Asian Journal of Chemistry; Vol. 26, No. 23 (2014), 8093-8097

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17370

A New Empirical Model for Heavy Metals Biosorption

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Received: 12 February 2014; *Accepted*: 20 August 2014; *Published online*: 15 November 2014; AJC-16301

A new model based on an empirical approach is proposed to apply to the biosorption of heavy metals. This model is implemented for four sets of experimental data to study the effect of concentration of Cr(III), Cr(VI), Cd(II) and Zn(II) on the sorption capacity by *Arenga pinnata* fruit shell. Six conventional models namely, Langmuir, Freundlich, Sips, Toth, Redlich-Peterson and Khan have been used for the comparison of new model on the biosorption process. Coefficient determination of four consecutive data for the effect of concentration of Cr(III), Cr(VI), Cd(II) and Zn(II) calculated using Langmuir, Freundlich, Sips, Toth, Redlich-Peterson and Khanishoterm are 0.76629, 0.72368, 0.88256, 0.80818, 0.84782 and 0.31096, respectively. On the other hand, coefficient determination of a new model using a non-linear regression with Levenberg-Marquardt algorithmis 0.91792. This means that a new proposed model shows more better results compared with other conventional reference models.

Keywords: New emperical model, Non-linear regression, *Arenga pinnata*, Biosorption isotherm, Coefficient of determination.

INTRODUCTION

Heavy metals in the environment has receive special concern because of their potential toxicity to the environment and human life[1,2]. There are several methods for treatment of toxic metals such as chemical precipitation, ultra filtration, ion exchange and membrane process using geological material[3-6]. However, its use is limited due to its relatively high costs. This has led to the investigation of alternative technologies, which consider low cost beside their abilities as adsorption materials[1,7-9]. Method for absorption of heavy metal ions using biological material known as biosorption. This method is on average relatively low-cost and safer than conventional absorption method. Research on biosorption devided into three researchs focus, namely biosorption isothermic, kinetic and thermodynamic. The present studies focussed on biosorption isotherm method.

Biosorption isotherm is the method used to study the relationship between the amount of a substance with absorbed of biological material that acts as an absorbent material with pressure or concentration at equilibrium under a constant temperature. The researchers are trying to understand this relationship through several modeling approaches, namely the theoretical approach, the emperical approach and the semi-emperical approach.

Many studies have been focussed on biosorption isotherm models, ranging from single-component approach to the multicomponent approach[10-12]. There are models that have set out the theoretical basis on the assumption of the ideal conditions. On the other hand, there are also models that are based solely on empirical data approach and based on merging of these two approaches. Among others, some ishoterm models such as a Freundlich, Langmuir, Langmuir-Freundlich (Sips), Redlich-Peterson, Khan, Toth, Brunauer, Emmett and Teller (BET), modified Langmuir-Freundlich, Radke-Prausnitz, Dubinin-Radushkevich, Flory-Huggins and Temkin are the most popular to study the biosorption ishoterm.

Each model has advantages and disadvantages. Some models are fit on a particular type of the data but does not fit the other data types. It is not possible to create a model that can cover all the biosorption phenomenon, because the mechanism of biosorption is very complex. Therefore we need to search a new ishoterm model that can be used fo any types of biosorption data.

EXPERIMENTAL

Preparation and characteristics of *Arenga pinnata* fruit shell: *Arenga pinnata* fruit shell, a by product of sugar palm fruit was collected from central production of sugar palm in Batusangkar district of West Sumatra Province, Indonesia. All the material was prepared according to the procedure described by Zein *et al.*[13]. The eipicarp (shell) of sugar palm fruit was separated from the fruit and shell was extensively washed with doubly distilled water to remove dirt and sand and other particulate material from their surface. After that it was dried at room temperature. Dried fruit shells was cuted and ground in a pestle and mortar and make a powder, sieved with diameter of particles ≤ 250 µm. The biosorbent was stored on a bottle for use as a sorbent.

