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AN ERROR ANALYSIS ON THE NONLINEAR BIOSORPTION KINETIC MODELS OF BIOWASTE ADSORBENT IN AN AQUEOUS SOLUTION

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Abstract. The adsorption kinetic experimental data were utilized to capture the intricate relationships behind the mechanism involving the biosorptive capability of a biowaste material to remove toxic substances from an aqueous solution using batch adsorption under specified experimental conditions. Several nonlinear models, such as the pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion, and MacArthur-Wilson were compared. The model parameters were estimated using the Gauss-Newton iterative method of nonlinear regression analysis. Results showed that the removal uptake increases with an increase in adsorbent dose and longer contact time. Removal uptake reflects a relatively slow initial and terminal increase rates against contact time with an overall kinetic process behaving under a pseudo-second order equation. Elovich model suggests higher initial adsorption rate, extent of surface coverage, and activation energy are favored at a lower adsorbent dose, while the intraparticle diffusion is noted to be relatively faster at a higher adsorbent dose. Analysis of the differential forms and the second degree derivatives of the Elovich and MacArthur-Wilson models revealed that it is negative over the entire range of contact time. Error analysis supports that intraparticle diffusion, Elovich, and McArthur-Wilson are possible nonlinear models which can optimally describe the nonlinear behavior of the kinetic processes presented in this study.

Keywords: nonlinear kinetic models; pseudo-first order; pseudo-second order; Elovich; intraparticle diffusion; MacArthur-Wilson; error analysis.

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Introduction

Biosorption is a physico-chemical process which makes use of biological materials to adsorb pollutants from aqueous solutions [3]. When dyes such as congo red enter the water systems, they can cause pollution, consequently harming humans and aquatic organisms [15]. Currently, activated carbon is one effective yet expensive biosorbent used in treating groundwater and industrial wastes as compared to conventional physical and chemical methods, thus biosorption studies are looking for easier and less costly treatment, often making use of agricultural wastes as bioadsorbents [10]. One reason that makes biosorption a potential alternative to the current commercial methods is the abundance of biomass [8].

Biosorption kinetics involve several factors, such as contact time, pH, temperature, adsorbent dose, ionic strength, and initial concentration. However, through circumspect and methodical observation, it has been determined that there exists an intricate and complex functional relationship linking one factor to another, and the biosorption rate is predicted using the values of these factors. Diverse agricultural wastes have been carefully examined by many experimental scientists over a number of observations on their potential to remove toxic substances in aqueous solutions, and they derived empirical relations among these variables using classic principles. It is now realized by many scientists and engineers that because of the intrinsically complex kinetic nature of biosorption, an adsorbent cannot be rigorously described by any overly simplified kinetic model at least within the range of ideal conditions where the assumptions hold.

In this paper, to capture the intrinsically complex kinetic behavior of adsorbents under specified conditions, nonstandard and non-ideal functional relationship among the kinetic factors, particularly the contact time and the adsorbent dose will be developed using a class of nonlinear models namely, the pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion, and MacArthur-Wilson models. Nonlinear models, in general, are more difficult to specify, identify, and estimate than linear models, and nonlinear iterative processes are involved in determining the solution [14]. Gauss-Newton, as one of the iterative methods employed in classic nonlinear regression analysis, was considered in estimating the parameters of nonlinear models in this study. The adequacy and sufficiency of the various models were individually assessed.

Most thermodynamic properties of some bioadsorbents are not always readily available to engineers and scientists, and sometimes only experimental values of these factors are reported. Hence, there is a need to consider inaccurate, imprecise, and unrealistic interpolation and graduation of the available data. Thus, if these adsorption kinetic models of any bioadsorbent can be modelled using the proposed nonlinear models, researchers will have more realistic and reliable choices, as to which appropriate model to use for a given experimental data. Certain set of criteria will be imposed in the selection of "best" model that fits the experimental data. Likewise, nonlinear regression will be used to estimate the parameters needed in the model so as to avoid the unrealistic procedure of linearizing the model in making parameter estimates.

