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Error Analysis Based on Isothermal Study Performed for Adsorption of Cr (III) with Hematite Nanosorbent Loaded on Rice Husk Biochar

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Abstract. Environmental safety and green technologies for the removal of harmful pollutants which burning issues now a days. In this regard research work was carried out for the sorption of Cr (III) from aqueous solution by three basic adsorbents named rice husk (RH), rice husk biochar (RHBC) and hematite loaded rice husk biochar (HLRHBC). The results revealed that rice husk nanomaterial as low cost adsorbent. Equilibrium studies were applied for error analysis to evaluate isotherm data. Linear and nonlinear analysis were used to calculate error functions. Linear errors were calculated from experimental results and non-linear error function data was calculated from error equations. Five errors i.e. sum square of errors, average relative error, sum of absolute error, chi square error and average percentage error were determined. Results indicated that all isotherms were supported by error data analysis both in linear and nonlinear approach. But chi square, sum square of errors and average relative error provided better determination for all adsorbents.

Keywords: hematite, equilibrium studies, error analysis, error equations, linear and nonlinear, adsorbents

Introduction

Agricultural and animal wastes have been used as adsorbents and recently, researcher's attention is to produce a low cost adsorbent called biochar with several environment friendly applications in adsorption processes (Mohan *et al*., 2014). Biosorption is an important technique to remove toxic metals from aqueous media and organic pollutants due to its simplicity, efficiency and cost effectiveness (Fertu *et al*., 2022; Lei *et al*., 2017). Selective adsorption by nano particles (Liu *et al*., 2010), fertilizer industrial waste, red mud, coal, biomass and algae have created great attention in this field. Different by products obtained from industries such as wasted iron, slags of iron, fly ash and hydrous titanium oxide are chemically modified to enhance their efficiency to remove metals from polluted water.

Biomass materials such as rice husk and straw, hazelnut shell, maize husk, hard covering of coconut etc. are used as sorbents in raw or chemically modified form, or pyrolysed into biochar or activated carbon through heating for the removal of heavy metals (Bansode *et al*., 2003). During past few years, biowaste materials are used for the removal of contaminants from aqueous media and industrial effluents. These biomaterials include plant or animal wastes, micro-organisms or their modified forms. Owing to their availability, low cost and efficiency in metal removal due to presence of certain functional groups such as amino or hydroxyl groups, these materials are now widely used as biosorbents (Michalak *et al*., 2013). Agricultural waste materials and industrial wastes are now focused for the removal of heavy metals due to ease in their accessibility and presence of chelated functional groups (Volesky, 2007). Use of ash or biochar of agricultural wastes is another addition to efficient biosorbents that can remove toxic metals from wastewater.

Adsorption isotherm models also depend on nature of adsorbent such as homogeneous or heterogeneous and also on possible interactions with adsorbate. Langmuir, Freundlich, Elovich, Dubinin-Radushkevich and Temkin adsorption isotherm models describe a relation among metal uptake to adsorbate concentration in the solution. Experimental data and analysis in adsorption isotherms is dependent on monolayer and multilayer surfaces. These adsorption isotherms are also applied in different equilibrium systems of gases, solids and liquids. The graphs obtained in isothermal study represent adsorption mechanism, interaction among adsorbents and contami-

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nants. Isothermal results vary with the error function to reduce gap of results among experimental and predicted data on isotherms (Ho *et al*., 2002). Previously, error analysis has been performed on different analytes. Linear and non-linear isotherms and error functions were performed for removal of methyl from soil. Less error values were obtained for Freundlich isotherm (Khandelwal *et al*., 2020). Five error functions were calculated from isotherm analysis data obtained for the removal of acid dyes from bamboo derived activated carbon. These error functions were nonlinear and gave favourable results (Chan *et al*., 2012). Leonardite was used as an adsorbent for uptake of cadmium and zinc from aqueous solutions. Adsorption study was applied on isotherms and nonlinear form of five error analysis (Terdputtakun *et al*., 2017).

Isothermal study for a single analyte component needs an error function to assess experimental data at equilibrium. The present study is focused on use of equilibrium isotherm data to evaluate error analysis for uptake of Cr (III) by RH, RHBC and HLRHBC. Parameters of Freundlich, Dubinin-Radushkevich, Langmuir, Elovich and Temkin isotherms were used to calculate linear and nonlinear error functions. These results were compared in terms of isotherms for minimum error analysis on adsorption data for removal of chromium by different forms of rice husk sorbents.

