



## EQUILIBRIUM AND KINETIC STUDY FOR THE UPTAKE OF A HEAVY METAL

Z. Idrees<sup>1</sup>, M. Kazmi<sup>1\*</sup>, M. Habib<sup>2</sup>, Q. Ali<sup>2</sup>, K. Shahzad<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, KSK Campus, UET Lahore.

<sup>2</sup>Department of Mathematics, University of Engineering and Technology, Lahore, Pakistan

<sup>3</sup>Centre for Coal Technology, University of the Punjab, Lahore.

### Abstract:

Regression analysis was carried out to explore the effects of almond shell activated carbon (ASAC) as a biosorbent for the uptake of Cr(VI) ions from synthetic waste water. The equilibrium and kinetics models for biosorption were examined to best describe the experimental data of Cr(VI) ions biosorption by ASAC using MatLab. Kinetic models (Pseudo 1st order and Pseudo 2nd order) were analyzed by least square method (linear and Non-linear). Two parameters (Langmuir and Freundlich) and three parameter (Redlich-Peterson, Sips, Toth, Koble-Corrigan and Radhke-Prausnitz) adsorption isotherm models were analyzed by both linear and non-linear least square method to obtain the best fit model. Non-linear regression presented a better fitting of model equations. The kinetics is best described by pseudo 2nd order model. The equilibrium data of Cr(VI) ion followed the Langmuir, Redlich-Peterson and Radke-Prausnitz isotherm models preferably than the other models.

**Keywords:** Regression analysis, ASAC, Biosorption, Kinetic models, Adsorption isotherms

---

\* Corresponding Author: [engrmakazmi@yahoo.com](mailto:engrmakazmi@yahoo.com)

## 1. Introduction

Developing countries mostly depends on large scale industrialization to make their economy strong. This economical development is largely achieved on the expense of production of significant quantities of metal, organic and inorganic contaminants. The existing industrial activities are altering the material's natural flow and introducing novel chemicals into our environment [1]. Toxic metals such as Pb, Cu, Zn, Cr, and Cd were listed as concerned pollutants by the U.S Environmental protection Agency (U.S EPA). The heavy metals anthropogenic sources find their ways to the industries as metal plating industries, nickel batteries, chemical manufacturing, mine drainage, tannery operations, leather tanning industries, pigments, stabilizers of alloys and as polluted ground water from hazardous waste locations [2]. Presence of these toxic metals/heavy metals is a major warning to environment and human life due to their toxicity, bio-accumulating tendency [3].

Chromium (Cr) is available in nature as an odorless, steel grey hard metallic element. It constitutes as one of the major environmental pollutant. Chromium exists in nature as stable hexavalent and trivalent forms [4]. Although micro quantity of chromium is necessary for human body as it control our glucose metabolism but surplus amount can leads to carcinogenic effect [5]. Human activities and natural processes are responsible for the chromium discharge in our environment. It may cause nosebleed, ulcers, weakened immune system, allergic reactions, liver damage, skin rash, genetic material alteration [6].

Waters and soil around industrial locations are contaminated by chromium and its removal from aqueous solution is very difficult. The most common physico-chemical techniques used for the Cr(VI) removal includes chemical reduction followed by precipitation with caustic soda. Other processes like electrolysis, reverse osmosis and ion-exchange are currently un-economical and inefficient [7].

Among all the processes, adsorption is accepted as an effectual and economic technique to make waste water free from heavy metal pollution. Activated carbon adsorption is extensively applied for the extraction of trace amount of heavy metals. This technique is relatively expensive. This fact turns the focus of the researchers to use other cost effective materials like industrial byproducts, agricultural waste, and natural substances [8]. Heavy metals biosorption by biomass has been much explored in recent years. In addition, biosorption is especially useful to handle dilute heavy metal contaminations. Biosorption is a process which is characterized as economical, efficient and generates less waste, and in some cases it may help in recovery of metal [9].

In the present study, Synthetic waste water containing Cr(VI) as heavy metal impurity is treated with almond shell activated carbon(ASAC). Number of experimental parameters for Cr(VI) ions adsorption from aqueous solutions were investigated in a batch study under different equilibrium conditions [10]. To determine the best fit equilibrium and kinetic models, the experimental data is fitted to Pseudo 1<sup>st</sup> order and Pseudo 2<sup>nd</sup> order kinetic models and adsorption isotherms. Two and three parameter adsorption isotherm were tested for their capability to specify the biosorption of Cr(VI) ions. Two parameter models include Langmuir and Freundlich adsorption isotherm. Similarly, three parameter models include Redlich-Peterson (R-P), Sips, Toth, Koble-Corrigan (K-C), and Radke-Prausnitz adsorption isotherm.