Currently, no biosorption studies have been conducted for calamansi (*Citrus microcarpa*) peels, although there have been for orange peels, which belong to the same family [1]. Finding potential uses for these discarded peelings may reduce waste and pollution. Hence, this study explores on unripe calamansi peels if it can adsorb significant amount of congo red at different adsorbent dose and under varying contact times using spectrophotometry. In particular, comparison on the percent removal of congo red from the aqueous solution using calamansi peels under constant pH, dye concentration, and temperature will be made. Only unripe calamansi peels as adsorbent with congo red as the adsorbate were used in this study. Further, factors such as the dye concentration, pH, and temperature were kept constant at 0.1 g/L, 4.00, and room temperature (27^{o}C), respectively. The bioadsorptive properties of calamansi peels were measured across different contact times, namely 10, 20, 30, 40, 50, and 60 minutes under two adsorbent doses of 0.25 grams and 0.50 grams.

We have to note that the parameter estimates obtained will vary over different nonlinear models and applicable for a specific biosorption kinetic property being modeled. This suggests that a new set of parameters has to be determined for another bioadsorbent in specified experimental conditions.

Methodology

The biosorption kinetic relationship between contact time and the amount of dye removed in an aqueous solution depicts a chaotic nonlinear interacting relationship. A nonlinear model was required reflecting an increase in the amount of dye adsorbed with an increase in contact time, and a levelling of the increase in the amount of dye adsorbed at some contact time value. This phenomenon can be captured using nonlinear models. The effect of contact time on the adsorption of dye revealed that uptake is rapid in the beginning and then becomes constant. The adsorption curves are single, smooth, and continuous leading to saturation and indicate the possible monolayer coverage on the surface of adsorbents by the dye molecules [9]. Further, since the adsorption capacity can be described using these mathematical models, predictive capability can be established on the removal of hazardous wastes as a function of contact time.

The Nonlinear Kinetic Models

1. The Pseudo-First Order Kinetic Model

The pseudo-first order kinetic model [7] is defined as

$$\frac{da_t}{dt} = c_1(a_e - a_t), \tag{1}$$

where a_t (mg g^{-1}) is the amount of dye adsorbed at time t, a_e (mg g^{-1}) is the adsorption capacity at equilibrium, c_1 (min^{-1}) is the pseudo-first order rate constant, and t is the contact time (min). The general solution to this pseudo-first order model is described as

$$\log(a_e - a_t) = \log(a_e) - \frac{c_1}{2.303}\, t. \tag{2}$$

2. The Pseudo-Second Order Kinetic Model

The pseudo-second order kinetic model [4] is given as

$$\frac{da_t}{dt} = c_2(a_e - a_t)^2, \tag{3}$$

where a_t (mg g^{-1}) is the amount of dye adsorbed at time t, a_e (mg g^{-1}) is the adsorption capacity at equilibrium, c_2 (g mg^{-1} min^{-1}) is the pseudo-second order rate constant, and t is the contact time (min). The general solution to this second order differential equation is defined as

$$\frac{t}{a_t} = \frac{1}{c_2(a_e)^2} + \frac{1}{a_e}\, t. \tag{4}$$

3. The Elovich Model

The Elovich model [2] is defined as

$$\frac{da_t}{dt} = \alpha e^{-\beta a_t} \, . \tag{5}$$

The solution to this differential equation describes the activated chemisorptions [12] and is given as

$$a_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t. \tag{6}$$

where a_t (mg g^{-1}) is the amount of dye adsorbed at time t, α (mg g^{-1} min^{-1}) is defined as the initial adsorption rate, β (g mg^{-1}) is the extent of surface coverage and activation energy for chemisorption, and t is the contact time (min).