Materials and Methods

Methods and equilibrium study. Adsorption equilibrium experiments were performed with rice husk adsorbents labelled as RH, RHBC and HLRHBC for removal of chromium through batch adsorption process. For this purpose standard solutions of chromium with varying concentrations (15-90 ppm) were prepared from chromium salt. Experimental results obtained by studying concentration parameter were applied on adsorption isotherm models and errors were calculated using equations. Linear and nonlinear errors were then used to compare isotherms, which revealed that isotherms with minimum error. Different isotherms are available in literature but five isotherm equations were used in this analysis to compare experimental results. These adsorption models were further validated by applying different errors, and comparing their high and low values in each case.

Error analysis. Error analysis is required with adsorption isotherm study for single component to evaluate experimental results. In this study linear and nonlinear error functions were applied on results obtained from Freundlich, Dubinin-Radushkevich, Langmuir, Elovich and Temkin isotherms eq (1).

Sum square of errors (ERRSQ/RSS). An important and widely used method in error function analysis is sum square of errors. This error function also has a limitation, as it shows good results at higher concentrations of adsorbate. With an increase in adsorbate concentration, an increase in error value and hence square of error occurs (Mane *et al*., 2007; Ng *et al*., 2002).

Mathematical expression to find ERRSQ is as under:

$$\text{ERRSQ/SSE} = \sum_{i=1}^{n} (q_{e.calc} - q_{e.meas})_i^2 \quad \text{.................... (1)}$$

Where, q_{ei} calc is calculated value at equilibrium and q_{ei} meas is measured value at equilibrium. In case of large no of experimental data values as in adsorption, low and high values are obtained. This error show favourable results towards high values as compared to low values. So, minimization of ERRSQ is required to attain favourable results. Otherwise, it is replaced by other error values such as average relative error and chi square error. To indicate a small error, values close to zero provides a better fit to error results and model results will be more useful (Mohd *et al*., 2022) in eq (2).

Average relative error (ARE). To minimize fractional error that spreads along whole concentration range, average relative error is used (Marquardt, 1963). To calculate error the difference between calculated and measured value is considered in relation to measured value.

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e.meas} - q_{e.calc}}{q_{e.meas}} \right|_i \quad \text{..........................(2)}$$

Sum of absolute error (EABS). Sum of absolute error provides better results for isothermal parameters at high concentrations. Thus, it shows a similarity with sum square error function in case that as value of error is increased and the results gets better (Kundu and Gupta, 2006; Porter *et al*., 1999) and show in eq (3).

$$\text{EABS} = \sum_{i=1}^{n} \left| q_{e.meas} - q_{e.calc} \right| \quad \text{............................ (3)}$$

Nonlinear chi-square test (X^2). Nonlinear chi-square test is used to analyse experimental data to attain best fitting results in adsorption. The equation for this analysis consist of difference of sum square of experimental data and standard data is taken proportionality and divided by standard value (Vimonses *et al*., 2009). Small value X^2 indicates a similarity among isothermal and experimental data, whereas, large value X^2 show a difference of results among isotherm and experimental data (Khamanur *et al*., 2017). The equation to calculate chi-square as under in eq (4).

$$\text{Chi-sq } (X^2) = \sum_{i=1}^{n} \frac{(q_{e.calc} - q_{e.meas})^2}{q_{e.meas}} \quad \text{.......................(4)}$$

Average percentage error (APE). Average percentage error helps to select isotherm with best fit of the experimental data. APE equation relates experimental and calculated data which was used to plot isotherms lines or curves (Subramanyam and Ashutosh, 2012).

$$\text{APE } (\%) = \frac{\sum_{i=1}^{n} (q_{e.meas} - q_{e.calc}) / q_{e.meas}}{N} \times 100 \quad \text{....... (5)}$$

Results and Discussion

Error distribution for equilibrium experimental results for chromium adsorption was calculated for all isotherms in linear and nonlinear forms. These values predict deviation among experimental and calculated data. Error data for isotherms under study is given in Table 1 and comparison among isotherms errors is shown to find the best fit results. Lowest error value predict best fit of data to isotherm results and minimum deviation from standard values.

Error analysis for RH. Error analysis was performed for parameters of different isotherms, indicating variation in error values in linear and nonlinear forms. Error data is given in Table 1 for both linear and non-linear models. This data proposed that for linear approach error minimization was high for Langmuir, Dubinin-Radushkevich and Elovich isotherm. So, Langmuir, Dubinin-Radushkevich and Elovich isotherm data supported linear analysis on adsorption experiments. While, for nonlinear approach Freundlich, Elovich, Temkin and Langmuir isotherms show less error values to favour adsorption data for removal of chromium by RH. Results indicate that rice husk worked as an efficient adsorbent with minimum error values on adsorption results. As experimental data performance on all forms of isotherms revealed that possible output of sorption analysis. Nonlinear model showed lower error values than linear model, indicating an increase in linearization increases the error results, which show in Table 1.

