Determination of best-fit isotherm model for the sorption of Lead (II) and Manganese (II) ions onto acid-activated shale using selected non-linear error functions

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ABSTRACT

The focus of this research is to apply the selected error function equation to establish the equilibrium isotherm model that best describes the adsorption of Pb^{2+} and Mn^{2+} onto acid-activated shale. Data collected from the batch experiment were analyzed using selected isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Sips and Redlich-Peterson). To compute the isotherm parameters used in choosing the best-fit isotherm model, selected non-linear error functions, namely, error sum of the square, normalized standard deviation, hybrid error function, root mean square error and Marquardt's percent standard deviation were employed. From the scanning electron microscope results, it was observed that the surface characteristics of the shale change considerably with calcination and acid treatment but the acid-treated shale shows better uneven porous surface characteristics. Error function computation shows that the Dubinin-Radushkevich isotherm model had the least sum of normalized error of 0.3623 for Pb^{2+} adsorption and 0.5465 for Mn^{2+} adsorption; hence, it was selected as the best isotherm model for explaining the sorption of $Pb(II)$ and $Mn(II)$ ions unto acid-activated shale.

1. Introduction

Environmental effluence toxic waste caused by the discharge of wastewater containing poisonous metals such as chromium, lead and manganese has been an issue of concern, which has become a widely studied area [1]. Unlike organic contaminants, which are mainly susceptible to biological degradation, heavy metals do not decompose into harmless end products. In addition, their occurrence in the environment can lead to bioaccumulation in living organisms, which can cause health problems [2].

Lead, chromium, and manganese are poisonous to the human bio-system and are among the popular worldwide pollutants arising from increasing industrialization [3]. These metals are used in most chemical industries for the manufacture of dry cell batteries, leather tanning, electroplating, and corrosion control [4]. Many of these metals find their way into surface and groundwater systems by direct fallout or via runoff from streams and infiltration [5].

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Constants' Identification			
A	Redlich-Peterson adsorption capacity constant ($= b_{RP} q_m$), (L/g)	NSD	Normalized standard deviation
a_s	Sips isotherm model constant (L/g)	p	Number of isotherm parameters
B	Redlich-Peterson isotherm constant (L/mg $^{1-1/A}$)	$\overline{q_{cal}}$	The average value of calculated metal uptake concentrations (mg/g)
b_{RP}	Parameter of Redlich-Peterson isotherm equation (L/mg $^{1-1/A}$)	q_{cal}	Equilibrium capacity obtained by calculating from the model (mg/g)
b_T	Temkin isotherm constant related to adsorbent-adsorbate interactions (J/mol)	q_e	Equilibrium metal uptake concentrations (mg/g)
C_0	Initial metal ion concentrations (mg/L)	q_{exp}	Experimental data of the equilibrium capacity (mg/g)
C_e	Equilibrium metal ion concentrations (mg/L)	q_m	Maximum adsorption capacity (mg/g)
g	An exponent between 0 and 1	q_{mDR}	Saturation capacity for Dubinin-Radushkevich (mg/g)
HYBRID	Hybrid fractional error function	R	Universal gas constant (J/mol/K)
K_{DR}	Dubinin-Radushkevich Constant indicative of adsorption energy (mol 2 /kJ)	R 2	Coefficient of determination
K_F	Freundlich isotherm constant indicative of adsorption capacity (mg $^{1-(1/n)}$ L $^{1/n}$ /g)	RMSE	Root mean square error
K_L	Langmuir isotherm constant (L/mg)	SEM	Scanning electron microscope
K_s	Sips isotherm model constant (L/mg)	SNE	Sum of normalized error
K_T	Temkin equilibrium binding constant (L/g)	SSE	Sum of square error
m	Mass of adsorbent used (g)	T	Absolute temperature (K)
MPSD	Marquardt's percent standard deviation	V	Aqueous sample volume (ml)
n	Adsorption intensity	XRF	X-ray fluorescence
$1/n_s$	Sips model exponent	<i>Greek letters</i>	
N	Number of experimental data points	β_s	Sips isotherm exponent
NE	Normalized error	ε	Polanyi potential
		η	Efficiency (%)

