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KINETIC & EQUILIBRIUM MODELLING OF COPPER BIOSORPTION

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Abstract

A thorough examination focused around non-linear and linear regression of different kinetic models (Pseudo 1st Order and Pseudo 2nd Order), two parameter isotherm models (Temkin, Dubinin-Radushkevich, Freundlich and Langmuir) and three parameter isotherm models (Radke-Prausnitz, Koble-Corrigan, Sips, Toth, Hill and Redlich-Peterson) were analysed to investigate different aspects of Cu (II) biosorption onto dead immobilized *Rhizopus Arrhizus* (DIRA). Six different error functions were utilized to demonstrate the integrity of the fit of a model. Non-linear regression was a more proper technique for getting parameters. Based on R^2, SSE, MSE, RMSE, SAE and ARE among three parameter models Redlich-Peterson and Radke-Prausnitz isotherm models enumerated the experimental data best and among two parameter models Langmuir isotherm model gave the better depiction of the work directed. Pseudo 2nd order kinetic model enumerated the biosorption of Cu^{+2} using DIRA best.

Keywords: DIRA, Kinetic Modelling, Equilibrium Modelling, Linear & Non-Linear Regression Analysis, Biosorption of Cu (II)

1. Introduction

Heavy metals discharged into the air by modern exercises tend to continue for an inconclusive period, flowing and at last aggregating all through the natural pecking order, therefore showing up as a deadly danger to all the livings and their surroundings [1]. Drinking water and wastewater tainted with Cd, Cu, Pb, Ni and Zn is a genuine continuous issue [2]. These pollutants are insistent poisons as well as they have an inclination to mount up in various nourishment cycles climaxing in a danger for all living creatures [3].

Copper finds far reaching applications in commercial enterprises and is an imperative component for different types of living in follow esteem. Then again, unbalanced copper can be destructive for the earth. In this manner, expulsion of copper from wastewater is fundamental not just to nurture water resources additionally to decelerate the rate of loss of copper holds.

The most ideal approach to remediate substantial metal tainted water is to treat it at source, *i.e.*, before scattering of wastewater to diverse biological communities [3]. To attain this objective a rundown of customary advances like evaporation, membrane separation, precipitation, sedimentation, adsorption, and so forth, is accessible. All these innovations can sequester or focus heavy metals from the contaminated water, yet they confront conservative and pragmatic limits like production of large volume of sludge, repeated alteration of filter which again requires most secure transfer [1, 4, 6].

Despite the fact that ion exchange is thought to be a finer option strategy, it is extravagant and mostly ion exchangers don't have great selectivity to point out metal ions over other metal ions. Adsorption system is thought to be among the most positive methodologies as a result of its high proficiency and complete evacuation of metal ions even at low concentrations. The proceeding increment in assortment and measure of risky chemicals in effluents makes customary adsorbents inefficient and once in a while indeed ineffectual. Therefore, the advancement of new and then some viable adsorbents has ended up crucial, yet in the meantime it should be of ease [6-8].

Over the recent decades biosorption has been widely examined as a potential contender for removal of lethal heavy metals, particularly at low concentrations, *i.e.*, short of what 100 ppm [9]. In biosorption uninvolved removal of lethal heavy metals comes about because of holding between binding sites of dead biomass and metallic species through different components [10]. Dead microorganisms (like bacteria, algae and fungi); industrial sludge and agricultural waste are three essential sorts of biomasses picked the metal sequestration [11-13]. They can be extracted from the environment or cultured in the lab. The cellular walls of biomass contain phenols, carboxylic acids, amide and amine groups which are responsible for heavy metals uptake [8, 14].

Current examination investigates the capability of dead immobilized *Rhizopus Arrhizus* (DIRA). It was chosen because of its non pathogenic nature for human and creatures and it can be created cheaply whether through simple fermentation or as industrial waste from industrial fermentation processes such as lactic acid and lipase fermentation processes [15]. So as to comprehend the mechanism and enhance the design parameters of a viable biosorption procedure process design a decent understanding of adsorption kinetics and isotherms is indispensable [10, 16]. Chemical kinetics lets us know about the rate of reaction furthermore decides the factors influencing the rate of reaction. The way of sorption process relies on physical and chemical characteristics of the adsorbent systems and operational conditions. The most commonly pseudo 2nd order and pseudo 1st order kinetic models are utilized to clarify the solid/liquid adsorption processes [17-19].