## 2. Modeling

### 2.1 Kinetic Models

#### 2.1.1 Pseudo First Order

Pseudo first order [11] equation suggested by Lagergren is a simple kinetic model that describes the process of sorption. There are some limitations of Pseudo first order kinetic model [12].

- (i)  $k_1 (q_e - q_t)$  does not correspond to the quantity of vacant biosorption sites.
- (ii) Intercept of plot between  $\log (q_e - q_t)$  and  $t$  does not compatible with  $\log (q_e)$ .
- (iii) It does not show linearity over the whole course of biosorption.

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

The general form is,

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

Where,

$k_1$  ( $\text{min}^{-1}$ ) is the pseudo 1<sup>st</sup> order rate constant.

$q_e$  and  $q_t$  are equilibrium and instantaneous uptake (mg/g).

#### 2.1.2 Pseudo Second Order

For the sorption process, the Pseudo 2<sup>nd</sup> order kinetics [13] is obtained by the following expression;

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

The general form is

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

Where,

$k_2$  (g/mg.min) is Pseudo 2<sup>nd</sup> order rate constant.

$q_e$  and  $q_t$  are equilibrium and instantaneous uptake (mg/g).

### 2.2 Isotherm Models

#### 2.2.1 Two Parameter Model

##### 2.2.1.1 Langmuir Isotherm

In 1916, Irving Langmuir proposed the isothermal model which deals the gas-solid adsorption. Later on empirical relations were developed for liquid-solid system. Langmuir adsorption isotherm is effective for both chemical and physical adsorption. In its formulation, this empirical model assumes monolayer adsorption and adsorption can occur at fixed number of specific

localized sites of the adsorbent. There is no further contact on adjoining sites and spatial interference among the adsorbed metal ions [14]. Langmuir also assumed that the energy of adsorption of each and every molecule of a given adsorbate is the same which means that the surface is energetically homogeneous [8]. Furthermore, Langmuir theory has explained that with the rise of the distance immediate reduction occurs in the intermolecular attraction forces.

The general form of Langmuir adsorption isotherm is represented by the following equation;

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (5)$$

The above mentioned equation is linearized into the following form;

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (6)$$

Where,

$q_e$  = Equilibrium uptake of the adsorbate (mg/g).

$C_e$  = Equilibrium concentration of the adsorbate (mg/L).

$q_{max}$  = Maximum adsorption capacity (mg/g).

$K_L$  = Langmuir isotherm constant associated to the affinity of the surface sites (L/mg).

### 2.2.1.2 Isotherm model of Freundlich

The Freundlich isotherm [15] model is proposed by Freundlich and Küster (1894). Non-ideal and reversible behaviour is initially described by Freundlich isotherm. This experiential model based on multilayer coverage because of the non-uniform affinities of the heterogeneous sites for the metal ions (adsorbate) [16]. Due to this, the sites with greater affinity occupied earlier resulting multilayer adsorption. The non-linear form of the Freundlich isotherm is described by the following relations;

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

When linearized the equation becomes;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

Where;

$K_F$  = the relative adsorption capacity of biosorbent in (mg/g).

$n$  = the extent of biosorption.

### 2.2.2 Three Parameter Isotherms

#### 2.2.2.1 Isotherm model of Redlich–Peterson

Redlich-Peterson (R-P) isotherm is obtained by merging the characteristics of both Freundlich and Langmuir isotherm [17]. In its formulation, it depends on the linear and exponential form of concentration to illustrate equilibrium over an extensive range of concentration [18]. Both homogeneous and heterogeneous surface adsorption phenomena can be analyzed by Redlich-

Peterson model. At high metal ion concentration, R-P model reduces to Freundlich model with exponent approaches to zero. At low metal ion concentration, it reduces to Langmuir model with exponent approaches to 1 [19]. Redlich-Peterson isotherm non-linear form is as follows;

$$q_e = \frac{k_{RP}C_e}{1+a_{RP}C_e^g} \quad (9)$$

Equation (10) describes the linear form of the model;

$$\frac{C_e}{q_e} = \frac{1}{k_{RP}} + \frac{a_{RP}}{k_{RP}} C_e^g \quad (10)$$

Where;

$k_{RP}$  = R-P isotherm model constant (L/g)

$a_{RP}$  = Constant of R-P model (L/mg)

$g$  = Redlich-Peterson model exponent (that lies between 0 & 1).

