Mathematical Modelling on Non-Thermal Innovative Food Preservation Processes

Cristina L.M. Silva

OUTLINE

→ Introduction

- Non-thermal Processes
- Mathematical Modelling
- Experimental Design and Data Analysis

→Cases Studies

- Ozone, UV-C, Thermosonication
- Red bell pepper / ozone
- Courgette / UV-C
- Watercress / thermosonication

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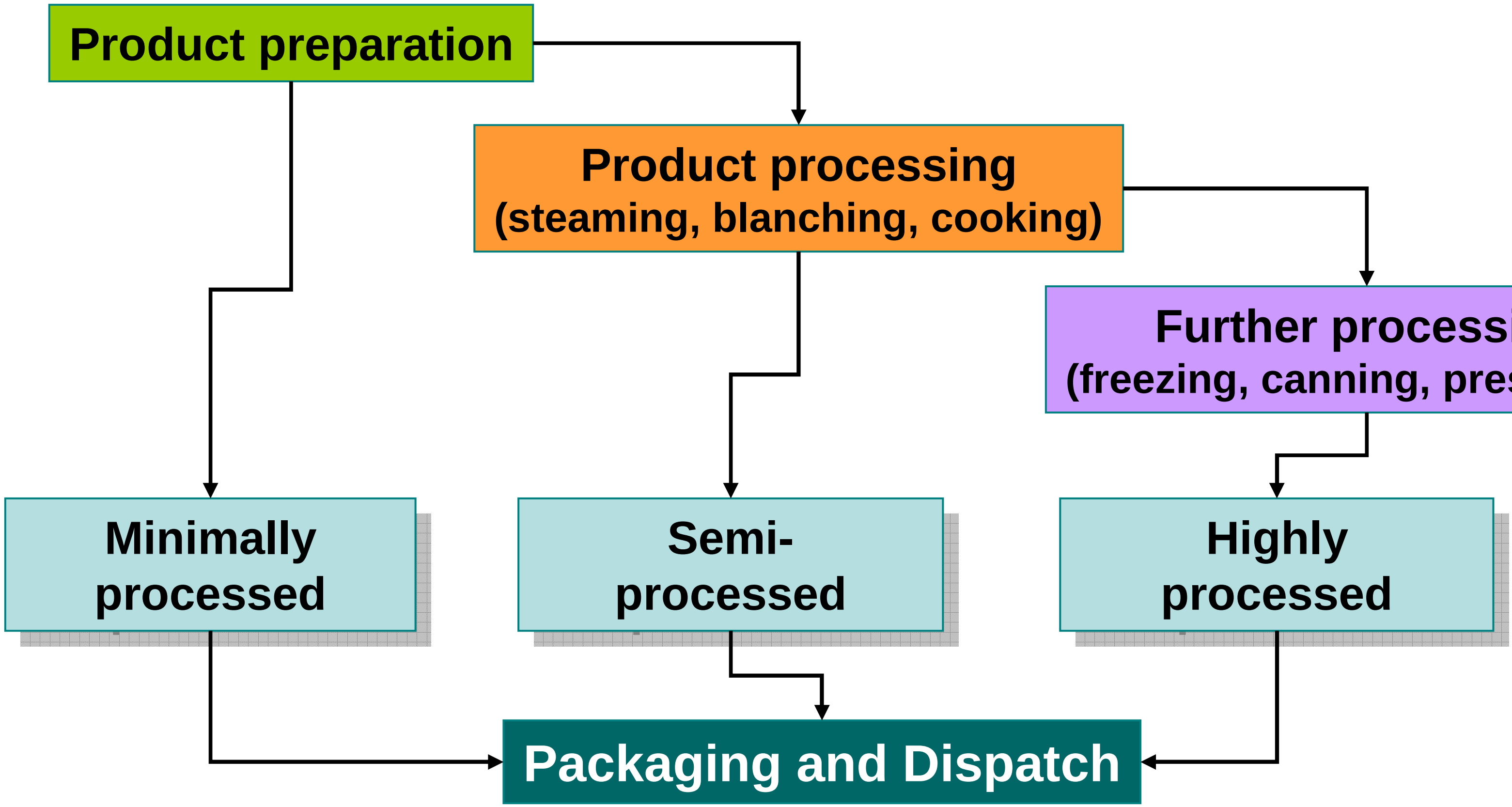
NON-THERMAL PROCESSES



NON-THERMAL PROCESSES

The problem is... Heating!

NEW TECHNOLOGIES

...uality attributes

NON-THERMAL PROCESSES

NON-THERMAL TECHNOLOGIES

little loss of:
- **colour**
- **flavour**
- **texture**
- **nutrients**

…but still retaining the desired shelf-life and safety!

NON-THERMAL PROCESSES

Pulsed Electric Fields	**Exposure of food to an intense electric field by means of controlled pulses of high voltage**
Ohmic Heating	**Generation of heat inside the food as a consequence of Joule effect**
Radio Frequency	**Exposure of food to electromagnetic waves in the radio-frequency range**
Microwave	**Exposure of food to controlled microwaves**
High Pressure	**Short-time exposure to extremely high pressure (up to 5000 bar)**

NON-THERMAL PROCESSES

Super Critical CO_2	**Contact of food with CO_2 at supercritical pressure**
Ozone	**Exposure of food to ozone**
Ultrasonication	**Exposure of foods to ultrasounds (US)** **US + mild temperatures (T) → thermosonication** **US + pressure (P) → manosonication** **US + T + P → manothermosonication**
UV-C	**Exposure of food to controlled pulses of UV rays**

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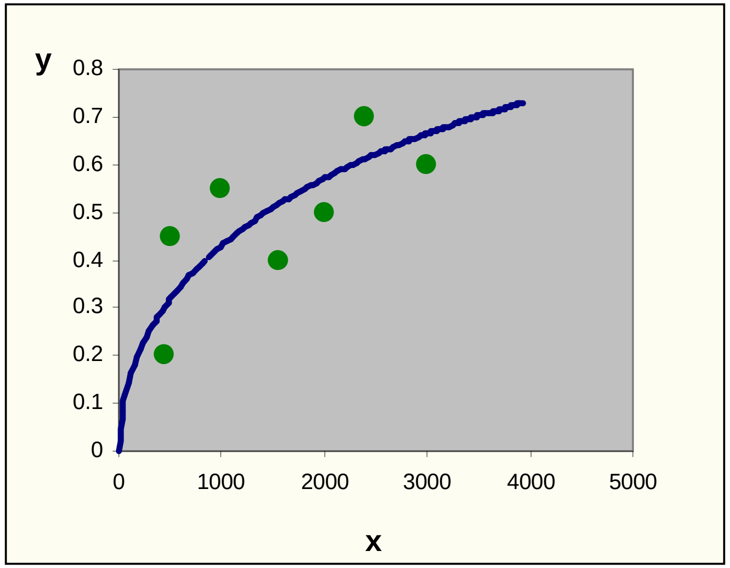
MATHEMATICAL MODELLING

Model → **mathematical expression**



$$y_i = f(x_{ij}, \theta_k) + \varepsilon_i$$

i=1,2,...,n (number of experimental runs/observations)
j=1,2,...,v (number of independent variables)
k=1,2,...,p (number of model parameters)

MATHEMATICAL MODELLING

Modeling and Simulation

Makes it possible to:

Gain more knowledge about the process and the effects on the product;

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Optimize the process with respect to different parameters, such as quality;

MATHEMATICAL MODELLING

Modeling and Simulation

Makes it possible to:

Gain more knowledge about the process and the effects on the product;

Reduce the number of experiments in the development stage;

Optimize the process with respect to different parameters, such as quality;

Study the influence on the product during process disturbances.