4. The MacArthur-Wilson Model

The MacArthur-Wilson model [11] is a two-parameter negative exponential model which takes the form

$$a_{t_i} = \beta_o\left(1 - e^{-\beta_1 t_i}\right) + \in_i, \tag{7}$$

where a_{t_i} (mg g^{-1}) is the amount of dye adsorbed at time t_i, β_o (mg g^{-1}) is a parameter defined as the asymptote or potential maximum, β_1 (min^{-1}) is defined as the rate at which the response variable approaches its potential maximum, t is the contact time (min), and $\in_i$ (mg g^{-1}) is the random error term. The linearized form of (7) is defined as

$$\ln\left(1 - \frac{a_t}{\beta_o}\right) = -\beta_1 t. \tag{8}$$

5. Intraparticle Diffusion Model

Another functional relationship identified to some adsorption processes is that the uptake varies almost proportionally with $t^{\frac{1}{2}}$ rather than with the contact time, t. The Weber-Morris plot allows to examine the relationship between a_t versus $t^{\frac{1}{2}}$ [16] using the equation

$$a_t = k_{id}\, t^{\frac{1}{2}} + C, \tag{9}$$

where a_t (mg g^{-1}) is the amount of dye adsorbed at time t, k_{id} is the intraparticle diffusion rate constant. The intercept, C, represents the thickness of boundary layer, a larger intercept suggests a greater boundary layer effect because of the instantaneous utilization of the readily available adsorbing sites on the adsorbent surfaces [5].

The Gauss-Newton Method

The NLIN (nonlinear regression) procedure of SAS was used to fit the models and estimate the parameters. In software computing algorithms such as SAS, in finding the least squares estimator in a nonlinear model, one of the most often methods used is the Gauss-Newton procedure. This method is iterative and requires starting value estimates for the parameters [11]. Inference on the coefficients using this method is based on the asymptotic variance-covariance matrix of the regression coefficients. Convergence of the parameter estimates depends on the specified initial values. Poor starting points can result the procedure to move in an undesired direction, and so convergence is never met. Hence, transformation of a nonlinear model to a linear form in estimating the parameters by linear regression is a possible solution and was employed in this study, and values obtained were taken as initial estimates.

Error Analysis

As a result of the parameter estimation procedure in the nonlinear models, three different error functions of nonlinear regression were utilized to determine the best-fit biosorption kinetic model to the experimental data.

1. Sum of Squares of the Errors (SSE)

The most commonly employed error function is SSE [13], and is defined as

$$\mathrm{SSE} = \sum_{i=1}^{n} \left(a_{e,pred} - a_{e,obs}\right)_i^2 , \tag{10}$$

where $a_{e,pred}$ and $a_{e,obs}$ are the predicted and the observed values of the adsorbate solid concentration in the solid phase (mg g^{-1}) at equilibrium, and n is the number of observations.

2. Sum of the Absolute Errors (SAE)

Parameter estimates employing the SAE describe a better fit as the value of the errors increases as it favors the fit towards the high-concentration observations [13]. The expression for SAE is defined as

$$\mathrm{SAE} = \sum_{i=1}^{n} \left|a_{e,pred} - a_{e,obs}\right|_i . \tag{11}$$

3. Average Relative Error (ARE)

This error function minimizes the fractional error distribution across the entire range of observations [6], and is computed using the expression

$$\mathrm{ARE} = \frac{100}{n} \sum_{i=1}^{n} \left|\frac{a_{e,pred} - a_{e,obs}}{a_{e,obs}}\right|_i . \tag{12}$$

Results and Discussion

The effect of contact time on the removal uptake of dye using different adsorbent doses is illustrated in Figure 1. The uptake of the dye is noted to be rapid from the start then gradually remains constant. Apparently, the adsorption curves are smooth, single, and continuous as they approach their respective saturations which possibly explains the monolayer coverage on the surface of adsorbent by the dye molecules. The equilibrium time were identified to be 50 and 30 minutes for 0.5 g and 0.25 g adsorbent dose, respectively. Further, the effect of adsorbent dose is also depicted in Figure 1, the amount adsorbed increases up to a certain threshold and then remains almost unchanged. An increase in the dose from 0.25 g to 0.5 g, the amount of dye adsorbed increases from 34-40%. The increase in adsorption with adsorbent dose explains the increased adsorbent surface area and availability of additional adsorption sites.