The absorption of fairly small quantities of these heavy metals over an elongated period by humans can lead to protracted toxicity together with several health challenges such as skin irritation, lung tumor and circulatory system [6]. The venomous effects of chromium, lead, and manganese ions in humans particularly when present above the threshold boundary in the hydrosphere is alarming and well documented [7]. The presence of these metals in the ecosystem is of great concern to engineers and scientists because of their harmful nature as well as other adverse impacts posed by the discharge of untreated effluents containing such metals on receiving water bodies [8].

Physico-chemical processes that have been employed in the treatment of wastewater containing heavy metals before being discharged into water bodies include chemical and electrolytic precipitation, reverse osmosis, electrodialysis, and ion exchange methods [9]. Adsorption offers good prospects over other treatment techniques owing to its flexibility and ease of operation [10]. Adsorption is a process that involves the movement of molecules of the fluid phase

(liquid or gas) to the surface of the solid. In adsorption, liquid or gas molecules diffuse from the bulk solution to the surface of the solid forming an adsorbed phase of distinct characteristics [11-12].

Over the years, linear transformation of the isotherm equations coupled with the application of the least square regression method to compute the R 2 -value, remains the most widely used technique. Because of this, the isotherm model having an R 2 -value closer to one was selected as the best-fit isotherm model [13-14]. Determination of R 2 -value and its subsequent application in the selection of best-fit isotherm model is not satisfactory owing to the alteration in the error structure associated with the transformation of the non-linear isotherm equation to its linear form. In addition, R 2 -value only accounts for the difference associated with each point fitted by the model concerning the overall average of the fitted curve.

Therefore, to have an accurate judgment in the selection of the best-fit isotherm model, non-linear error functions were employed. Error functions such as SSE, NSD, HYBRID, RMSE, and MPSD unlike R 2 , accounts for the

difference associated with each point fitted by the model concerning each experimental point measured. Furthermore, since each of the selected error functions produced non-identical sets of isotherm constraints, an overall optimal isotherm parameter set was hard to find directly. To overcome this limitation and make a more significant comparison between the parameter sets, a technique for normalizing the computed error functions was assumed to produce a single combination of the minimized error called the SNE for each selected isotherm parameter [15].

In this paper, selected non-linear error functions and their subsequent minimization using the SNE was utilized to determine the isotherm model that best describes the adsorption of Pb^{2+} and Mn^{2+} onto acid-activated shale.

2. Methodology

2.1. Collection and Preparation of Adsorbent

Shale was extracted from its deposit in Okada. To remove any carbonaceous matter, which could interfere with the shale's metal adsorption capability, the shale was first soaked in a plastic containing 5 % H_2O_2 . It was then treated with purified water to eliminate any water-soluble impurities before being used. The dried shale was then finely ground and sieved with a 212 m sieve before being used according to Krishna and Susmita [16]. 500 g of dried sieved shale was calcined in a furnace at 550 °C for 10 h before being put in a desiccator to cool before using. Acid activation was achieved by mixing 200 g of calcinated shale with 1 liter of H_2SO_4 (0.25 M). Before use, the shale was dried for 30–45 min at 100 °C, ground with a mortar and pestle, sieved to 212 m, and stored in a desiccator.

2.2. Characterization of Adsorbent

To characterize the shale material for use as an adsorbent, a SEM and an XRF were employed to assess the microstructural arrangement and the chemical composition of the shale material after acid-activation [17–18].

2.3. Preparation of Aqueous Solution

To prepare the adsorbate, a stock solution of lead (II) nitrate and manganese (II) chloride tetrahydrate were employed. The salts were dissolved in 1 liter of distilled water and stirred to mix. The required concentration of adsorbate was prepared by further diluting the stock solution while the metal ion concentration was determined with the aid of

atomic absorption spectrophotometer. To regulate the pH of the solution, dropwise addition of HNO_3 (1 M) or NaOH (1 M) was adopted.