#### 2.2.2.2 Sips isotherm model

Sips [20] proposed new equation to anticipate the heterogeneous adsorption system. Sips isotherm is also a combined form of Freundlich and Langmuir isotherm. The concentration of adsorbate expresses inverse relation as compared to Redlich-Peterson isotherm. At a smaller amount of adsorbate it becomes Freundlich isotherm and thus Henry's law is not obeyed. At high concentration of adsorbate, it predicts the single layer biosorption which is the essential characteristic of the isotherm of Langmuir. The sips isotherm can be given by the following expression;

$$q_e = \frac{K_s C_e^{B_s}}{1+a_s C_e^{B_s}} \quad (11)$$

The Sips equation has another simple linear form called as Pseudo linear form represented as;

$$\frac{1}{q_e} = \frac{a_s}{K_s} + \frac{1}{K_s C_e^{B_s}} \quad (12)$$

Where;

$K_s$  = Sips constant (Litre/gram).

$a_s$  = Sips constant (Litre/milligram).

$B_s$  = Sips model of adsorption exponent.

#### 2.2.2.3 Koble-Corrigan isotherm model

Koble-Corrigan [21] model is similar to Sips isotherm model. Like R-P isotherm and Sips isotherm, it is formulated with the combination of Freundlich and Langmuir isotherm. The equation of model is given below;

$$q_e = \frac{A_k C_e^{n_k}}{1 + B_k C_e^{n_k}} \quad (13)$$

The above expression is re-arranged to give the following linear expression

$$\frac{1}{q_e} = \frac{1}{A_k C_e^{n_k}} + \frac{B_k}{A_k} \quad (14)$$

Where;

$A_k$  = Koble-Corrigan constant (L·mg/g).

$B_k$  = Koble-Corrigan constant (Litre/milligram).

$n_k$  = Adsorption intensity.

#### 2.2.2.4 Toth isotherm model

Studies showed that heterogeneous system can be described well with the help of the Toth isotherm model that is derived by the potential theory [22]. Toth isotherm can be represented by following expression;

$$q_e = \frac{K_T C_e}{(a_T + C_e)^{\frac{1}{t}}} \quad (15)$$

Where,

$K_T$  = Toth adsorption isotherm constant (mg/g).

$a_T$  = Toth adsorption isotherm constant (L/mg).

$t$  = Toth model exponent.

The linearization of Toth equation results in the following equation.

$$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t} \ln(a_T + C_e) \quad (16)$$

#### 2.2.2.5 Isotherm model of Radke–Prausnitz

Isotherm model of Radke-Prausnitz is mostly estimated by high RMSE value. Model equation is given as follow [1];

$$q_e = \frac{q_m k_R C_e}{1 + k_R C_e^p} \quad (17)$$

The linearized form of the model equation is given below;

$$\frac{C_e}{q_e} = \frac{1}{q_m k_R} + \frac{1}{q_m} C_e^p \quad (18)$$

### 2.3 Regression Analysis

Regression analysis is a statistical tool for the investigation of relationship between variables, usually 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 major

problem is the linearization step. The modification of the original equation can violate the theories existing behind the model so in fact the parameter estimation gives the best fitting parameters for the linear form of the model, not necessarily for the original nonlinear model. Nonlinear regression is a more general method that can be used to estimate model parameters [23].

In this study all the model parameters in Table [4, 5, and 6] were analyzed by linear regression and non-linear regression using curve fitting tool of MatLab. The validity of kinetic and equilibrium models were checked by the estimation of error functions. The Best model selection was done on the basis of coefficient of determination ( $R^2$ ), SSE (Sum of square error), MSE (Mean square error), RMSE (Root mean square error), ARE (Average relative error), and SAE (Sum of absolute error) as represented by Table 1.