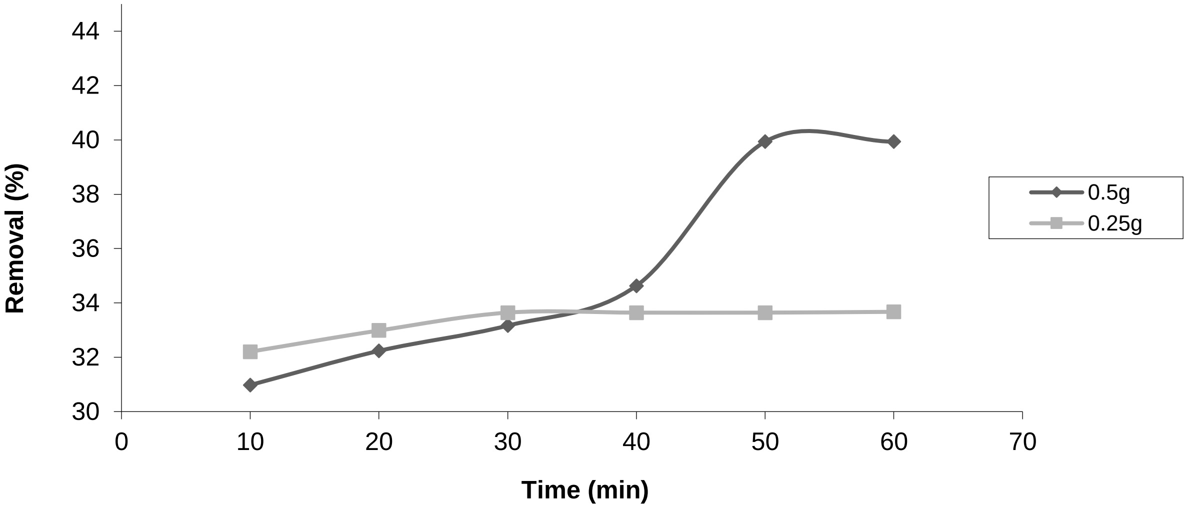

Figure 1: The effect of contact time and adsorbent dose on the removal uptake of dye.

Parameter Estimates and Analysis

In the pseudo-first order kinetic model, the value of c_1 can be calculated from the linear plots of $\log(a_e - a_t)$ against t, and is given in Table 1. Due to the inherent disadvantage of correctly estimating the equilibrium adsorption capacity as obtained from the linearity of the curve, the relationship does not necessarily reflect the pseudo-first order mechanism. Further, the a_e values obtained from the linear plots are different from the observed a_e values, the pseudo-first order adsorption kinetic model is inadequate to describe the given rate processes as justified by the coefficients of determination significantly deviating from unity.

It is important to note that the a_e observed and a_e predicted values obtained in the pseudo-second order biosorption kinetic model are almost the same (R^2=0.99) which suggests that the adsorption phenomenon can be modelled approximately using the pseudo-second order kinetic equation for the different adsorbent doses.

Results of the Elovich model suggest that higher initial adsorption rate, extent of surface coverage, and activation energy are favored at a lower adsorbent dose (R^2=0.93). The parameter estimates for the McArthur-Wilson model are also reflected in Table 1. Further, the a_e observed and a_e predicted values (β_0) obtained using the McArthur-Wilson model are very close to each other as justified by the coefficients of determination which are close to unity (R^2=0.99). This suggests that the adsorption phenomenon can be modelled approximately using the McArthur-Wilson model for the different adsorbent doses. However, the rate at which the uptake approaches its potential maximum is relatively faster at a lower adsorbent dose.

Table 1: Adsorption kinetic parameter estimates of the models at varying adsorbent doses.

