Jordan Journal of Civil Engineering, Volume **3**, No. **4**, **2009**

Exponential Model for Predicting the Sorption Isotherms-Evaluation, Statistical Appraisal and Comparison with Existing Models

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ABSTRACT

A nonlinear model simulating the relationship between the mass of solute sorbed on clay mineral surfaces and in equilibrium with the concentration of solute in the pore fluid has been discussed in this work. The model and the procedure for obtaining the parameter *(β)* associated with the model were presented. The predicted cadmium isotherms for two types of clayey soils using the exponential model were in excellent agreement with experimental results (Shackelford and Daniel, 1991). Sorption isotherm predicted by the exponential model was compared with other existing models such as Freundlich model and Langmuir model. Seven statistical goodness-of-fit measures were used to evaluate prediction accuracy of the exponential model as well as the Langmuir model and the Freundlich model. All seven statistical goodness-of-fit measures indicated that the exponential model has the best prediction accuracy among the sorption isotherm prediction models. For instance, the error norm for the exponential model was N_e = 0.15 (best value of N_e is zero) for the kaolinite clay, while N_e = 2.95 and N_e = 6.1 for Langmuir model and Freundlich model, respectively. Furthermore, for Lufkin clay, the error norm for the exponential model was N_e = 1.6, while N_e = 264.4 and N_e = 15.1 for Langmuir model and Freundlich model, respectively. The modeling efficiency (*EF*), Nash-Sutcliffe coefficient-of-efficiency (*E*) and the index-of-agreement (*d*) values (best value for *EF*, *E* and *d* is one for the three measures) are best for the exponential model and for the two considered soils. For example, *EF* = 0.992, *E* = 0.999, and *d* = 0.999 for the exponential model (Lufkin clay). However, *EF* = -0.71, *E* = -20.5 and *d* = 0.07 for Langmuir model, and *EF* = 0.79, *E* = 0.93 and *d* = 0.95 for Freundlich model for the same clay.

KEYWORDS: Geo-environment, Diffusion, Sorption isotherm, Modeling, Freundlich model, Langmuir model, Statistical appraisal, Goodness-of-fit.

INTRODUCTION

The relationship between the mass of a specific solute (chemical species) sorbed onto the solid phase (clay mineral surfaces measured as dry mass of solid mg/kg) in equilibrium with the concentration of that specific solute present in the pore fluid (mg/L) is called *adsorption isotherm*, or *sorption isotherm* (Sorption or adsorption will be used interchangeably). Adsorption isotherms are determined experimentally according to *ASTM ES-10-85* and *D4319 - 93*.

Generally, adsorption isotherms assume a nonlinear relationship between the mass of a solute "q (mg/kg)" sorbed on soil particles and the equilibrium concentration of that specific solution "c (mg/L)" in the pore fluid (Fig. 1). The slope of the adsorption isotherm is called the distribution ratio "K_p", where:

$$K_p = \frac{dq}{dc}. \qquad (1)$$

Accepted for Publication on 1/10/2009.

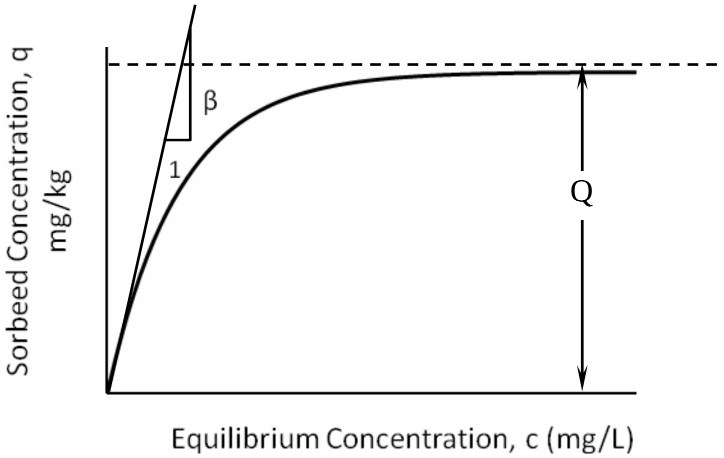


Fig. (1): Typical Adsorption Isotherm for Active Clay.