All reagents used were of analytical grade obtained from Merck (Darmstad, Germany. The apparatus used were screener Octagon 200 (Endcots, London, Englandinspect F50, FEI Co., USA), an analytical balance (AA-200 Denver Instrument Company), a sheker (Haake SWB 20), FTIR spectrocopy (model 460 plus, Jasco, Japan), scanning electron microscop (model 460 plus, Jasco, Japan) and atomic absorption spetrometer (AAS, Raylight WFX-320, BRAIC, China). Cr(III), Cr(VI), Cd(II) and Zn(II) working standard solution was prepared from 1000 mg L^{-1} stock standard solution.

Removal studies: Dried sugar palm fruit shell were shoaked with 0.1 mol L^{-1} nitric acid for about 4 h and then were filtered and finally washed with ultra pure water until neutral and dried at room temperature. Working standard solutions was prepared from a 1000 mg/L stock standard solution of Cr(III), Cr(VI), Cd(II) and Zn(II). All the concentration of metal ions during the experiment were measured by atomic absorption spectrophotometric method.

RESULTS AND DISCUSSION

Linear regression and non-linear regression to the model: Langmuir and Freundlich models are the two most widely used models because it can be linearized and only has two parameters that can be applied to a simple linear regression on both models. In general each model have more than two parameters that can not be estimated using linear regression, because of it, an alternative, non-linear regression should be used.

Linear regression method is a method based on a purely statistical method of least squares, making it easy to implement. Non-linear regression method is a method based on numerical algorithms, since it estimates the values of the parameters is done by first giving an initial estimate of the value of each parameter are then recursively repaired .

The main weaknesses of the non-linear regression estimation lies in the provision of initial value. If the initial estimate is not appropriate, then the regression will not work and will generate an error value. The simpler form of the model, the model is more tolerant to the value of the initial estimate, on the contrary, the model is more complex and more sensitive to the value of the initial estimate. For a suitable initial estimate, the regression will usually result in parameter values that give shape to the curve of the coefficient of determination better than linear regression. Non-linear regression algorithm used in the study is the Levenberg-Marquardt algorithm (LM). This algorithm is an optimization algorithm that is most widely used today.

Zein *et al.*[13], investigated the relationship between the concentration of metal ion absorption capacityusing Langmuir ishoterm models. Langmuir parameters for each set of data obtained through the use of linear regression. The results acquired can be seen in the Table-1.

The results shows the high scores for the coefficient of determination, which shows that the dynamics of the data according to the model of Langmuir. Unfortunately, the results obtained, which is the best result for the linearity of the Langmuir models are not the best result for the Langmuir model in their original form, as it turns out when the parameters obtained from Langmuir linearity applied to the model in the form of the original Langmuir, showed lower as shown in the Table-2.

Application of non-linear regression on the Langmuir isoterm model, generally provide better results, shown by the coefficient of determination higher than the results obtained from the linear regression if the data and the model are plotted in its original form. Fig. 1 shows the visualization difference in the results of linear and non-linear regression.

New model proposed: Based on empirical approaches, this research proposed a new isotherm model called as EMZHA (Edison, Mimi, Zulfi and Hermansyah approach) model that is formulated in the form of equation as following:

$$q_e = \left(\frac{\alpha\beta C_e^{1/n}}{1+\alpha C_e}\right) e^{-(\delta+\beta C_e^{1/n})} \quad (1)$$

where α, β, δ and n are parameters of model.