Adsorption isotherms are portrayed by an equilibrium relationship which is attained when an adsorbate interact with a specific adsorbent at a given temperature. Thus fitting information of residual adsorbate concentration and equilibrium amount on adsorbent is obliged to perform precise examination for design of adsorption/biosorption based separation method. Different adsorption isotherms initially inferred for gas-solid have been utilized by the researchers in order to empirically define liquid-solid equilibria in heavy metal biosorption [20-21]. These models may be classified based upon their number of parameters viz, two parameter models and there parameter models.

Different kinetic and adsorption equations commonly used in the literature were tried for their ability to count the kinetic and equilibrium sorption data. Coefficient of determination (R^2) was taken as the criteria for assertion between model and experimental values. However, error functions like sum of the square of the errors (SSE), mean square error (MSE), root mean square error (RMSE), sum of the absolute errors (SAE) and average relative error (ARE) were likewise utilized to support the result of R^2. This encouraged the determination of the finest parameters set and consequently provided precise kinetic and equilibrium isotherm models.

2. Materials and Methods

2.1. Preparation of DIRA, chemicals and biosorption studies

Details of chemicals and methods are mentioned in N. Feroze *et al.*, [22].

3. Theoretical Background

3.1. Kinetic Study

3.1.1. Pseudo 1st Order Kinetic Model

It is given by the accompanying differential equation [23].

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

Where, q_t and q_e are instantaneous and equilibrium uptakes (mg.g^{-1}) respectively. k_1 (min^{-1}) is the pseudo 1st order rate constant. Eq. (1) results in the accompanying linearized form for the conditions of $q_t = 0$ at $t = 0$

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

And non-linear type is as follows

$$q_t = q_e\,[1 - \exp(-k_1 t)] \tag{3}$$

Linear plots ln ($q_e - q_t$) vs. t indicate the graphical conduct of pseudo first order kinetic model.

3.1.2. Pseudo 2nd Order Kinetic Model

Pseudo 2nd order kinetics can be determined using following rate equation [11].

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

Where, k_2 (g.mg^{-1}.min^{-1}) is pseudo 2nd order rate constant. Eq. (4) creates a linear equation on integration with initial conditions of at $t = 0$, $q_t = 0$:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{5}$$

The term $k_2 q_e^2$ is termed as initial sorption rate represented by h (mg.g^{-1}.min^{-1}) [7] and non-linear form is as follows

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6}$$

A linear plot of $\frac{t}{q_t}$ vs. t demonstrates the graphical conduct of pseudo 2nd order kinetic model.

3.2. Adsorption Isotherm Study

3.2.1. Two Parameters Models

3.2.1.1. Langmuir Isotherm Model

Fundamental assumptions of this model are [4]
a) Single layer homogeneous adsorption
b) Adsorption can occur only at finite sorption sites with same affinity for metal ions
c) No tangential interaction and steric interruption between the adsorbed ions
Mathematical non-linear type of this model is given by

$$q_e = \frac{b q_{max} C_e}{1 + b C_e} \tag{7}$$

Where, q_e (mg.g^{-1}) is equilibrium uptake corresponding to C_e (mg.L^{-1}) the equilibrium concentration of Cu^{+2}. b (L.mg^{-1}) and q_{max} (mg.g^{-1}) are the Langmuir constants. Linearized type of equation is

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\,b} + \frac{C_e}{q_{max}} \tag{8}$$

q_{max} is the concentration of adsorbate forming monolayer on the biosorbent surface. The constant b which represents the apparent energy of adsorption is used to calculate very important information regarding the effectiveness of the biosorption process namely separation factor (R_L) as given by the expression

$$R_L = \frac{1}{1 + b C_o} \tag{9}$$

C_o (mg.L^{-1}) is the initial Cu^{+2} concentration. Estimation of R_L somewhere around 0 and 1 speaks to the favourable adsorption. $R_L > 1$ represents the unfavourable adsorption while $R_L = 0$ denotes the irreversible process [4].

3.2.1.2. Freundlich Isotherm Model

This generally utilized relationship expects the vicinity of heterogeneous sites with different affinities for the adsorbate [24]. Sites with greater affinity are possessed prior bringing about multilayer adsorption with random magnitude of adsorption heat over the surface. Nonlinear type of this model is as under

$$q_e = K_F C_e^{1/n} \tag{10}$$

K_F (mg.g^{-1}) and n are Freundlich constants. K_F represents the relative adsorption capacity of the biosorbent. Estimation of n connotes the strength of biosorption. A greater value of 'n' symbolizes stronger bonding while $n = 1$ demonstrates linear adsorption. Freundlich parameters can be ascertained utilizing after linearized form of Freundlich model

