Evaluation of Linear Regression Equations and Methods of Solving Linear Equations: Adsorption Kinetics Model

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Research Paper

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As a follow up on previous studies such as Kumar (2006); Oke (2013), Ho (2014), Guasian et al., (2014) Oke et al. (2014) and Fehintola et al., (2015), this paper presents a report on the comparison between linear regression methods and linear equation of the pseudo second kinetics model. Selected materials (clay soil, activated carbon, egg shells, corn cobs and used dry batteries) were collected from selected locations in Nigeria. The materials collected were washed with distilled water, air-dried, ground into powder (powdered corn cob, PCC; powdered eggshell, PES and powdered carbon rod, PCR) as the case may be and classified using British Standard sieve. The mineral contents of these materials (adsorbents) were determined. Linear equations of adsorption kinetics models were derived. Adsorption capacities of powdered adsorbents were examined on synthetic lead solution prepared by using standard methods. Adsorption kinetics models (pseudo second) parameters were determined using linear regression methods (least squared, graphical, iteration, Gaussian elimination and Microsoft excel Solver methods) and linear equations. The methods and linear equations derived were evaluated statistically using a model of the selection criterion, total error, coefficient of determination, correlation coefficient (R) and mean The study revealed that these materials are good error. adsorbents based on the adsorption capacities. The linear pseudo second-order kinetics and the adsorption theory were found of getting violated by linear regression B

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

Statistical evaluation revealed that Microsoft excels solver method is the best method to be used for analysis adsorption pseudo second kinetics model based on the highest average Model of selection criterion (3.6584) and average Coefficient of Determination (0.9729); R (0.9875); low average total error (0.0190) and mean error (0.0383). It was concluded that in the determination of engineering parameters Microsoft excels solver should be used for linear pseudo second order kinetics parameter determination to prevent failure of adsorption reactors and processes. The equation $\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} - k_2 t$ which has been in use by many researchers is wrong.

Key words: Pb^{2+} removal, PCC, PES; PCR, aqueous solution, regression methods, environmental pollution control.

INTRODUCTION

Rapid population growth and higher living standards have led to ever increasing demands for good quality municipal and industrial water. In addition, high water quality will be required on essential environmental concerns such as aquatic life, wildlife refuges, recreation and scenic values. Thus, increased competition for quality water and effective waste management are expected. This will require intensive management and international cooperation (Bouwer, 2003; Oke, 2013). Literature has reported that water resources management should be flexible so as to be able to cope with changes in availability and demands for water quality and quantity. This called for integrated water management where all pertinent factors are considered in the decision making process. While, proper solid wastes and water management must be integrated with other waste management and environmental objectives (Oke, 2013). In order to achieve high quality of water and wastewaters, water and wastewaters are to be treated using conventional and innovative techniques. Conventional wastewater and water treatment processes are pH adjustment, chemical treatment, adsorption, electrochemical, ion exchange, precipitation, evaporative recovery and membrane processes. Out of all these treatment processes, adsorption has been found economical and applicable at all levels (Bhide et al., 1996; Ozer et al., 1997).

Khashimova et al. (2008) reported that the use of adsorption for separation of pollutants from mixtures has been increasing continuously and that the main advantages of adsorption include: its high selectivity compared with other separation techniques and relatively high capacity of the adsorbents for the pollutant removal (even at low concentrations). Ho (2007) reported that about 9058 articles have been published on adsorption of materials**.** It is well known that in the adsorption dynamic relationship between sorbents and sorbates are described by adsorption kinetics models. Table 1 presents adsorption kinetics models. Adsorption kinetics models give the capacity of adsorbent for adsorbate. Kinetics can be obtained by examining batch reactions at fixed operational conditions.

In practice, kinetics parameters are required by environmental, water, chemical and process engineers to select and design appropriate water and wastewater processes needed. Linear regression methods are frequently used to determine the best-fitting kinetics models.