MATHEMATICAL MODELLING

Models should:

predict the response variable **accurately**

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↑

adequacy of the model

MATHEMATICAL MODELLING

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adequacy of the model

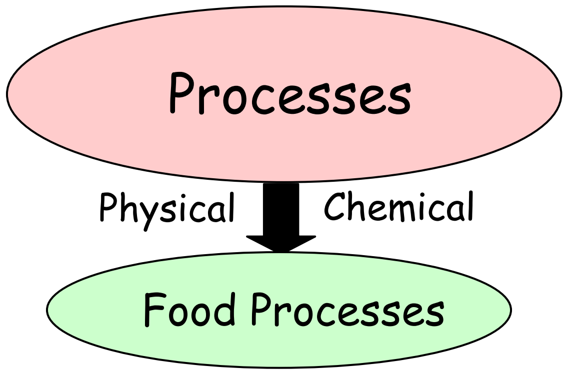
parameters quality

MATHEMATICAL MODELLING

Transport phenomena
- heat transfer
- mass transfer
- momentum transfer

Reaction kinetics

Properties



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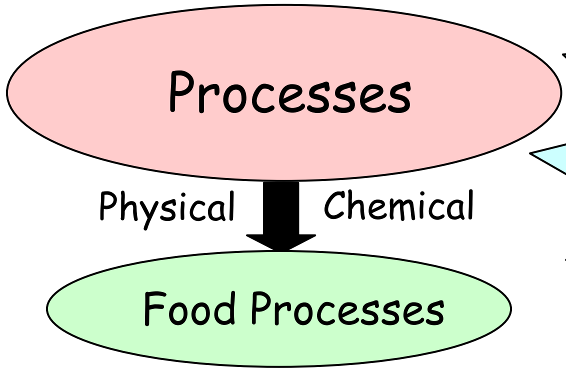
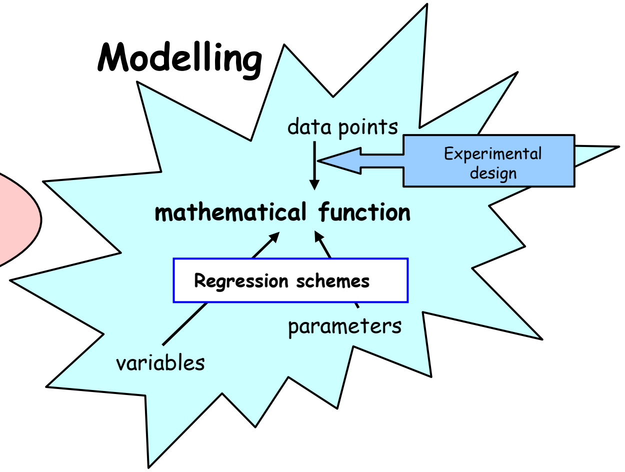
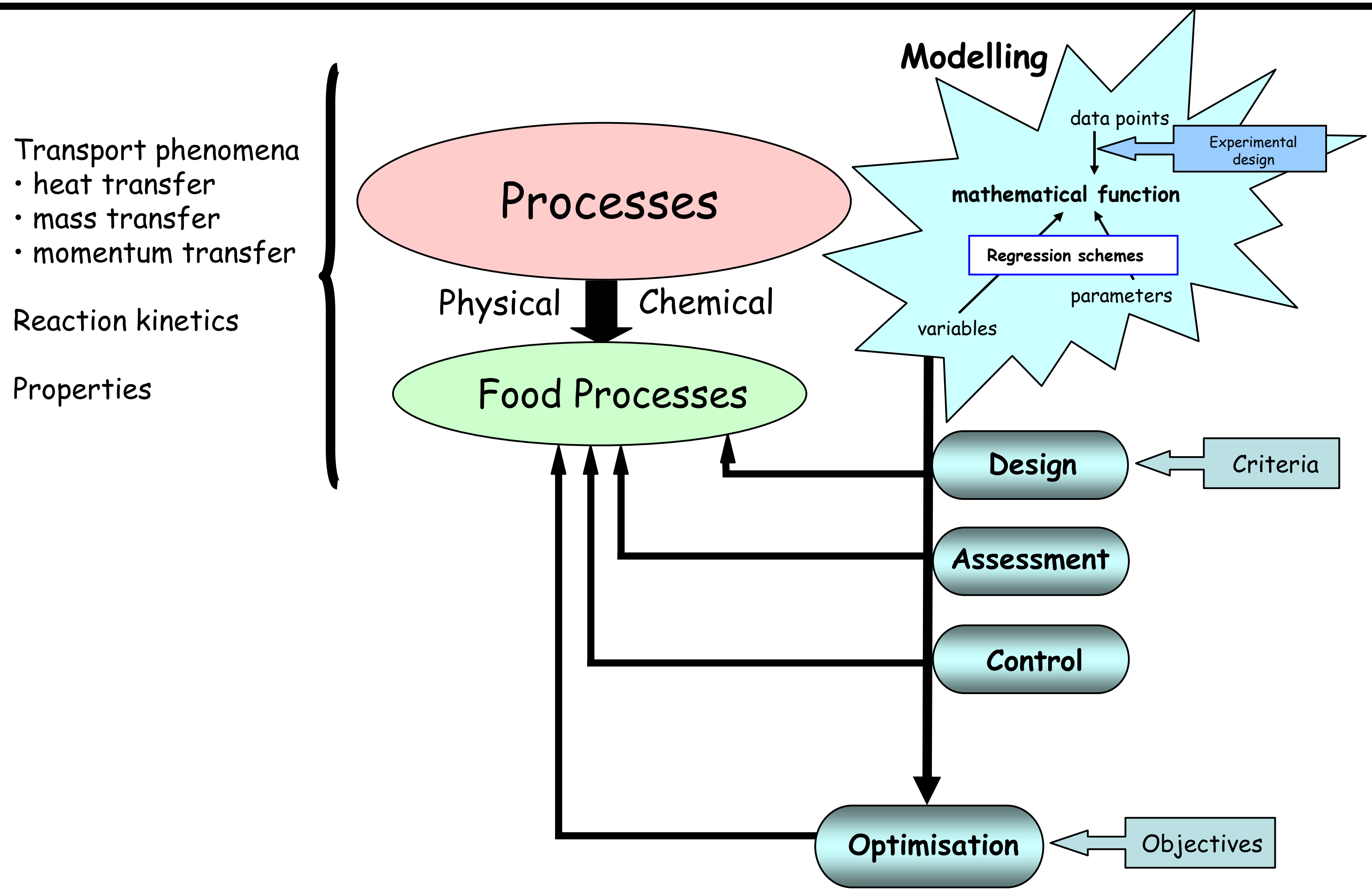




MATHEMATICAL MODELLING



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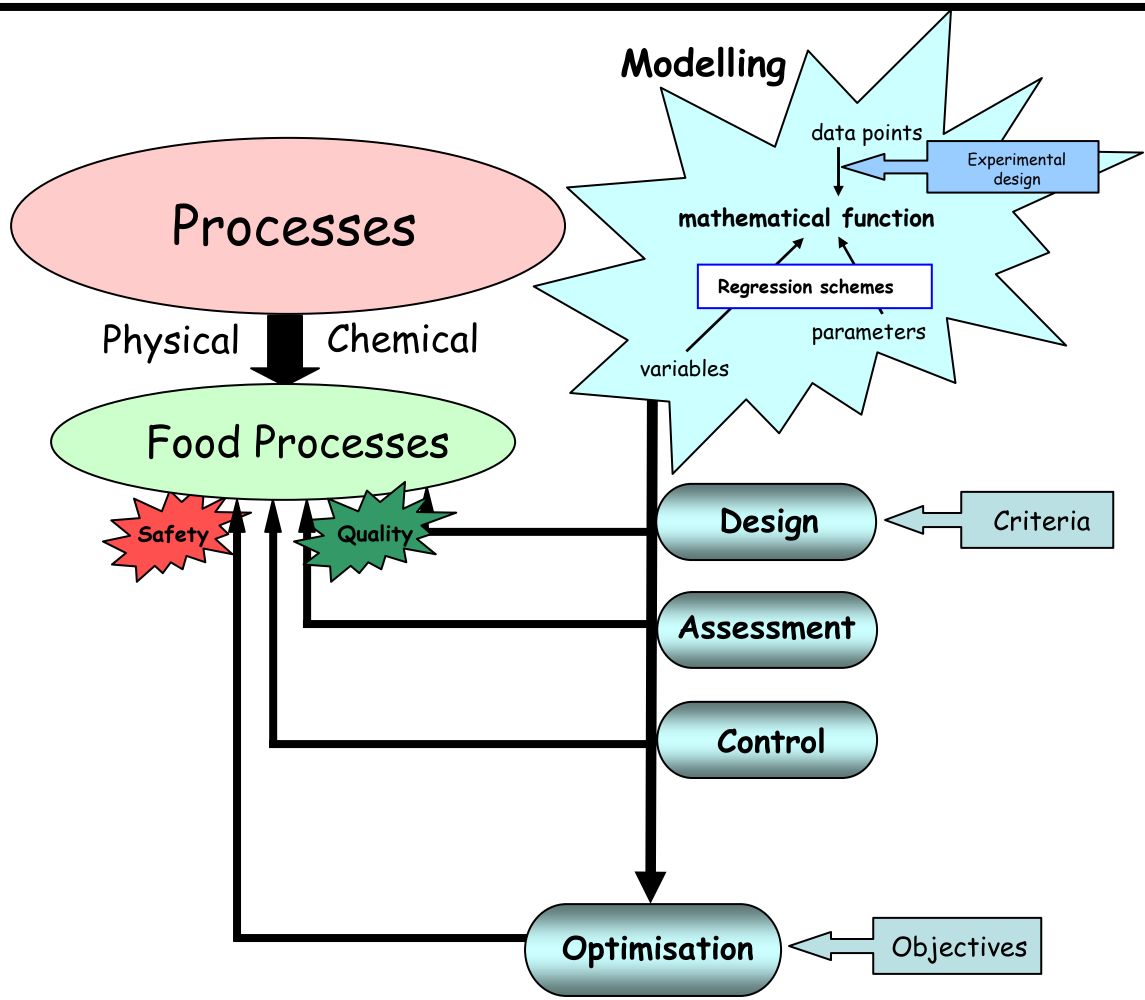

MATHEMATICAL MODELLING

- Mechanistic models are more complex, but in general allow accurate predictions

- Empirical models are much simple, but usually are appropriate to limited practical uses

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- Mechanistic models are more complex, but in general allow accurate predictions
- Empirical models are much simple, but usually are appropriate to limited practical uses

Balance of the advantages and disadvantages, depending on the final purpose.