For nonreactive solutes and/or nonreactive soils (Cation Exchange Capacity (*CEC*) = *0*), the distribution ratio K_p is zero. The distribution ratio is used to determine the "*retardation factor* R_d" (Shackelford and Daniel, 1991), and is given as:

$$R_d = 1 + \frac{\rho_d}{\theta} K_p \, , \tag{2}$$

where ρ_d is the dry density of the soil and θ is the volumetric moisture content ($m^3 \, m^{-3}$) which is defined as the volume of water divided by the total volume of soil (V_w/V), also $\theta = n\,S$. The retardation factor is utilized in Fick's second law for reactive solute diffusive transport subject to reversible sorption reaction during diffusive transport. The Fick's second law of solute diffusive transport is given as:

$$\frac{\partial c}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 c}{\partial x^2} \tag{3}$$

$$D^* = D_0 \, \tau \, , \tag{4}$$

where D^* is the effective diffusion coefficient of chemical species, D_0 is the limiting free-solution diffusion coefficient and τ is tortuosity factor (Shackelford and Daniel, 1991).

Since the sorption isotherm assumes a nonlinear relationship, and given that the distribution factor is the slope of this relation, thus the distribution factor K_p has an infinite number of values (Eq.1). Consequently, the retardation factor, which is dependent on the distribution factor, has an infinite number of values (Eq.2). Therefore, virtually it is not possible to implement a nonlinear sorption isotherm relationship in a mathematical analysis of solute transport. However, numerical analysis such as the finite element analysis can easily handle nonlinear relationships such as the sorption isotherm relation. Therefore, sorption isotherm models are very useful in finite element analysis with the objective of achieving results having high accuracy.

SCOPE OF WORK

The purposes of this work were to:

1. Present an exponential model to simulate the adsorption isotherms. The exponential model consists, primarily, of one parameter. The parameter *(β)* of the model is easy to determine using a simple procedure.
2. Compare the adsorption isotherm predicted by the exponential model with that predicted by Freundlich

model and by Langmuir model with cadmium sorption isotherm for two types of soil obtained from (Shackelford and Daniel, 1991).

3. Present statistical evaluation of the sorption isotherms predicted by the exponential model as well as the other two existing models using seven well-known goodness-of-fit measures.

Table (1): Values of the Fitting Parameters Associated with the Three Models.

Soil Type	Freundlich Model		Langmuir Model		Proposed Model	
	K	***N***	***a***	***b***	***Q***	***β***
Kaolinite Clay	31.18	0.298	0.42	0.0042	198	0.009177
Lufkin Clay	84.454	0.466	0.0446 0.0446	0.0007* 0.000954**	1048	0.0202987

* b is determined using the $\frac{1}{c}$ vs $\frac{1}{q}$ construction.

** b is determined as $b = \frac{1}{\lim_{c\to\infty q}}$

EXISTING ADSORPTION ISOTHERM MODELS

Presently, there is a number of isotherm models, and the most used models are: the linear model, the Freundlich sorption isotherm (power model) and the Langmuir sorption isotherm (hyperbolic model).

The linear sorption isotherm model assumes a linear relationship between the sorbed mass of the solute by the clay particles with the equilibrium concentration of the solute in the pore fluid. The linear model is represented by the simple equation:

$$q = K_p\, c\,. \tag{5}$$

The Freundlich sorption isotherm assumes a nonlinear relationship (power function) between the sorbed mass of the solute by the clay particles with the equilibrium concentration of the solute in the pore fluid. The Freundlich model is represented by the equation:

$$q = K\, c^N\,, \tag{6}$$

where *K* and *N* are parameters associated with the model. These two parameters are determined by plotting the experimental results on a log – log scale. The experimental results represent a straight line on the *log q – log c* domain (Fig. 2), since

$$\log q = \log K + N \log c \tag{7}$$

N represents the slope of the best straight line fit of the experimental resulted plotted on *log q – log c* domain (Fig. 2).

The Langmuir sorption isotherm, also, assumes a nonlinear relationship (hyperbolic function) between the sorbed mass of the solute by the clay particles with the equilibrium concentration of the solute in the pore fluid. The Langmuir model is represented by the equation:

$$q = \frac{c}{a + b\,c} \tag{8}$$

where *a* and *b* are parameters associated with the model. These two parameters are determined by plotting the experimental results on $\frac{1}{q} - \frac{1}{c}$ domain, where the experimental results represent a straight line (Fig. 3), since

$$\frac{1}{q} = b + a\frac{1}{c}\,. \tag{9}$$

Therefore, the intercept of the best straight line fit represents parameter *b* and the slope of the straight line represents parameter *a.*

