ESCOLA SUPERIOR AGRÁRIA DE COIMBRA

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Removal of Pb (II) from aqueous solutions using eggshell composting products

Micaela A. R. Soares[1,2], **Margarida M.J. Quina**[2], Licínio Gando-Ferreira[2], Rosa Quinta-Ferreira[2]

[1] Instituto Politécnico de Coimbra, ESAC, CERNAS – Natural Resources, Environment and Society Research Centre, Coimbra, Portugal

[2] CIEPQPF- Research Centre on Chemical Processes Engineering and Forest Products, Department of Chemical Engineering, **University of Coimbra, Portugal**

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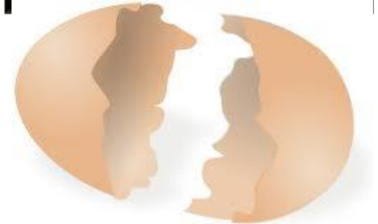
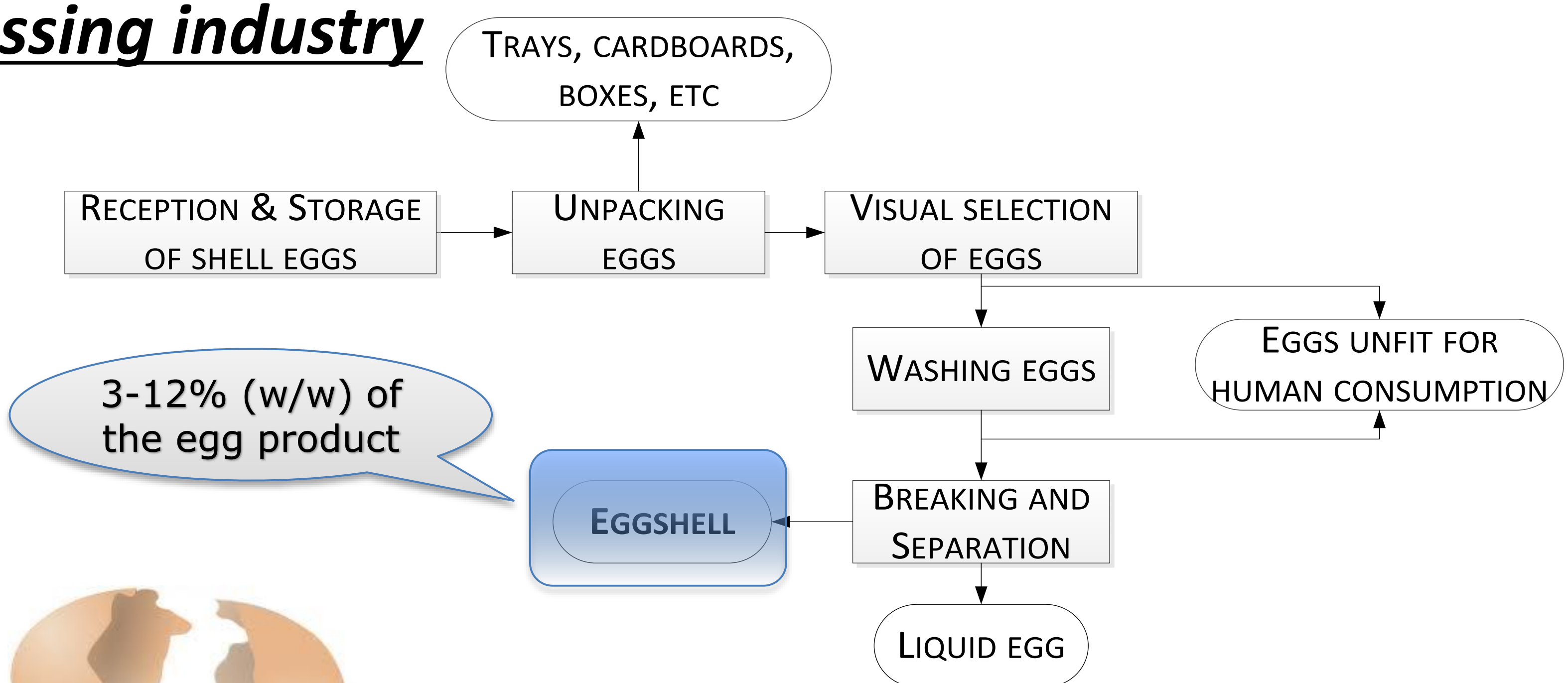
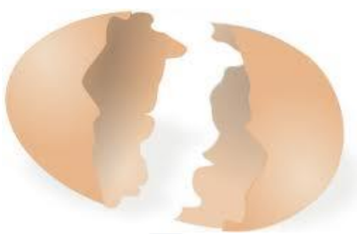


1- Introduction

Egg processing industry





The annual production of ES in Europe may ascend to 350 thousand ton!