$$\log (q_e) = \log (K_F) + \frac{1}{n} \log (C_e) \tag{11}$$

3.2.1.3. Dubinin-Radushkevich Isotherm Model

This model is infrequently applied onto liquid phase biosorption due to its complex nature. It accept heterogeneous surface with Gaussian energy distribution [4]. It characterizes an imperative parameter to be specific mean free energy which is utilized to differentiate the physical and chemical adsorption as takes after

$$q_e = q_{DR} \exp (-k_d \varepsilon^2) \tag{12}$$

k_d (mol^2.kJ^{-2}) and q_{DR} (mg.g^{-1}) can be computed from emulating linearized equation

$$\ln (q_e) = \ln (q_{DR}) - k_d\, \varepsilon^2 \tag{13}$$

ε can be computed by the accompanying expression

$$\varepsilon = RT \ln (1+\frac{1}{C_e}) \tag{14}$$

Where, k_d speaks to adsorption energy and q_{DR} is the saturation capacity of biosorbent. k_d is utilized to estimate mean free energy by the following expression

$$E = \frac{1}{\sqrt{2\, k_d}} \tag{15}$$

Value of E less than 1 to 8 kJ/mol corresponds to the physical adsorption while, 8 to 16 kJ/mol correspond to chemical adsorption. The graph is drawn between ln (q_e) vs. ε^2.

3.2.1.4. Temkin Isotherm Model

Temkin adsorption isotherm accept that decline in the heat of adsorption is a linear function rather than logarithmic. The adsorption heat of all molecules in the layer would diminish linearly with the coverage due to the adsorbent/adsorbate interactions. It is excellent adsorption isotherm for the determination of gas phase equilibrium. It can be utilized for the distribution of binding energies. The non-linear form of Temkin adsorption isotherm has been applied in following form [25].

$$q_e = \frac{RT}{b_T} \ln (A_T\, Ce) \tag{16}$$

The linear form of Temkin adsorption isotherm is given below

$$q_e = \frac{RT}{b_T} \ln (A_T) + \frac{RT}{b_T} \ln (C_e) \tag{17}$$

b_T is Temkin constant related to the adsorption heat (J/mol) and A_T is Temkin adsorption equilibrium binding constant (L/g). The graph is drawn between q_e vs. ln C_e.

3.2.2. Three Parameters Models

3.2.2.1. Redlich-Peterson Isotherm Model

This is a three parameter isothermal model which covers the wide range of adsorbate concentration by incorporating a linear relation in the numerator and an exponential function in the denominator [26]. It is a hybrid form of Freundlich and Langmuir equations as follows

$$q_e = \frac{K_{RP}\ C_e}{1+ a_{RP}\ C_e^g} \tag{18}$$

Where, K_{RP} (L.g^{-1}), a_{RP} (L.mg^{-1})^g and g are Redlich-Peterson constants. These parameters can be calculated using following linearized form

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{a_{RP}}{K_{RP}}\, C_e^g \tag{19}$$

Graph is plotted between $\frac{C_e}{q_e}$ vs. $\mathrm{C_e^g}$.

3.2.2.2. Sips Isotherm Model

This adsorption isotherm is a hybrid form of Freundlich-Langmuir adsorption isotherm model. This empirical equation is actually deduced from the system of heterogeneous adsorption. The mathematical non linear form of Sips adsorption isotherm is given below [25].

$$q_e = \frac{K_S\ C_e^{\beta S}}{1+ a_S\ C_e^{\beta S}} \tag{20}$$

On the other hand, the linear form of this model will be like this

$$\frac{1}{q_e} = \frac{a_S}{K_S} + \frac{1}{K_S}\frac{1}{C_e^{\beta S}} \tag{21}$$

Where, K_S is Sips model isotherm constant (L.g^{-1}), a_S is Sips model constant (L.mg^{-1}) and β_S is Sips adsorption model exponent. By using the linear form of above equation, we can plot the graph between $\frac{1}{q_e}$ vs. $\frac{1}{C_e^{\beta S}}$.

3.2.2.3. Toth Isotherm Model

This model is aimed at improving the Langmuir model to predict the behaviour of adsorption on heterogeneous surface [26]. In its non-linear type it is given as follows

$$q_e = \frac{K_T\, C_e}{(a_T + C_e)^{1/t}} \tag{22}$$

K_T (L.g^{-1}) and a_T (L.mg^{-1}) are toth constants and t which is toth model exponent can be calculated through following linearized equation

$$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t}\ln(a_T + C_e) \tag{23}$$

In this case, graph is drawn between $\ln\left(\frac{q_e}{K_T}\right)$ vs. $\ln(C_e)$.