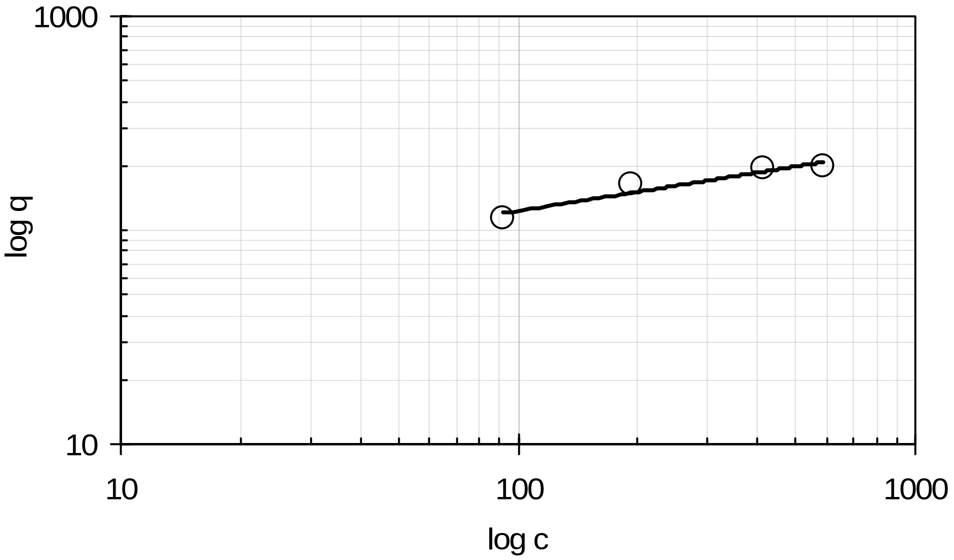


Fig. (2): The log q *vs.* log c Domain for Calculating Parameters *K* and *N* Associated with the Power Model. Data Are for Lufkin Clay after (Shackelford and Daniel, 1991).

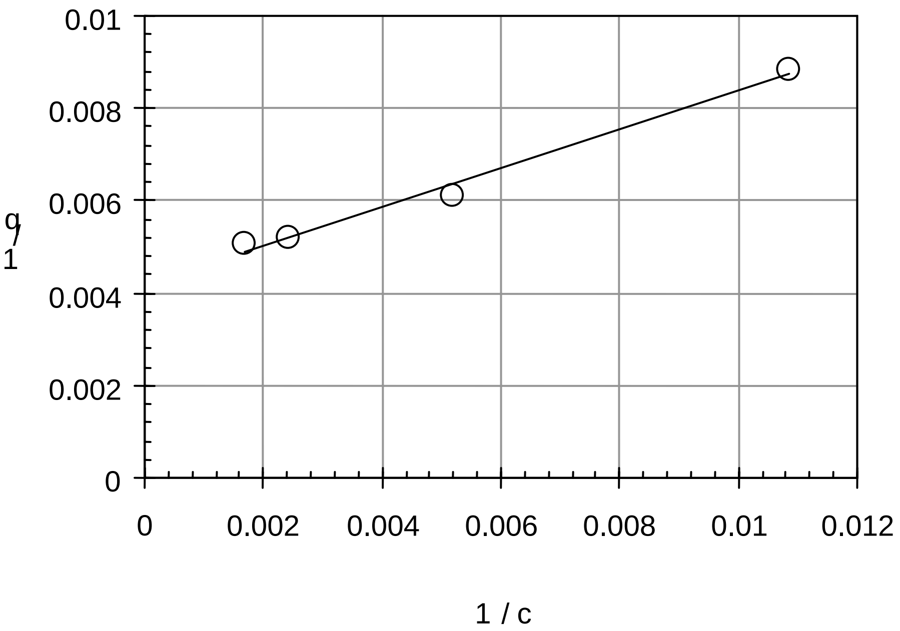


Fig. (3): The 1/q *vs.* 1/c Domain for Calculating Parameters "a" and "b" Associated with the Langmuir Model. Data Are for Lufkin Clay after (Shackelford and Daniel, 1991).

Table (2): Goodness-of-Fit of the Predicting Models (Kaolinite Clay).