Biomineralized composite structure of calcite crystals embedded in an organic framework of protein fibres

Porous structure
92-96% $CaCO_3$ (calcite)
2-5% organic matter

1- Introduction

Disposal or use: legal framework

(Regulation (EC) Nº 1069/2009 of the European Parliament and the Council).

Methods for disposal/use

- Incineration
- Thermal processing
- Composting
- Biogas production
- Production of petfood
- Other authorized methods /uses

Eggshell sanitation

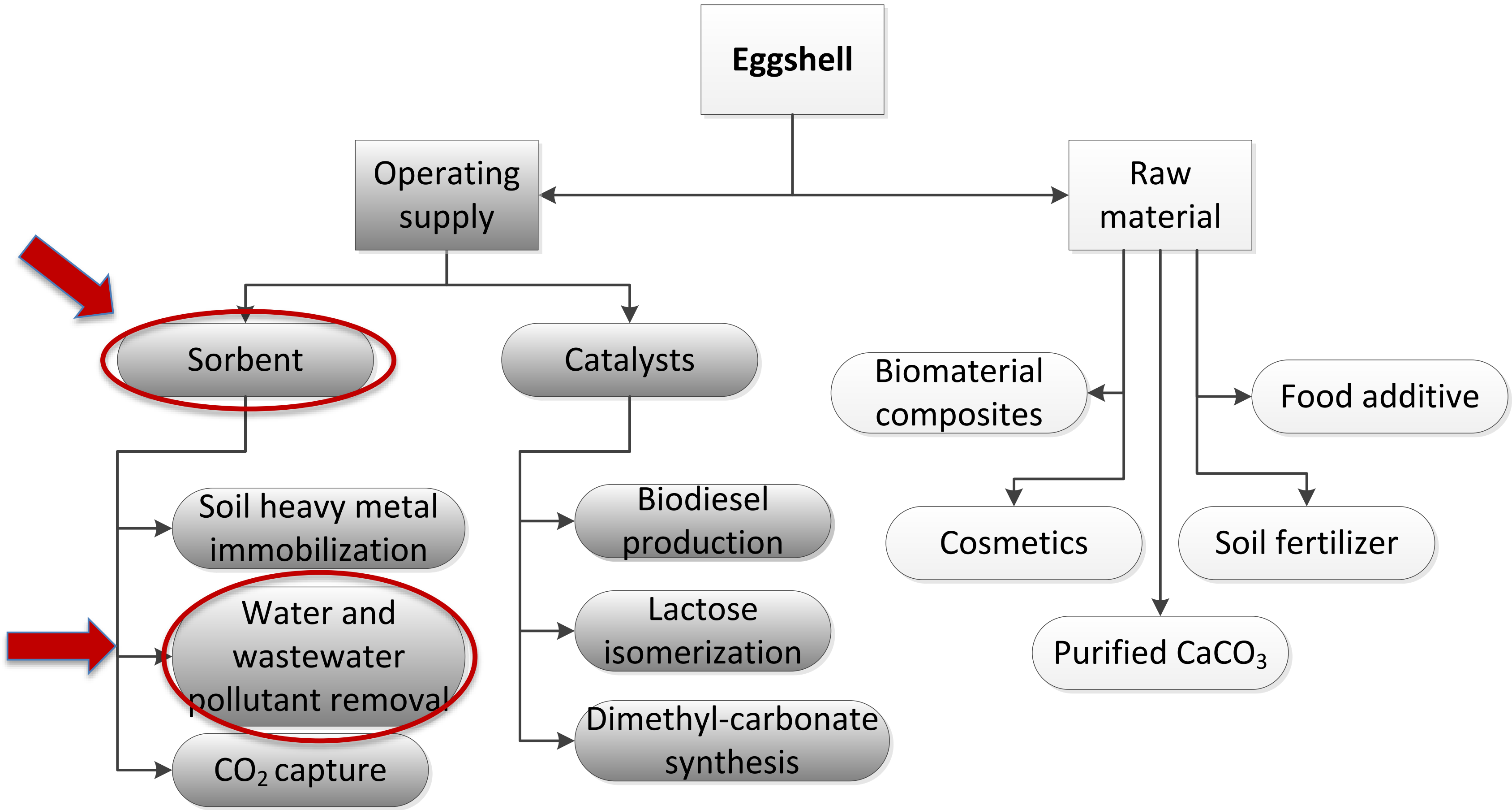
Biological heat produced during composting

Requirement: **70ºC for 1 h**

Pathogen thermal inactivation

1- Introduction

Other valorization options addressed in the literature



1- Introduction

Objective

Evaluate the feasibility of a mature compost (CES), obtained from ***industrial eggshell composting***, to be further used as low-cost sorbent for Pb (II) removal from aqueous matrices.