3.2.2.4. Koble-Corrigan Isotherm Model

It is a well known three-parameter adsorption isotherm model which resembles with the sips adsorption isotherm equilibrium model. Koble-Corrigan also incorporates the features of the Freundlich and Langmuir adsorption equilibrium isotherms for representing the adsorption equilibrium isotherm data. The original mathematical non linear form of the Koble-Corrigan adsorption equilibrium isotherm is as follows [25].

$$q_e = \frac{A_{KC}\ C_e^{p}}{1+ B_{KC}\ C_e^{p}} \tag{24}$$

The linear form of the KC adsorption equilibrium isotherm is given below

$$\frac{1}{q_e} = \frac{1}{A_{KC}\ C_e^{p}} + \frac{B_{KC}}{A_{KC}} \tag{25}$$

Where, A_{KC} (L^p.mg^{1-p}/g) and B_{KC} (L/mg)^p are Koble-Corrigan isotherm constants and p is adsorption intensity. Graph is drawn between $\frac{1}{q_e}$ vs. $\frac{1}{C_e^{p}}$.

3.2.2.5. Radke-Prausnitz Isotherm Model

The mathematical non linear type of the Radke-Prausnitz can be expresses as follows [27]

$$q_e = \frac{q_m K_R C_e}{1+K_R C_e^{p}} \tag{26}$$

When we reduce the above equation to linear form then it can be written as follows

$$\frac{C_e}{q_e} = \frac{1}{q_m K_R} + \frac{1}{q_m} C_e^{p} \tag{27}$$

Where, q_m and K_R are Radke-Prausnitz isotherm model constants and p is model exponent. Graph is plotted between $\frac{C_e}{q_e}$ vs. C_e^{p}.

3.2.2.6. Hill Isotherm Model

Hill equation was hypothesized to depict the binding of different species onto homogeneous substrates. The model accept that adsorption is an agreeable phenomenon, with the ligand binding ability at one site on the macromolecule, may impact different binding sites on the same macromolecule [26]. Non linear form of hill model is given below [25].

$$q_e = \frac{q_{sH} C_e^{nH}}{K_D + C_e^{nH}} \tag{28}$$

And linear form is generalized as

$$\log\left(\frac{q_e}{q_{sH} - q_e}\right) = n_H \log(C_e) - \log(K_D) \tag{29}$$

$$K_D = K_d^{n_H} \tag{30}$$

Where, q_{SH} and K_D are the Hill isotherm constants. K_d is dissociation constant per site (mg/L) and n_H is Hill coefficient of binding interaction. Along these lines, three potential outcomes can happen

(1). $n_H > 1$, shows positive mutual binding
(2). $n_H = 1$, shows non-agreeable or hyperbolic binding
(3). $n_H < 1$, shows negative cooperation in binding [5].

Graph is plotted between $\log\left(\frac{q_e}{q_{sH} - q_e}\right)$ vs. $\log(C_e)$.

3.3. Linear & Non-linear Regression Analysis

Regression analysis is a factual tool for the examination of relationship between variables, typically the change in one dependent variable (decision/response variable) with respect to change in one or more than one independent variables. Regression analysis can be linear or non-linear depending upon the nature of mathematical equation.

For linearized regression, the real issue is the linearization step. The adjustment of the original equation can abuse the speculations existing behind the model so truth to be told the parameter estimation gives the best fitting parameters for the linear form of the model, not so much for the original nonlinear model. Nonlinear regression is a more general method that can be utilized to estimate model parameters [28].

In this study all the model parameters in Table 2, 3 & 4 were assessed by linear and non-linear regression utilizing curve fitting tool of MATLAB. The legitimacy of kinetic and equilibrium models were checked by the estimation of error functions as shown in the Table 1**.**

Table 1: Abbreviations and mathematical expression of six error functions

Error Functions	**Abbreviation**	**Mathematical Expression**
Coefficient of Determination	R^2	$= \frac{(q_{e,exp} - \overline{q_{e,model}})^2}{\sum(q_{e,exp} - \overline{q_{e,model}})^2 + (q_{e,exp} - q_{e,model})^2}$
Sum of the Squares of the Errors	SSE/ERRSQ	$= \sum_{i=1}^{n} (q_{e,model} - q_{e,exp})_i^2$
Mean Square Error	MSE	$= \frac{1}{n-2} \sum_{i=1}^{n} (q_{e,exp} - q_{e,model})^2$
Root Mean Square Error	RMSE	$= \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} (q_{e,exp} - q_{e,model})^2}$
Sum of the Absolute Errors	SAE/EABS	$= \sum_{i=1}^{n} \lvert q_{e,exp} - q_{e,model} \rvert_i$
Average Relative Error	ARE	$= \frac{100}{n} \sum_{i=1}^{n} \left\lvert \frac{q_{e,exp} - q_{e,model}}{q_{e,exp}} \right\rvert_i$