MATHEMATICAL MODELLING

Difficulties in food processes modelling:

MATHEMATICAL MODELLING

Difficulties in food processes modelling:

- Dynamic processes

MATHEMATICAL MODELLING

Difficulties in food processes modelling:

- Dynamic processes
- Complexity and heterogeneity of products

MATHEMATICAL MODELLING

Difficulties in food processes modelling:

- Dynamic processes
- Complexity and heterogeneity of products
- Structural and physicochemical changes

MATHEMATICAL MODELLING

Kinetic Studies:

Allow the quantification of the extension and rate of production/consumption of any substance

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Allow the quantification of the extension and rate of production/consumption of any substance

Safety

MATHEMATICAL MODELLING

Kinetic Studies:

Allow the quantification of the extension and rate of production/consumption of any substance

Safety

Quality

MATHEMATICAL MODELLING

Safety and **Quality** depend on:

Intrinsic factors

Extrinsic factors

MATHEMATICAL MODELLING

Safety and **Quality** depend on:

Intrinsic factors

- pH
- a_w
- **others**

Extrinsic factors

MATHEMATICAL MODELLING

Safety and **Quality** depend on:

Intrinsic factors
- **pH**
- **a_w**
- **others**

Extrinsic factors
- **T**
- **pH**
- **humidity**
- **gas concentration**
- **others**

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EXPERIMENTAL DESIGN AND DATA ANALYSIS

Model Validation:

- **Heuristic sampling**
- **Experimental design**

Minimize variance of:

- ***predicted response***
- ***parameter estimates***

EXPERIMENTAL DESIGN AND DATA ANALYSIS

Data Analysis:

- **Regression schemes**

$$SSR = \sum_{i=1}^{n} e_i^2 = \sum_{i=1}^{n} \left[y_i - f\left(x_{ij}, \theta_k\right)\right]^2$$

Least-squares method

- **Analysis of residuals**

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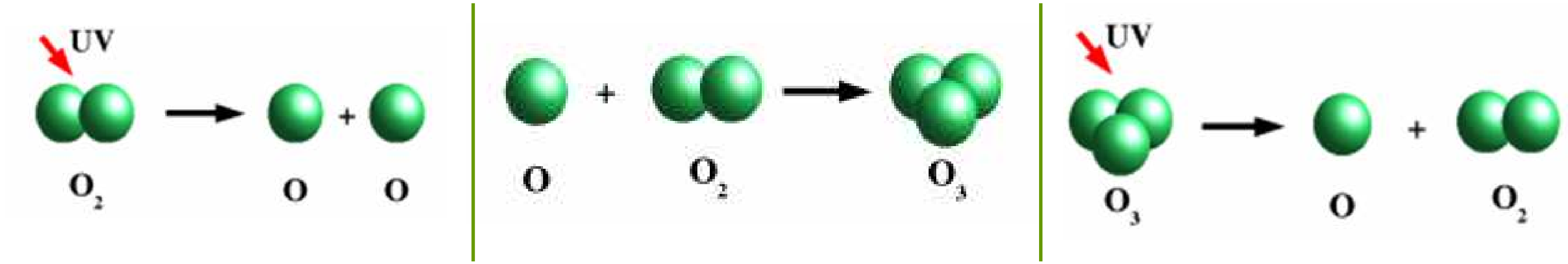
CASE STUDIES

Ozone	**Exposure of food to ozone**
Ultrasonication	**Exposure of foods to ultrasounds (US)** **US + mild temperatures (T) → thermosonication** **US + pressure (P) → manosonication** **US + T + P → manothermosonication**
UV-C	**Exposure of food to controlled pulses of UV rays**

CASE STUDIES

OZONE

- Gas formed by 3 oxygen atoms
- Highly instable
- In nature it is formed by the action of sun UV light (185 nm)



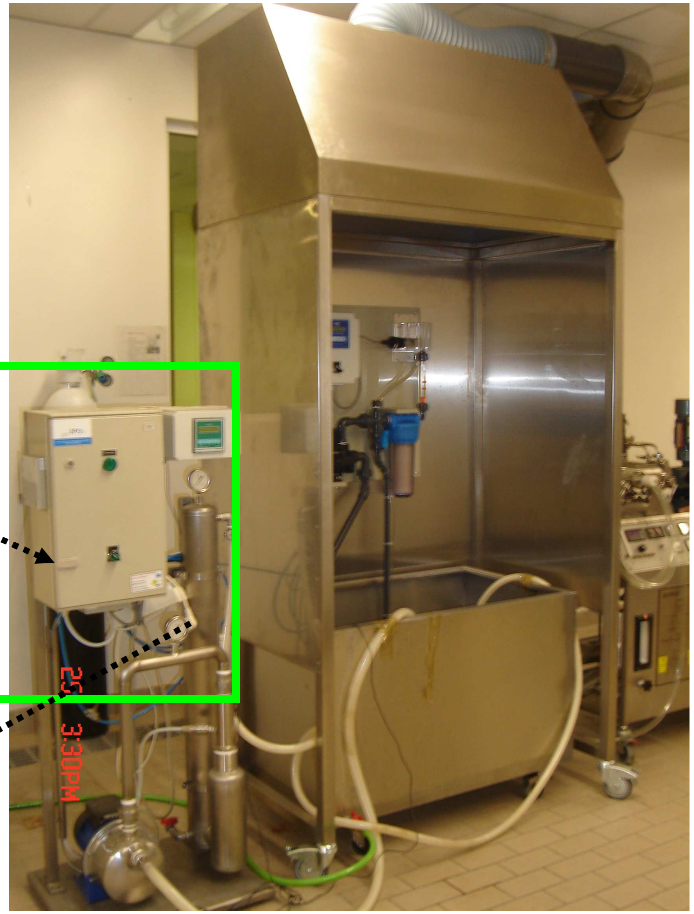
CASE STUDIES

OZONE

-<u>Commercially</u>:

Ozone generated by

Electrical Discharge



CASE STUDIES

OZONE

-**Powerful antimicrobial agent → strong oxidant**

-**Lethal or inhibitory effect on microorganisms due to its reaction with:**

- **intracellular enzymes**
- **nucleic material**
- **membrane components → destruction of coating of spores and viral capsules**

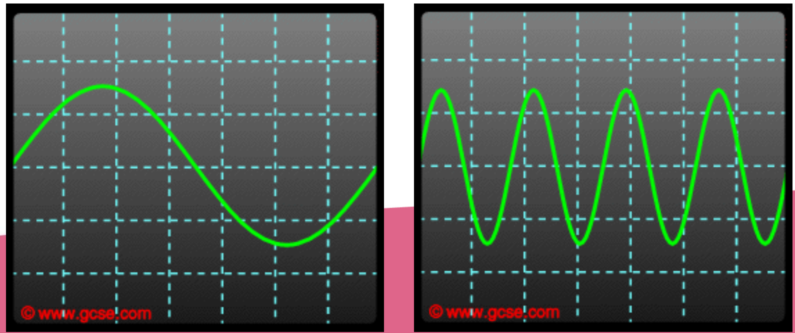
CASE STUDIES

ULTRASOUNDS

- **Vibrations similar to sound waves**

- **Very high frequencies: 18 kHz – 500 MHz → greater than upper limit of human hearing!**

- **Some animals, such as dogs, dolphins, and bats, have an upper limit that is greater than that of the human ear and thus can hear ultrasound.**