For comparison, natural eggshell (ES) and a mature compost without eggshell (CWES) were also tested for their sorption capacity towards lead ions.

CES

ES

CWES

2- Materials & methods

Sorbents tested

Compost with industrial eggshell (CES)

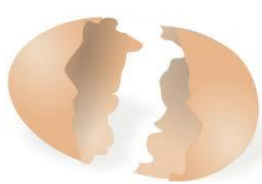
- Industrial potato peel (35.4%)
- Grass clippings (22.7%)
- Rice husks (11.9%)
- Industrial Eggshell (30%)

Compost without industrial eggshell (CWES)

- Industrial potato peel (50.6%)
- Grass clippings (32.4%)
- Rice husks (17.0%)

Composting performed in a laboratorial self-heating reactor of 105 L with forced aeration. Both composts with 144 days of maturation.

Natural industrial eggshell (ES)



Prior to laboratorial studies, each sorbent was air dried and subsequently ground and sieved to particle size between 25 and 500 µm

2- Materials & methods

Sorbents properties

	Sorbent		
Parameters	CWES	CES	ES
pH	9.3	8.9	8.3
pHzpc (L/S=100 L kg^{-1})	7.0	8.2	9.7
ANC (pH=4) (meq g^{-1})	0.64	18.2	19.7
CE (dS m^{-1})	0.85	1.10	-
Equivalent $CaCO_3$ (g $CaCO_3$ 100 g^{-1})	5.0±0.1	61.4±1.7	89.4±0.2
Organic matter (%)	79.4±0.5	28.5± 0.3	6.3± 0.1
TOC/TN	21.0	11.9	2.1
Respiration rate (mg C-CO_2 g^{-1}C d^{-1})	5.31±1.1	3.55±0.2	-
$Cd_{aqua\ regia}$ (mg kg^{-1})	0.70±0.01	0.40±0.01	-
$Cr_{aqua\ regia}$ (mg kg^{-1})	12.4±1.0	4.2±0.01	-
$Pb_{aqua\ regia}$ (mg kg^{-1})	12.7±0.01	7.3±0.02	3.55±0.02
$Cu_{aqua\ regia}$ (mg kg^{-1})	8.2±0.2	5.2±0.2	-
$Zn_{aqua\ regia}$ (mg kg^{-1})	47±0.3	11.9±0.1	4.95±0.1

- The pH at which the sorbent surface is neutral is dependent of the sorbent type.
- CES and ES present higher ANC, in comparison to CWES.
- Both composts present mature properties due low respiration rate.
- Heavy metals content in the tested sorbent (CWES, CES and ES) is low.

2- Materials & methods

Sorption equilibrium experiments

Sorbent

CWES

[Pb (II)] $_{initial}$= 300-2500 mg L^{-1}

CES

[Pb (II)] $_{initial}$= 100-1500 mg L^{-1}

ES

[Pb (II)] $_{initial}$= 100-1500 mg L^{-1}

<u>Operating conditions:</u>

- liquid to solid ratio (L/S) fixed at 10 L kg^{-1}
- T=25 ±2°C
- pH control at 5±0.5
- Equilibrium time = 180 min

<u>Analytical determinations:</u>

Pb(II) was measured by FAA spectrometry (Perkin Elmer – 3000), after centrifugation at 4000 rpm and filtration with a quantitative filter paper, at time t=0 and when the equilibrium was reached.