This model was implemented in the four sets of experimental data to study the effect of concentration on the sorption capacity of the *Arenga pinnata* fruit shell, against metal ions

TABLE-1
COEFFICIENT OF DETERMINATION OF LANGMUIR MODEL IN LINEAR FORM

Effect of metal ion concentration	Langmuir parameter		Coefficient Determination
	q_m	B	R_L^2
Cr (III)	1.06	0.0218	0.983
Cr (VI)	7.81	0.0721	0.972
Cd (II)	-0.15	-0.0011	0.906
Zn (II)	-1.3	-0.0711	0.907

TABLE-2
DIFFERENCE IN THE COEFFICIENT OF DETERMINATION OF LINEAR FORM AND ORIGINAL FORM

Metal ion	Langmuir plarameter		Coefficient Determination	
	q_m	b	Linear form (R_L^2)	Original form (R^2)
Cr(III)	1.06	0.0218	0.983	0.641
Cr(VI)	7.81	0.0721	0.972	0.804
Cd(II)	-0.15	-0.0011	0.906	-1.168
Zn(II)	-1.3	-0.0711	0.907	-148.5

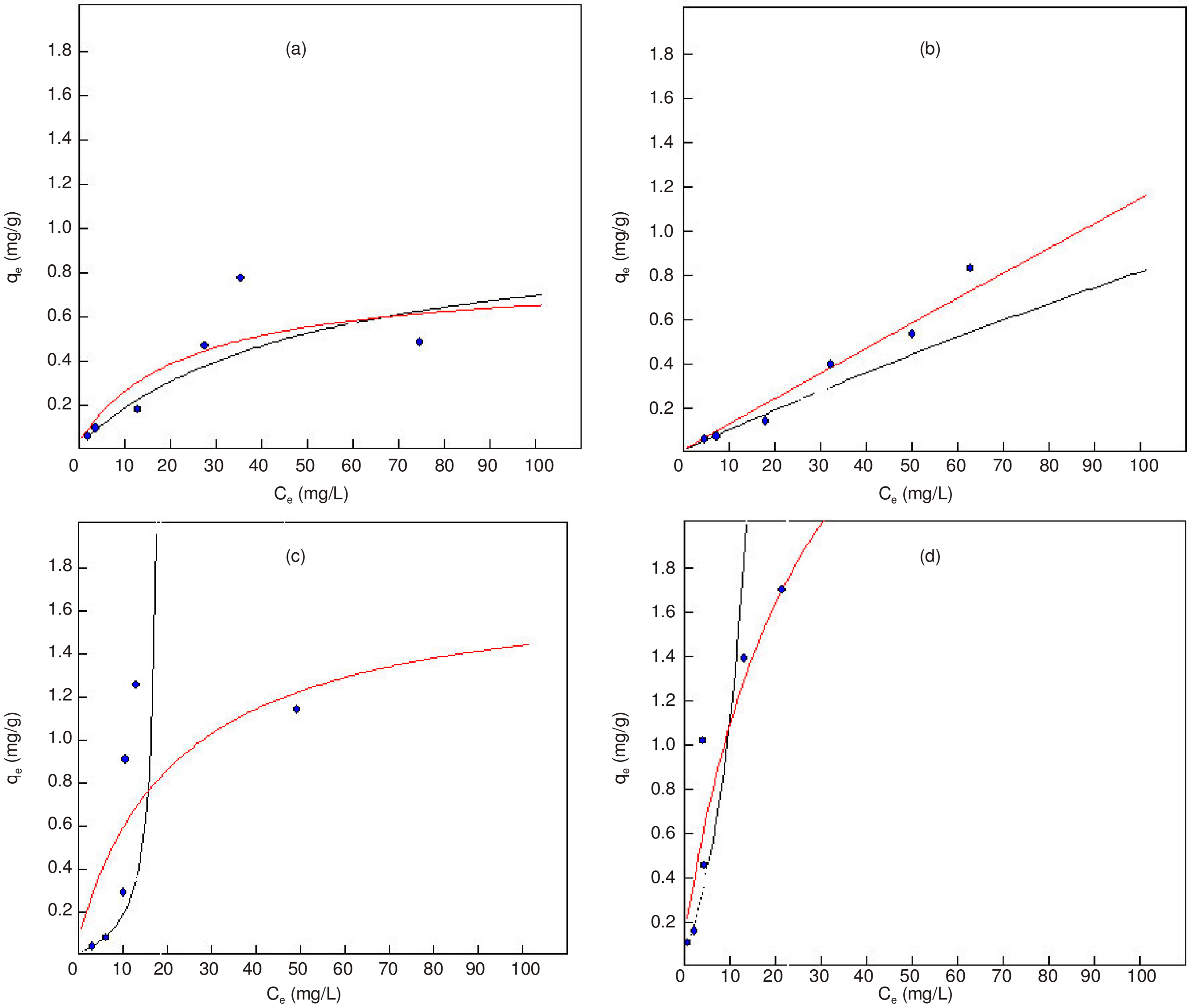

Fig. 1. Langmuir curve by linear regression (black) and non-linear regression (red)

Cr(III), Cr(VI), Cd(II) and Zn(II) at concentration 5; 10; 25; 50; 75 and 100 mg /L.

Implementation of the new models to experimental data

Effect of concentration of Cr(III): Implementation of new model and six other popular models (Langmuir, Freundlich, Sips, Toth, Redlich-Peterson and Khan) as reference to experiments that studied the effect of concentration on the absorption ability of the fruit skin *Arenga pinnata* against metal ion Cr(III) is shown in the Fig. 2. The parameters and coefficients of determination obtained through non-linear regression approach (Levenberg and Marquardt algorithm). In this experiment, Redlich-Peterson model has the highest coefficient of 0.89922 and a new model in the second with a coefficient of determination 0.89531.

Effect of concentration of Cr(VI): Implementation of new model and six other models as reference to experiments that studied the effect of concentration on the absorption ability of the fruit skin *Arenga pinnata* against Cr(VI) can be seen in the Fig. 3. In this experiment, Sips model have the highest coefficient of 0.98305, followed Redlich-Peterson model with a coefficient of determination 0.97994. The new model was fourth with a coefficient of determination 0.97602.

Effect of concentration of Cd(II): Implementation of new model and six other models as reference to experiments that studied the effect of concentration on the absorption ability of the fruit skin *Arenga pinnata* against Cd(II) can be seen in the Fig. 4. In these experiment, the new model has the highest coefficient of 0.90755 and Sip models in the second with a coefficient of determination 0.83266.

Effect of concentration of Zn(II): Implementation of new model and six other models as reference to experiments that studied the effect of concentration on the absorption ability of the fruit skin *Arenga pinnata*against metal ion Zn(II). In these experiments, the new model has the highest coefficient of 0.89279 and sips model in the second with a coefficient of determination 0.89214.

Average value of the coefficient of determination: The average value of the coefficient of determination for all four models were applied to the experimental data. The new model has the highest average score, outperformed all of the reference model.