The least-squares method with linearly transformed kinetics equations has also been widely applied to confirm experimental data (kinetics) using coefficients of determination, but derivation of these equations are rare in literature. In recent years, the literature has highlighted the use of nonlinear regression methods in solving environmental engineering problems (Kumar, 2006; Ho, 2006; Oke, 2013; Ho, 2014; Gusani et al.,2014). These called for statistical evaluation of linear regression methods to ascertain their accuracy, reliability, good fitting and predictability to prevent engineering failure of adsorption reactor. There are several error analysis methods that have been used to determine the best-fitting isotherm equation (Oke, 2013). With advances in computer software, solving equations should not be a major issue or problem. Literature such as Bowman, (1962); Loveday, (1980); Krasnov et al., (1990); Stroud, (1990) stated that linear and non- linear equations can be solved by using statistical and mathematical methods. Some of the linear methods are Gaussian elimination, Gauss-Jordian elimination, Matrix, least squared, Microsoft excel solver, Newton Raphson technique and iteration (numerical) methods. Previous studies on Microsoft excel Solver or similar package in solving non-linear regression equations include Barati, (2013) and Bhattacharjya, (2010) used solver for groundwater flow; Gay and Middleton, (1971) developed solutions for pipe network, Jewell, (2001) and Huddleston et al. (2004) used excel sheet for pipe network analysis; Canakci, (2007) used solver for pile foundation design while Tay et al. (2014) used solver for solving nonlinear equation. Briti et al. (2013); Elis and Simpson, (1996) used the solver for pipe network analysis. Kumar (2006) provides various linear equations of the pseudo second kinetics model, but derivations of these equations were not provided. The author used a graphical method to determine the kinetics parameters and evaluated the equations using squared correlation coefficient. In this study, derivations of the linear regression equations and methods of widely adsorption kinetics model (Pseudo second) were provided and evaluated statistically using lead adsorption onto low cost adsorbents with particular attention to the accuracy of the equations and methods for determining the parameters in pseudo second kinetics model equation.

MATERIALS AND METHODS

Selected materials (clay soil, activated carbon, egg shells, corn cobs and used dry batteries) were collected from selected locations in Nigeria. They (the materials collected) were washed with distilled water, air-dried, ground into powder and classified using British Standard (BS) sieve. These adsorbents were selected on the basis of their availability and their lower initial cost of production. Powdered adsorbents with sieve sizes of 300-425 μm, 212-300 μm, 75-150 μm and 150-212 μm were separated and stored in different desiccators. The mineral contents of these adsorbents were determined by using AAS after acid digestion of 2 g samples of the adsorbents (APHA, 1998; Oke, 2013).

Structures (Micrograph) of the adsorbent were examined to ascertain its nature and porosity (presented

Table 1. Adsorption kinetics models (Kumar, 2006; Ho, 2014; Oke et al., 2014; Fehintola et al., 2015).

Type	Relationship	Parameters
Pseudo First-order (Non- Linear)	$q_t = q_e\left(1-\exp^{k_1 t}\right)$	k_i and q_e
Pseudo First-order (Linear),	$\log_e(q_e - q_t) = \log_e(q_e) - \frac{k_i}{2.303}t$	k_i and q_e
Pseudo Second-order (Non- Linear)	$q_t = \frac{k_2 (q_e)^2 t}{1+k_2 (q_e)t}$	q_e and k_2
Pseudo Second-order (Linear)	$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}t$	q_e ; h and k_2
Linear Regression A_1	$\left(\frac{q_t}{t}\right) = k_2(q_e)^2 - k_2(q_e)q_t$	q_e and k_2
Linear Regression B_1	$q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$	q_e and k_2
Linear Regression C_1	$\left(\frac{1}{q_t}\right) = \frac{1}{k_2(q_e)^2}\left(\frac{1}{t}\right) + \frac{1}{q_e}$	q_e and k_2
Linear Regression D_1	$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} - k_2 t$	q_e and k_2
Linear Regression E_1	$\left(\frac{1}{t}\right) = \frac{k_2(q_e)^2}{q_t} - k_2(q_e)$	q_e and k_2
Elovich	$q_t = \frac{1}{\beta}\log_e(\alpha\beta) + \frac{1}{\beta}\log_e(t)$	α and β
Intraparticle diffusion	$R = k_{id}(t)^a$	K_{id} and a
	$R = k_{id}\sqrt{(t)} + I$	K_{id} and I

Where; qt is the adsorption capacity at time t (mg/g); qe is equilibrium solid-phase concentration of sorbate (mg/mg); t is the time and k i is the rate constant of pseudo first-order adsorption k2 is the rate constant of pseudo second-order adsorption. h (mg/g• h) is h = k2 (qe)2; b is the desorption constant during any one experiment and a is the initial adsorption rate; R is the percentage of pollutant adsorbed (%); a is the gradient of linear plots and kid is the intraparticle diffusion rate constant (/h).