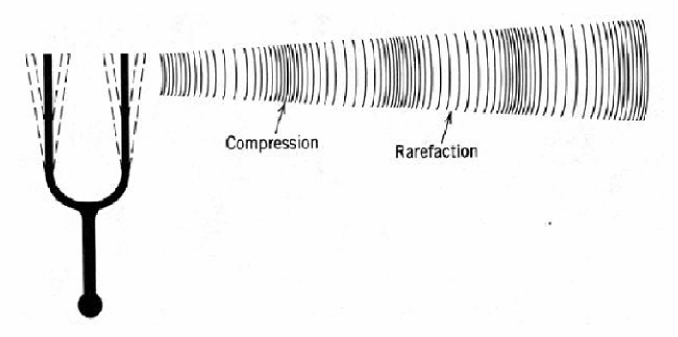


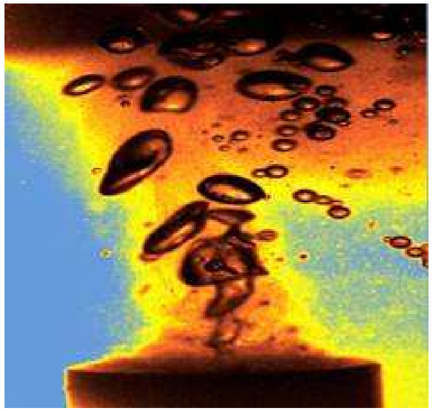
CASE STUDIES

ULTRASOUNDS

- **In a biological medium: production of compression and expansion cycles**

  → CAVITATION phenomenon





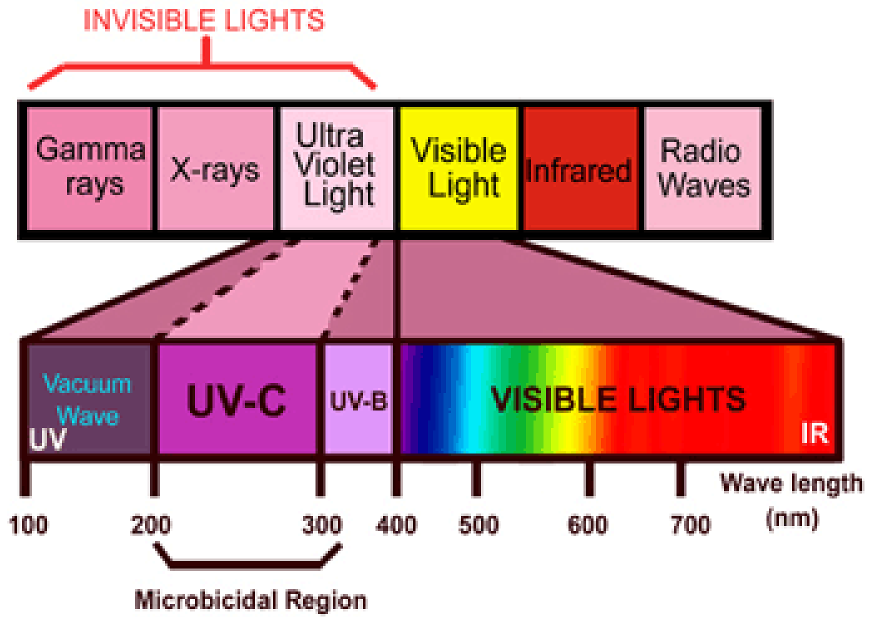
- **The implosion of gas bubbles → high temperature and high pressure spots**

  → Cell disruption → cellular death

CASE STUDIES

ULTRAVIOLET RADIATION

- Ultraviolet light in the non-ionizing region of the electromagnetic spectrum, between X-rays (200 nm) and visible light (400 nm)

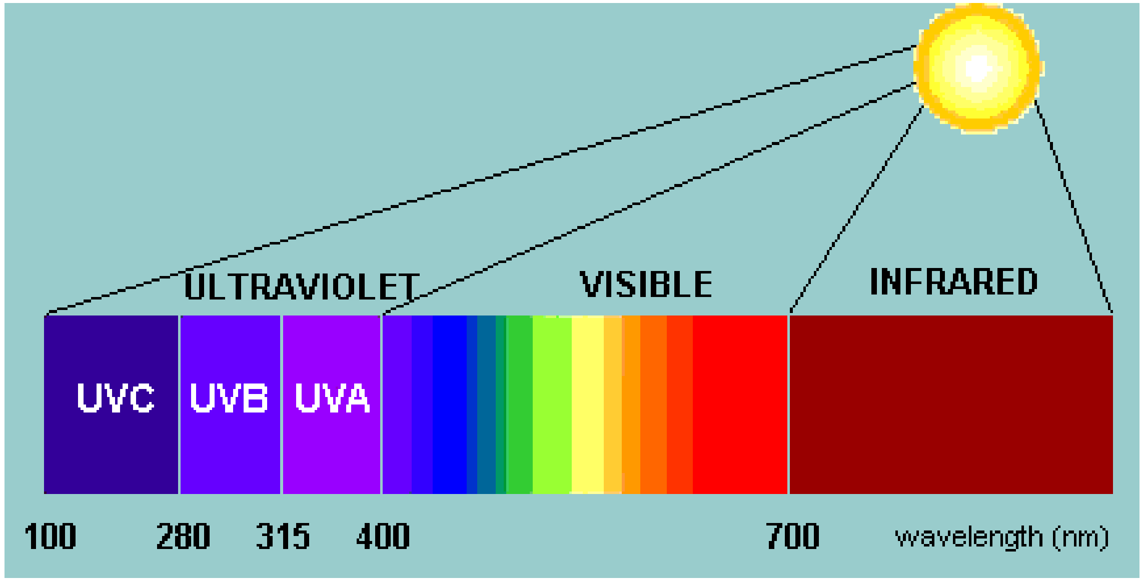


CASE STUDIES

ULTRAVIOLET RADIATION

UV light can be divided into three regions:

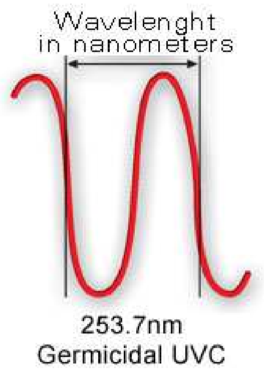
- UVA: 320-400 nm – therapeutic effects (dermatological);
- UVB: 280-320 nm – sun burn and plant damage
- **UVC**: 100-280 nm – dangerous to life – maximum lethal effect at 254 nm

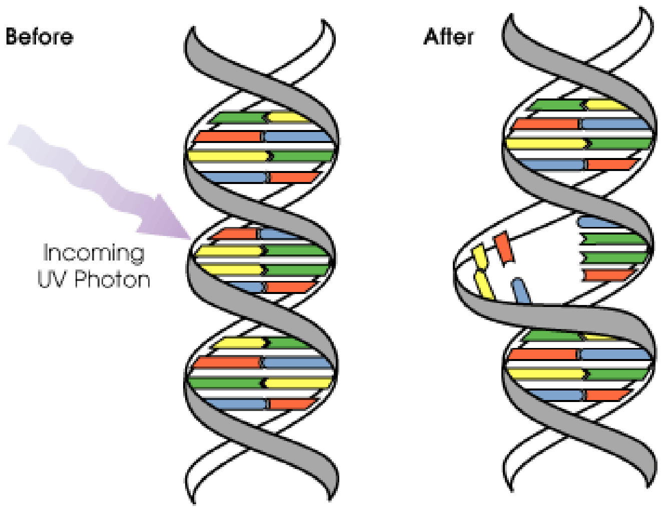


CASE STUDIES

ULTRAVIOLET RADIATION - UVC

Lethal effect (254 nm) due to its destroying action on DNA chains → decreasing or inactivation of vital functions of cells