2.4. Adsorption Studies

Adsorption studies were conducted to investigate the effects of selected adsorption variables, namely; adsorption temperature, contact time, adsorbent dose, and pH. A mixture of varying doses of adsorbent and 50 ml adsorbate solution was stirred at 150 rpm for diverse contact times and constant pH. Separation of the adsorbent from the adsorbate solution of heavy metal was achieved with the aid of filtration process using 150 ml Whatman filter paper while the residual metal ions removed during the process was deduced using the proposed mass balance equation by Badmus et al. [3]:

$$q_e = \frac{V}{m} [C_0 - C_e] \quad (1)$$

Where, q defines the equilibrium metal uptake concentration (mg/g); C_0 and C_e are the initial and equilibrium metal ion concentrations (mg/l), V is the aqueous sample volume (ml) and m is the mass of adsorbent used (g).

The efficiency (η) of metal ion removal was calculated using the mass balance equation of the form expressed in equation (2) [3].

$$\eta = \left(\frac{C_0 - C_e}{C_0} \times 100 \right) \quad (2)$$

2.5. Equilibrium Isotherm Studies

To study the equilibrium relationship between the amount of metal ions removed and the amount of metal ions remaining, batch experimental data were analyzed using selected linear isotherm models presented in Table 1.

2.6. Error Analysis

Linear regression analysis can be used to specify the best-fitting correlation, which quantifies the distribution of adsorbates as well as validation of the consistency of the theoretical adsorption models. Nevertheless, the error structure of measured or experimental dataset normally varied during the linear transformation of adsorption isotherms [28]. As a consequence, nonlinear regression analysis gives a statistically rigorous approach for establishing adsorption parameters [29]. Nonlinear regression typically entails the minimization of error distribution between the computed isotherm and measured data based on its convergence criteria [26]. The selected error functions utilized are presented in Table 2.

Table 1 Linear isotherm equations.

Isotherm model	Definition	Equation
Langmuir [19]	$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot C_e + \frac{1}{q_m K_L}$	(3)
Freundlich [20]	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$	(4)
Temkin [21]	$q = a + b \ln C_e$	(5)
Dubinin-Radushkevich [22]	$q = q_D \exp \left(-K_{ad} \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right)$	(6)
Sips [23,24]	$\ln \left(\frac{q_e}{q_0 - q_e} \right) = \ln b + n \ln C_e$	(7)
Redlich-Peterson [25-27]	$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln B$	(8)

Table 2 Definition of selected error functions.

Error function	Definition	Equation
R ² [30]	$\frac{\sum_{i=1}^N (q_{exp} - \bar{q}_{cal})_i^2}{\sum_{i=1}^N [(q_{exp} - \bar{q}_{cal})_i^2 + (q_{exp} - q_{cal})_i^2]}$	(9)
SSE [24]	$\sum_{i=1}^N (q_{exp} - q_{cal})_i^2$	(10)
HYBRID [31]	$\frac{100}{N-p} \sum_{i=1}^N \left[\frac{(q_{exp} - q_{cal})_i^2}{q_{exp}} \right]_i$	(11)
NSD [32]	$100 \times \sqrt{\frac{1}{n-1} \sum_{i=1}^N \left[\frac{(q_{exp} - q_{cal})_i^2}{q_{exp}} \right]_i}$	(12)
RMSE [32]	$\sqrt{\frac{1}{N-1} \sum_{n=1}^N (q_{exp} - q_{cal})^2}$	(13)
MPSD [31]	$100 \times \sqrt{\frac{1}{N-p} \sum_{i=1}^N \left[\frac{(q_{exp} - q_{cal})_i^2}{q_{exp}} \right]_i}$	(14)

