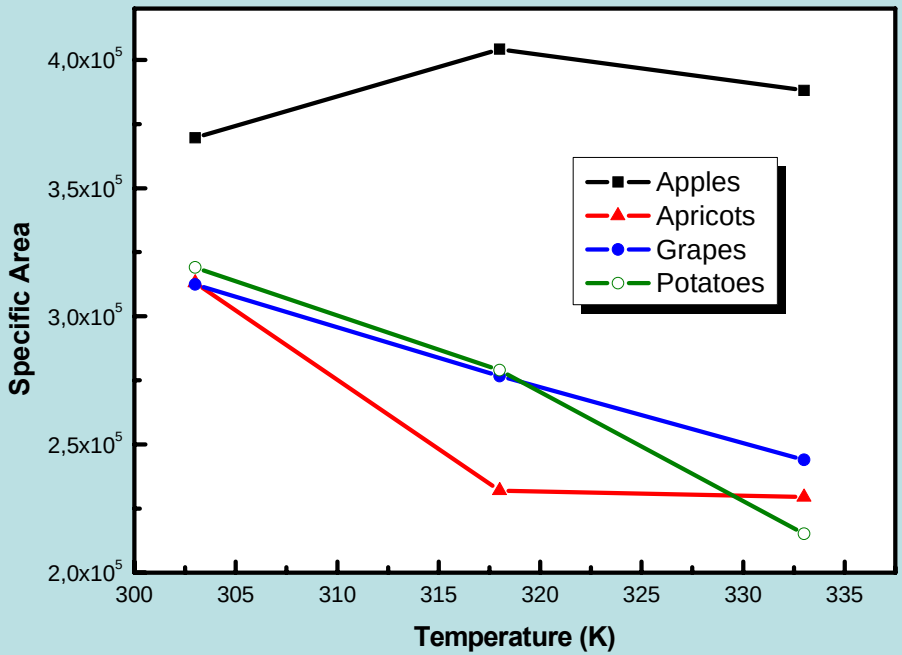
Density of receptor sites N_M



vegetables

Monolayer adsorbed quantity Q_0 and Specific Area

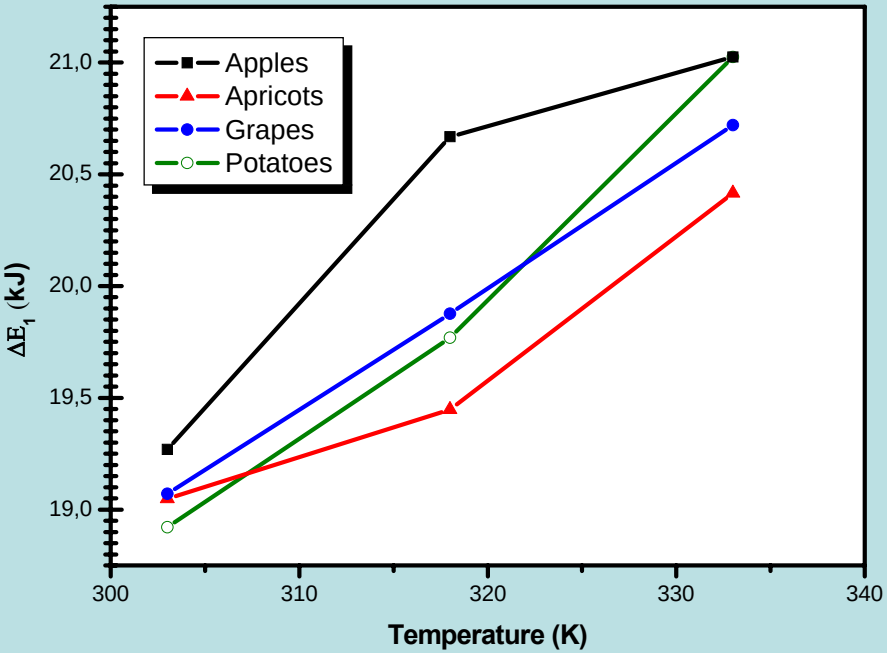


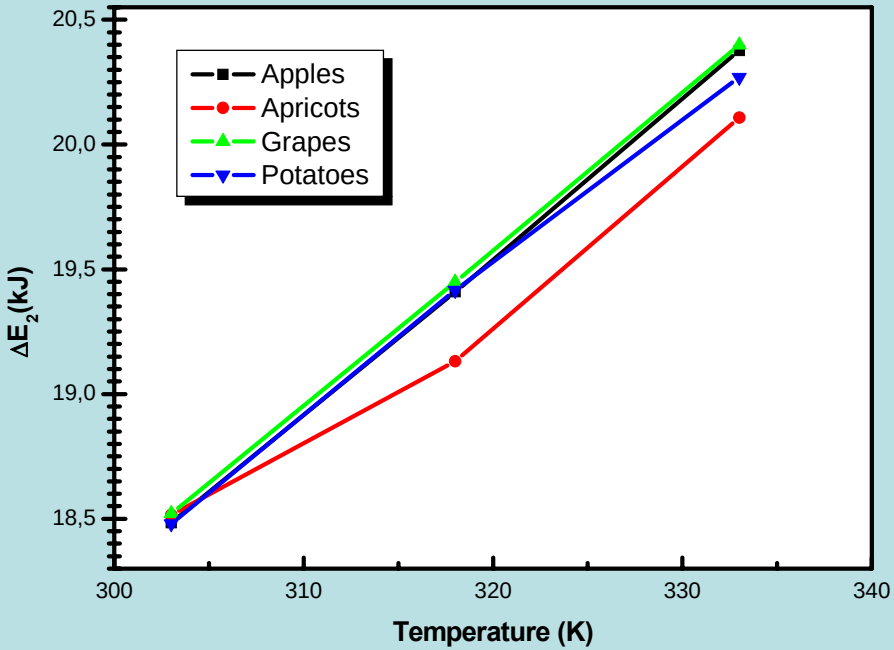


Apples>Potatoes>Grapes>Apricots

Vegetables

Adsorption Energies





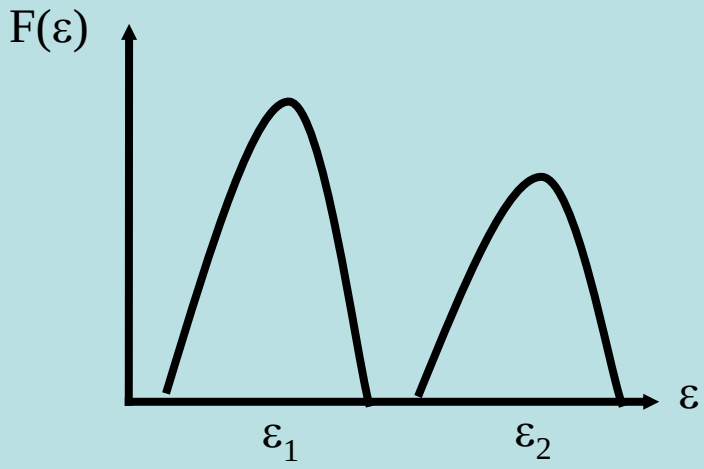
Conclusions

❖ Modeling of water vapor isotherms of four dietary cereals and vegetables using a statistical physics treatment allows to:

- ✓ Give concrete significance to parameters in relation with physicochemical parameters: the number of molecules per sites, the density of receptor sites, adsorption energy, chemical potential.
- ✓ Interpret the adsorption mechanism at microscopic level.
- ✓ The study of parameters behavior versus the temperature.
- ✓ Compare the properties of studied food to adsorb water.

Perspectives

❖ Improvement of the modeling using continuous function of energy distribution



❖ Applied the model to obtain the Pore Size distribution of receptor sites

Thank
You