4. Results and Discussions

4.1. Kinetic Modelling

4.1.1. Pseudo 1st Order Kinetics

This kinetic model assumed that the biosorption of Cu^{+2} onto DIRA was proportional to the log of difference of uptake at equilibrium, q_{eq} and uptake at any time, q_t [4]. Pseudo first order kinetics has few downsides: (i) k_1 (q_{eq} - q_t) does not remained for quantity of vacant biosorption sites; (ii) Intercept of plot between ln (q_e-q_t) vs. t does not compares to ln (q_e); (iii) It does not indicate linearity over the entire course of biosorption [23]. Because of these downsides the kinetic study was further reached out to the pseudo second order kinetics to have better estimation of kinetic order for biosorption of Cu^{+2} onto DIRA. Table 2 introduces the details of pseudo 1st order and pseudo 2nd order models with linear and additionally non-linear forms for the fitting to the experimental data.

4.1.2. Pseudo 2nd Order Kinetics

This model is focused around the presumption that the rate of coverage of adsorption sites is directly related to the square of the uncovered adsorption sites [4]. The estimation of correlation of determination for Cu^{+2} biosorption onto DIRA was greatly high (R^2 is 0.999 for linear and 0.982 for non-linear) while SSE, MSE and RMSE were very low. Accordingly pseudo second order model gave the best fit between the experimental and anticipated values. The value of q_e calculated (2.967 mg/g for linear) through second order model was in agreement with experimental value (2.96 mg/g) as given in Table 2. That is why pseudo 2nd order is selected.

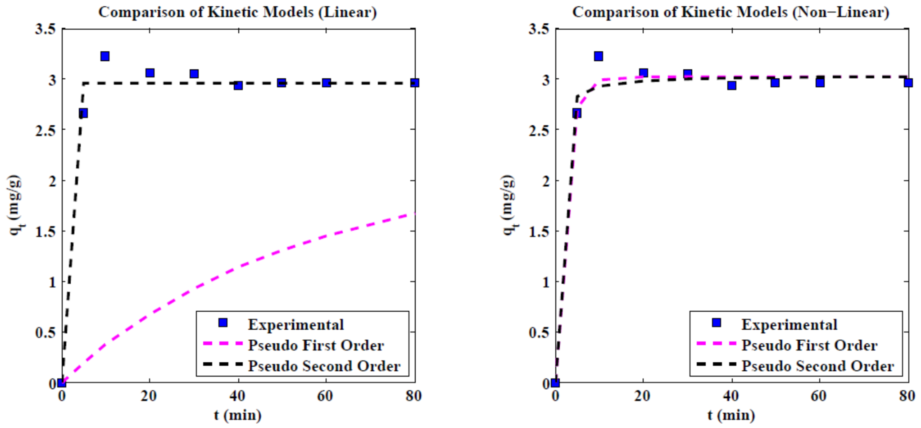

Figure 1: Comparison of linear & non-linear kinetic models for Cu (II) adsorption onto DIRA

4.2. Equilibrium Modelling

4.2.1. Two Parameters Models

4.2.1.1. Langmuir Isotherm Model

DIRA demonstrated a high level of fitting to this model in both cases as can be analyzed from R^2, SSE, MSE, RMSE and SAE values in Table 3. This demonstrated the likelihood of the removal of Cu (II) by DIRA in the form of a single layer. Since the R^2 was not unity, so it could be conceivable that there might be some heterogeneity in the system so there was a need to search for a finer description of the process. The monolayer capacity as indicated by the Langmuir constant q_{max} was 13.29 and 14.74 mg.g^{-1} for linear and non-linear, respectively. The parameter b which signifies the energy of adsorption was assessed to be 0.077 and 0.057, respectively. This constant was further used to ascertain the separation factor for various C_o. Values of R_L were in typical range of 0 and 1 on all the initial concentrations showing favourable biosorption of Cu^{+2} onto DIRA in range of 2-100 mg.L^{-1}.