Products

Strawberry

Red bell pepper

Watercress

Brocoli

Courgette / squash

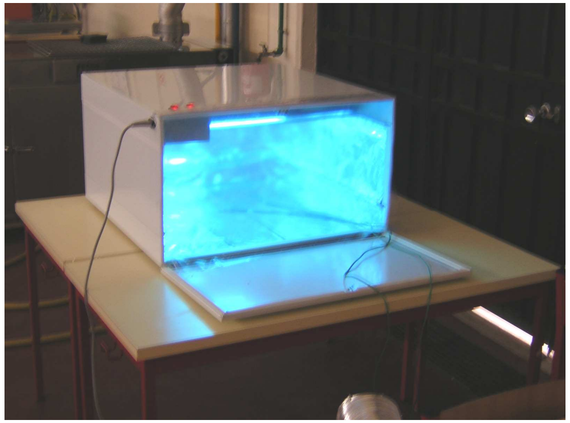
pumpkin

Technologies

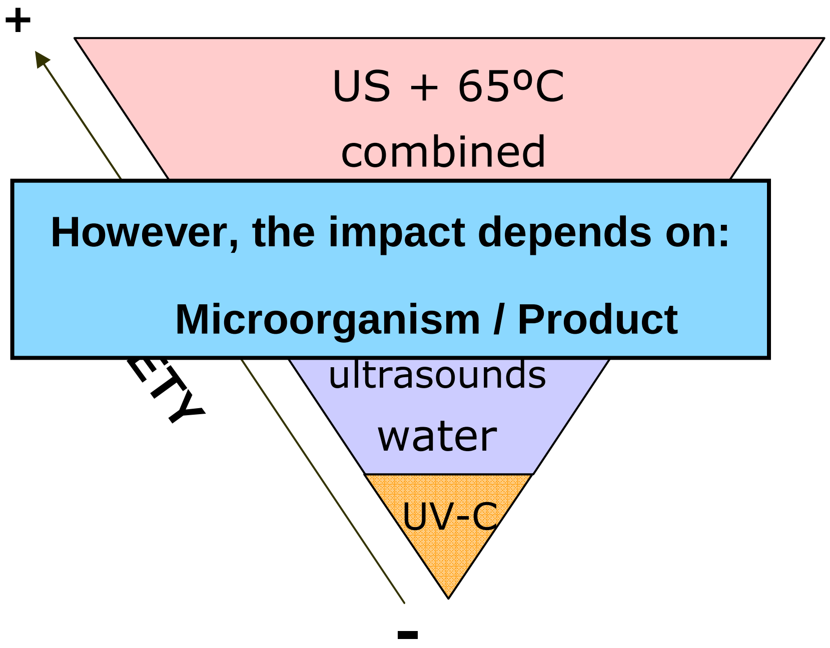
Ozone

Ultrasounds

UV-C



SAFETY

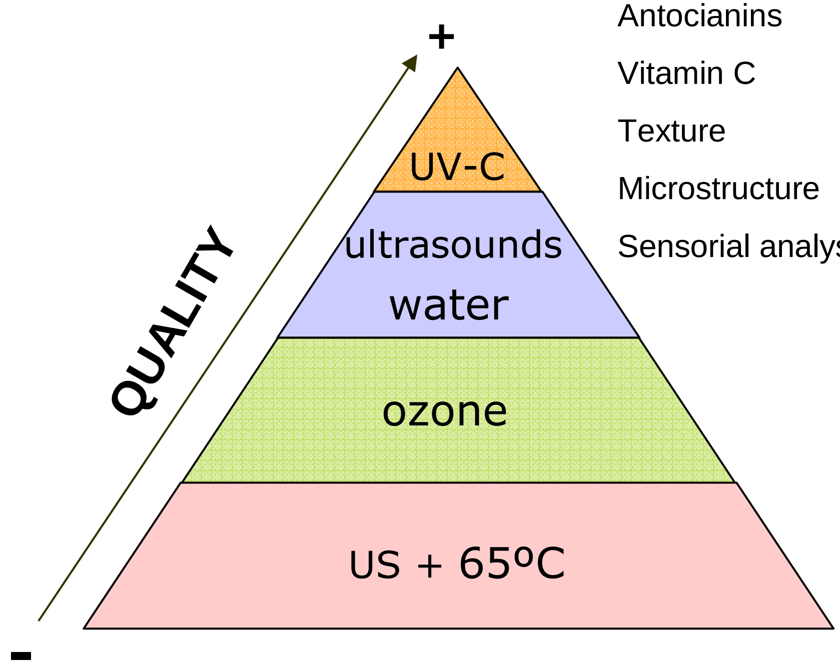


However, the impact depends on:

Microorganism / Product

QUALITY

Colour
pH
Antocianins
Vitamin C
Texture
Microstructure
Sensorial analysis



Compromise: safety + quality

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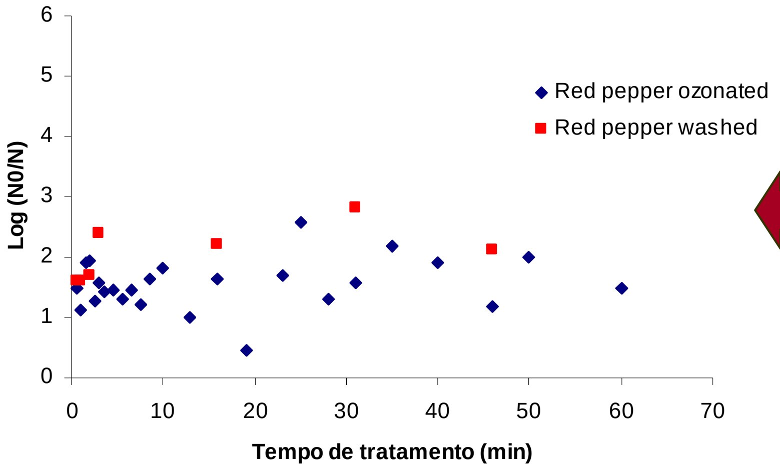
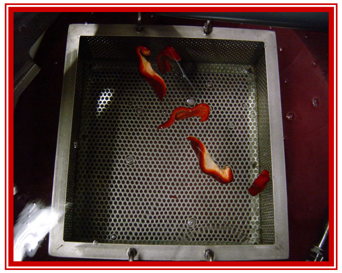
Kinetc behaviour

