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

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ABSTRACT

This study aims to evaluate a mature compost (CES) obtained by composting industrial eggshell waste with other organic materials to be further used as a low cost sorbent for Pb (II) removal from aqueous solutions. A set of batch sorption experiments were performed at 25ºC to assess the influence of initial metal concentration and

equilibrium time on Pb (II) efficiency removal from synthetic solutions. The equilibrium data were fitted to two-parameters and three parameters sorption isotherms models. For the purpose of comparison, natural industrial eggshell (ES) and mature compost without eggshell (CWES) were also studied for their sorption capacity towards lead ions.

The results obtained in this work have empowered a specific application of eggshell composting products for lead removal from aqueous media. In fact, CES presented an additional sorption capacity towards Pb(II), in comparison to ES. Nevertheless, CWES (compost without ES) was still the sorbent with higher capacity for uptaking lead ions from aqueous solutions.

Key words

Industrial eggshell waste; compost applications; heavy metal; sorption.

Introduction

Eggshell (ES) waste is the main by-product from the hen egg processing industry. The disposal of this waste is a matter of great concern due to its significant production, environmental risk (mainly associated to microbial proliferation or growth of pathogens) and financial burden. Therefore, options for adding value to this industrial waste should be developed (Russ and Meyer-Pittroff, 2004).

In 2011, European countries produced about 10 600 million ton of eggs from which about 30% were used to egg industrial processing (Agra CEAS Consulting Ltd, 2008; FAO, 2012) and the annual production of ES in Europe may ascend to 350 thousand ton (Soares et al., 2013).

According to Regulation (EC) Nº 1069/2009 of the European Parliament and the Council, ES is considered as an animal by-product not intended to human consumption, which requires pre-treatment to reduce pathogen spreading risk. Composting prior to soil incorporation is one of the treatment alternatives foreseen by the European regulation. As a result of ES composting, an enriched calcium compost can be obtained for value-added applications, namely in acidic soils with deficit in calcium, but also for heavy metal removal from aqueous media (water and wastewater).

In fact, some efforts in using ES as a sorbent for heavy metals uptake from contaminated water have been reported in the literature (de Paula et al., 2008; Park et al., 2007). Additionally, composting end-products have also been indicated as adequate for heavy metal removal due to the presence of humic substances, with negatively charged functional groups (Farrell and Jones, 2009; Paradelo and Barral, 2012). But to our knowledge, the effect of calcium carbonate rich organic compost for lead removal is scarcely addressed in the literature.

This study aims to evaluate the possibility of a mature compost (CES), obtained from industrial eggshell composting with other organic materials, to be further used as a

low cost sorbent for Pb (II) removal from aqueous solutions. For comparison, natural industrial eggshell (ES) and mature compost without eggshell (CWES) were also tested regarding their sorption capacity to lead ions.

Materials and methods

The composting products tested as sorbents were obtained at labscale by using self-heating reactors of 105 L with forced aeration, as described by Soares et al. (2013). After 25 days of active composting, solid mixtures were allowed to conclude the maturation phase in small piles until 144 days of composting.

The starting ingredients of the composting mixture for producing compost referred as CES were industrial potato peel, grass clippings, rice husk and industrial eggshell (ES) waste in the proportions of 35.4%, 22.7%, 11.9% and 30.0%(w/w), respectively. CWES compost was obtained in the same conditions as CES, but without eggshell in the initial mixture and keeping the relative proportions of the other ingredients.

For comparison purposes with CWES and CES, industrial eggshell (ES) was also considered as a sorbent material for lead aqueous removal.

Prior to laboratorial studies, each sorbent was air dried and subsequently ground and sieved to particle size between 25 and 500 µm. The main properties of the tested

sorbents are presented in Table 1. The sorbents had alkaline pH and low metal concentrations. In addition, CES and ES presented similar acid neutralization capacity.

Table 1 – Main properties of the sorbents tested (mean±standard deviation).

Parameters	Sorbent		
	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	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

CES: compost with industrial eggshell; CWES: compost without industrial eggshell; ES: industrial eggshell waste; pH$_{zpc}$: pH at zero point charge; ANC: acid neutralization capacity; EC: electrical conductivity; TN: total nitrogen; TOC: total organic carbon; concentration units are presented in a dry weight basis.