**Table 1:** Mathematical expressions of Error Functions

Function s	Formulas	Function s	Formulas
SSE	$\sum_{i=1}^n (q_{e,model} - q_{e,exp})_i^2$	ARE	$\frac{100}{n} \sum_{i=1}^n \left  \frac{q_{e,exp} - q_{e,model}}{q_{e,exp}} \right _i$
MSE	$\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,model})_i^2$	SAE	$\sum_{i=1}^n  q_{e,exp} - q_{e,model} _i$
RMSE	$\sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,model})_i^2}$	$R^2$	$\frac{\sum (\overline{q_{e,exp}} - q_{e,model})^2}{\sum (\overline{q_{e,exp}} - q_{e,model})^2 + \sum (q_{e,exp} - q_{e,model})^2}$

### 3 Result and Discussion

#### 3.1 Pseudo First Order Kinetic

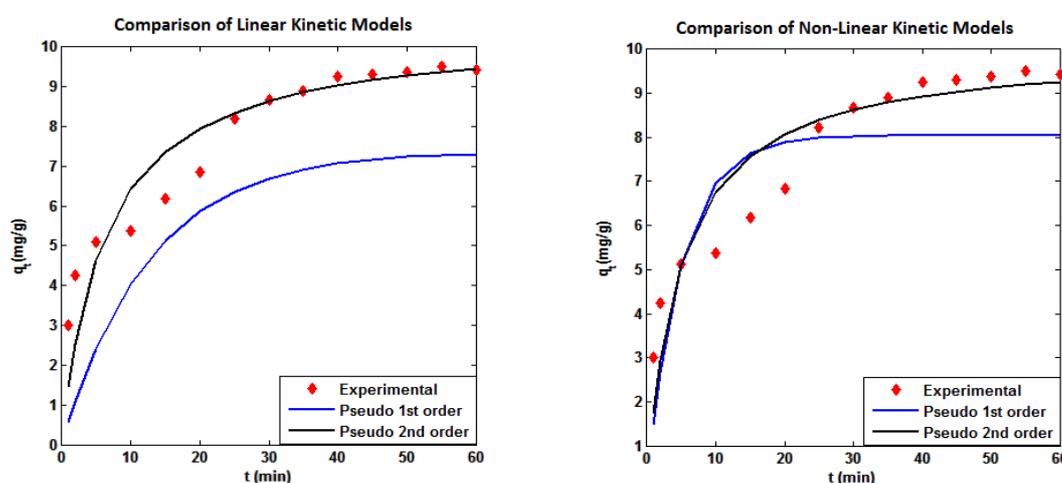
Equilibrium constant  $k_1$  and equilibrium capacity  $q_e$  (mg/g) obtained by linear regression as well as non-linear method. The  $q_e$  value is much lower than the experimental value representing that the Pseudo 1<sup>st</sup> order is not appropriate for the Cr(VI) removal kinetics. Figure 1 justifies that there is a poor correspondence between the first order model and the experimental data. The value of the parameters and coefficient of correlation is given in the Table 4. Due to the limitations the kinetic study was further extended to second order kinetics in order to obtain good fit for the Cr(VI) biosorption on ASAC.

#### 3.2 Pseudo Second Order

Four different Pseudo 2<sup>nd</sup> order linear forms are mentioned in Table 2. Pseudo 2<sup>nd</sup> order I is used in this study, as it is the most preferable linear form [24]. Using linear and non-linear least-square regressive method,  $k_2$  and  $q_e$  was determined. The values demonstrate that the model explains sorption in better way confirming a chemisorptions process. This kinetic model gave best fit between the predicted and experimental values in Figure 1. The value of the parameters and coefficient of correlation is given in Table 4.

**Table 2:** Linear Forms of Pseudo 2<sup>nd</sup> Order Kinetic Model.

Models	Linearized form	Plot
Pseudo 2 <sup>nd</sup> order I	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ vs $t$
Pseudo 2 <sup>nd</sup> order II	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{q_t}$ vs $\frac{1}{t}$
Pseudo 2 <sup>nd</sup> order III	$q_t = q_e - \left(\frac{1}{k_2 q_e}\right) \frac{q_t}{t}$	$q_t$ vs $\frac{q_t}{t}$
Pseudo 2 <sup>nd</sup> order IV	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	$\frac{q_t}{t}$ vs $q_t$

**Figure 1:** Comparison of Linear and Non-Linear plots of Pseudo 1<sup>st</sup> and 2<sup>nd</sup> order kinetic model of Cr(VI) removal using ASAC.