Type of Measure	Freundlich Model	Langmuir Model	Proposed Model
MAE	7.738	3.292	0.153
RMSE	9.2425	4.49	0.226
CRM	0.002108	0.00175	-0.000699
E	0.98403	0.99623	0.99999
EF	0.981014	0.98632	0.99706
d	0.995998	0.999061	0.999998
N_e *(%)*	6.0753	2.9516	0.1485

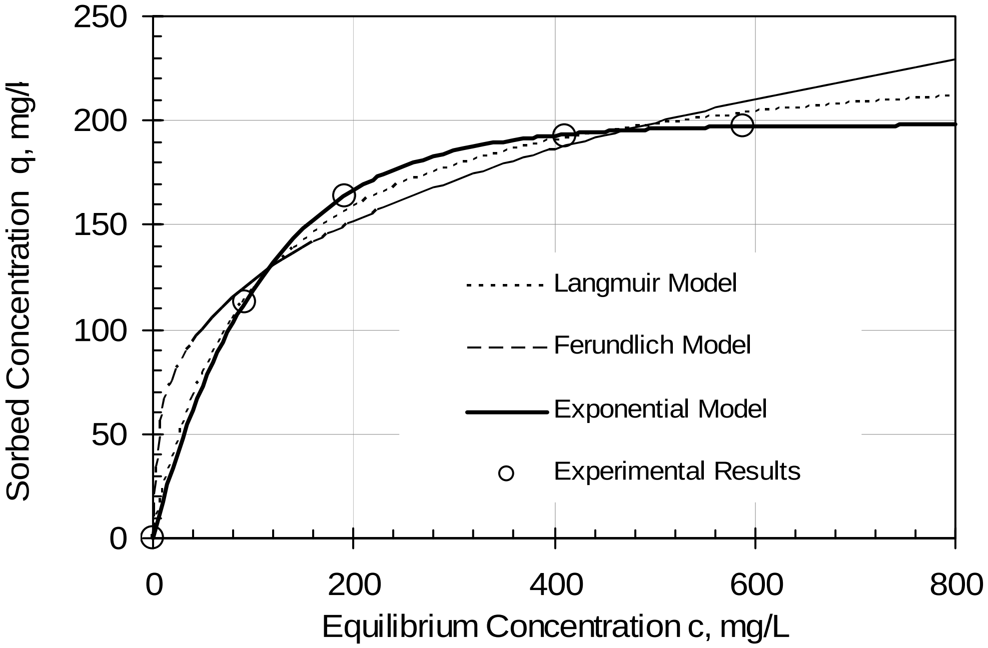


Fig. (4): Cadmium Sorption Isotherms for the Kaolinite Clay as Predicted by the Three Models and the Experimental Results.

THE EXPONENTIAL SORPTION ISOTHERM MODEL

The exponential model assumes a nonlinear relationship between the sorbed mass of the solute by the clay particles with the equilibrium concentration of the solute in the pore fluid. The exponential model is expressed as:

$$q = Q\left\lfloor 1 - e^{-\beta c} \right\rfloor \tag{10}$$

where q = mass of the solute sorbed on the clay particle surfaces per dry mass of soil (mg/kg), c = equilibrium concentration of the solute in the pore fluid (mg/L), Q = limiting value of q (from Eq. 10; $\lim_{c\to\infty} q = Q$) and as shown in Fig. (1) and β = parameter associated with the exponential model. β represents the initial tangential slope of the sorption isotherm relationship.

By differentiating Eq. 10 with respect to c we get the slope of the exponential model's function:

$$\frac{dq}{dc} = Q\,\beta\, e^{-\beta c}\,. \tag{11}$$

The initial tangential slope of the exponential model's function is then

$$\left.\frac{dq}{dc}\right]_i = Q\ \beta \tag{12}$$

$$\beta = \frac{1}{Q}\left.\frac{dq}{dc}\right]_i \tag{13}$$

EXPERIMENTAL RESULTS AND THE ISOTHERMS AS PREDICTED BY THE THREE MODELS

Shackelford and Daniel (1991) presented experimental results for cadmium adsorption isotherms using two types of clay, kaolinite clay having *CEC* = 5 meq/100g, and Lufkin clay, a naturally occurring smectitic clay having *CEC* = 25 meq/100g. The adsorption isotherms were obtained from batch equilibrium tests using 1:4 soil:solution by mass, and mixing time was 48 hours at a temperature of 23°C ± 2°C (Shackelford and Daniel, 1991).

The exponential model, the Freundlich model and the Langmuir model were utilized to simulate the experimental results given by Shackelford and Daniel (1991). Initially, the parameters associated with each model were determined using the procedure mentioned above and are given in Table (1).

The adsorption isotherms for cadmium predicted by the exponential model as well as Freundlich model, Langmuir model and the experimental results (Shackelford and Daniel, 1991) for the kaolinite clay and Lufkin clay are shown in Fig. (4) and Fig. (5), respectively.