Model	**Parameter**	**Adsorbent Dose Levels**	
		0.5 g	**0.25 g**
Pseudo-first order	a_e obs (mg g^{-1})	2.800	2.370
	a_e pred (mg g^{-1})	5.029	0.119
	c_1 (min^{-1})	0.110	0.044
	R^2 (%)	85.88	82.25
Pseudo-second order	a_e obs (mg g^{-1})	2.800	2.370
	a_e pred (mg g^{-1})	2.818	2.385
	c_2 (g mg^{-1} min^{-1})	0.093	0.714
	R^2 (%)	99.63	99.99
Elovich	α (mg g^{-1} min^{-1})	10.69	$2.17x10^{14}$
	β (g mg^{-1})	2.758	16.837
	R^2 (%)	88.00	93.39
MacArthur-Wilson	β_o (mg g^{-1})	2.562	2.347
	β_1 (min^{-1})	0.163	0.320
	R^2 (%)	99.37	99.99
Intraparticle Diffusion	k_{ip} (mg/g $min^{½}$)	0.148	0.022
	C (mg g^{-1})	1.613	2.205
	R^2 (%)	92.37	88.65

Table 2 reflects that the intraparticle diffusion and Elovich models provide the best fit in the uptake of the dye in any adsorbent dose, with error values noted to be smaller at lower adsorbent dose. However, the McArthur-Wilson model can also be considered as an alternative option in defining the kinetic processes involved in this adsorption phenomenon.

Table 2. Error analysis of the different adsorption models at varying adsorbent doses.

Model	**SSE**		**SAE**		**ARE**	
	0.5 g	0.25 g	0.5 g	0.25 g	0.5 g	0.25 g
Pseudo-first order	2.472	0.602	4.035	2.214	60.721	12.012
Pseudo-second order	7.286	0.089	8.351	0.782	6.676	0.412
Elovich	0.168	0.002	1.352	0.132	4.594	0.470
MacArthur-Wilson	0.464	0.003	2.277	0.139	7.667	0.472
Intraparticle Diffusion	0.109	0.004	1.008	0.181	0.411	0.078

Conclusion

The removal uptake reflects a relatively slow initial and terminal increase rates against contact time. Analysis of the differential forms and the second degree derivatives of the Elovich and McArthur-Wilson models point out that these are negative over the entire range of contact time.

The adsorption kinetics was investigated under specified experimental conditions and findings revealed that removal uptake increases with an increase in adsorbent dose and prolonged contact time.

The maximum removal of 40% and 34% were noted at 0.5 g and 0.25 g doses, respectively, suggesting that adsorption is favored at a higher adsorbent dose.

Exploration on various mathematical models revealed that the kinetic processes involved in this study shows that the adsorption reaction behaves under a pseudo-second order kinetic model.

The results of Elovich model suggest that higher initial adsorption rate, extent of surface coverage, and activation energy are favored at a lower dose.

The intraparticle diffusion model offers an adequate fit for the experimental data involving higher adsorbent dose, and the intraparticle diffusion is noted to be relatively faster at a higher adsorbent dose. This is possibly a result of the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

Findings involving error analysis support that the intraparticle diffusion, Elovich, and McArthur-Wilson models are possible nonlinear models which can optimally describe the nonlinear behavior of the kinetic processes presented in this study.

Given the results of the experiment, the removal of dye from an aqueous solution by adsorption on calamansi peels has been found possible. Further research can be done relevant to this study as to assess the possible effects of varying the pH, temperature, and concentration of the dye in the solution on biosorption kinetic processes. Removal efficiency can likewise be compared with other available bioadsorbents. Nonetheless, with the information obtained in this study, it is possible to create a design that will optimize a treatment procedure employing calamansi peels as a bioadsorbent. Moreover, having a better understanding of the meaning and interpretation of the parameters, the physical system being studied, and the mathematics of the models, a researcher accomplishes efficient parameter estimation.

Conflict of Interests

The authors declare that there is no conflict of interests.

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