previous studies such as Oke et al., 2014; Ismail et al., 2009; Fehintola et al., 2015a and b). Micrographs were also obtained from literature to ascertain applicability of the materials elsewhere. Adsorption capacities of powdered adsorbents were examined on synthetic lead solution prepared by dissolving a known mass of lead salt in distilled water. Specifically, a known mass (1.599 g) of lead nitrate ($Pb(NO_3)_2$) was dissolved in 200ml of distilled water and 10 ml of concentrated HNO_3 was added. The mixture was diluted to 1000 ml mark using distilled water and working solutions were prepared from the stock solution. In the determination of adsorption capacities 300ml of the lead solutions containing 150.00 mg/L of Pb^{2+} each were taken into different beakers and known masses of the adsorbent were added at a known initial pH. The mixtures were stirred at 60 revolutions per minute (rpm) for 3 minutes and allowed to stand for 24 hours. The supernatants were filtered through a filter paper Number 40 (Whatman) to remove suspended solids and lead concentration in the filtrate was determined (Concentration of Pb^{2+} in the solution was determined hourly). The laboratory determinations of lead concentrations in synthetic solutions were conducted using procedures as specified in APHA (1998) using the Alpha 4 Atomic Absorption Spectrophotometer (AAS) (Chem Techn Analytical) at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria. The final concentrations of Pb^{2+} were determined. The amount of solute removed (adsorbed) was calculated using equation (1). The percentage of lead ion removed

(R_R %) from the solution was calculated using equation (2).

$$q_t = \frac{(C_0 - C_t)}{M} V \tag{1}$$

$$R_R = 100 \frac{(C_0 - C_t)}{C_0} \tag{2}$$

Where; q_t is the adsorption capacity at time t (mg/g); R_R *is* the percentage of the pollutant adsorbed (%); M is adsorbent mass (mg); C_0 is the initial liquid-phase concentration of sorbate ; C_t is the experimental concentration in the solution at time t (mg/l) and V is the volume of solution (0.3 L). The adsorption capacities of the adsorbent through adsorption kinetics models of the PCC were analyzed using five methods of solving linear regression (numerical techniques for solving the equations and sigma plot for plotting the graphs, linear least-squares and Microsoft excel Solver, Gaussian elimination). The statistical evaluations of these linear adsorption kinetics models (Second Pseudo order) were expressed as the coefficient of determination (CD), the sum of the squares of the errors (total error), mean errors; model of selection criterion (MSC) and Correlation coefficient (R) to ascertain best fitting, accuracy and validity of the obtained output, . The total error, which is the sum of the squares of the errors between the obtained adsorption capacity and the expected adsorption capacity, can be interpreted as a measure of variation in the values expected left unexplained by the values obtained. The lower the value of total error the higher the accuracy, validity and good fitness of the methods. Total error (Err^2) can be computed using equation (3a) while mean errors (MErr) were computed using equation (3b):

$$Err^2 = \sum_{i=1}^{n} (Y_{obsi} - Y_{cali})^2 \tag{3a}$$

Where; Y_{obsi} is observed concentration and Y_{cali} is calculated concentration.

$$MErr = \frac{\sum_{i=1}^{n} (Y_{obsi} - Y_{cali})}{N} \tag{3b}$$

Where; N is total number of samples.

The coefficient of determination *(CD)* can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and good fitness of the device. CD can be expressed as follows(Oke, 2013; Oke et al., 2014):

$$CD = \frac{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y}_{cali}\right)^2 - \sum_{i=1}^{n} (Y_{obsi} - Y_{cali})^2}{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y}_{cali}\right)^2} \tag{4}$$

where, $\overline{Y}_{obsi}$ is the average of observed concentration c and $\overline{Y}_{cali}$ is the average of calculated concentration.

The model selection criterion (MSC) is interpreted as the proportion of expected data variation that can be explained by the obtained data. Like, CD the higher the value of the MSC, the higher the accuracy, validity and the good fitness of the device. MSC can be computed using equation (5) as follows (Oke, 2013):

$$MSC = \ln \frac{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y}_{obsi}\right)^2}{\sum_{i=1}^{n} (Y_{obsi} - Y_{cali})^2} - \frac{2p}{n} \tag{5}$$

Where; p is the number of parameters and n is the number of samples.

Correlation coefficient (R)

The correlation coefficient is interpreted as the proportion of expected data variation that can be explained by the obtained data. Like, CD the higher the value of R, the higher the accuracy, validity and the good fitness of the method. R can be computed using equation (6) as follows:

$$R = 1 - \frac{\sum_{i=1}^{n} (Y_{obsi} - Y_{cali})^2}{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y}_{cali}\right)^2} \tag{6}$$

Where; R is the correlation coefficient. These errors and statistical values were evaluated using analysis of variance (ANOVA).