The results depicted in Fig. (4) and Fig. (5) indicated that the Freundlich model represents reasonably good agreement with the experimental results of the sorption isotherm for the two types of clay soils. Sorption isotherm prediction using the Langmuir model, on the other hand, has shown contradicting precisions. The Langmuir model has shown very good representation of the sorption isotherm for the kaolinite clay soil. The Langmuir model well predicted the sorption isotherm for most of the equilibrium solute concentration in the pore fluid c range, except at large values of c, where the model yielded some inaccuracy. Conversely, for the Lufkin clay soil, the Langmuir model has inadequately represented the experimental results (Fig. 5). The exponential model, however, has shown very good agreement with the experimental results for the entire range of the equilibrium solute concentration in the pore fluid c and sorbed mass of solute by the clay minerals q for the kaolinite clay as well as the Lufkin clay.

PROBLEMS ASSOCIATED WITH LANGMUIR MODEL

Langmuir model, as mentioned above, simulated the sorption isotherms with contrasting accuracies (Fig. 5). It simulated the sorption isotherm of the kaolinite clay with high precision; however, it had poorly simulated the sorption isotherm of the Lufkin clay. This problem is not inherited in the model itself rather than the procedure of obtaining the parameters of the model (*a* and *b*). Mathematically, the Langmuir model is a square hyperbolic function. The hyperbolic function is nonlinear and, towards both ends of the function, becomes asymptotic to two perpendicular straight lines. The linearization process; i.e. $\frac{1}{q} - \frac{1}{c}$ construction used to determine the parameters of the straight line "*a*" and "*b*" is very sensitive to deviation of the experimental points from an ideal hyperbolic function, especially at small values of the abscissa; i.e. concentration of solute in the pore fluid "*q*". Therefore, the less the scatter of the experimental data points the better the Langmuir model simulates the sorption isotherms. There is an alternative simple procedure for getting the parameters of the model "*a*" and "*b*" other than the one mentioned earlier. Parameter "*b*" is the limiting value of q, and parameter "*a*" is the initial tangent (slope at $c = 0$) of the q *vs.* c relationship (Eqs. 14a and 14b).

$$b = \frac{1}{\lim_{c\to\infty} q} \qquad (14a)$$

$$a = \left.\frac{dq}{dc}\right]_{c=0} . \qquad (14b)$$

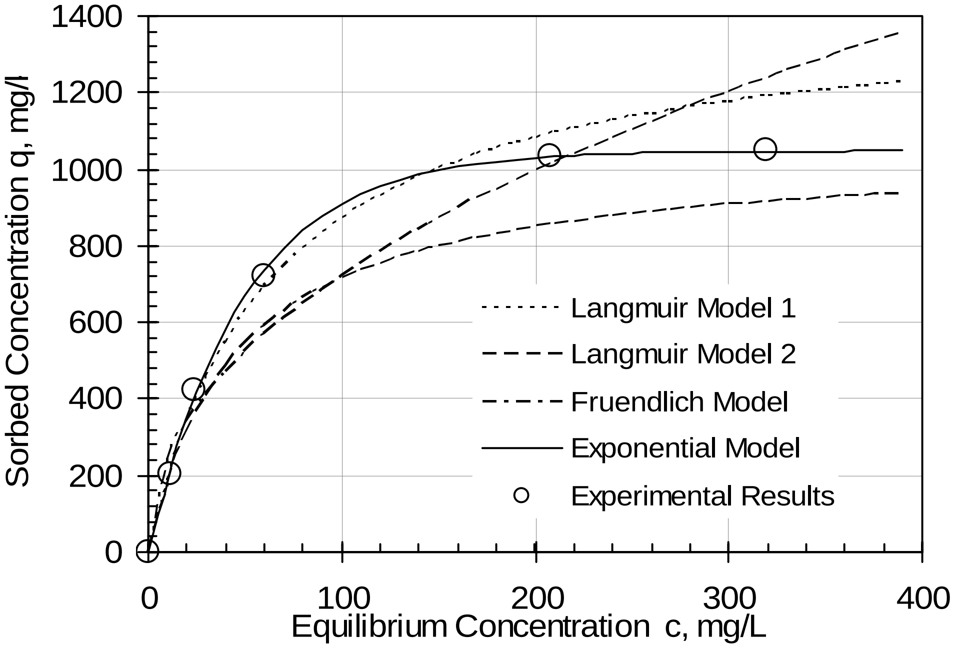
Determining the initial tangent for an explicitly defined function (function containing either polynomial or transcendental functions or both) is a simple matter. However, finding the initial tangent for an implicitly defined function; i.e. set of experimental data points where the function is defined, only, at a discrete number of data points, is highly dependent on the first data point since the only available option of finding the tangent is the forward technique. Alternatively, one may manually fit a curve through the data points, merely, to get a better estimate for the initial tangent instead of using the numerical forward technique.