### 3.3 Two Parameter Models

#### 3.3.1 Langmuir Isotherm Model

Equation of Langmuir isotherm can be linearized into four altered forms given in the Table 3. Langmuir I is used because of least deviation from the fitted equation that results from best error distribution [25]. Figure 2 shows that both linear and non-linear model fitted well to the experimental data for Cr(VI) biosorption onto ASAC. The parameters of the Langmuir equation  $q_{max}$  and  $K_L$  estimated by NL (Non-linear) and L (Linear) regression are 20.28 (mg/g), 0.0635 (L/mg) and 19.89 (mg/g), 0.06562 (L/mg). The  $q_{max}$  predicts the monolayer capacity and  $K_L$  expresses the energy of adsorption used to calculate the separation factor  $R_L$  [10]. Langmuir model represented a good fit of experiment data for the sorption of Cr(VI) ions on ASAC in both cases, as the coefficient of determination ( $R^2$ ) was 0.9819 by linear regression and 0.9818 by non-linear regression. Since  $R^2$  is slightly less than unity indicates that there is might be some heterogeneity in the adsorption process of Cr(VI) ions on ASAC. The error functions (SSE, MSE, RMSE, ARE, SAE) also indicating a good fit of Langmuir model and are shown in Table 5.

Table 3: Different Linear Models of Langmuir Isotherm equation.

Sr No.	Linear Model	Plot
Langmuir I	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{b \cdot q_{max}}$	$\frac{C_e}{q_e}$ vs $C_e$
Langmuir II	$\frac{1}{q_e} = \frac{1}{b \cdot q_{max}} \cdot \frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Langmuir III	$\frac{q_e}{C_e} = b \cdot q_{max} - b \cdot q_e$	$\frac{q_e}{C_e}$ vs $q_e$
Langmuir IV	$q_e = q_{max} - \frac{1}{b} \cdot \frac{q_e}{C_e}$	$\frac{q_e}{C_e}$ vs $q_e$

### 3.3.2 Freundlich isotherm model

Figure 2 represents the compatibility of Freundlich isotherm for equilibrium data, the non linear model follows the experimental data for the biosorption of Cr(VI) ions a bit more than the linear model. The calculated values of Freundlich constant  $K_F$  and exponent  $n$  were 1.812 (mg/g) and 1.925 in the case of linear analysis and 2.691 (mg/g) and 2.404 for non linear analysis. As the values of  $R^2$  (0.9424, 0.9536) and other correlation given in Table 5 predicting favourable conditions in the result of both non-linear and linear regression for the sorption of Cr(VI) on ASAC. The adsorption intensity  $1/n$  ranges between 0 and 1 deduce the heterogeneous nature of the system [15]. The values are below unity, suggesting the chemisorptions process.

### 3.4 Three Parameter Models

#### 3.4.1 Redlich-Peterson(R-P) Isotherm

Figure 2 delivers the comparison between experimental equilibrium data and R-P model. The Redlich-Peterson model has presented high  $R^2$  0.9802, 0.9834 and other correlation for the biosorption of Cr(VI) ion in both linear and non-linear model fitting in Table 6. The exponent  $g$  (0.8002 and 0.9023) approaches to unity specifying that the biosorption is homogeneous in nature with the formulation of monolayer on the surface of adsorbent [26]. Figure 2 also verified that R-P model goes well with the Langmuir isotherm model.

#### 3.4.2 Sips Isotherm Model

The unknown parameters of the Sips isotherm model were evaluated through linear and non-linear curve fitting method. The linear model presented a poor fit of experimental data as  $R^2$  is 0.4400 as compared to non-linear model showing best fit of equilibrium data with  $R^2$  0.9818 and acceptable values of error functions in Table 6. For  $B_s=1$ , the Sips model reduces to Langmuir model [27]. Non-linear model gave  $B_s = 0.938$  slightly less than unity predicting Sips model overlapping the Langmuir model as shown in Figure 2.