RESULTS AND DISCUSSION

The results of this study were presented and discussed in the following categories: the adsorbents and their properties, adsorption of lead by these adsorbents (adsorption capacities), derivation of the linear equation form of pseudo second kinetics models and statistical evaluation of the methods and equations.

The adsorbents and their properties

The adsorbents are available as either agricultural waste, household (domestic) waste or both, which indicated that

Table 2. Chemical and Physical Properties of the Adsorbents (Oke *et* al., 2008; Adie et al., 2008; Ismail et al., 2009).

	Properties	Powdered Corn Cobs		Powdered Egg Shells		Powdered Carbon Rods		Clay soil	
		Average	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**
Physical	Ash content (%)	2.33	0.061	97.58	1.84	99.78	0.02	84.38	0.831
	Volatile (%)	86.89	1.007	2.31	0.42	0.22	0.02	0.67	0.011
	Moisture content (%)	10.78	0.278	1.06	0.36	0.25	0.00	4.08	0.040
	Density (g/cm^3)					1.48	0.02		
	Mass (g)					5.53	0.08		
Chemical	Magnesium (mg/g)	54.40	0.30					1.48	0.015
	Aluminium (mg/g)	0.010	0.001	13.45	0.001			10.31	0.106
	Solubility in water (%)	0.52	0.034	0.64	0.07	3.43	0.05	0.41	0.050
	Solubility in 0.25 M HCl (%)	4.56	0.98	2.96	0.72	5.98	0.08	0.74	0.015
	Calcium (mg/g)	1.70	0.10	407.44	0.032			0.25	0.013
	Iron (mg/g)	131.00	2.40	27.60	0.002			4.90	0.156
	Zinc (mg/g)	0.01	0.001			0.05	0.00	0.00	0.000
	Cadmium (mg/g)	0.02	0.001			0.00	0.00	0.00	0.000
	Chromium (mg/g)	0.000	0.000			0.00	0.00	0.00	0.000
	Nickel (mg/g)	0.01	0.001			0.00	0.00	0.00	0.000
	Lead (mg/g)	0.000	0.000			0.00	0.00	0.00	0.000
	Carbon (%)	54.79	2.04			0.01	0.00		
	Hydrogen (%)	8.03	0.64						
	Nitrogen (%)	0.4	0.02						
	Sulphate(mg/g)					0.00	0.00		
	Chloride (mg/g)					0.00	0.00		
	As(mg/g)					0.00	0.00		
	Copper (mg/g)					0.00	0.00		
	Manganese (mg/g)					0.01	0.00		
	Silicon (%)							26.98	0.309
	Potassium (%)							3.97	0.048
	Sodium (%)							0.51	0.007
	Oxygen (%)							42.53	0.433

utilization of the wastes would be a method of reducing environmental problem (solid waste management) often caused by rapid urbanization and industrialization. More on adsorption and on these adsorbents can be found in literature such as Oke et al., (2014). Table 2 presents composition of these adsorbents. The study revealed that clay soil, powdered egg shells; powdered corn cobs, activated carbon and powdered carbon rods were made of pores, carbon, nitrogen, hydrogen, aluminum, iron and calcium, without cadmium, chromium and lead. These compositions make these materials good adsorbents. Micrographs of these adsorbents have been presented in previous studies and literature such as (Oke et al., 2008); Ismail et al., 2009); Oke et al., 2014); Oke, 2014); Fehintola et al., 2015a and b). More on micrographs of these adsorbents can be found in literature such as (Bohor and Randall, 1971; Sengupta et al., 2008; Ketcha et al., (2012). Figure 1 presents some of the scanning electron microscopy (SEM) obtained from literature. From these micrographs it can be seen that there are pores on the adsorbent, which are common features of adsorbents on the waste materials. These indicated that these materials can be used as adsorbents for pollutant removal from water and wastewater or as water and wastewater purification.