4.2.1.2. Freundlich Isotherm Model

There is a richness of equilibrium studies which are favourably specified by Freundlich model. The nonlinear model takes after the experimental data for the biosorption of Cu^{+2} using DIRA demonstrated generally preferable fitting of Freundlich model over the linear model as shown in Figure 2. The parameter n has its value greater than unity which recommends that DIRA surface for sorption is heterogeneous [21]. As indicated by this model an estimation of n between 1 and 10 contrasts with favourable adsorption [21]. R^2 was evaluated as 0.991 (non-linear case) which was more than other models except Langmuir model. The adsorption intensity $1/n$ ranges somewhere around 0 and 1 reason the heterogeneous nature of the system [25]. Freundlich isotherm is broadly utilized to translate equilibrium data yet does not supply information on monolayer adsorption.

4.2.1.3. Temkin Isotherm Model

It represents the change of energy, which happens when heavy metals associate with the biosorbents. The appropriateness of Temkin isotherm model for equilibrium data is short of what the Langmuir and Freundlich model. Yet the linear and non-linear model of Temkin isotherm similarly fulfils the data of Cu (II) removal as indicated in Figure 2. It expects that the heat of sorption varies linearly, as the process of uptake proceeds. Table 3 demonstrates a moderately good fit of Temkin model for DIRA as R^2 is greater than 0.8. On the other hand, SSE and ARE were genuinely high for this situation. The constant A_T and b_T used to show up biosorption potential and heat of biosorption, separately. In both cases b_T is in the typically quoted range of physiosorption *i.e.*, less than 8 kJ/mol. Henceforth, it recommends that bonding of Cu (II) with DIRA is feeble [16].

4.2.1.4. Dubinin-Radushkevich Isotherm Model

To focus the nature of biosorption of Cu^{+2} *i.e.*, whether it is chemisorption or physiosorption, the Dubinin-Radushkevich model was concentrated on [4]. R^2 magnitude for D-R model was lower than other models considered in this study. k_d obtained from the linear equation used to calculate the mean free energy acquired from D-R model was 2.146 kJ.mol^{-1} which showed that process of adsorption of Cu^{+2} upon DIRA may be considered as physiosorption [24]. Plainly DR model underpinned the conclusion of Temkin isotherm. As contrasted with linear, non-linear model show better fit for the experimental data as demonstrated in Figure 2. The metal uptake of 9.382 (mg/g) is lower than Langmuir model. This demonstrates the lower efficiency of adsorption process.

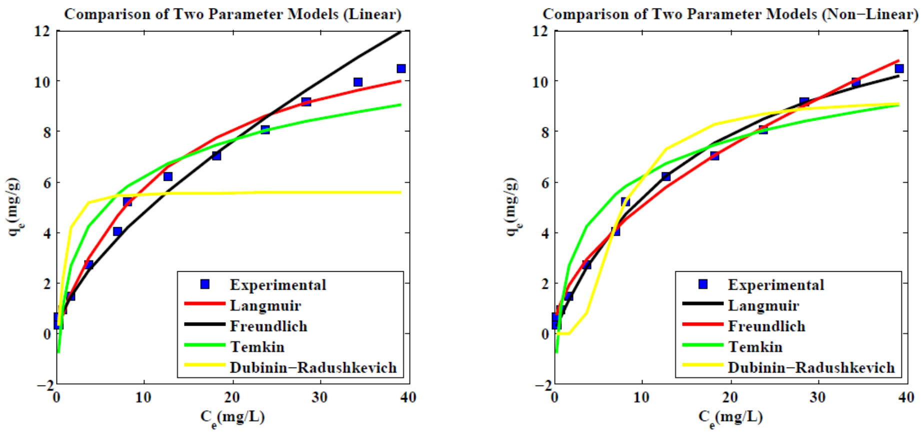

Figure 2: Comparison of linear & non-linear two parameter isotherm models for Cu (II) adsorption onto DIRA

4.2.2. Three Parameters Models

4.2.2.1. Redlich-Peterson Isotherm Model

Redlich-Peterson (R-P) model constants namely a_{RP}, K_{RP} and g were calculated using curve fitting tool and given in the Table 4. R^2 values for R-P model were 0.996 and 0.982 for non-linear and linear case, respectively. Since the values of g are 0.684 and 0.664, respectively. These were more close to 1 than 0 so it supported the result of Langmuir *i.e.*, the existence of homogenous system in the biosorption of Cu^{+2} onto DIRA with slight heterogeneity in the range of 2-100 mg.L^{-1}. Furthermore, the estimation of g lies between 0 and 1, indicating favourable adsorption. This model has shown high R^2 values and low values for SSE, MSE, RMSE and ARE (for both linear and non-linear models) among all other three parameters models except Radke-Prausnitz model.