Sorption modelling

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

$$Pb(II)\ removal\ (\%) = \frac{(C_0 - C)}{C_0} \times 100$$

Table – Summary of the sorption isotherms models evaluated in this study

	Isotherm	Model	Model Linear Form	Model Parameters
Two parameters models	Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$K_L;\ q_m$
	Freundlich	$q_e = K_F C_e^{1/n_F}$	$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$	$K_F;\ n_F$
Three parameters models	Langmuir-Freundlich	$q_e = \frac{q_m K_{LF} C_e^{1/n_{LF}}}{1 + K_{LF} C_e^{1/n_{LF}}}$	-	$K_{LF};\ q_m;\ n_{LF}$
	Toth	$q_e = \frac{K_T C_e}{(A_T + C_e^{T_a})^{1/T_a}}$	-	$A_T;\ K_T;\ C_e$

2- Materials & methods

To evaluate the fitting of the experimental data to the sorption models

Objective: Low value

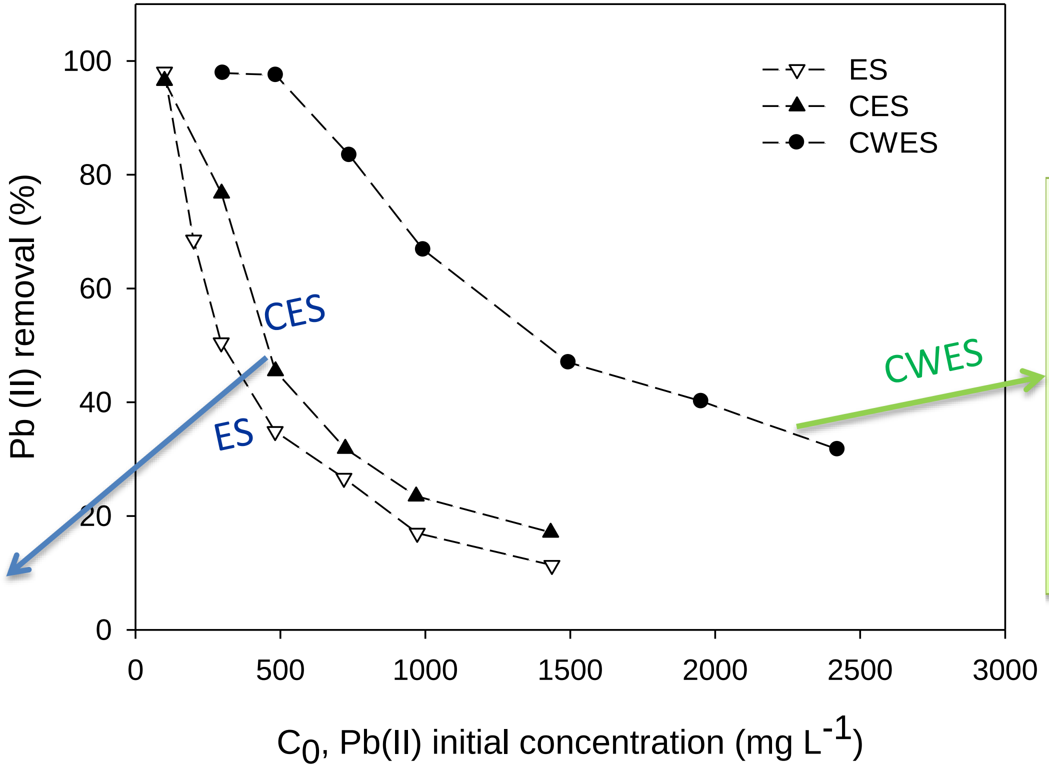
Error function	Equation
Sum of the square of errors - SSE	$SSE = \sum_{i=1}^{n} (q_{model} - q_{exp})_i^2$
Sum of the absolute errors - SAE	$SAE = \sum_{i=1}^{n} \lvert q_{model} - q_{exp} \rvert_i$
Average relative errors - ARE	$ARE = \frac{100}{n} \sum_{i=1}^{n} \left\lvert \frac{q_{exp} - q_{model}}{q_{exp}} \right\rvert_i$
Marquardt's percent standard deviation - MPSD	$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{q_{exp} - q_{model}}{q_{exp}} \right)_i^2}$
Percent standard deviation - σ	$\sigma = 100 \sqrt{\frac{SSE}{n-1}}$
Chi-square - χ^2	$\chi = \sum_{i=1}^{n} \frac{(q_{model} - q_{exp})_i^2}{q_{model}}$
R^2 adjusted – R^2_{adj}	$R^2_{Adj} = 1 - \frac{SSE / n-p}{\sum_{1=1}^{n} (q_{exp} - \overline{q_{exp}})^2 / n-1}$
Coefficient of determination – r^2	$r^2 = 1 - \frac{SSE}{\sum_{1=1}^{n} (q_{exp} - \overline{q_{exp}})^2}$

Objective: High value

3- Results & discussion

3.1- Influence of sorbent type and Pb (II) initial concentration

For all sorbents, the ***removal efficiency decrease with the increase of C_0*** ,due to the rise of Pb cations that gradually occupies the sorbent active sites, until saturation is reached.