Derivations and determinations of kinetics parameters using linear equations and numerical techniques

The derivations of linear forms of Pseudo second order kinetics are as presented in equations (7) to equations (17). From these equations it can be seen that six different linear equations can be derived. The derivations of the linear equations used are as follows:

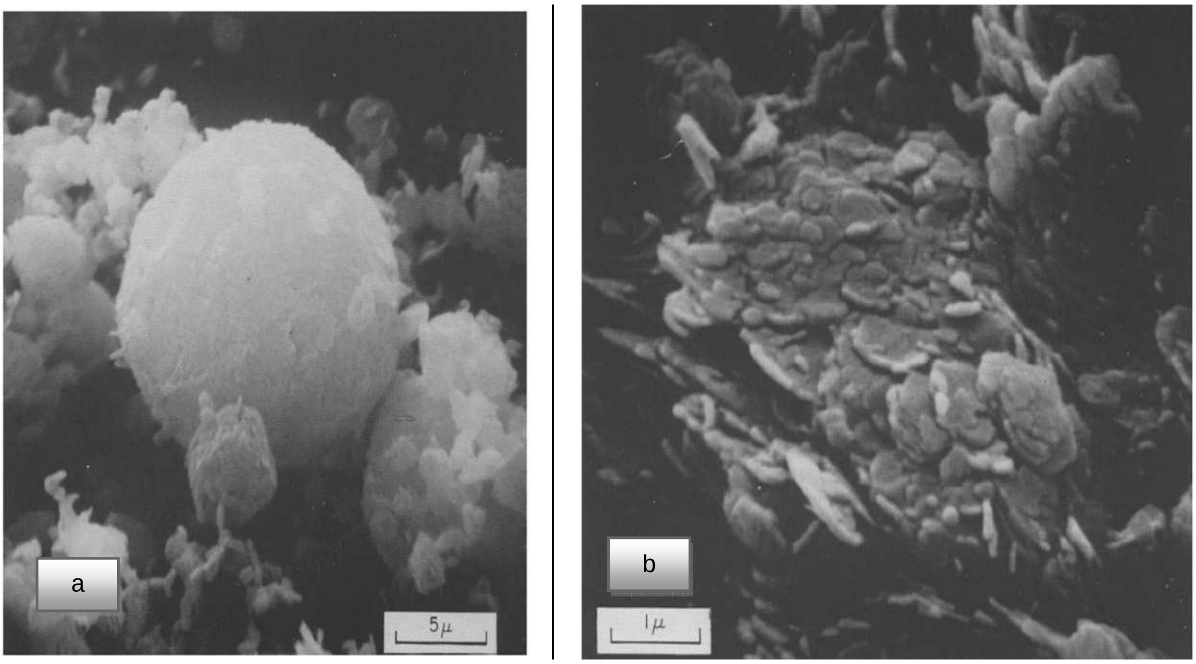

Figure 1.SEM of kaolin rich clay (Source: Bohor and Randall, 1971).

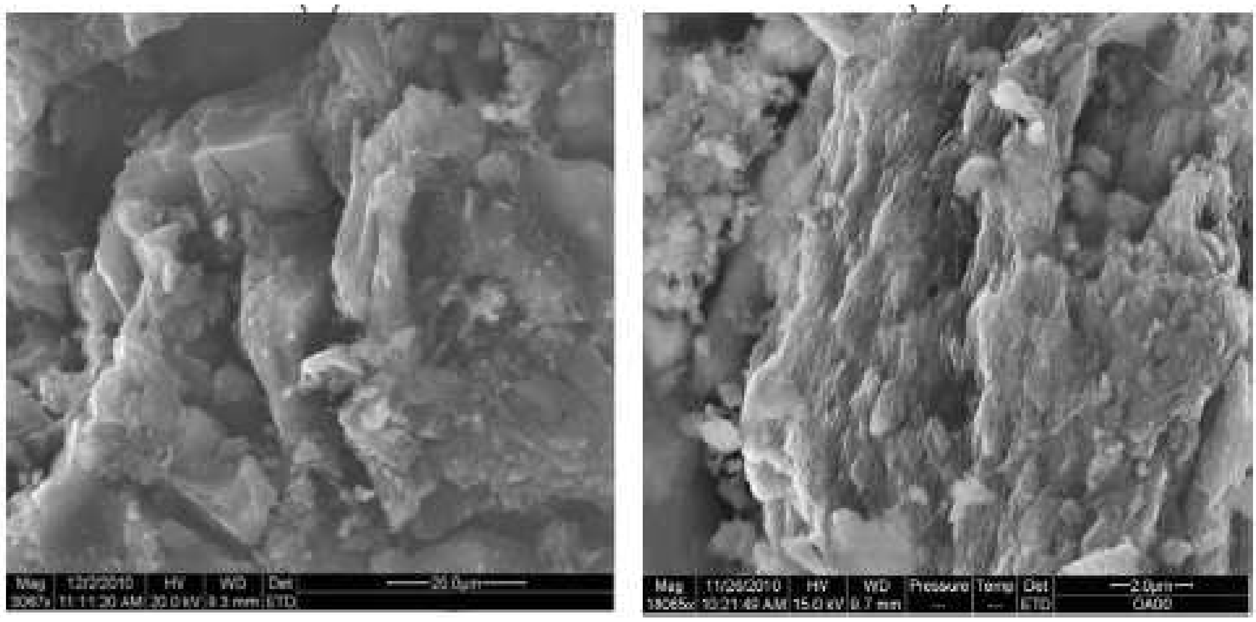

Figure 1c. SEM of activated carbon at various magnifications (Bohor and Randall, 1971).