4.2.2.2. Radke-Prausnitz Isotherm Model

This model has demonstrated high R^2 values and low values for SSE, MSE, RMSE and ARE (for both linear and non-linear models) like Redlich-Peterson model. It speaks to the Langmuir model for $p = 1$ and Henry's model for $p = 0$ [29]. The values of p by linear and non-linear regression were 0.664 and 0.684, respectively. Non-linear model was marginally better for Cu (II) ion adsorption onto DIRA with minimization of error functions while value of R^2 resulted to be 0.996. Figure 3 shows experimental data of Cu (II) adsorption as well as model. Values of parameters are given in Table 4.

4.2.2.3. Koble-Corrigan Isotherm Model

This model is valid only when $p > 1$[30]. The constant p is less than unity, implying that the model is not able to depict the data in spite of the high estimation of R^2. The non linear regression of Koble-Corrigan model gave parameters values like the Sips model affirming the theoretical correspondence of these two models as shown in the Table 4. The parameters got as a result of the linear regression and coefficient of determination as well as other functions given in Table 4 does not fulfil the experimental data.

4.2.2.4. Toth Isotherm Model

It is an alternate empirical equation created to enhance Langmuir isotherm fittings (experimental data), furthermore valuable in portraying heterogeneous adsorption systems [25]. Linear and non-linear trends of Toth model are shown in Figure 3 which depicts a poor fit for linear model and a fine correlation in case of non-linear model. This is stated by comparing the values of R^2 and other error functions given in Table 4. When t is less than 1, it suggests that adsorption occurs on a heterogeneous surface. For homogeneous adsorbents t is equal to 1. The Toth model exponent t assessed by non-linear regression lies between 0 and 1 recommending a decent correspondence of Toth isotherm with Langmuir isotherm as shown in Table 3 & 4.

4.2.2.5. Sips Isotherm Model

For $\beta_S = 1$, the Sips equation reduces to the Langmuir model [31], as apparent from the estimations of parameters. The Sips isotherm fitted for the experimental equilibrium data covers with the Langmuir isotherm, hence, demonstrating a great fit. Degree of heterogeneity, β_S was less than one which demonstrates that some kind of heterogeneity in the surface. The linear model introduced a poor fit of experimental data as R^2 was 0.861 as contrasted to non-linear model demonstrating best fit of equilibrium data with R^2 0.995 and adequate estimations of error functions in Table 4.

4.2.2.6. Hill Isotherm Model

The Hill isotherm model fitted well the experimental data of Cu^{+2} ion uptake onto DIRA by estimating R^2 has values of 0.944 and 0.995 for linear and non-linear case, respectively and adequate values of the error functions are presented in Table 4. The hill model constant n_H values are 1.123 by linear and 0.778 by non-linear regression analysis, which demonstrates that value greater than unity indicating positive mutual binding of metal ions on the surface of DIRA. While less than unity value by non-linear regression tells that there is negative cooperation in the binding of metal ions on the surface of DIRA. The non-linear form gave better elucidation of experimental data as shown in Figure 3.

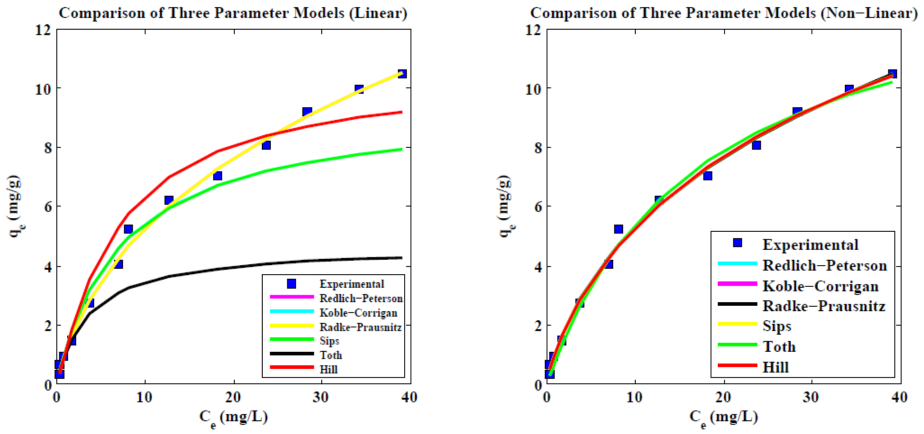

Figure 3: Comparison of linear & non-linear three parameter isotherm models for Cu (II) adsorption onto DIRA