Linear approach. RSS= Dubinin-Radushkevich > Freundlich > Elovich > Temkin > Langmuir; EABS= Elovich > Freundlich > Temkin > Langmuir > Dubinin-Radushkevich; Chi-square (X^2) = Dubinin-Radushkevich > Freundlich > Langmuir > Temkin > Elovich; APE= Elovich > Freundlich > Langmuir > Temkin > Dubinin-Radushkevich; ARE = Elovich > Temkin > Freundlich > Langmuir > Dubinin-Radushkevich.

Nonlinear approach. RSS= Langmuir > Temkin > Dubinin-Radushkevich > Freundlich > Elovich; EABS= Langmuir > Temkin > Dubinin-Radushkevich > Elovich > Freundlich; Chi-square (X^2) = Freundlich > Dubinin-Radushkevich > Langmuir> Elovich > Temkin; APE= Freundlich > Elovich > Dubinin-Radushkevich > Temkin > Langmuir; ARE = Temkin > Freundlich > Langmuir > Elovich > Dubinin-Radushkevich.

Error analysis for RHBC. In case of RHBC application of adsorption data on errors show better adsorption of chromium and evaluate RHBC as an efficient adsorbent. Error function for Elovich and Langmuir models have small values for both linear and nonlinear forms. Which suggests these isotherms strongly supports experimental data with acceptable results of both linear and nonlinear error models,while error values of Dubinin-Radushkevich, Temkin and Freundlich isotherms also favours adsorption results. Linear and nonlinear errors are applicable on experimental study for removal of chromium by RHBC as indicated by final values given in Table 2. Langmuir isotherm give small RSS value in linear and nonlinear forms, while Freundlich, Dubinin-Radushkevich and Temkin isotherm reveals smallest APE value. Elovich isotherm shows lower chi-square value, favouring isotherm analysis.

Linear approach. RSS= Langmuir > Dubinin-Radushkevich > Temkin> Freundlich > Elovich; EABS= Langmuir > Dubinin-Radushkevich > Temkin > Freundlich > Elovich; Chi-square (X^2) = Freundlich > Dubinin-Radushkevich > Langmuir > Temkin > Elovich; APE= Freundlich > Elovich > Dubinin-Radushkevich > Temkin > Langmuir; ARE = Elovich >Temkin > Langmuir > Freundlich > Dubinin-Radushkevich.

Table 1. Error analysis for removal of Cr (III) by RH

Error function	RSS	EABS	Chi-square (X^2)	APE	ARE
Linear form					
Freundlich	0.0037	0.9301	0.5593	4.4309	0.0091
Langmuir	-0.0002	-0.0002	0.0002	0.0724	-0.072
Elovich	148.34	12.179	-2.984	49.74	17.909
Dubinin-Radushkevich	2470.8	-49.707	121.46	-232.4	-83.664
Temkin	$3.57*10^{-6}$	0.0018	-0.0918	-0.0314	0.5508
Nonlinear form					
Freundlich	$1.05*10^{-6}$	0.00213	0.00169	315457	19.42
Langmuir	0.0026	0.1467	-0.1467	-5.992	5.992
Elovich	$1.62*10^{-8}$	0.00012	-6.000	-0.0002	$-7.2*10^{-5}$
Dubinin-Radushkevich	$3.54*10^{-5}$	0.0059	$-1.1*10^{-6}$	-0.0146	-0.00529
Temkin	$3.65*10^{-5}$	0.0060	-6.286	-0.1007	37.716

Table 2. Error analysis for removal of Cr (III) by RHBC

Error function	RSS	EABS	Chi-square (X^2)	APE	ARE
Linear form					
Freundlich	0.0189	2.9060	4.1946	2.7616	0.047
Langmuir	0.00013	0.0001	-0.00013	0.0660	-0.0660
Elovich	84.358	9.1846	-1.9363	32.272	11.617
Dubinin-Radushkevich	597.12	-24.436	32.682	-116.63	-41.988
Temkin	0.0005	0.0226	-0.0841	-0.3780	0.5047
Nonlinear form					
Freundlich	$1.08*10^{-6}$	0.0022	0.0017	30930	21.45
Langmuir	0.0026	0.0672	-0.0672	-5.988	5.988
Elovich	$1.01*10^{-8}$	0.0001	-6.000	-0.0001	$-5.6*10^{-5}$
Dubinin-Radushkevich	$3.6*10^{-5}$	0.0060	$-1.1*10^{-6}$	-0.014	-0.0053
Temkin	$1.89*10^{-5}$	0.0043	-4.048	-0.072	24.291