To demonstrate the sensitivity of the Langmuir model to the procedure of obtaining its parameters, the "*b*" parameter only was obtained according to Eq. 14a, while "*a*" was obtained as defined previously. The Langmuir model, again, for the Lufkin clay did not achieve satisfactory results (Fig. 5).

STATISTICAL APPRAISAL OF THE PREDICTION MODELS

The sorption isotherms predicted by the exponential model, the Freundlich model and the Langmuir model were evaluated using six well-known goodness-of-fit measures. One additional measure, to reduce sensitivity to extreme values, was proposed in the present work and used for the statistical appraisal.

In order to quantify evaluation of the predicted sorption isotherms, an appropriate criterion that reflects the quality-of-fit of the model is needed. The coefficient of correlation *"r"* and the coefficient of determination "R^2" are extensively used to appraise regressed data. At present, however, it has become a well established fact that the correlation-based criterion can be greatly influenced by the relationship between the two variables at one extreme outlier. Legates and Davis (1997) and Moore (1991) demonstrated that correlation-based measures are more sensitive to outliers than to observations near the mean. Consequently, this oversensitivity to outliers leads to a bias toward extreme events if correlation-based measures are employed in model evaluation. Thus, a high value of correlation-based measures does not, necessarily, indicate high-quality fit (Willmott, 1981; Willmott et al., 1985; Kessler and Neas, 1994; Legates and Davis, 1997). Therefore, correlation-based measures were not used in this work and six accredited statistical criteria, plus one more proposed criterion, were used to evaluate the goodness-of-fit of the exponential model, the Langmuir model and the Freundlich model. These measures were briefly explained below, and for more details the reader is referred to other publications (Willmott, 1981; Willmott et al., 1985; Kessler and Neas, 1994; Legates and Davis, 1997).



Langmuir Model 1➔ b is determined using the $\frac{1}{q} - \frac{1}{c}$ construction.

Langmuir Model 2➔ b is determined as $b = \dfrac{1}{\lim_{c\to\infty} q}$.

Fig. (5): Cadmium Sorption Isotherms for the Lufkin Clay as Predicted by the Three Models and the Experimental Results.

Index-of-Agreement (*d*)

The index-of-agreement measure was developed by Willmott (1981) to overcome the insensitivity of the correlation-based measures to differences in the observed and correlation-based means and variances. The index-of-agreement (d) is given as:

$$d = 1 - \frac{\sum_{i=1}^{i=N} \left(q_{m,i} - q_{p,i}\right)^2}{\sum_{i=1}^{i=N} \left(\left| q_{p,i} - \overline{q}_m \right| + \left| q_{m.i} - \overline{q}_m \right| \right)^2}, \qquad (15)$$

where:

d = index-of-agreement,
N = number of data points,
$q_{m,i}$ = i^{th} observed q value,
$q_{p,i}$ = i^{th} predicted q value and
$\overline{q}_m$ = mean of the entire q values.

The index-of-agreement d, varies from 0.0 for a poor model to 1.0 for a perfect model. The index of agreement represents an improvement over the coefficient-of-determination R^2, yet it is also sensitive to extreme values (due to squared differences).

Root Mean Square Error (*RMSE*)

The *RMSE* quantifies the error in terms of the units of the variable. The *RMSE* is non-negative statistics that have no upper bound. The root mean square of the error is given as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{i=N} \left(q_{m,i} - q_{p,i}\right)^2}{N}}. \qquad (16)$$

Table (3): Goodness-of-Fit of the Predicting Models (Lufkin Clay).