5. Conclusions

Linear and non-linear optimisation techniques were applied to determine isotherm and kinetic parameters. For the best models distinguished, the non-linear calculation of isotherm and kinetic parameters introduced in this paper produced comparable data to those acquired utilizing the linear method based on the least squares calculation. Based on the error analysis, Langmuir, Redlich-

Peterson and Radke-Prausnitz equations, in both their linear and non-linear forms, appear to be suitable models for Cu (II) biosorption onto DIRA. For these best models, the estimations of isotherm constants were very close when figured utilizing linear and non-linear equations. Pseudo second order kinetics prevalently specified the kinetic data in case of linear regression analysis and on the basis of both non-linear & linear regression analysis pseudo second order showed optimized results as compared to pseudo first order model.

Table 2: Comparison of Kinetic Models

Kinetic Models	**Unknown Parameters**		**Different Error Functions**				
Pseudo 1st Order	k_1 **(min^{-1})**	q_{e1} **(mg/g)**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**
Linear	0.019	0.712	0.316	4.545	0.568	0.753	21.263
Non-linear	0.459	3.022	0.990	0.080	0.009	0.094	0.630
Pseudo 2nd Order	k_2 **(g/mg.min)**	q_{e2} **(mg/g)**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**
Linear	2538	2.967	0.999	0.260	0.032	0.180	0.794
Non-linear	0.893	3.041	0.982	0.141	0.015	0.125	0.850

Table 3: Comparison of Two Parameters Models

Isotherm Models	**Unknown Parameters**		**Error Functions**					
Langmuir	b **(L/mg)**	q_{max} **(mg/g)**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	0.077	13.290	0.962	0.499	0.038	0.196	2.051	14.120
Non-linear	0.057	14.740	0.994	1.122	0.086	0.293	3.119	11.299
Freundlich	K_F **(mg/g)**	n	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	1.029	1.494	0.975	0.075	0.005	0.076	0.719	13.327
Non-linear	1.406	1.797	0.991	1.370	0.105	0.324	3.382	20.424
Dubinin-Radushkevich	k_d **(mol^2/kJ^2)**	q_{DR} **(mg/g)**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	0.217	5.590	0.928	3.781	0.290	0.539	5.936	53.046
Non-linear	6.831	9.382	0.936	13.231	1.017	1.008	11.060	41.948
Temkin	b_T **(kJ/mol)**	A_T **(L/mg)**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	1.231	2.156	0.914	14.075	1.082	1.040	11.868	64.147
Non-linear	1.231	2.156	0.914	14.075	1.082	1.040	11.868	64.147

Table 4: Comparison of Three Parameters Models

Isotherm Models	**Unknown Parameters**			**Error Functions**					
Redlich-Peterson	K_{RP} **(L/g)**	a_{RP} **(L/mg)^g**	g	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	1.487	0.395	0.664	0.982	0.234	0.018	0.134	1.378	10.119
Non-linear	1.439	0.354	0.684	0.996	0.630	0.048	0.220	2.373	9.255
Koble-Corrigan	A_{KC} **(L^{p}mg^{1-p}/g)**	B_{KC} **(L/mg)^p**	p	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	1.294	0.136	0.991	0.861	1.472	0.113	0.336	2.067	18.238
Non-linear	1.164	0.053	0.778	0.995	0.673	0.051	0.227	2.374	9.765
Radke-Prausnitz	q_m **(mg/g)**	K_R	p	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	3.756	0.395	0.664	0.982	0.234	0.018	0.134	1.378	10.119
Non-linear	4.063	0.354	0.684	0.996	0.630	0.048	0.220	2.369	9.257

Sips	**K_S (L/g)**	**a_S (L/mg)**	**βs**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	1.293	0.136	0.991	0.861	1.472	0.113	0.336	2.068	18.260
Non-linear	1.164	0.053	0.778	0.995	0.673	0.051	0.227	2.374	9.765
Toth	**K_T (mg/g)**	**a_T (L/mg)**	**t**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	3.113	3.616	1.500	0.979	0.346	0.026	0.163	1.437	17.540
Non-linear	16.990	17.310	0.867	0.994	1.122	0.086	0.293	3.116	11.292
Hill	**q_{sH} (mg/g)**	**K_D**	**n_H**	**R^2**	**SSE**	**MSE**	**RMSE**	**SAE**	**ARE**
Linear	10.503	8.664	1.123	0.944	0.502	0.041	0.204	8.054	16.739
Non-linear	21.630	18.590	0.778	0.995	0.673	0.051	0.227	2.379	9.764

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