3. Results and Discussion

3.1. Adsorbent Characterization

Results of adsorbent characterization are shown in Fig. 1 and Table 3. A SEM was used to confirm the existence of microspores in the shale structure. The surface properties of the shale materials change dramatically with calcination and acid treatment, as shown in Fig. 1(a)-(c), with the acid-treated shale having a stronger random porous surface structure. From the chemical analysis of the shale material, it was observed that the dominant oxides found in shale were aluminum oxide and silicon oxide. The alumina content of raw shale was found to be 21.33 weight percent, rising to 24.41 weight

percent for calcinated shale and decreasing to 18.13 weight percent for acid-activated shale, presumably due to the shale's acid dealumination caused by acidification.

From the results of Fig. 1 (a)–(c), it was observed that acid treated shale showed more porous surface characteristics than the raw and calcinated shales. The reason being that acid treatment tends to open up the pore spaces better than calcination alone. The higher number of microporous structures seen with acid-activated shale indicates a greater surface area. This assertion is due to the fact that as bio-sorbent materials present larger numbers of microporous structure, it adsorbs greater amount of nitrogen, which resulted to a higher surface area.

Fig. 1 SEM (a) raw shale, (b) calcinated shale, and (c) acid-activated shale.

3.2. Adsorption Isotherm Modeling

The adsorption isotherm models were fitted to explain the relationship between the adsorbate and adsorbent materials thus providing relevant data that can be useful in assessing the adsorption potential of the adsorbents. Results of the two parameters isotherm modeling are presented in Fig. 2. When the sorption data were analyzed based on the linear form of the Langmuir isotherm model presented in Fig. 2(a), it was observed based on the R^2 -value that Langmuir isotherm produces a very strong fit for the sorption of Pb(II) and Mn(II) onto acid-activated shale.

The linear Freundlich isotherm graph presented in Fig. 2(b), appears to produce a reasonable fit for sorption in all two systems with Mn(II) ion adsorption showing a better fit than Pb(II) ions adsorption. Analysis of sorption data based on the linear form of Temkin isotherm model presented in Fig. 2(c), revealed the suitability of the Temkin isotherm model in providing a reasonable fit for the

Fig. 2 Isotherm models for Pb(II) and Mn(II) ions adsorption (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin-Raduskevich.

sorption of Pb(II) and Mn(II) onto acid-activated shale with Mn(II) ion adsorption showing better fit compared to the adsorption of Pb(II). More also, the results of Fig. 2(d), showed that the linear form of the Dubinin-Radushkevich isotherm model can also provide a good fit for sorption in all two systems.

The simplicity of the two-parameter isotherm model in providing a reasonable fit to adsorption data was based on the fact that the model variables can easily be transformed so that the overall equation was converted to a linear form for which linear regression can

then be applied. These transformations do not seem to be possible with three-parameter isotherms such as the Sips and Redlich-Peterson isotherm model. Based on this, a trial-and-error method was introduced to determine one of the constraints thus paving way for the application of linear regression analysis. Since the transformation of non-linear to linear equations indirectly modifies their error structure and can also violate the error variance, alternative isotherm parameter sets were determined by non-linear regression analysis using the non-linear form of the isotherm equation.

Table 3 Predicted isotherm by minimizing the error distribution using different error functions for Pb(II) ion adsorption onto acid activated shale.