#### 3.4.3 Koble-Corrigan (K-C) Isotherm

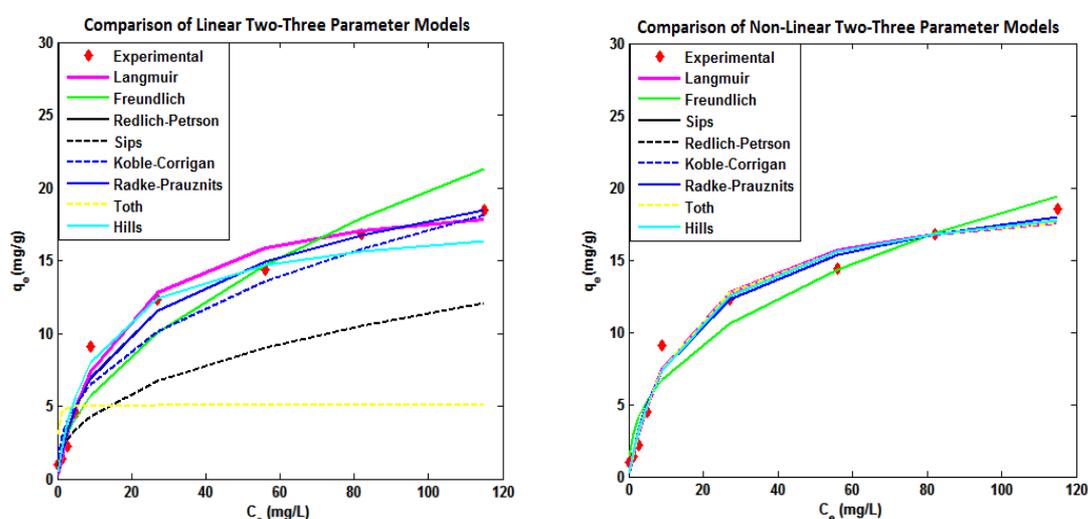
The non linear regression of Koble-Corrigan model gave parameters  $A_{KC}$ ,  $B_{KC}$ ,  $n_{KC}$  values 1.446, 0.069, and 0.938 similar to the Sips model confirming the theoretical correspondence of these two models. Like Sips model, it is also coinciding with the Langmuir model as value of  $n_{KC}$  was 0.938 as depicted in Figure 2. K-C model follows the equilibrium data providing  $R^2$  0.9818 and suitable values of errors are analyzed in Table 6. The parameters obtained as a result of the linear regression and coefficient of determination given in Table 6 does not satisfy the experimental data as justified by Figure 2.

### 3.4.4 Toth Isotherm

Figure 2 depicts a poor fit for linear model and a fine correlation in case of non-linear model of Toth isotherm. This is presented by the comparison of  $R^2$  and error values in Table 6. The Toth model exponent  $t$  estimated by non linear regression was 0.1784 (lies between 0 and 1) suggesting a good correspondence of Toth isotherm with Langmuir isotherm in Figure 2. **Error! Reference source not found.**

### 3.4.5 Radhke-Prasnitz Isotherm

The curve fitting of linear and non-linear model of Radhke-Prasnitz isotherm came up with good results. Figure 2 shows conformity between the Radhke-Prasnitz model and experimental data of Cr(VI) adsorption. Non-linear model slightly better toward the Cr(VI) ion adsorption onto ASAC with  $R^2$  value of 0.9834 and minimization of error functions. The parameters  $K_R$ ,  $k_R$  and  $p$  were estimated at 12.59, 0.1232 and 0.9023.



**Figure 2:** Comparison of Linear and Non-Linear plots of two-three parameter models of Cr(VI) removal using ASAC.

## 4 Conclusions

Various mathematical equation models were used in this study to evaluate the equilibrium and kinetics of Cr(VI) ion removal. It is concluded that non-linear regression analysis of the adsorptive behavior of Cr(VI) ions onto ASAC imparts more acceptable results. Pseudo 2<sup>nd</sup> order model delineated the kinetics of the process better, suggesting a chemisorptions process. Among models of two parameter isotherms, Langmuir isotherm showed the best results. For three parameter isotherms, both, the Redlich-Peterson and Radke-Prasnitz were found to be the best choice.

**Table 4:** Comparison of Kinetic Model.

Sr No	Models	Parameters		Values Of Different Error Functions					
		$k_1$ (1/min)	$qe_1$ (mg/g)	SSE	MSE	RMSE	ARE	SAE	$R^2$
1	Pseudo 1 <sup>st</sup> Order								

2	Linear	0.0792	0.7382	38.38	4.2643	2.0650	36.92	17.483	0.556
	Non-Linear	0.2001	8.041	11.87	1.3192	1.1486	19.75	8.9937	0.8133
	<b>Pseudo 2<sup>nd</sup> Order</b>	$k_2$ (g/mg.min)	$qe_2$ (mg/g)	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	0.01541	10.43	9.46	0.6761	0.8223	11.837	7.946	0.9046
	Non-Linear	0.02082	10	8.94	0.6385	0.7990	11.73	8.818	0.8946