For CES and ES

- The trend of lead removal is similar
- CES capacity to retain lead is in average 1.4 times higher than for ES

- Removal near to 100% for C_0<500 mg L^{-1}
- At the highest concentration (2500 mg L^{-1}) is still possible a removal efficiency near to 30%.

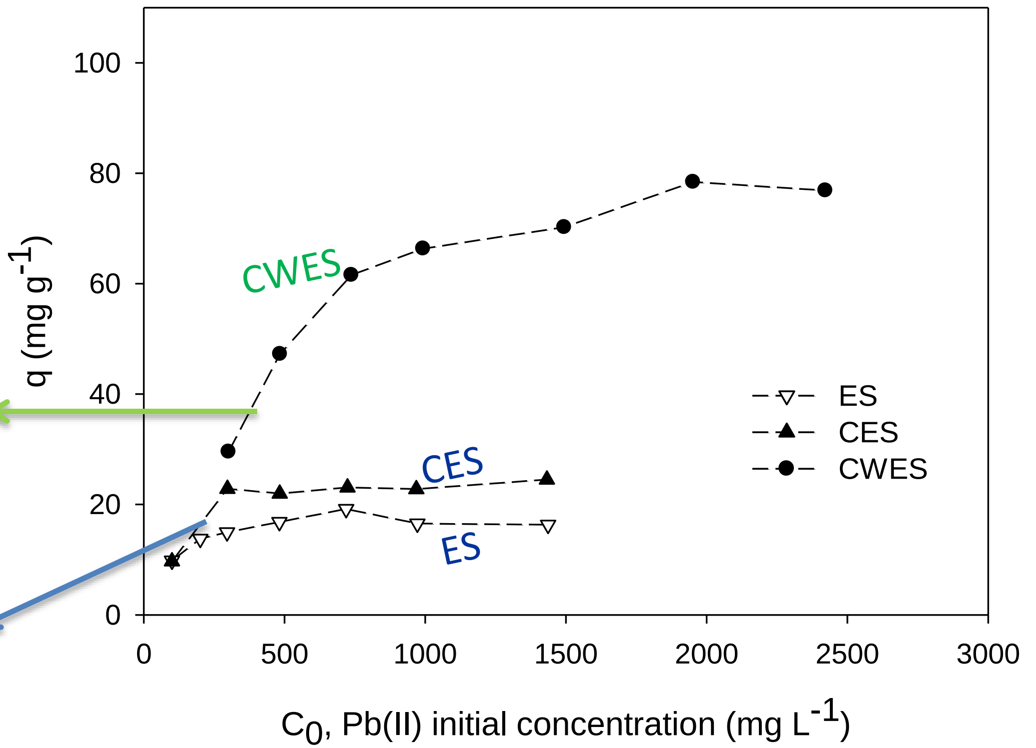
3- Results & discussion

3.1- Influence of sorbent type and Pb (II) initial concentration

The type of sorbent is also determinant to the uptake value attained (q)

CWES is the sorbent with higher organic content, and the maximum q ~ 80 mg g^{-1}, due to the negative charged functional groups associated to humic substances.

CES and **ES** present smaller maximum q values of 24 mg Pb(II) g^{-1} and 16 mg Pb(II) g^{-1}, respectively