Sorption experiments

Sorption experiments for equilibrium studies consisted in putting each sorbent in contact with solutions with different initial lead concentrations, under constant agitation. The initial concentrations ranged from 100-1500 mg L^{-1} when CES and ES were tested and 100-2500 mg L^{-1} in the case of CWES. All lead solutions used were prepared from a stock solution of 3000 mg L^{-1}, by performing the adequate dilutions.

The operating conditions imposed for equilibrium experiments consisted in a liquid to solid ratio (L/S) fixed at 10 L kg^{-1}, temperature maintained at 25 ±2ºC and the pH kept

at 5±0.5 by adding standard solutions (0.01, 0.2 and 0.5 M) of HNO$_3$ and NaOH, as required.

Previously kinetic studies indicated that a contact time of 3 h ensured equilibrium conditions.

The concentration of lead in the aqueous phase was measured by flame atomic absorption 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 isotherms modelling

The amount of lead sorbed by unit mass of sorbent in equilibrium conditions (q$_e$, in mg g^{-1}) was calculated according to Eq.(1).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where C$_0$ (mg L^{-1}) represents the initial aqueous phase concentration in lead, m (g) denotes the amount of sorbent used in each test, V (L) the initial volume of aqueous phase in contact with each sorbents during sorption tests and C$_e$ (mg L^{-1}) is the lead equilibrium concentration after sorption.

The percentage of lead sorbed by each sorbent (Pb(II) removal) was calculated by Eq.(2).

$$Pb(II)\ removal\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

The sorption capacity of the sorbent can be obtained from experimental data by using sorption isotherms models. In this study two and three parameters models were studied (Table 2).

In addition, for the two-parameters equations (Langmuir model and Freundlich model) the influence of equation linearization over the sorption models parameters estimation and functions errors was assessed.

Table 2 – Summary of the sorption isotherms models evaluated in this study (Malamis and Katsou, 2013).

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

A_T - Toth isotherm constant (L mg^{-1})$^{\text{Ta}}$; C_e - equilibrium metal concentration in aqueous media (mg L^{-1}); C_0 - the initial metal concentration in aqueous media (mg L^{-1}); K_L - the Langmuir constant (L mg $^{-1}$); K_F - the Freundlich constant (mg g^{-1} (L mg $^{-1}$)$^{\text{nF}}$); K_{LF} - the Langmuir-Freundlich isotherm constant (L mg^{-1})$^{\text{nF}}$; K_T - the Toth isotherm constant (mg g^{-1} L mg $^{-1}$); n_F - the Freundlich affinity constant; n_{LF} - the Langmuir-Freundlich isotherm exponent; q_m - the maximum adsorption capacity (mg g^{-1}); T_a - the Toth isotherm exponent.

To evaluate the fitting of the sorption models to the experimental data, several error function were assessed, according to the equations indicated in Table 3.

Table 3 – List of error functions used in this study (Foo and Hameed, 2010).

Error function	Equation
Sum of the square of errors - SSE	$$SSE = \sum_{i=1}^{n} \left(q_{model} - q_{exp}\right)_i^2$$
Sum of the absolute errors - SAE	$$SAE = \sum_{i=1}^{n} \left|q_{model} - q_{exp}\right|_i$$
Average relative errors - ARE	$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left|\frac{q_{exp} - q_{model}}{q_{exp}}\right|_i$$
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	$$\chi = \sum_{i=1}^{n} \frac{\left(q_{model} - q_{exp}\right)_i^2}{q_{model}}$$
R^2 adjusted – R^2_{adj}	$$R^2_{Adj} = 1 - \frac{SSE/n-p}{\sum_{1=1}^{n}\left(q_{exp} - \overline{q_{exp}}\right)^2 / n-1}$$
Coefficient of determination – r^2	$$r^2 = 1 - \frac{SSE}{\sum_{1=1}^{n}\left(q_{exp} - \overline{q_{exp}}\right)^2}$$

q_{exp} is the experimental value of the sorbent capacity, in equilibrium conditions; q_{model} is equilibrium capacity obtained from the sorption isotherm model.