$$q_t = \frac{k_2(q_e)^2 t}{1 + k_2(q_e)t} \qquad (7)$$

Linearizing the equation gives equations (8) and (9) as follows:

$$\frac{1}{q_t} = \frac{1}{k_2(q_e)^2 t} + \frac{k_2(q_e)t}{k_2(q_e)^2 t} \qquad (8)$$

$$\frac{1}{q_t} = \frac{1}{k_2(q_e)^2 t} + \frac{1}{(q_e)} \qquad (9)$$

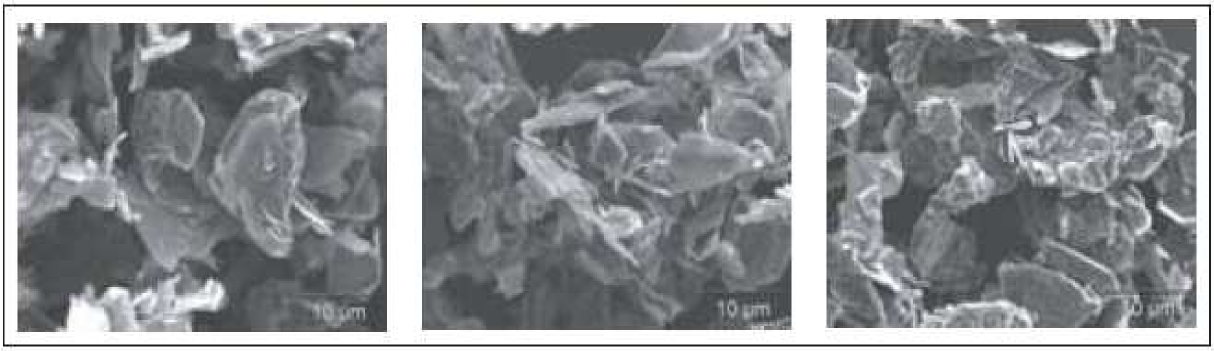

Figure 1d. SEM pictures of three 25 μm grades of Graphite. (Source: Juri et al., 2015).

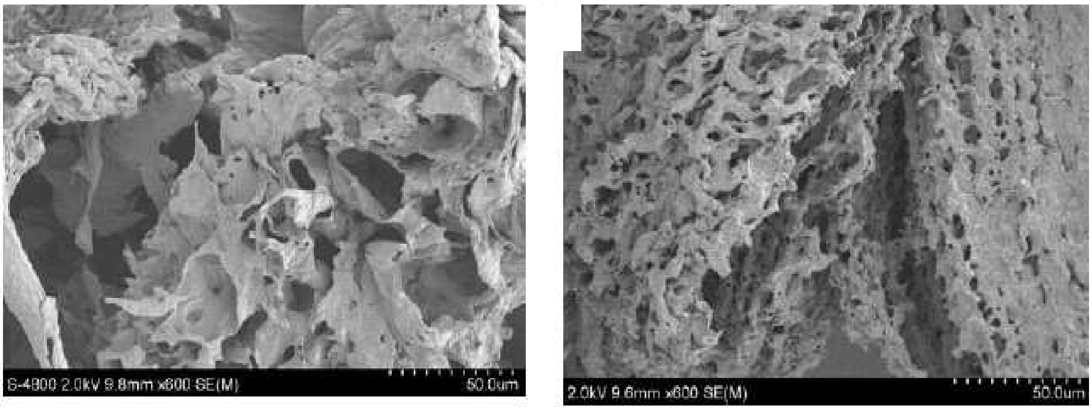

Figure 1e. Scanning electron microscope images of corn cobs, (i) Corn cobs after pretreatment with 0.75% KOH at 120°C for 25 min; and (ii) Corn cobs after pretreatment with 2% KOH at 120°C for 25 min. (Source: Wanitwattanarumlug *et al.,* 2012).