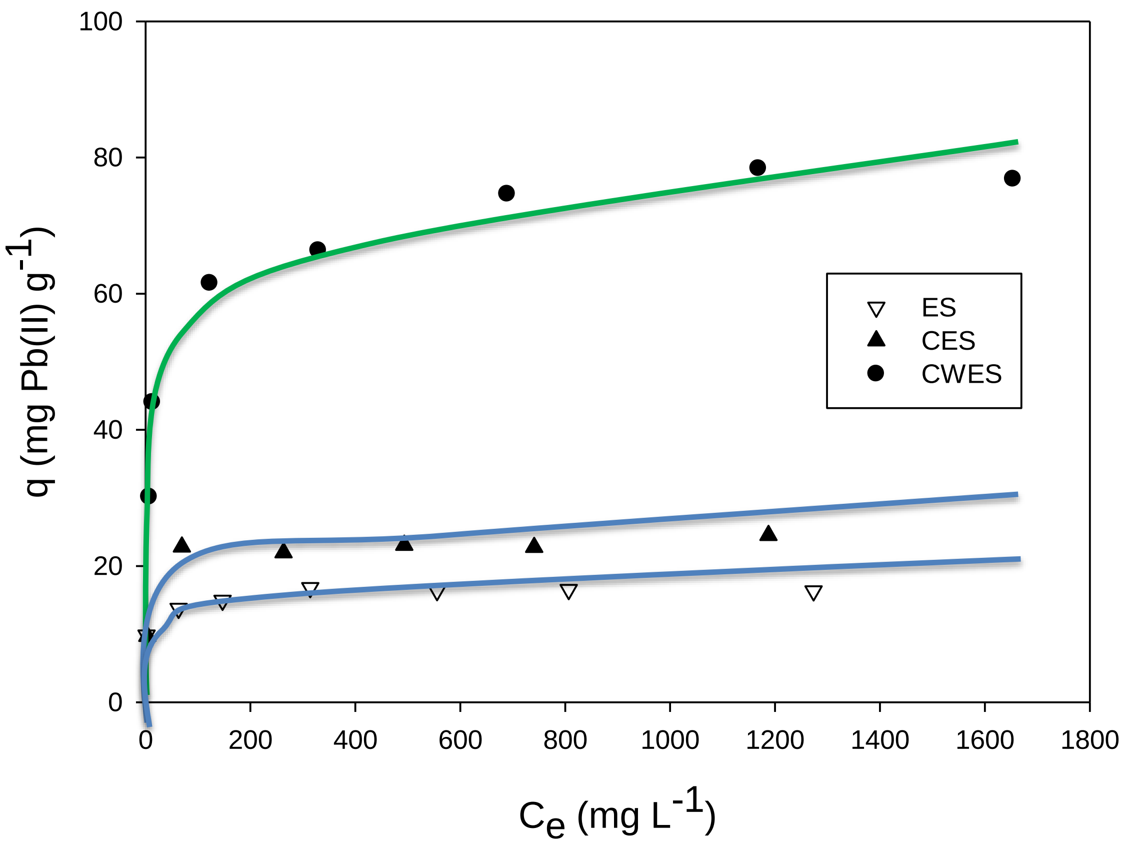
In terms of $CaCO_3$....

q_{CES}=39 mg Pb(II) g^{-1} $CaCO_3$

q_{ES}=18 mg Pb(II) g^{-1} $CaCO_3$

Such difference can only be attributed to the presence of humic substances in CES.

3.2- Equilibrium studies



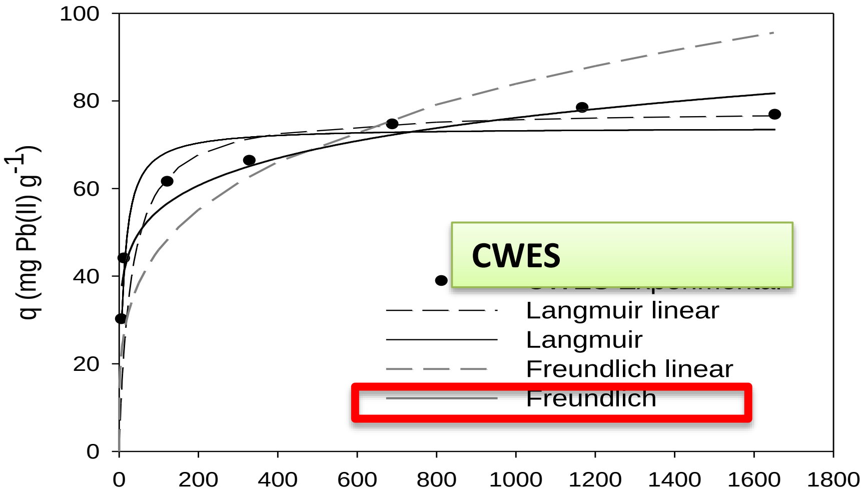
What Model?