**Table 5:** Comparison of Two Parameter Models

Sr No	Isotherms	Parameters		Values of the Different Error Functions					
1	<b>Langmuir</b>	$q_m$ (mg/g)	$K_L$ (L/g)	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	20.28	0.0635	7.174	0.7972	0.8929	19.03	6.666	0.9819
	Non-Linear	19.89	0.06562	7.100	0.777	0.8819	19.12	6.525	0.9818
2	<b>Freundlich</b>	$n$	$K_F$ (L/g)	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	1.925	1.812	27.399	3.0444	1.7448	21.93	11.938	0.9424
	Non-Linear	2.404	2.691	16.387	1.821	1.349	34.19	9.7200	0.9536

**Table 6:** Comparison of Three Parameter Models.

Sr No	Isotherms	Parameters			Values of the Different Error Functions					
1	<b>Redlich-Peterson</b>	$a_{RP}$ (1/mg)	$K_{RP}$ (L/g)	$g$	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	0.2275	1.786	0.8002	7.497	0.8330	0.9127	21.04	6.107	0.9802
	Non-Linear	0.1232	1.552	0.9023	6.2977	0.6997	0.8365	20.82	5.947	0.9834
2	<b>Koble-Corrigan</b>	$A_{KC}$ (L <sup>n</sup> mg <sup>1-n</sup> /g)	$B_{KC}$ (L/mg) <sup>n</sup>	$n_{KC}$	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	1.768	1.03e-10	0.4053	164.71	18.301	4.278	33.57	30.612	0.4406
	Non-Linear	1.446	0.069	0.938	6.9202	0.7689	0.8769	20.06	6.4169	0.9818
3	<b>Toth</b>	$K_T$ (mg/g)	$a_T$ (L/mg)	$t$	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	2.009	0.1347	1.965	940.47	104.49	10.222	73.99	71.575	0.0001
	Non-Linear	3.548	15.24	0.1784	6.9997	0.7777	0.8819	19.12	6.5240	0.9818
4	<b>Sips</b>	$B_S$	$a_S$ (L/mg)	$K_S$ (L/g)	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	0.4052	1.715e-9	1.768	164.91	18.323	4.2806	33.575	30.628	0.4400
	Non-Linear	0.938	0.07	1.446	6.9202	0.7689	0.8769	20.05	6.4145	0.9818
5	<b>Radke-Prausnitz</b>	$q_m$	$k_R$	$p$	<b>SSE</b>	<b>MSE</b>	<b>RMSE</b>	<b>ARE</b>	<b>SAE</b>	<b>R<sup>2</sup></b>
	Linear	7.852	0.2287	0.8002	7.455	0.8283	0.9101	21.14	6.0958	0.9803
	Non-Linear	12.59	0.1232	0.9023	6.2976	0.6997	0.8365	20.79	5.9443	0.9834