Langmuir	q_e	K_L	OF ^a	NE	SNE = 1.1774
R ²	11.7191	2.9741	1.000	0.2538	
SSE	10.9513	3.1491	1.366E-08	0.2875	
HYBRID	13.4747	1.9878	1.420E-11	0.1475	
NSD	13.3833	2.4345	4.417E-08	0.1819	
RMSE	13.5848	2.2300	5.153E-09	0.1642	
MPSD	13.3970	1.9226	1.029E-06	0.1435	
Freundlich	K_F	$1/n$	OF ^a	NE	SNE = 3.7953
R ²	2.4588	1.0000	1.000	0.4067	
SSE	3.1620	0.8985	3.669E-08	0.2842	
HYBRID	1.1106	1.0000	1.357E-30	0.9004	
NSD	1.6057	1.0177	4.498E-06	0.6338	
RMSE	1.5926	0.9432	7.167E-07	0.5922	
MPSD	1.0259	1.0033	2.153E-06	0.9780	
Temkin	K_T	b_T	OF ^a	NE	SNE = 3.8129
R ²	3.6137	4.8903	1.000	0.7390	
SSE	3.9229	4.7683	5.493E-08	0.8227	
HYBRID	2.2704	4.2016	1.383E-30	0.5404	
NSD	2.8847	4.8299	3.495E-06	0.5973	
RMSE	2.6387	4.6420	1.495E-08	0.5684	
MPSD	2.3479	4.3072	1.023E-08	0.5451	
Dubinin-Radushkevich	q_{mDR}	K_{DR}	OF ^a	NE	SNE = 0.3623
R ²	11.1568	0.5789	1.000	0.0519	
SSE	10.3021	0.3844	7.466E-09	0.0373	
HYBRID	12.9970	0.9184	6.808E-18	0.0707	
NSD	12.8588	0.8214	2.782E-06	0.0639	
RMSE	13.0756	0.8728	1.091E-09	0.0667	
MPSD	12.9306	0.9290	7.652E-10	0.0718	
Sips	q_0	b	n	OF ^a	SNE = 2.4933
R ²	1.8180	0.9219	0.9631	1.000	
SSE	1.7725	0.8196	1.1548	3.712E-08	
HYBRID	1.8527	0.9307	0.6448	2.195E-16	
NSD	1.8320	0.9086	0.7856	8.436E-07	
RMSE	1.8357	0.9072	0.7274	1.729E-06	
MPSD	1.8369	0.8956	0.6434	2.202E-06	
Redlich-Peterson	A	B	g	OF ^a	SNE = 1.3467
R ²	1.7294	0.7294	1.000	1.000	
SSE	1.9068	0.9137	0.9596	3.632E-09	
HYBRID	1.0553	0.0553	1.000	1.437E-30	
NSD	1.3729	0.2926	0.9983	9.906E-07	
RMSE	1.2041	0.1997	0.9996	2.504E-07	
MPSD	1.0197	0.0146	1.0038	7.752E-06	

OF^a: Objective function for the minimum error distribution between experimental and predicted isotherm

Table 4 Predicted isotherm by minimizing the error distribution using different error functions for Mn(II) ion adsorption onto acid activated shale.