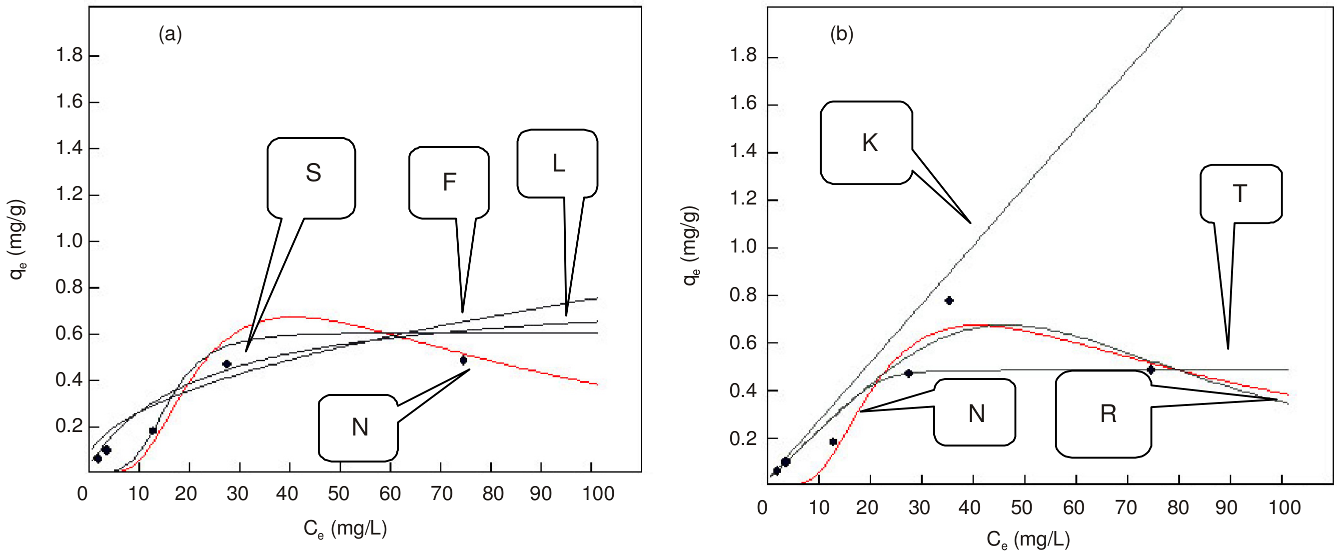

Fig. 2. Visualization effect of concentration of Cr(III) according to the new model and six reference models. (N = New model, L = Langmuir, F = Freundlich, S = Sips, R = Redlich-Peterson, T = Toth, K = Khan)

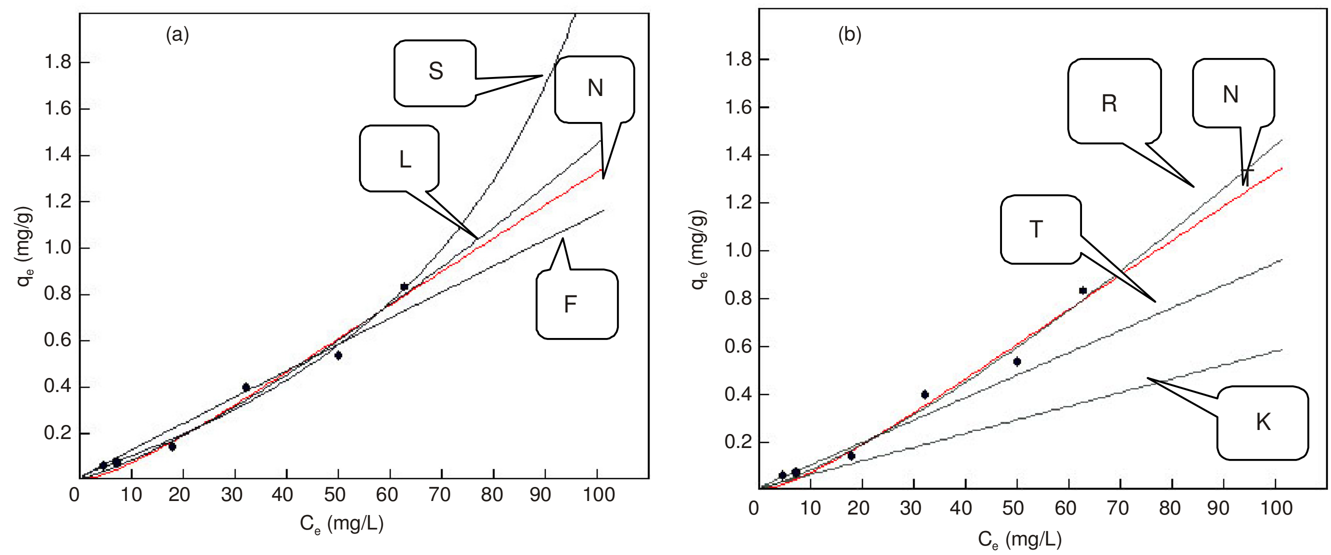

Fig. 3. Visualization effect of concentration of Cr(VI) according to the new model and six reference models. (N = New model, L = Langmuir, F = Freundlich, S = Sips, R = Redlich-Peterson, T = Toth, K = Khan)