Results and discussion

Influence of sorbent type and initial concentration on Pb(II) sorption

Figure 1 shows the influence of the type of sorbent on lead(II) removal, by varying the initial concentration from 100 to 2500 mg Pb(II) L^{-1}.
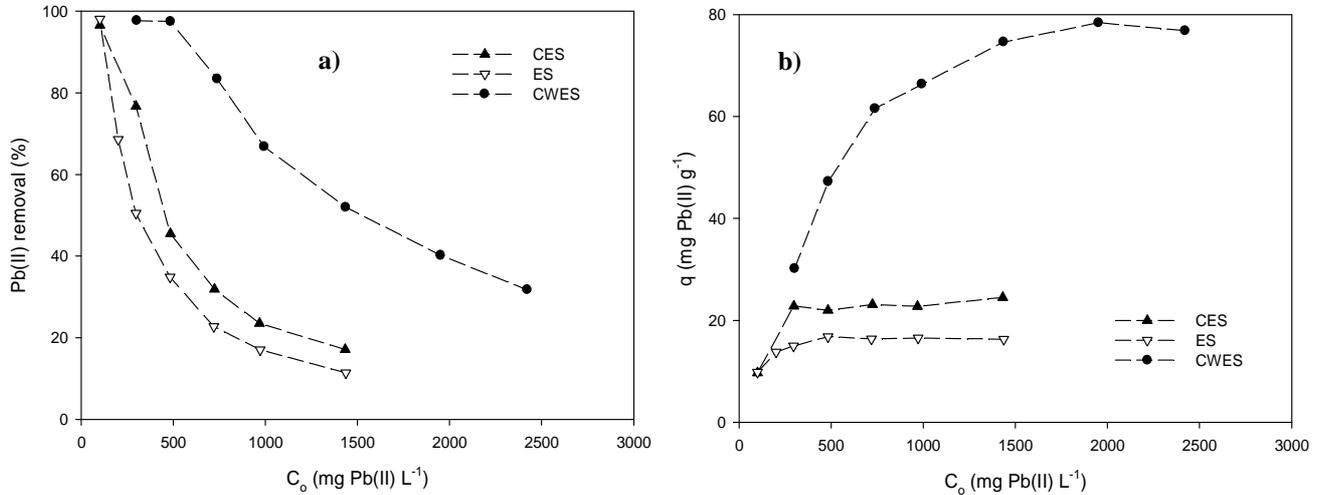
Figure 1 – Influence of the initial concentration of lead on metal a) removal and b) uptake from aqueous solution, in equilibrium conditions.

The behavior of lead removal for the sorbents that contain eggshell (CES and ES) is very similar (Figure 1a). For the lowest initial concentration (100 mg L^{-1}) there is a high removal capacity (near 100%), which is sharply inhibited when the initial concentration is increased. Nevertheless, in case of initial concentration Pb(II) is greater than 100 mg L^{-1}, the CES capacity to retain lead is in average 1.4 times higher than for ES. Vijayaraghavan & Joshi, 2013 studied the sorption of lead by chicken eggshell waste and achieved a removal efficiency of 30.7% (at 25ºC, pH=5 and L/S= 500 Lkg^{-1}, C$_o$=1045 mg L^{-1}) which is almost twice the removal recorded in this study (16%), for the same concentration level. In addition, S. M. Shaheen et al., 2013 observed a removal efficiency of 99% (at ambient temperature, pH not controlled, L/S=20 L kg^{-1} and C$_o$=700 mg L^{-1}) while in this study only 22% of Pb(II) was removed from aqueous solution with ES. This significant difference can be attributed to the lack of pH control

during the sorption tests performed by S. M. Shaheen et al. (2013), and thus probably occurred an increase of the aqueous pH to alkaline levels due to partial ES dissolution. In consequence, adequate conditions for the precipitation of lead ions in the form of hydroxides are available and lead removal is enhanced through this route, which masks the quantitative sorptive ability of the sorbent.

Regarding CWES, this sorbent enables lead removal at levels near to 100% for a broader range of initial concentrations (200 to 500 mg L^{-1}) in comparison to CES. Then, a smoother decrease of lead removal is observed when C_o is increased. However, at the highest concentration tested (2500 mg Pb(II) L^{-1}) is still possible to attain a removal efficiency near 30%.

Independently of the sorbent tested, the decrease of lead removal efficiency with the increase of Co is due to the rise of the number of metal cations that gradually occupies the sorbent active sites, until saturation is reached (Malamis and Katsou, 2013).