Plot $\frac{1}{q_t}$ against $\frac{1}{t}$ to give $Y = mx + C$ where; m is the slope ($\frac{1}{k_2(q_e)^2}$) and C is the intercept ($\frac{1}{(q_e)}$).

Form these, the unknown kinetics parameters were determined. Multiplying equation (9) by t gives equations (10) and (11) as follows:

$$\frac{t}{q_t} = \frac{t}{k_2(q_e)^2 t} + \frac{1}{(q_e)}t \qquad (10)$$

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{(q_e)}t \qquad (11)$$

Plot $\frac{t}{q_t}$ against t in equation (11) to give $Y = mx + C$ where; m is the slope ($\frac{1}{k_2(q_e)^2}$) and C is the intercept ($\frac{1}{(q_e)}$). From these, the unknown kinetics parameters were determined. Rearranging equation (11) and making t the subject of the formulae in

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

gives equations (12) and (13) respectively as follows:

$$q_e\frac{t}{q_t} = \frac{q_e}{k_2(q_e)^2} + t \qquad (12)$$

$$t = q_e\frac{t}{q_t} - \frac{1}{k_2(q_e)} \qquad (13)$$

$$q_t = -\frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right) + q_e$$

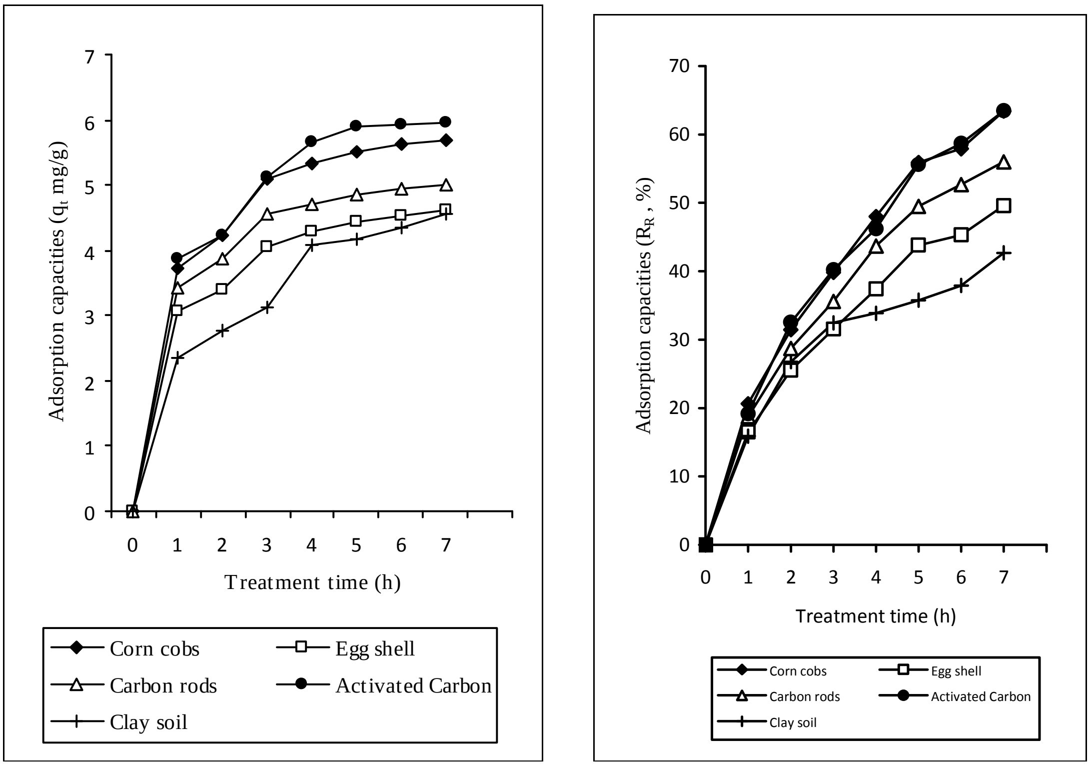

Figure 2. Adsorption capacities and kinetics of lead ion unto the selected solid wastes.
(a).Non-linear plot of Adsorption capacity of Lead onto these Adsorbents.
(b).Non linear plot of Adsorption of lead onto these adsorbents (intra-particle).

