Praise Worthy Prize

Development of Heavy Metal Sorption Isotherm
Using Fractional Calculus

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Abstract – *Lead is a heavy metal effluent pollutant, which can be generated by different chemical plants. Literature reports different approaches for lead removal, however, great attention has been given to water hyacinths. Mathematical modeling of heavy metal sorption represents an important tool for in-depth process studies. This work proposes a new approach for modeling heavy metal isotherm sorption by using fractional calculus formalism. A novel isotherm based on Mittag-Leffler function is developed for lead sorption experimental data equilibrium modeling, in order to provide more accurate equilibrium information for sorption dynamic modeling. Experimental data were obtained using Eicchorniacrassipes as the hyacinth. Simulation results were compared to classical equilibrium sorption models. It was shown that the proposed isotherm, Epslon, provides better results when compared to classical models.* **Copyright © 2011 Praise Worthy Prize S.r.l. - All rights reserved.**

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Nomenclature

C_e	Heavy metal concentration in fluid phase in equilibrium	[mg/L]
C_{e_norm}	Normalized heavy metal concentration in fluid phase in equilibrium	[dimensionless]
$E_{\alpha,\beta}(z)$	Mittag-Leffler function	
k_1	Isotherm parameter	
k_2	Isotherm parameter	
k_3	Isotherm parameter	
p	Dummy variable	
q	Heavy metal concentration in solid phase in equilibrium	[mg/g]
q_norm	Heavy metal concentration in solid phase in equilibrium	[dimensionless]
R^2	Coefficient of determination	
r	Mass of wet water hyacinth in grams per volume of contaminated solution in liters	[g/L]
X_{MAX}	Highest value of the set to be normalized	
X_{MIN}	Lowest value of the set to be normalized	
X_{NORM}	Normalized variable	
X	Variable	
y	Dummy variable	
z	Dummy variable	

Greek symbols

α	Dummy variable
β	Dummy variable
ε	Epslon function
Γ	Gamma function

I. Introduction

Lead is widely recognized as being hazardous to human health and an environmental aggressive heavy metal, which can be continuously generated by different chemical plants, for example, in the battery industry [1]. Literature reports different approaches for lead removal, such as chemical precipitation [2], ion exchange [3], electrochemical [4]. On the other hand, the use water hyacinths represents an environmental friendly and sustainable approach [5] for lead removal as they can be used either *in natura* or as a dried and processed biomass.

The availability of mathematical models represents an important tool for in-depth process studies, optimization and control. Heavy metal sorption modeling usuallyconsists of two steps. The first step is related to equilibrium isotherm modeling, which represents an important way towards the establishment of equilibrium conditions.

The most common approach used for this task consists on the use of classical models [6], such as Langmuir, Freundlich, Redlich-Peterson, among others, followed by proper parameter estimation and model discrimination analysis. The second step deals with the study and description of the dynamic behavior of the sorption process, which can be conducted either in batch, semi-

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batch or continuous mode. The dynamic behavior can be modeled by different approaches. Literature reports, for example, the use of reaction rate curves[7], mass transfer approach [8], among others [6], which are again followed by proper parameter estimation and model discrimination analysis.

Fractional calculus represents a novel approach and a growing research field for process modeling, being based on derivates of arbitrary order [9]. Literature reports different applications, for example in systems engineering [10], diffusion processes [11], heat transfer [12], among others [13].

This manuscript presents the use of a new approach for modeling heavy metal isotherm sorption by using fractional calculus formalism. A novel isotherm model, based on Mittag-Leffler[9] function, is proposed for lead sorption experimental data equilibrium modeling, in order to provide an alternative tool for heavy metal sorption modeling.

II. Methodology

II.1. Experimental

Synthetic lead effluent was prepared by using $Pb(NO_3)_2$, supplied by ECIBRA (Brazil) and used as received. *Eicchorniacrassipes* hyacinths were collected in lakes in the neighborhood of Maringá, Brazil, and used for lead sorption.

Experimental runs were carried out in plastic buckets of 20L placed in a greenhouse. For different hyacinth concentrations, r, five different initial lead concentrations (10 mg/L; 15 mg/L; 30 mg/L; 60 mg/L; 120 mg/L) were used in order to establish sufficient experimental data for isotherm calculation. Samples of water were periodically taken and, after specific treatment, analyzed by atomic absorption spectroscopy (SPECTR AA 10 PLUS, Varian).

Further details regarding experimental procedures can be found elsewhere [1].

II.2. Modeling

Table I presents classical models, which are commonly used for isotherm sorption description. However, in some scenarios, these models may not be able to successfully describe the equilibrium behavior,for example, when porous and non-uniform structures, i.e. fractal structures, are used as the solid phase of the sorption process.