The type of sorbent is also determinant to the uptake value attained (Figure 1b). Indeed, CWES is the sorbent with higher organic content, featuring a maximum q value near 80 mg Pb(II) g^{-1}, probably due to the presence of negative charged functional groups associated to humic substances. On the other hand, CES and ES present smaller maximum q values of 24 mg Pb(II) g^{-1} and 16 mg Pb(II) g^{-1}, respectively. Nevertheless, if the lead uptake is expressed in terms equivalent mass of $CaCO_3$, q value for CES and

ES becomes 39 mg Pb(II) g^{-1} $_{CaCO3}$ and 18 mg Pb(II) g^{-1} $_{CaCO3}$, respectively. Such difference can only be attributed to the presence of humic substances in CES.

Equilibrium sorption modelling

Sorption isotherms are mathematical equations which describe the equilibrium between the mass of a solute sorbed in a solid phase and the soluble concentration of that solute in an aqueous medium, for a specific temperature. The equilibrium conditions are attained when aqueous concentration of the solute remains constant, after being in contact with a sorbent for a given period of time (Hossain et al., 2012).

In practice, equilibrium sorption modelling allows to compare the performance of different sorbents towards the solute removal from the aqueous medium, at several operating conditions. Additionally, the sorption isotherms contain parameters that express the surface properties and affinity of the sorbent, at a given operating conditions (Malamis and Katsou, 2013).

In this work, the application of several isotherm models with two and three parameters, detailed in Table 2 were addressed to characterize the sorption of Pb(II) in the tested sorbents.

The experimental sorption isotherms for Pb(II), obtained according to the experimental conditions previously described, are presented by the symbols in Figure 2 a), b) and c), respectively for CES, ES and CWES.
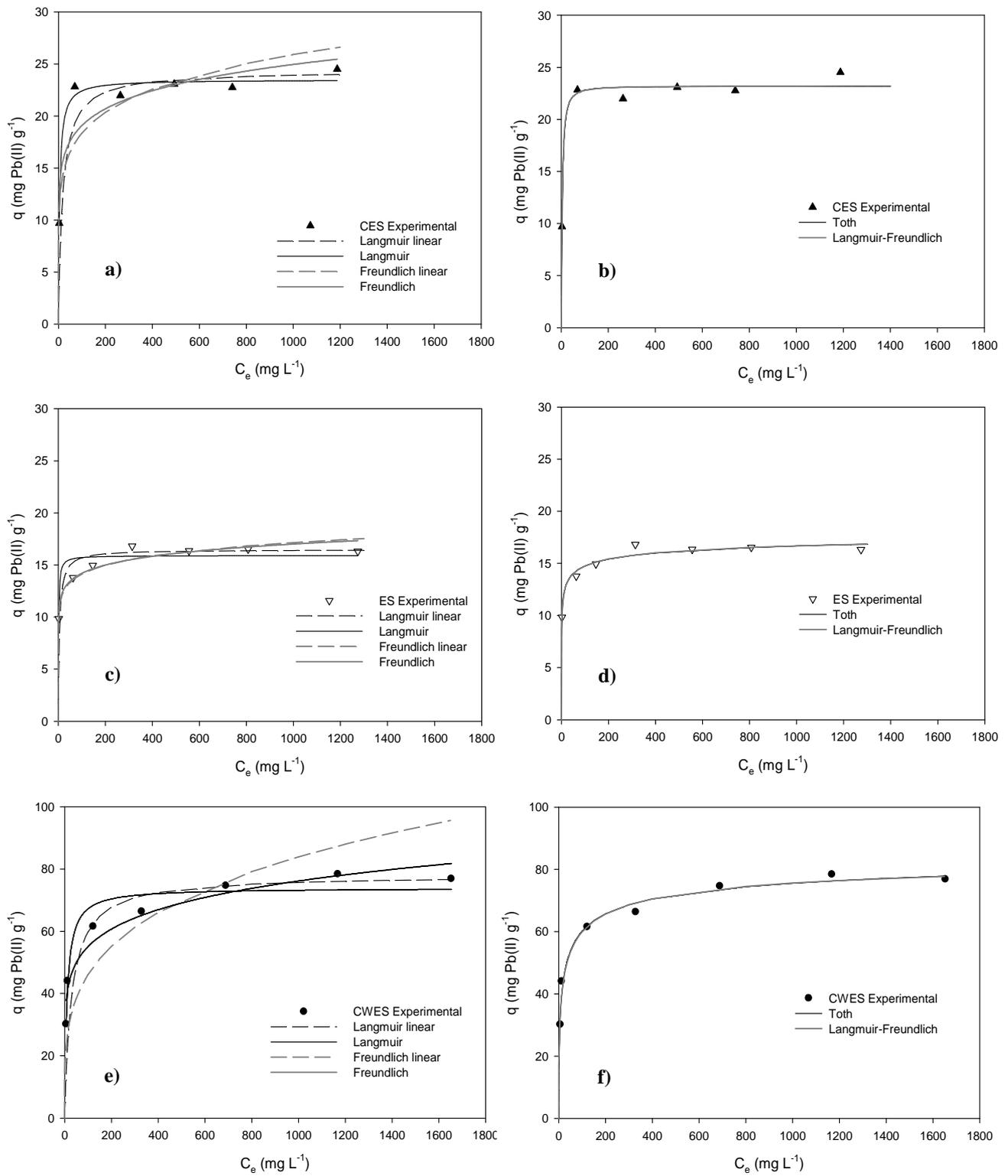
Figure 2 – Sorption experimental data and model sorption fitting: a) CES - two parameters models, b) CES – three parameters models, c) ES - two parameters models; d) ES – three parameters models; e) CWES – two parameters models; f) CWES – three