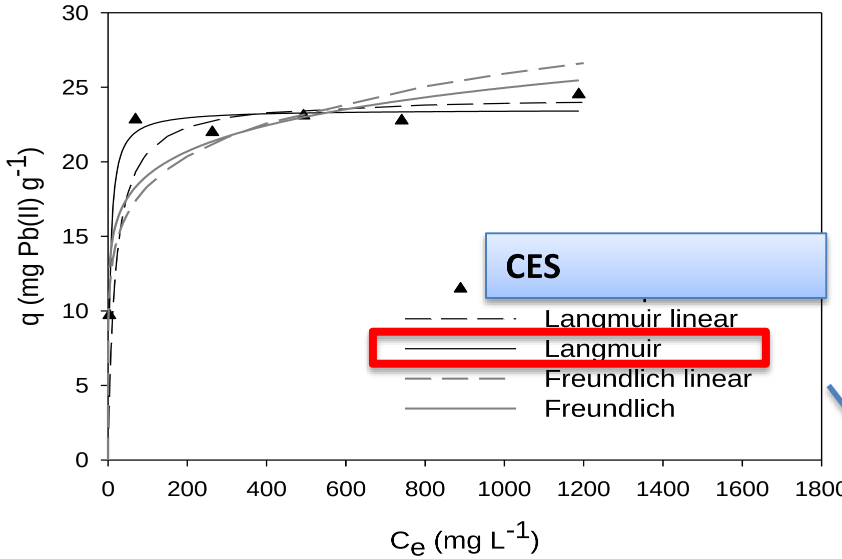
Independently of the sorbent tested, results from equilibrium sorption studies describe a high affinity sorption isotherm, classified as H-class isotherm: high uptake at low metal concentrations, which is defined by a curve with a relevant steep slope.