Red bell pepper / *Listeria innocua*

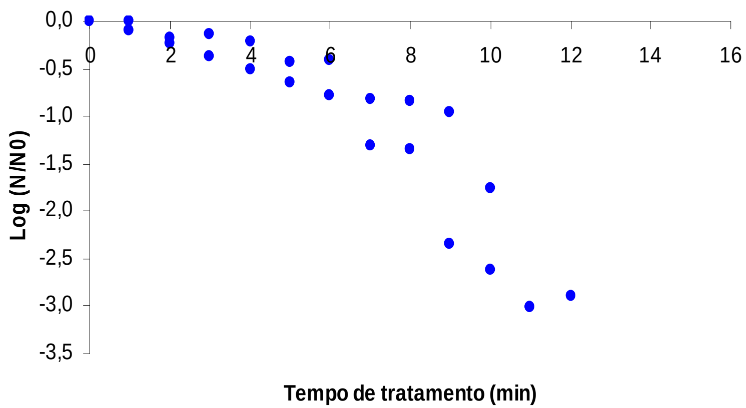


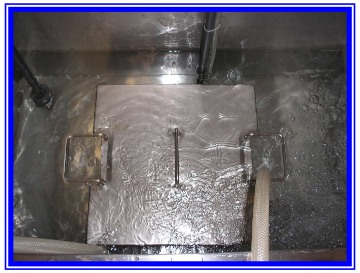
Ozone

red bell pepper



Water / *Listeria innocua*

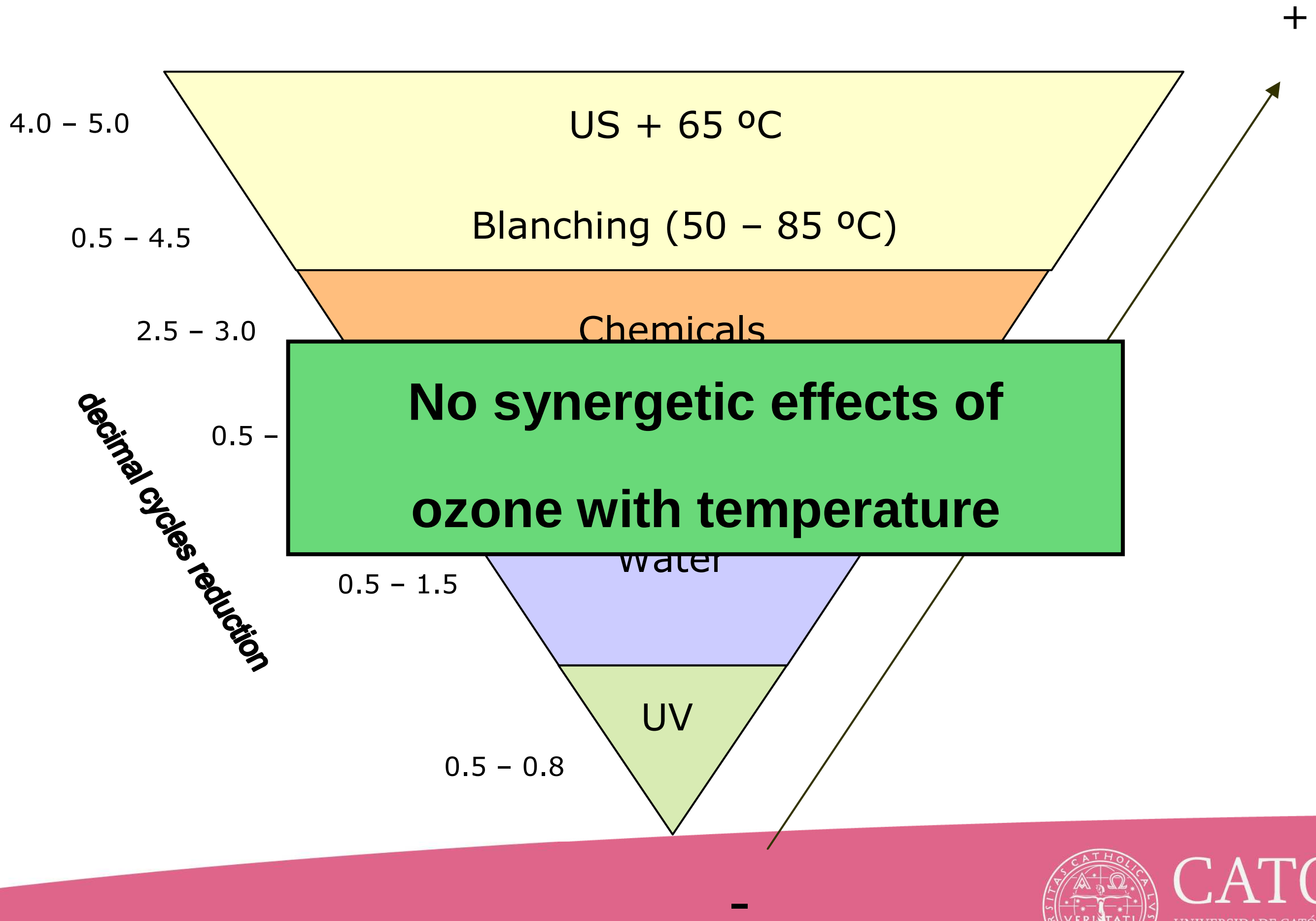




Ozone

Water

SAFETY (total mesophyls)



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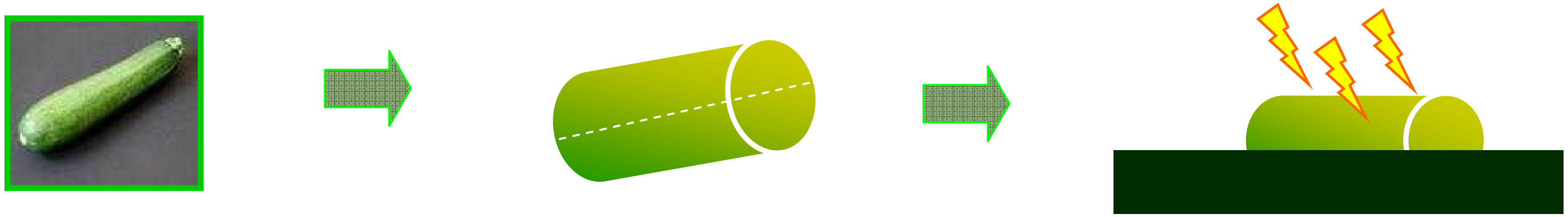
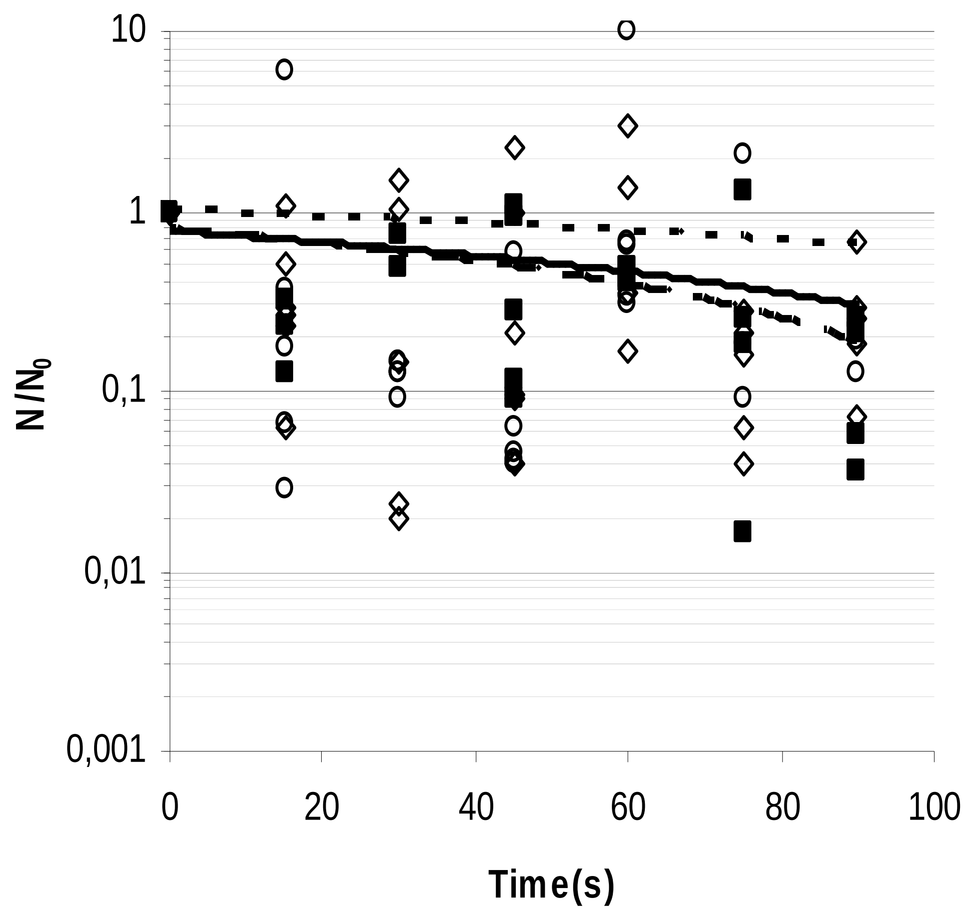
Fonte: www.deltaohm.com

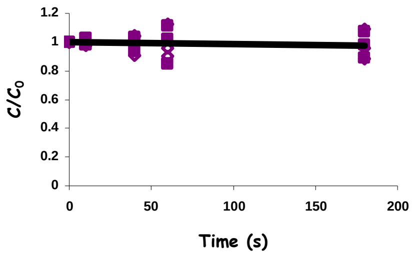


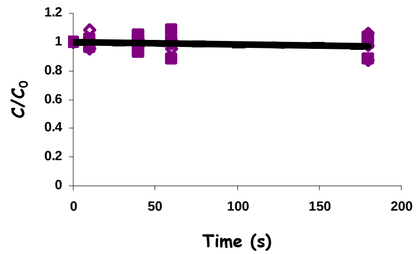


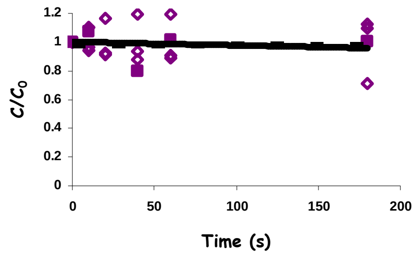
total mesophyls at 30 ºC

(◇) — 11 J/m²
(■) -- 8 J/m²
(○) ··· 5 J/m²

Effect on Peroxidase ....

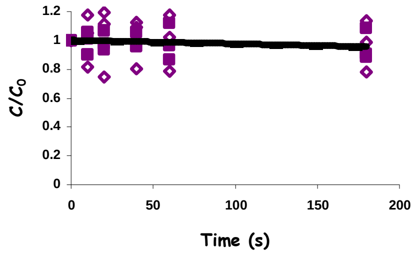


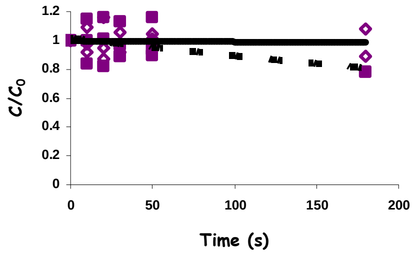


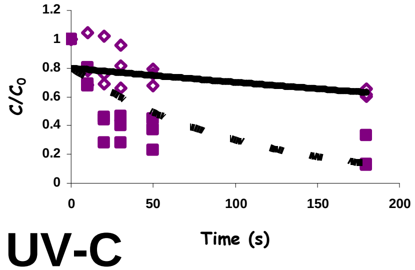


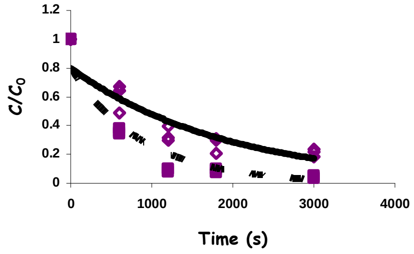
Temp. and UV-C

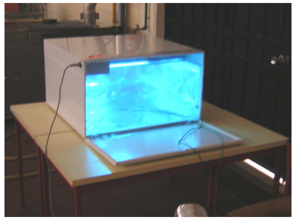
(11 J/m²)