Type of Measure	Freundlich Model	Langmuir Model	Proposed Model
MAE	77.60486	1139.384	7.018
RMSE	104.875	1838.881	10.83308
CRM	-0.00699	-1.99466	0.001017
E	0.930124	-20.4828	0.999254
EF	0.790425	-0.71195	0.991597
d	0.949768	0.07169	0.999223
N_e (%)	15.07951	264.4045	1.557639

Mean Absolute Error (*MAE*)

The mean absolute error quantifies the error in terms of the units of the variable. The *MAE* is non-negative statistics that have no upper bound.

$$MAE = \frac{\sum_{i=1}^{i=N} \left| q_{m,i} - q_{p,i} \right|}{N} . \qquad (17)$$

The *RMSE* is a dimensioned goodness-of-fit measure; i.e. it expresses the average model-prediction error in the units of the variable of interest. Though the *RMSE* is widely used, however, its use as a goodness-of-fit measure is inappropriate (Willmott and Matsuura, 1999). One of the disturbing characteristics of *RMSE* (according to Willmott and Matsuura, 1999) is that it tends to become increasingly larger than *MAE*. Willmott and Matsuura (1999) concluded that *MAE*, as a goodness-of-fit measure, is an unambiguous measure of average error magnitude and it is more appropriate to use than *RMSE*.

Nash-Sutcliffe Coefficient-of-Efficiency (*E*)

Nash and Sutcliffe (1970) developed the coefficient-of-efficiency (*E*) to overcome the inaccuracy of the correlation-based measures. The coefficient-of-efficiency, *E* is defined as:

$$E = 1 - \frac{\sum_{i=1}^{i=N} \left(q_{m,i} - q_{p,i}\right)^2}{\sum_{i=1}^{i=N} \left(q_{m,i} - \overline{q}_m\right)^2} . \qquad (18)$$

The coefficient-of-efficiency, *E* varies from minus infinity for a poor model to 1.0 for a perfect model. The coefficient-of-efficiency represents an improvement over the coefficient-of-determination R^2, yet it is, also, sensitive to extreme values (due to squared differences).

Modeling Efficiency (*EF*)

The modeling efficiency represents an improvement over the coefficient-of-determination R^2, yet it is also sensitive to extreme values (due to squared differences). The modeling efficiency measure is defined as:

$$EF = \frac{\sum_{i=1}^{i=N} \left(q_{m,i} - \overline{q}_m\right)^2 - \sum_{i=1}^{i=N} \left(q_{m,i} - q_{p,i}\right)^2}{\sum_{i=1}^{i=N} \left(q_{p,i} - \overline{q}_m\right)^2} . \qquad (19)$$

Coefficient of Residual Mass (*CRM*)

The coefficient of residual mass represents a normalized error criterion and is given as the difference of the sum of the square of the observed data points and the square of those predicted by the model. The coefficient of residual mass is defined as:

$$CRM = \frac{\sum_{i=1}^{i=N} q_{m,i}^2 - \sum_{i=1}^{i=N} q_{p,i}^2}{\sum_{i=1}^{i=N} q_{m,i}^2}. \qquad (20)$$

Error Norm (N_e)

The Error Norm N_e as a goodness-of-fit measure is proposed in this work. It is intended to remove the influence of outlier values by normalizing the error. The error norm N_e is non-negative statistics that have no upper bound and is given as percentage away from perfect prediction. For perfect prediction, the error norm N_e = 0 %. The error norm N_e is defined as:

$$N_e = \sqrt[2]{\frac{\sum_{i=0}^{i=N} \left(q_{m,i} - q_{p,i}\right)^2}{\sum_{i=0}^{i=N} q_{m,i}^2}} \times 100\%. \qquad (21)$$

The i^{th} error "e_i" involved in predicting each observed data point (experimental result) is defined as:

$$e_i = \left| q_{m,i} - q_{p,i} \right|. \qquad (22)$$

The error norm N_e is then defined as:

$$N_e = \sqrt[2]{\frac{\sum_{i=0}^{i=N} e_i^2}{\sum_{i=0}^{i=N} q_{m,i}^2}} \times 100\%, \qquad (23)$$

where $q_{m,i}$ is the i^{th} observed "*measured*" value of sorbed mass of solute in equilibrium with concentration "*c*" of the solute in pore fluid, $q_{p,i}$ is the i^{th} "*predicted*" value of sorbed mass using one the models, *i* is used to denote the i^{th} observed data point (experimental results), *N* is the number of data points and *i* is the index for *N*.