Langmuir	q_e	K_L	OF ^a	NE	SNE = 1.4469
R ²	8.4117	2.5745	1.0000	0.3061	
SSE	7.7417	2.7483	1.029E-09	0.3550	
HYBRID	9.2649	1.6942	8.232E-12	0.1829	
NSD	9.6035	2.1170	4.103E-08	0.2204	
RMSE	9.5870	1.9337	6.801E-09	0.2017	
MPSD	9.1548	1.6552	6.398E-08	0.1808	
Freundlich	K_F	$1/n$	OF ^a	NE	SNE = 4.2156
R ²	2.0534	1.0000	1.0000	0.4870	
SSE	2.3534	1.0051	3.797E-08	0.4271	
HYBRID	0.8058	1.0000	1.994E-30	0.8058	
NSD	1.4323	0.9503	2.204E-05	0.6635	
RMSE	1.0491	1.0058	3.210E-07	0.9587	
MPSD	1.0047	0.8776	3.781E-06	0.8735	
Temkin	K_T	b_T	OF ^a	NE	SNE = 4.3056
R ²	2.9517	3.5577	1.0000	0.8297	
SSE	3.2498	3.4015	7.020E-09	0.9554	
HYBRID	1.7437	2.8297	0.0000	0.6162	
NSD	2.2790	3.4718	2.062E-07	0.6564	
RMSE	2.0560	3.2609	1.547E-08	0.6305	
MPSD	1.8048	2.9230	1.125E-08	0.6174	
Dubinin-Radushkevich	q_{mDR}	K_{DR}	OF ^a	NE	SNE = 0.5465
R ²	7.8820	0.6065	1.0000	0.0769	
SSE	7.1659	0.4648	1.888E-09	0.0649	
HYBRID	8.8531	0.9396	1.849E-19	0.1061	
NSD	9.1287	0.8448	2.993E-06	0.0925	
RMSE	9.1381	0.8950	2.433E-09	0.0979	
MPSD	8.7611	0.9479	1.701E-06	0.1082	
Sips	q_0	b	n	OF ^a	SNE = 2.2295
R ²	1.7561	0.8649	0.8862	1.0000	
SSE	1.7089	0.7626	1.1271	9.394E-07	
HYBRID	1.8146	0.8832	0.5285	5.398E-10	
NSD	1.7972	0.8794	0.6705	2.538E-06	
RMSE	1.8015	0.8717	0.6112	2.580E-09	
MPSD	1.8076	0.8649	0.5190	3.570E-06	
Redlich-Peterson	A	B	g	OF ^a	SNE = 0.9067
R ²	1.5267	0.5267	1.0000	1.0000	
SSE	1.7160	0.6935	0.9396	6.088E-09	
HYBRID	0.8058	0.0000	1.0000	0.0000	
NSD	1.1518	0.1488	1.0021	3.745E-10	
RMSE	1.0328	0.0289	1.0091	4.347E-08	
MPSD	0.7431	0.0004	1.0001	5.472E-07	

OF^a: Objective function for the minimum error distribution between experimental and predicted isotherm

To perform the non-linear regression and estimate the isotherm parameters, a solver add-in with Microsoft's Excel spreadsheet was employed. Since each of the selected error functions produced non-identical sets of isotherm parameters, an overall optimal isotherm parameter set was difficult to identify directly. To overcome this limitation and make a more meaningful comparison between the parameter sets, a procedure of normalizing the computed error functions was adopted to produce a single combination of the minimized error called SNE for each selected isotherm parameter [33]. The SNE was thereafter employed to choose the isotherm that best described the adsorption of

Pb²⁺ and Mn²⁺ onto acid-activated shale since the lower the sum of normalized error, the better the ability of the isotherm to describe the adsorption data. Results of the predicted isotherm by minimizing the error distribution using the selected error functions are presented in Tables 3 and 4 representing Pb²⁺ and Mn²⁺ adsorption onto shale. To select the isotherm model that best explains the adsorption data for specific metal ion removal, a graphical relationship between the computed SNE and the selected isotherm model for the sorption of Pb(II) and Mn(II) ion onto acid-activated shale were obtained and presented in Fig. 3.

Fig. 3 Selection of best-fit isotherm for (a) Pb (II) ion adsorption and (b) Mn(II) ion adsorption.

From the results of Fig. 3, it was noted that the Dubinin-Radushkevich isotherm model was the most suitable model to satisfactorily described the sorption of Pb^{2+} and Mn^{2+} onto acid-activated shale. Based on these findings, the sorption capacity of acid-activated shale was taken as 11.1568 mg/g. The average free energy of sorption per mole of the sorbate (E) as it is transferred to the surface of the solid from infinite distance in the solution was deduced using $E = 1/\sqrt{2K_{DR}} = 0.9294 \text{ kJ/mol}$; where $K_{DR} = 0.5789$, the positive value indicates endothermic reaction.

4. Conclusion

The application of non-linear error function for the selection of isotherm model that best explained the experimental data for the sorption of Pb^{2+} and Mn^{2+} onto acid-activated shale has been investigated. Based on the computed SNE, it was observed that the Dubinin-Radushkevich model provides the best-fit for the experimental data. Isotherm modeling using error function analysis is relevant in studying the potentials of materials as suitable adsorbents for water and wastewater treatment. It will also help determine the sorption capacity of adsorbents.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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