## References

- [1] M. Faisal and S. Hasnain, "Comparative study of Cr(VI) uptake and reduction in industrial effluent by *Ochrobactrum intermedium* and *Brevibacterium* sp.," *Biotechnol. Lett.*, vol. 26, pp. 1623–1628, 2004.
- [2] R. ; B. E. ; Arunachalam; S. Thomas, "Removal of lead and cadmium from aqueous waste streams using granular activated carbon (GAC) columns," *Environ. Prog.*, vol. 13, no. 1, pp. 60–64, 1994.
- [3] Jude C. Igwe and A. A. Abia, "Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk," *Electron. J. Biotechnol.*, vol. 10, no. 4, Oct. 2007.
- [4] B. J. Alloway, *Chromium and Nickel; Heavy Metals in Soil*. New York: McGrath, S. P. and Smith, 1999.
- [5] M. Cieślak-Golonka, "Toxic and mutagenic effects of chromium(VI). A review," *Polyhedron*, vol. 15, pp. 3667–3689, 1996.
- [6] M. Owlad, M. K. Aroua, W. A. W. Daud, and S. Baroutian, "Removal of hexavalent chromium-contaminated water and wastewater: A review," *Water. Air. Soil Pollut.*, vol. 200, no. 1–4, pp. 59–77, 2009.
- [7] M. Sen and M. Ghosh. Dastidar, "Chromium Removal Using Various Biosorbents," vol. 7, no. 3, pp. 182–190, 2010.
- [8] A. B. Pérez-Marín, V. M. Zapata, J. F. Ortuño, M. Aguilar, J. Sáez, and M. Lloréns, "Removal of cadmium from aqueous solutions by adsorption onto orange waste," *J. Hazard. Mater.*, vol. 139, no. 1, pp. 122–131, 2007.
- [9] L. Dupont and E. Guillon, "Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran," *Environ. Sci. Technol.*, vol. 37, no. 18, pp. 4235–4241, 2003.
- [10] M. Kazmi and N. Feroze, "Biosorption Of Cr ( VI ) On Activated Carbon From Almond Shell," *J. Pakistan Inst. Chem. Eng.*, vol. 42, no. 2, pp. 45–52, 2014.
- [11] T.-Y. Kim, S.-K. Park, S.-Y. Cho, H.-B. Kim, Y. Kang, S.-D. Kim, and S.-J. Kim, "Adsorption of heavy metals by brewery biomass," *Korean J. Chem. Eng.*, vol. 22, no. 1, pp. 91–98, 2005.
- [12] Y. Sağ and Y. Aktay, "Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*," *Biochem. Eng. J.*, vol. 12, no. 2, pp. 143–153, 2002.
- [13] M. A. Hossain, M. Kumita, Y. Michigami, and S. Mori, "Kinetics of Cr(VI) Adsorption on Used Black Tea Leaves," *J. Chem. Engg Japan*, vol. 38, no. 6, pp. 402–408, 2005.
- [14] K. Vijayaraghavan, T. V. N. Padmesh, K. Palanivelu, and M. Velan, "Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models," *J. Hazard. Mater.*, vol. 133, no. 1–3, pp. 304–308, 2006.
- [15] J. Appel, "Freundlich's adsorption isotherm," *Surface Science*, vol. 39, no. 1. pp. 237–

244, 1973.

- [16] A. W. A. P. G. ADAMSON, *Physical Chemistry of Surfaces*, Sixth., vol. 210, no. Part\_1, 1997.
- [17] O. D. L. P. Redlich, "A Useful Adsorption Isotherm," *J. Phys. Chem.*, no. 63, pp. 1024–1026, 1959.
- [18] J. C. Y. Ng, W. H. Cheung, and G. McKay, "Equilibrium studies of the sorption of Cu(II) ions onto chitosan.," *J. Colloid Interface Sci.*, vol. 255, no. 1, pp. 64–74, 2002.
- [19] a. W. Marczewski, a. Derylo-Marczewska, and M. Jaroniec, "Unified theoretical description of physical adsorption from gaseous and liquid phases on heterogeneous solid surfaces and its application for predicting multicomponent adsorption equilibria," *Chem. Scripta*, vol. 28, pp. 173–184, 1988.
- [20] R. Sips, "Combined form of Langmuir and Freundlich equations," *J. Chem. Phys.*, vol. 16, pp. 490–495, 1948.
- [21] R. A. T. E. C. Koble, "Adsorption Isotherms for Pure Hydrocarbons," *Ind. Eng. Chem.*, vol. 44, pp. 383–387, 1952.
- [22] J. Toth, "State equations of the solid gas interface layer," *Acta Chem. Acad. Hung.*, vol. 69, pp. 311–317, 1971.
- [23] B. Nagy, C. Mănzatu, A. Măicăneanu, C. Indolean, L. Barbu-Tudoran, and C. Majdik, "Linear and nonlinear regression analysis for heavy metals removal using *Agaricus bisporus* macrofungus," *Arab. J. Chem.*, 2014.
- [24] Y. S. Ho, "Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods," *Water Res.*, vol. 40, no. 1, pp. 119–125, 2006.
- [25] B. Armagan and F. Toprak, "Optimum isotherm parameters for reactive azo dye onto pistachio nut shells: Comparison of linear and non-linear methods," *Polish J. Environ. Stud.*, vol. 22, no. 4, pp. 1007–1011, 2013.
- [26] M. Kazmi, N. Feroze, H. Javed, M. Zafar, and N. Ramzan, "Biosorption of Copper ( II ) on Dry Fruit by Product : Characterization , Kinetic and Equilibrium Studies," vol. 34, no. 6, pp. 1356–1365, 2012.
- [27] J. U. K. Oubagaranadin, Z. V. P. Murthy, and P. S. Rao, "Applicability of Three-parameter Isotherm Models for the Adsorption of Mercury on Fuller ' s Earth and Activated Carbon," vol. 49, no. September, pp. 196–204, 2007.