This possibly happens due to the key role played by memory effects [14]. Towards this, one can notice that Redlich-Peterson model have features of both Langmuir and Freundlich, improving experimental data fitting and modeling.

Literature [6] also reports other different isotherm models which turn out to be modifications of classical models by adding other fitting parameters.

TABLE I
EQUILIBRIUM SORPTION ISOTHERM

Langmuir	Freundlich	Redlich-Peterson
$q = \dfrac{k_1 \cdot C_e}{1 + k_2 \cdot C_e}$	$q = k_1 \cdot (C_e)^{k_2}$	$q = \dfrac{k_1 \cdot C_e}{1 + k_2 \cdot (C_e)^{k_3}}$

According to reported extensive amount of experimental results on equilibrium systems regarding heavy metals, for lower concentrations of heavy metal in the fluid phase the equilibrium concentration in the solid phase may considerably change for a change in the concentration of the fluid phase. However, for higher concentrations in the fluid phase, this change may not be significantly enough. When carefully analyzed, these features resemble a somewhat exponential behavior. It is also interesting to note that this behavior may arise fromfirst order differential equations. Consequently, an exponential model for heavy metal sorption isotherm, as (1) may explain some experimental results:

$$k_1 \cdot \frac{dq}{dC_e} + k_2 \cdot q = 1 \qquad q(C_e = 0) = 0$$

$$q = \left(\frac{1}{k_2}\right) \cdot \left(1 - e^{-(k_2/k_1) \cdot C_e}\right) \tag{1}$$

Therefore, a natural generalization of (1) can provide better results. In this context, fractional calculus has powerful tools, for example, the Mittag-Leffler function [9]. Consequently, a novel isotherm, named Epslon [15], can be obtained after generalization, yielding (2):

$$k_1 \cdot \frac{d^{k_3} q}{dC_e^{k_3}} + k_2 \cdot q = 1 \qquad q(C_e = 0) = 0$$

$$q = \left(\frac{1}{k_1}\right) \cdot \varepsilon_0 \left(C_e, \frac{-k_2}{k_1}; k_3, k_3 + 1\right) \tag{2}$$

where:

$$\varepsilon_0(p, y; \alpha, \beta) = p^{\beta-1} \cdot E_{\alpha,\beta}\left(y \cdot p^\alpha\right)$$

Mittag-Leffler function: $E_{\alpha,\beta}(z) = \sum_{j=0}^{\infty} \dfrac{z^j}{\Gamma(\alpha \cdot j + \beta)}$

It is important to note that by considering k_3 equal to 1,(2) reestablishes (1). On the other hand, the most important aspect of (2) is parameters k_3, which, according to its values turns Mittag-Leffler function into a different mathematical function [15].

Before performing parameter estimation, experimental data were normalized, by using (3), in order to avoid numerical convergence problems. Parameter estimation tasks used minimum least squares as objective function and algorithms already used for fractional identification[10]:

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$$X_{NORM} = \frac{x - x_{MIN}}{x_{MAX} - x_{MIN}} \qquad (3)$$

III.   Results & Discussions

Experimental data obtained from two different hyacinths concentrations r=10g/L and r=20g/L were used for validation of the proposed isotherm model. The original and normalized data used for parameter estimation are presented in Table II.

TABLE II
EXPERIMENTAL DATA USED FOR PARAMETER ESTIMATION

r = 10 g/L					
C_e– [mg/L]	0.74	3.75	18.05	45.5	105
q– [g/mg]	12.44	14.04	15.59	20.24	18.37
Ce_norm	0	0.02887	0.1660	0.4293	1
q_norm	0	0.2698	0.5312	1.3154	1
r = 20 g/L					
C_e– [mg/L]	0.49	0.61	4.31	30	87.8
q– [g/mg]	5.89	9.09	16.22	19.15	20.33
Ce_norm	0	0.001374	0.04375	0.3379	1
q_norm	0	0.2216	0.7154	0.9183	1

Table III presents the parameter estimation results for each isotherm. From these results one can observe that Epslon isotherm model provides better results, specially for the case of r=20g/L, when compared to the other models. Comparison of Epslon model to Lagmuir and Freundlich is not as reasonable as it seems to be as Epslonisotherm contains three parameters while the others contain two. Even though, Epslon presented better coefficient of determination (R^2) values and lower value of the objective function for both study cases, as might be expected. A much reasonable comparison is stated between Epslon and Redlich-Peterson models, as they present the same number of parameters.

It can be seen from Table III that for both cases studied, Epslon model presents much better results. This probably happened due to the fractional calculus based feature of Epslon model, which considers memory effects. This is an important aspect as the heavy metal sorption is a complex process and the hyacinth roots and cell membrane are a highly nonuniformmicroporous media. Finally, it is important to stress that parameter k_3 of Epslon model represents a somewhat fractional order of the equilibrium, which, in both cases is not integer, once more corroborating the hypothesis that memory effects play a key role in lead sorption.