(◊) heat (■) heat and UV-C

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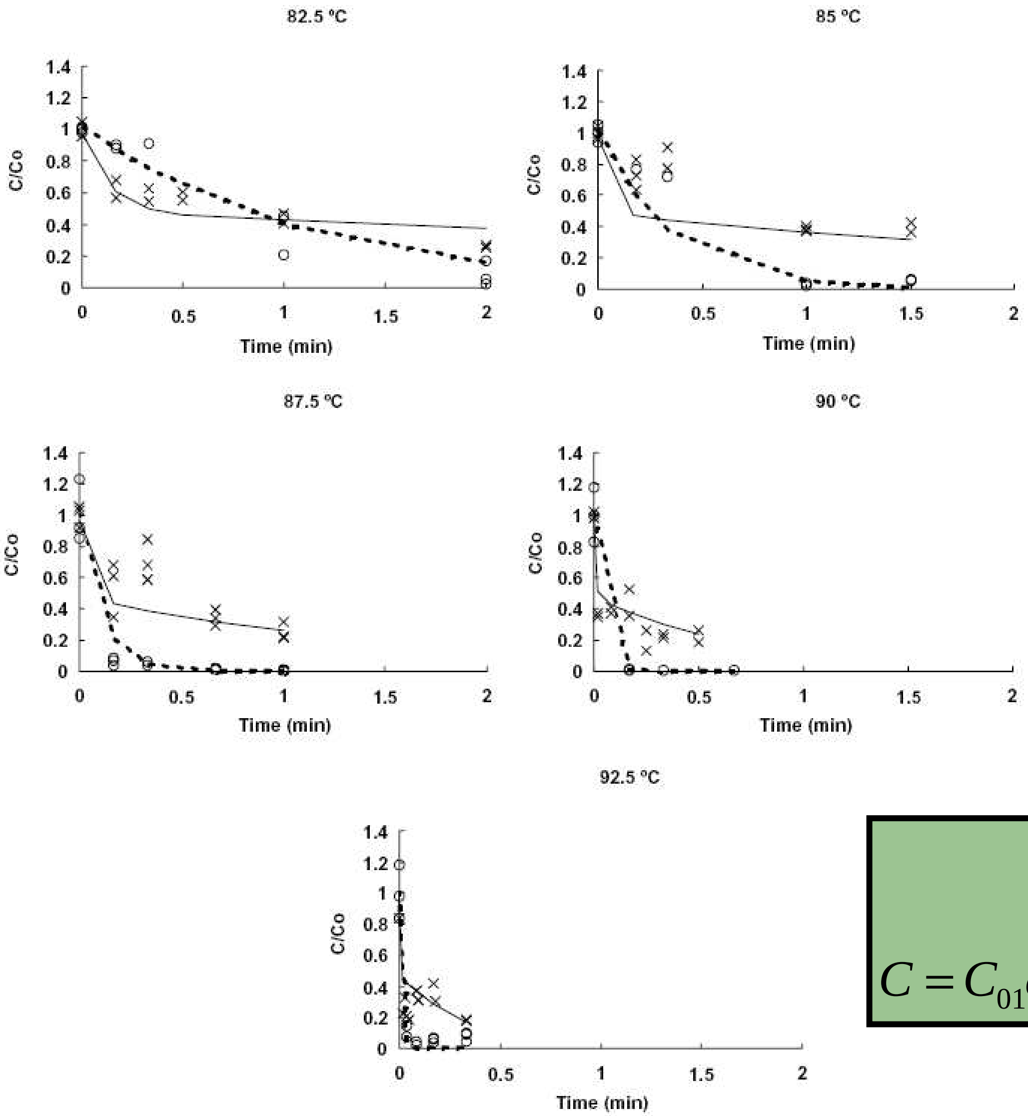
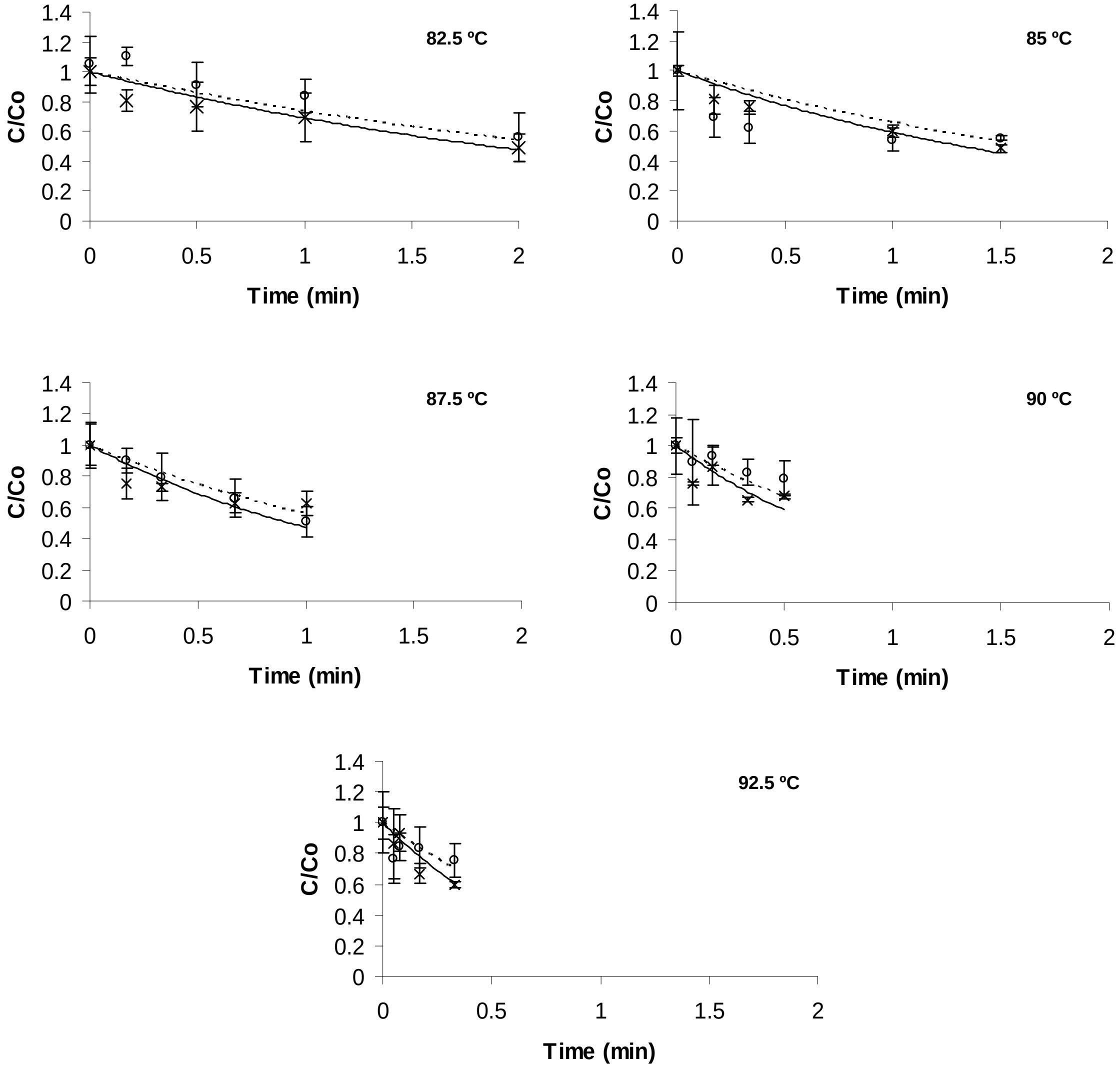
Effect on Peroxidase ....