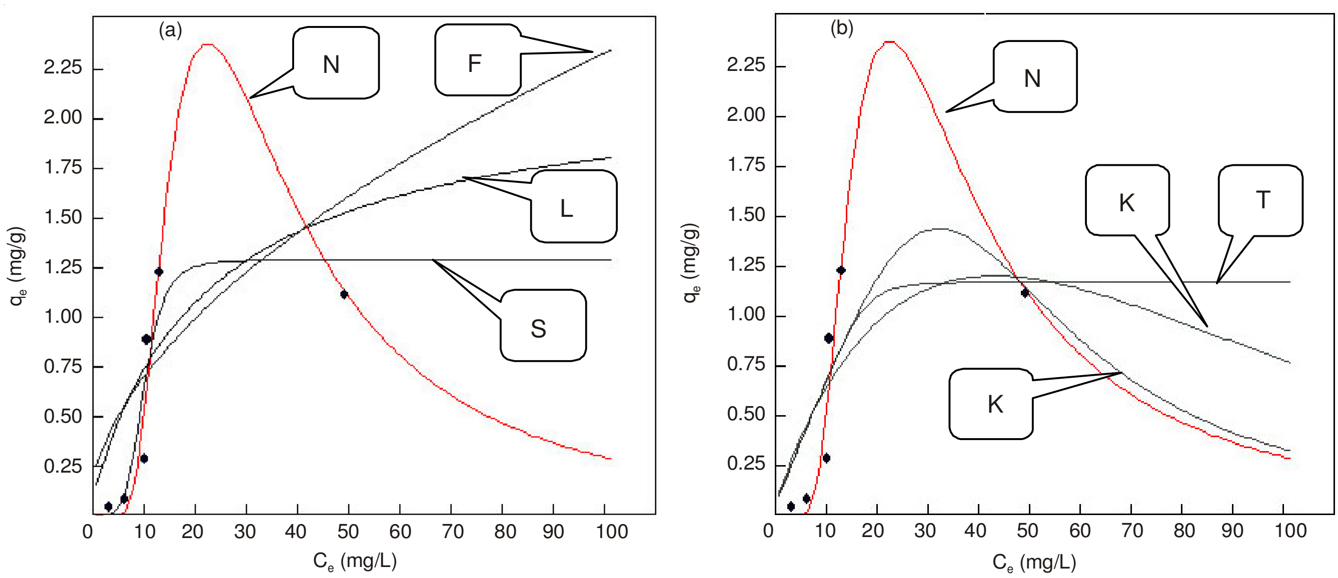

Fig. 4. Visualization effect of concentration of Cd(II) according to the new model and six reference models. (N = New model, L = Langmuir, F = Freundlich, S = Sips, R = Redlich-Peterson, T = Toth, K = Khan)

Conclusion

Generally, application of non-linear regression on the Langmuir isoterm model provide better results, shown by the coefficient of determination higher than the results obtained from the linear regression if the data and the model are plotted in its original form.

The proposed new model, when applied to the four sets of experimental data to study the effect of concentration on the absorption ability of the fruit skin *Arenga pinnata* against Cr(III), Cr(VI), Cd(II) and Zn(II), gave satisfactory results. It can be seen from results that the model's ability to fit the four sets of experimental data. Using non-linear regression (Levenberg-Marquardt algorithm) obtained coefficients of determination for the fourth consecutive data set is 0.89531; 0.97602; 0.90755 and 0.89279 for the effect of ion concentration of Cr(III), Cr(VI), Cd(II) and Zn(II), respectively.

For the fourth set of experimental data above, the new model shows an advantages compared to the reference models, as shown by the fact that the new model has an average value of the highest coefficient of determination, which is 0.91792.

ACKNOWLEDGEMENTS

The authors thank Dean of Faculty of Mathematics and Natural Sciences for the grant offer (Contract No. : 009/UN.16.03.D/PG/2013, September 17, 2013).

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