The seven statistical criteria, described above, were used to evaluate the performance of the exponential model as well as Langmuir model and Freundlich model. The values of the seven statistical goodness-of-fit measures for the cadmium sorption isotherms for the kaolinite clay and Lufkin clay are given in Table (2) and Table (3), respectively. The results reported in Table (2) and Table (3) clearly demonstrate that the exponential model yielded best result as appraised by "*all seven*" goodness-of-fit measures and for the two considered types of soil. The Langmuir model produced second best result for the kaolinite clay, and the Freundlich model yielded second best result for the Lufkin clay. For instance, the error norm N_e for the exponential model (kaolinite clay) yielded the lowest N_e = 0.15 (best N_e = 0). The Langmuir model and the Freundlich model both produced error norm N_e higher than that yielded the exponential model by 20 folds and by 40 folds, respectively (Table 2). Similar trend was, also, observed for the Lufkin clay; the Langmuir model and the Freundlich model produced error norm N_e higher than that yielded the exponential model by 165 folds for the Langmuir model and by 10 folds for the Freundlich model, respectively (Table 3). The same trend can be traced for the Mean Absolute Error (*MAE*) and the Root Mean Square Error (*RMSE*) yielded similar results (as that of the error norm N_e) for the two types of clays (Table (2) and Table (3).

For the kaolinite clay and for the three considered models, the modeling efficiency (*EF*), Nash-Sutcliffe coefficient-of-efficiency (*E*) and index-of-agreement (*d*) all are close to the best value (1.0), bearing in mind that *E*, *EF* and *d* values are closer to the best value (1.0) for the exponential model in comparison with the other models.

For Lufkin clay, the modeling efficiency (*EF*), Nash-Sutcliffe coefficient-of-efficiency (*E*) and index-of-agreement (*d*) vary significantly for the three considered models. The exponential model yielded best values among the three models having values very close to one.

Good values for E and d were achieved by Freundlich model. Moderate value for the modeling efficiency (EF = 0.79), however, was obtained for the Freundlich model. The Langmuir model yielded poor values for modeling efficiency (EF), Nash-Sutcliffe coefficient-of-efficiency (E) and index-of-agreement (d).

SUMMARY AND CONCLUSIONS

An exponential model for predicting the sorption isotherms was discussed in this paper. The predicted isotherm using the exponential model was compared with experimental results for cadmium isotherms (Shakelford and Daniel, 1991). The exponential sorption isotherm model was also compared with other existing well-known nonlinear models, namely; Freundlich model and Langmuir model. Seven goodness-of-fit measures were used to evaluate the prediction performance of the exponential model as well as Freundlich model and Langmuir model.

The predicted cadmium isotherms using the exponential model for the two clayey soils were in excellent agreement with the experimental results presented by Shakelford and Daniel (1991). The sorption isotherm produced by the exponential model as appraised by the seven goodness-of-fit measures yielded values very close to the optimum (best) values.

The exponential model yielded better sorption isotherms for the two types of clayey soil as compared with the Freundlich model and Langmuir model. The Langmuir model produced conflicting prediction accuracy; it achieved good prediction results for the kaolinite clay, while it yielded poor results for the Lufkin clay as can be observed visually (Fig. (4) and Fig. (5)) and as evaluated by the seven goodness-of-fit measures as well (Table (2) and Table (3)). The procedure associated with obtaining the parameters of the Langmuir model is attributed to the contrasting prediction accuracy of that model.

Lowest values of the error norm (N_e = 0.15 for kaolinite soil and 1.6 for Lufkin soil) were obtained for the exponential model and compared to (N_e = 2.95 for kaolinite soil and 264.4 for Lufkin soil) for the Langmuir model, and (N_e = 6.1 for kaolinite soil and 15.1 for Lufkin soil) for the Freundlich model.

APPENDIX I

NOMENCLATURES

a and b = parameters associated with the Langmuir model,
c = concentration of specific solute in the pore fluid (mg/L),
CEC = cation exchange capacity,
CRM = Coefficient of Residual Mass,
d = index-of-agreement,
D^* = effective diffusion coefficient of chemical species,
D_0 = limiting free-solution diffusion coefficient,
e_i = error involved in data point i,
E = Nash-Sutcliffe coefficient-of-efficiency,
EF = modeling efficiency,
K and N = Parameters associated with the Freundlich model,
N_e = error norm,
K_p = distribution ratio,
MAE = Mean Absolute Error,
q = mass of a specific solute sorbed onto the clay mineral surfaces measured as dry mass of solid (mg/kg).

$q_{m,i}$ = i^{th} observed q value,

$\underline{q}_{p,i}$ = i^{th} predicted q value, and

q_m = mean of the entire q values.

R_d = retardation factor,

RMSE = Root Mean Square Error,

β = parameter associated with the exponential model,

ρ_d = dry density of the soil,

θ = volumetric moisture content and

τ = tortuosity factor.

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