Synergetic effect of

Temperature and ultrasonication

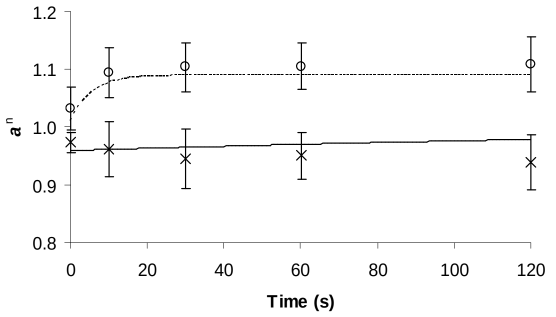


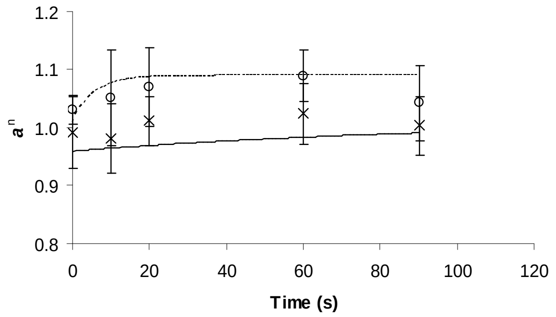
$$C = C_{01} e^{\left[-k_{1ref} e^{\left(\left(-\frac{Ea_1}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right)} t \right]} + C_{02} e^{\left[-k_{2ref} e^{\left(\left(-\frac{Ea_2}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right)} t \right]}$$



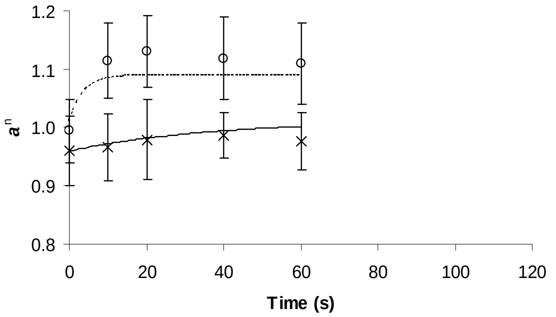
Vitamina C

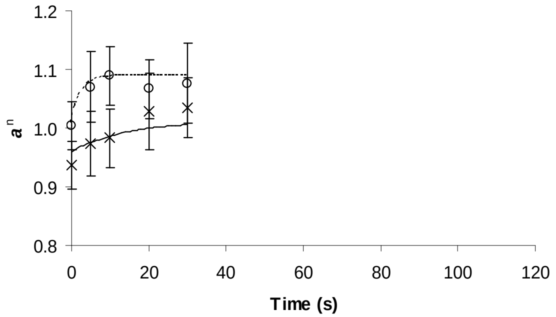
$$\frac{C}{C_0} = e^{\left\{-k_{\text{ref}}\, e^{\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_{\text{ref}}}\right)\right]} t\right\}}$$



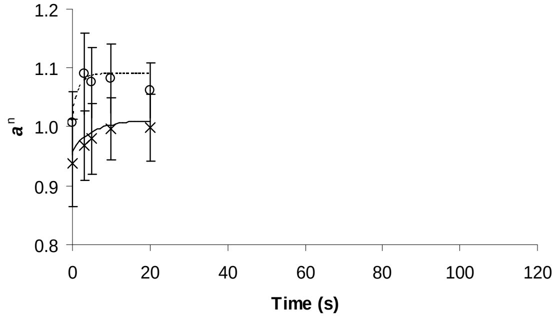


Colour a*



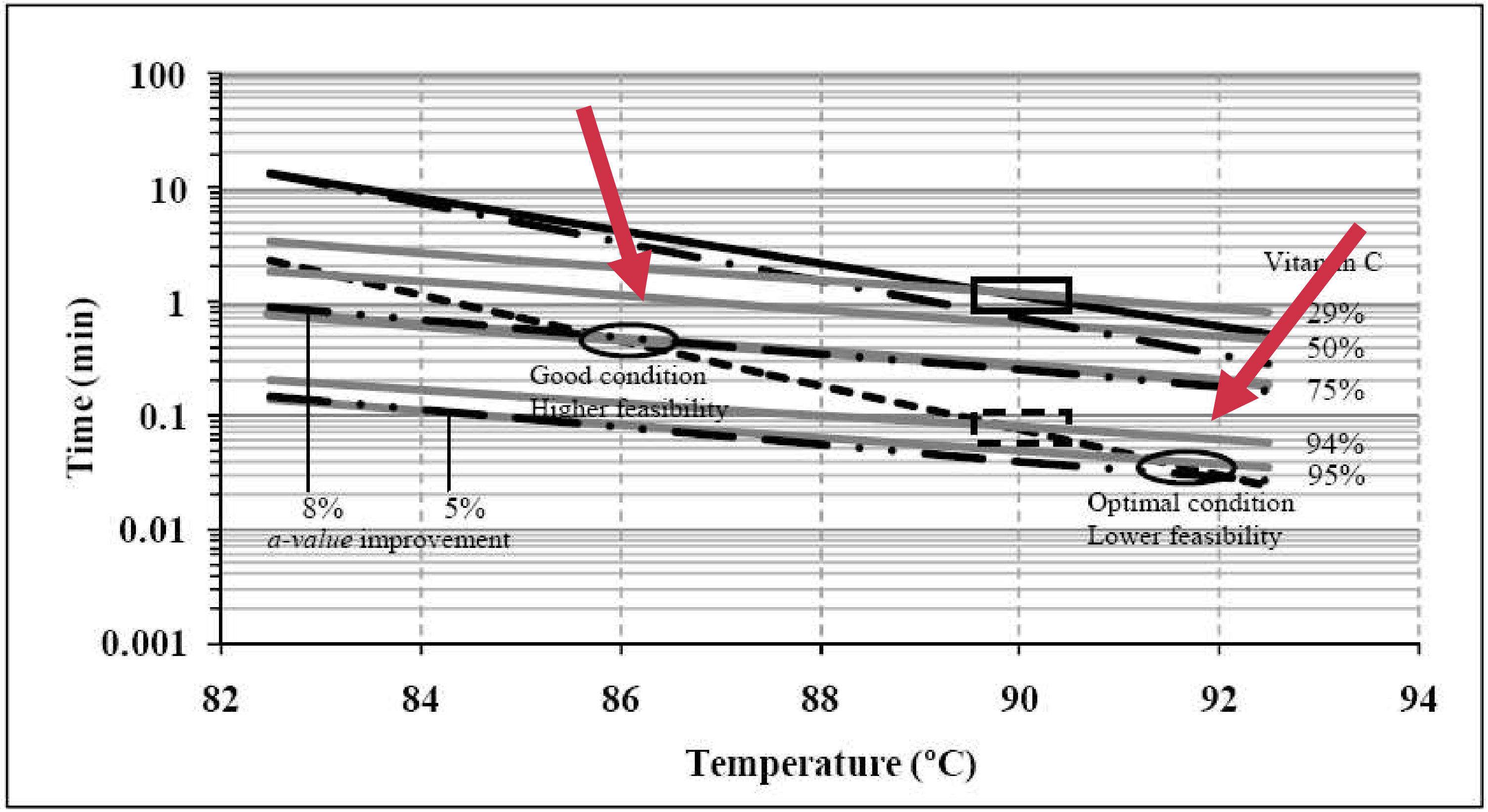


$$\frac{C - C_e}{C_0 - C_e} = e^{\left\{ -k_{ref}\, e^{\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} t \right\}}$$



Quality parameter	Treatment	Model	Kinetic parameter		Reference
Peroxidase	Heat	*Biphasic first-order*	C_{01} (µmol.min^{-1}.mg protein^{-1}) $k_{1\ 84.6°C}$ (min^{-1}) E_{a1} (kJ.mol^{-1}) C_{02} (µmol.min^{-1}.mg protein^{-1}) $k_{2\ 84.6°C}$ (min^{-1}) E_{a2} (kJ.mol^{-1}) R^2	0.49±0.08 18.01±13.98 420.72±114.94 0.48±0.06 0.24±0.14 351.65±80.91 0.94	Cruz et al. (2006)
	Thermosonication*	*First-order*	C_0 (µmol.min^{-1}.mg protein^{-1}) $k_{87.5°C}$ (min^{-1}) E_a (kJ.mol^{-1}) R^2	1.01±0.05 9.64±2.21 496.45±65.52 0.97	
Colour (*a* parameter)	Heat	*Reversible first-order*	C_0 C_e E_a (kJ.mol^{-1}) $k_{87.5°C}$ (s^{-1}) R^2	0.96±0.01 1.01±0.02 422.37±126.63 0.028±0.024 0.99	Cruz et al. (2007)
	Thermosonication*	*Reversible first-order*	C_0 C_e E_a (kJ.mol^{-1}) $k_{87.5°C}$ (s^{-1}) R^2	1.01±0.01 1.09±0.01 187.70±160.07 0.28±0.18 0.99	
Vitamin C	Heat	*First-order*	C_0 E_a (kJ.mol^{-1}) $k_{87.5°C}$ (min^{-1}) R^2	1 150.47±42.81 0.75±0.10 0.98	Cruz et al. (2008)
	Thermosonication*	*First-order*	C_0 E_a (kJ.mol^{-1}) $k_{87.5°C}$ (min^{-1}) R^2	1 136.20±60.97 0.58±0.11 0.97	

*Ultrasound at 20 kHz and 125 W


100
10
1
0.1
0.01
0.001
Time (min)
82
84
86
88
90
92
94
Temperature (°C)
Vitamin C
29%
50%
75%
94%
95%
Good condition
Higher feasibility
Optimal condition
Lower feasibility
8%
5%
a-value improvement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