Independently of the sorbent tested, results from equilibrium sorption studies (Figure 2) describe a high affinity sorption isotherm, classified as H-class isotherm (Hinz, 2001). For this type of isotherm, sorbent presents high uptake at low metal concentrations, which is defined by a curve with a relevant steep slope.

In order to evaluate the ability of some sorption models to correlate with the experimental data, two-parameters and three-parameters equations were appraised, by analyzing the error functions associated to these models. In this study, the most adequate model to describe the isotherm data was considered as the one with higher value of r^2 and R^2_{adj} and lower values of other error functions considered (SSE, SAE, ARE, MPSD, σ and $\chi2$), indicated in Tables 4 to 6 with bold and italic number formatting. According to these criteria, is possible to verify that the three parameters models are the ones that better describe the sorbents affinity towards lead in aqueous solution (Table 4 to 6), independently of the sorbent type. In fact, for CES, ES and CWES, Figures 2 b), d) and f) present an overlay for Langmuir-Freundlich and Toth models curves, although for CES and ES the Langmuir-Freundlich sorption model is more adequate, while the Toth model is for suitable for CWES.

It is also important to highlight that selection of one sorption model is better achieved when combining several errors function, instead of basing the selection in only one error function. Nevertheless for the sorbents studied, only MPSD and R^2_{adj} error functions indicated the Langmuir model (two-parameter equation) as more adequate.

Table 4 – Isotherm parameters and fitting error values for lead (II) adsorption onto CES using two and parameters models.

Model type	Model Parameters	Error functions							
		SSE	SAE	ARE	MPSD	σ	χ2	R^2_{Adj}	r^2
Langmuir $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m=23.50 mg g^{-1} K_L=0.207 L mg^{-1}	3.55	3.96	2.77	**4.08**	84.2	0.154	**0.971**	0.977
Langmuir linear parameters $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m=24.35 mg g^{-1} K_L=0.055 L mg^{-1}	48.3	12.1	4.57	8.38	311	0.738	0.602	0.681
Freundlich $q_e = K_F C_e^{1/n_F}$	K_F=11.17 (L mg^{-1})$^{8.6}$ n_F=8.6	33.90	10.7	5.47	10.6	260	1.25	0.720	0.776
Freundlich linear parameters $q_e = K_F C_e^{1/n_F}$	K_F=9.21 (L mg^{-1})$^{6.7}$ n_F=6.7	40.79	12.0	7.66	13.6	286	2.07	0.663	0.731
Lagmuir-Freundlich $q_e = \frac{q_m K_{LF} C_e^{1/n_F}}{1+K_{LF} C_e^{1/n_F}}$	q_m=23.21 mg g^{-1} K_{LF}=0.145 (L mg^{-1})$^{0.78}$ n_F=0.78	**3.22**	**3.20**	**2.29**	4.44	**80.2**	**0.139**	0.965	**0.979**
Toth $q_e = \frac{K_T C_e}{\left(A_T+C_e^{Ta}\right)^{1/Ta}}$	K_T=23.20 L mg^{-1} A_T=11.98 (mg L^{-1})$^{1.4}$ T_a=1.4	3.24	3.20	2.29	4.45	80.4	0.140	0.964	**0.979**

Table 5 – Isotherm parameters and fitting error values for lead (II) adsorption onto ES using two and three parameters models.