Nonlinear approach. RSS= Langmuir > Dubinin-Radushkevich > Temkin > Freundlich > Elovich; EABS= Langmuir > Dubinin-Radushkevich > Temkin > Freundlich > Elovich; Chi square (X^2) = Freundlich > Dubinin-Radushkevich > Langmuir > Temkin > Elovich; APE= Freundlich > Elovich > Dubinin-Radushkevich > Temkin> Langmuir; ARE = Temkin > Freundlich > Langmuir > Elovich > Dubinin-Radushkevich

Error analysis for HLRHBC. Results of error analysis for HLRHBC as an adsorbent are given in Table 3. These results revealed that nanosorbents as an efficient sorbent with minimum error values. Dubinin-Radushkevich, Elovich and Temkin isotherms error functions analysis show that these values favours adsorption data for linear and nonlinear forms of isotherms. For linear form Elovich model gave high APE, EABS and ARE error values, while low chi-square value. Whereas, for nonlinear form Elovich model show small EABS and RSS values, Dubinin-Radushkevich also show minimum error for three errors i.e. EABS, APE and ARE in linear form, while, ARE and EABS in nonlinear form. Each error value show variation for each isotherm. These results revealed that minimum error and high adsorption capacity of HLRHBC adsorbent for uptake of chromium.

Linear approach. RSS= Dubinin-Radushkevich > Elovich > Freundlich > Temkin > Langmuir; EABS= Elovich > Temkin > Langmuir > Freundlich > Dubinin-Radushkevich; Chi-square (X^2) = Dubinin-Radushkevich > Freundlich > Langmuir > Temkin > Elovich; APE= Elovich > Freundlich > Langmuir > Temkin > Dubinin-Radushkevich; ARE = Elovich > Temkin > Freundlich > Langmuir >Dubinin-Radushkevich.

Table 3. Error analysis for removal of Cr (III) by HLRHBC

Error function	RSS	EABS	Chi-square (X^2)	APE	ARE
Linear form					
Freundlich	0.0128	-2.5741	4.3723	2.7623	0.033
Langmuir	0.4127	0.4127	-0.4127	0.05	-0.05
Elovich	145.61	12.066	-2.444	40.739	14.666
Dubinin-Radushkevich	4131.1	-64.274	197.52	-297.04	-106.93
Temkin	$6.05*10^{-5}$	0.0077	-0.1089	-0.1296	0.6535
Nonlinear form					
Freundlich	$3.18*10^{-7}$	0.0007	0.0006	30938	18.62
Langmuir	0.0025	0.0662	-0.0662	-5.971	5.971
Elovich	$2.35*10^{-9}$	$4.84*10^{-5}$	-6.000	$-7*10^{-5}$	$-2.5*10^{-5}$
Dubinin-Radushkevich	$3.61*10^{-5}$	0.6000	$-1.1*10^{-6}$	-0.0148	-0.0053
Temkin	$6.56*10^{-5}$	0.0081	-9.024	-0.1350	54.149

Nonlinear approach. RSS= Langmuir > Temkin > Dubinin-Radushkevich > Freundlich > Elovich; EABS= Langmuir > Temkin > Freundlich > Dubinin-Radushkevich > Elovich; Chi-square (X^2) = Freundlich > Dubinin-Radushkevich > Langmuir > Elovich > Temkin; APE= Freundlich > Elovich > Dubinin-Radushkevich > Langmuir > Temkin; ARE = Temkin > Freundlich > Langmuir >Elovich > Dubinin-Radushkevich.

Conclusion

Certain errors may arise in the results of adsorption isotherms owing to fluctuations in adsorption experiments or in measurement of adsorption data. All analysis was performed using error equations through implication of experimental results on linear and non-linear forms. Error study indicates that isotherm study is important but alone it cannot conclude adsorption findings without evaluating error results. Their application to complete equilibrium data indicated favourable results with the fact that error models can play efficient role in the analysis of sorption processes. Error analysis indicated minimum errors results for HLRHBC as an efficient adsorbent for Cr (III) uptake from aqueous media. EABS, ARE, APE showed minimum error i.e. -64.274, -106.93 and -297.04 values for Dubinin-Radushkevich isotherm in linear form. For nonlinear form RSS and EABS gave minimum error i.e. $2.35*10^{-9}$ and $4.84*10^{-5}$ for Elovich isotherm whereas, chi-square and APE results were minimum i.e. -9.024 and -0.1350 for Temkin isotherm. In comparison with RHBC small error results favoured Elovich, Freundlich and Langmuir isotherms. Also, or RH adsorbent equilibrium error results supported all isotherms with minimum error value in one case or other. So, the results of this study revealed that both linear and nonlinear error analysis supported all adsorption isotherm data for the removal of chromium by RH, RHBC and HLRHBC.

Conflict of Interest. The authors declare that they have no conflict of interest.

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