Fig. 1 and Fig. 2 present the comparison between experimental lead concentration in the hyacinth and the model predictions of lead concentration in the hyacinth. For both cases studies, Epslon isotherm provides better prediction results. It can be concluded that Epslon isotherm represents an important alternative tool for isotherm modeling.

TABLE III
SUMMARY PARAMETER ESTIMATION

r = 10 g/L				
	Epslon	Redlich-Peterson	Langmuir	Freundlich
k_1	0.1508	3022.72	9.5137	1.1968
k_2	0.8503	2525.21	7.1845	0.3242
k_3	0.9509	0.6768	-------	------
R^2	0.88	0.79	0.86	0.79
Objective Function	0.14	0.24	0.16	0.23
r = 20 g/L				
	Epslon	Redlich-Peterson	Langmuir	Freundlich
k_1	0.1692	2861.57	117.044	1.0608
k_2	0.8840	2717.07	123.848	0.1764
k_3	0.4887	0.8358	-------	------
R^2	0.99	0.97	0.98	0.96
Objective Function	0.0014	0.023	0.018	0.029
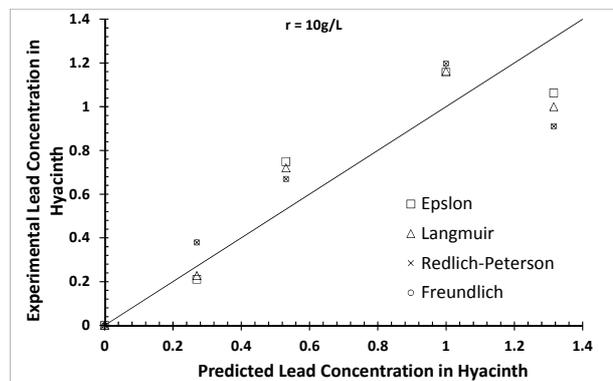
Fig. 1. Case r=10g/L – Normalized lead concentrationin Hyacinth: experimental versus predicted
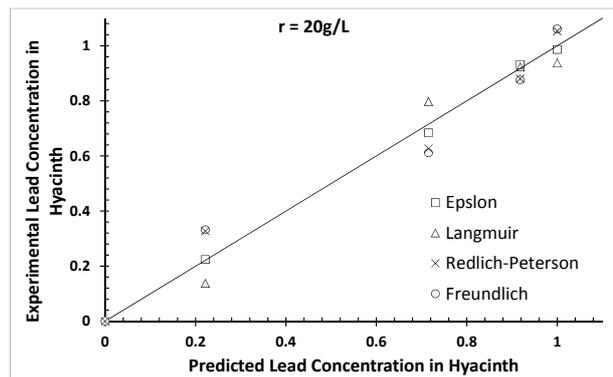
Fig. 2. Case r=20g/L – Normalized lead concentrationin Hyacinth: experimental versus predicted

In Fig. 3, experimental data and simulations results concerning normalized lead concentration in hyacinth are plotted against normalized lead concentration in water for case r=20g/L. Firstly, it can be observed the exponential-like behavior of the equilibrium concentrations. Secondly, although the behavior of all

isotherms looks similar, Epslon isotherm resembles much better experimental data, specially for high concentrations.
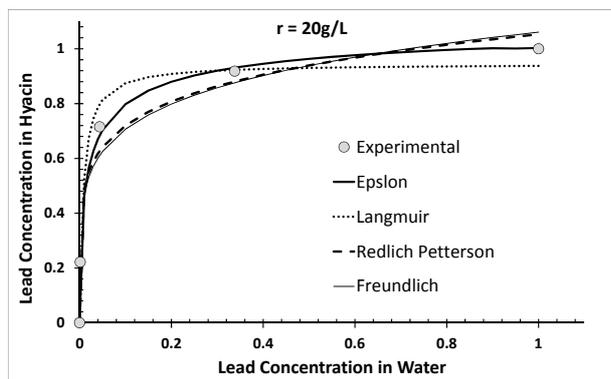
Fig. 3. Case r=20g/L – Normalized lead concentration: In Hyacinth versus in Water

IV. Conclusion

A new approach, based on fractional calculus, was proposed for equilibrium sorption isotherm modeling. This approach, which is based on exponential features of heavy metal sorption isotherms, was successfully used to model experimental data of lead sorption using water hyacins (*Eicchorniacrassipes*). Simulationswere performed in order to compare the proposed approach to to classical equilibrium sorption models. It was shown that the proposed isotherm, Epslon, provides better results when compared to classical models for the experimental conditions simulated. Consequently, Epslon isotherm can be used as an alternative tool for heavy metal sorption studies.

Acknowledgements

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