Model type	Model Parameters	Error functions							
		SSE	SAE	ARE	MPSD	σ	χ2	R^2_{Adj}	r^2
Langmuir $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m=15.91 mg g^{-1} K_L=0.801 L mg^{-1}	5.81	5.32	4.86	7.35	98.4	0.368	0.814	0.845
Langmuir linear parameters $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m= 16.47 mg g^{-1} K_L=0.199 L mg^{-1}	31.0	8.58	3.22	5.88	227	0.228	0.006	0.172
Freundlich $q_e = K_F C_e^{1/n_F}$	K_F=9.899 (L mg^{-1})$^{12.8}$ n_F=12.8	3.18	3.60	2.63	4.54	72.8	0.175	0.898	0.915
Freundlich linear parameters $q_e = K_F C_e^{1/n_F}$	K_F=9.58 (L mg^{-1})$^{11.9}$ n_F=11.9	3.34	3.65	2.96	4.90	74.6	0.199	0.893	0.911
Lagmuir-Freundlich $q_e = \frac{q_m K_{LF} C_e^{1/n_F}}{1+K_{LF} C_e^{1/n_F}}$	q_m=19.23 mg g^{-1} K_{LF}=0.845 (L mg^{-1})$^{3.4}$ n_F= 3.4	**1.56**	**2.37**	**2.07**	**3.87**	**50.9**	**0.0988**	**0.938**	**0.958**
Toth $q_e = \frac{K_T C_e}{\left(A_T+C_e^{Ta}\right)^{1/Ta}}$	K_T=19.94 L mg^{-1} A_T=0.21 (mg L^{-1})$^{0.23}$ T_a=0.23	1.60	2.40	2.10	3.92	51.6	0.101	0.936	0.957

Table 6 – Isotherm parameters and fitting error values for lead (II) adsorption onto CWES using two and three parameters models.

Model type	Model Parameters	Error functions							
		SSE	SAE	ARE	MPSD	σ	$\chi2$	R^2_{Adj}	r^2
Langmuir $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m= 73.94 mg g^{-1} K_L= 0.098 L mg^{-1}	121	25.3	4.93	***6.92***	416	1.78	0.974	0.977
Langmuir linear parameters $q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	q_m= 78.42 mg g^{-1} K_L=0.038 L mg^{-1}	553	43.5	13.0	25.2	889	24.0	0.880	0.897
Freundlich $q_e = K_F C_e^{1/n_F}$	K_F= 28.49 (L mg^{-1})$^{7.0}$ n_F= 7.0	131	25.3	6.80	12.3	433	2.79	0.971	0.976
Freundlich linear parameters $q_e = K_F C_e^{1/n_F}$	K_F= 26.14 (L mg^{-1})$^{6.4}$ n_F= 6.4	147	27.5	6.89	10.9	459	2.88	0.968	0.973
Lagmuir-Freundlich $q_e = \frac{q_m K_{LF} C_e^{1/n_F}}{1+K_{LF} C_e^{1/n_F}}$	q_m= 86.81 mg g^{-1} K_{LF}= (0.244 L mg^{-1})$^{2.1}$ n_F= 2.1	48.1	15.1	4.03	7.56	262	1.11	0.987	0.991
Toth $q_e = \frac{K_T C_e}{\left(A_T + c_e^{Ta}\right)^{1/Ta}}$	K_T=89.45 L mg^{-1} A_T=1.021 (mg L^{-1})$^{0.39}$ T_a=0.39	***44.9***	***14.9***	***3.92***	7.19	***254***	***1.03***	***0.988***	***0.992***

Conclusion

In this study, a mature compost (CES), obtained by composting a mixture of industrial eggshell with other organic materials, was tested as a low cost sorbent for Pb (II) removal from liquid solutions. The efficiency of removal of CES was compared with natural industrial eggshell (ES) and mature compost without eggshell (CWES). The results showed that 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.

Initial metal concentration in liquid solutions strongly affected the sorbents capacity, though CWES was more robust to that 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, being the non-linear one more adequate.

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

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