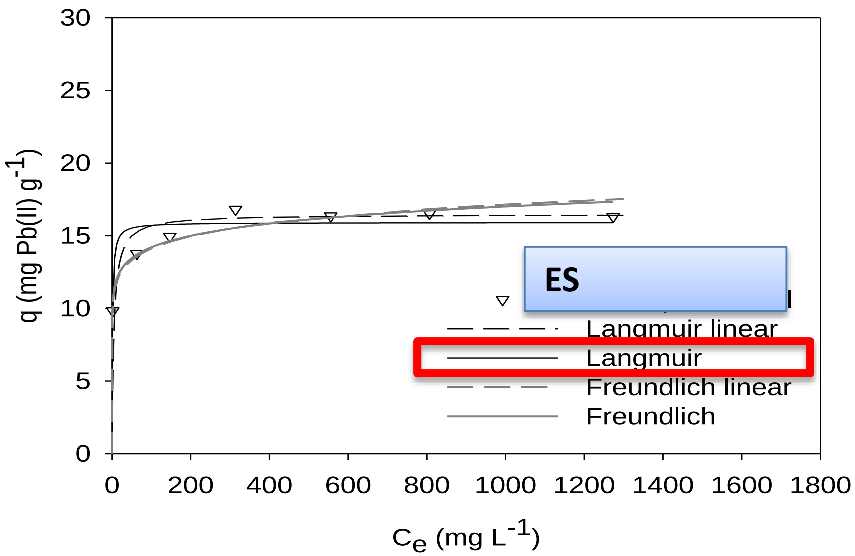
3- Results & discussion

Removal of Pb (II) from aqueous solutions using eggshell composting products

3.3- Equilibrium sorption modelling: Two parameters models



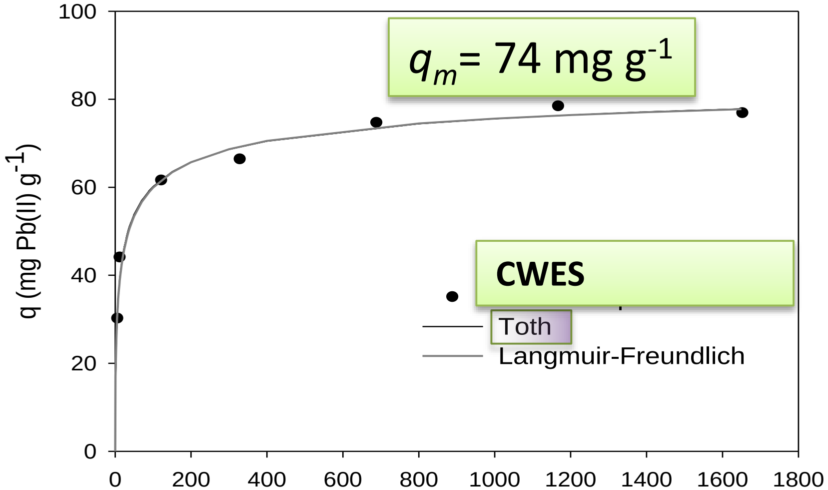


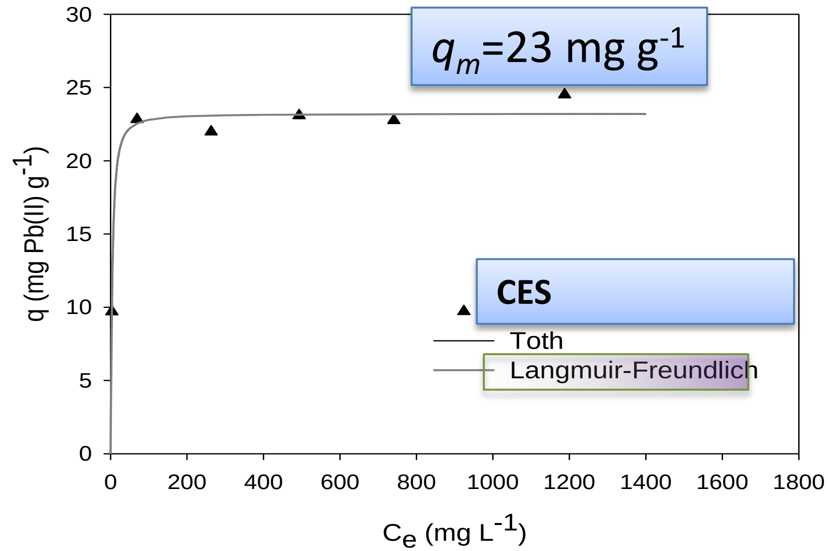


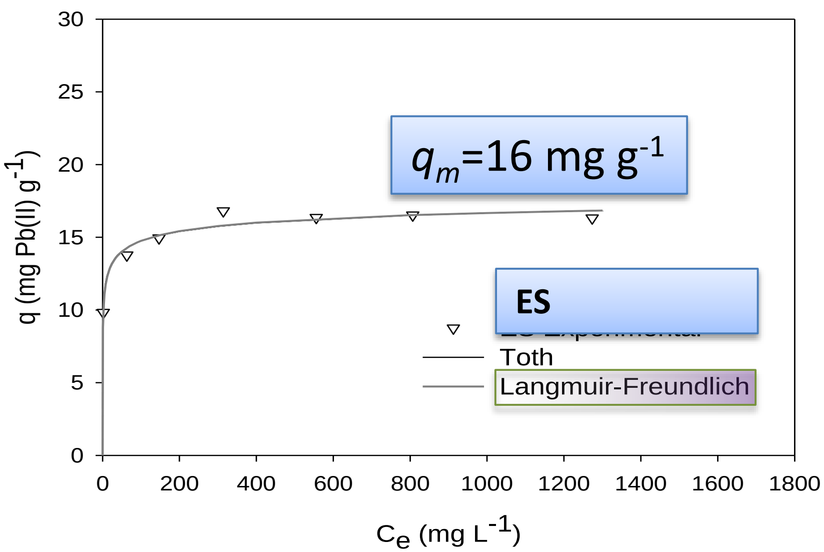
The influence of equation linearization over the sorption models parameters estimation was assessed.

Model type	Model Parameters	SSE	r^2
Langmuir $q = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m=23.50 mg g^{-1} K_L=0.207 L mg^{-1}	3,548	0,977
Langmuir linear parameters $q = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m=24.35 mg g^{-1} K_L=0.055 L mg^{-1}	48,245	0,681
Langmuir linear $\frac{C_e}{q} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	q_m=24.35 mg g^{-1} K_L=0.055 L mg^{-}	4,147	0,998

3.3- Equilibrium studies: Three parameters models







Higher value of r^2 and R^2_{adj} and lower values of other error functions considered (SSE, SAE, ARE, MPSD, σ and χ2)

4- Conclusions

- CES presented an additional affinity (about 40% higher) towards the metal studied in comparison to ES. Nevertheless, CWES was the material with higher capacity to lead(II) sorption (74 mg g-1).

- Initial metal concentration in liquid solutions strongly affected the sorbents capacity, though CWES was more robust to this variable.

- Independently of the sorbent tested the equilibrium experimental data for lead sorption was more adequately described by a three-parameters sorption model namely Langmuir-Freundlich for CES and ES and Toth for CWES.

- The method used to estimate the model parameters may have a significant influence in the goodness of the fitting, and the non-linear regression is the most adequate one.

Eggshell composting product (CES) may be an interesting sorbent material for Pb(II), better than unprocessed eggshells (ES) but with lower performance when compared to the compost obtained with the same organic material and without eggshell (CWES).

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Thank you for your attention.