Plot t against $\frac{t}{q_t}$ in equation (13) to give $Y = mx + C$ where; m is the slope (q_e) and C is the intercept ($\frac{1}{(k_2 q_e)}$). From these, the unknown kinetics parameters were be determined. Multiply $\frac{1}{q_t} = \frac{1}{k_2(q_e)^2 t} + \frac{1}{(q_e)}$ (equation (9)) by q_t gives equation (14) and making q_t the subject of the formula gives equation (15).

$$\frac{q_t}{q_t} = \frac{q_t}{k_2(q_e)^2 t} + \frac{q_t}{(q_e)} \qquad (14)$$

Rearranging equation (14) to give an equation (15) as follows:

$$q_t = -\frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right) + q_e \qquad (15)$$

Plot q_t against $\frac{q_t}{t}$ in equation (15) to give $Y = mx + C$ where; m is the slope and C is the intercept. From these, the unknown kinetics parameters were determined. From equation (15) make $\left(\frac{q_t}{t}\right)$ the subject of the formula. Then equation (15) becomes equation (16) as follows:

$$\left(\frac{q_t}{t}\right) = -k_2(q_e)q_t + k_2(q_e)^2 \qquad (16)$$

Multiply equation (9) by $\left(\frac{1}{q_t}\right)$ and making $\left(\frac{1}{t}\right)$ the subject of the formula. Then equation (9) becomes equation (17)

$$\left(\frac{1}{t}\right) = -k_2(q_e) + k_2(q_e)^2\frac{1}{q_t} \qquad (17)$$

These derivations revealed that the expression

Table 3. Kinetics parameters for adsorption of Pb2+ onto selected adsorbents.

Linearized Equation	Parameters	Least Squared	Microsoft excel solver	Elimination	Graphical	Iteration	Overall Average
Linear regression A	K_2	0.02859	0.02855	0.02859	0.02861	0.02860	0.02859
$\left(\frac{t}{q_t}\right) = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t$	q_e	3.0665	3.0668	3.0668	3.0665	3.0668	3.06668
Linear regression B	K_2	0.06449	0.06088	0.06028	0.06019	0.06028	0.06122
$\left(\frac{1}{q_t}\right) = \frac{1}{k_2(q_e)^2}\left(\frac{1}{t}\right) + \frac{1}{q_e}$	q_e	2.1763	2.2401	2.2401	2.2422	2.2401	2.22776
Linear regression C	K_2	0.04258	0.04873	0.04783	0.04784	0.04783	0.04696
$q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$	q_e	2.6007	2.4763	2.4763	2.4760	2.4763	2.50112
Linear regression D'	K_2	0.03193	0.03593	0.03193	0.03157	0.03584	0.03344
$\left(\frac{q_t}{t}\right) = k_2(q_e)^2 - k_2(q_e)q_t$	q_e	2.8404	2.7938	2.9323	2.9462	2.7932	2.86118
Linear regression E	K_2	0.05934	0.06068	0.05760	0.05720	0.05970	0.05890
$\left(\frac{1}{t}\right) = -k_2(q_e) + k_2(q_e)^2\frac{1}{q_t}$	q_e	2.2544	2.2495	2.2838	2.2901	2.2492	2.26540
Linear regression F	K_2	0.04171	0.04296	0.04178	0.04170	0.04233	0.04210
$t = q_e\frac{t}{q_t} - \frac{1}{k_2(q_e)}$	q_e	2.6170	2.6038	2.6175	2.6170	2.6037	2.61180

$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} - k_2t$ described in Ho (2006) and Kumar (2006), which is in used by many researchers, is wrong and needs to be verified. This observation is similar to Ho, (2014) and Kumar, (2006) conclusion on the evaluation of other linear equations. In line with this observation, the expression $\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} - k_2t$ was expanded and the expansion gave $q_t = \frac{k_2(q_e)^2t}{1 - k_2(q_e)t}$ not actual pseudo second kinetics equation of

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

Adsorption of lead unto PCC

Adsorption kinetics are important ingredients in environmental pollution control. In order to investigate in detail of the mechanism of adsorption rate for the adsorption of Pb^{2+} onto the adsorbents, the rate constants were determined by applying the linear equations of pseudo second kinetic order and numerical methods. Figure 2a and b) presents adsorption kinetics of lead onto the adsorbent. From the figure it can be seen that adsorption of lead by the adsorbent increases with time. This observation agrees with the literature on adsorption of lead by various adsorbents. Table 3 shows the values of pseudo second order kinetics model's parameters (K_2 and q_e) for each of the linear equations derived and evaluated. K_2 and q_e were in the range of 0.02855 to 0.06449 and 2.1763 to 3.0668 respectively. The lowest K_2 (0.02855) came from linear regression A solved by Microsoft excel Solver method and the highest value of K_2 came from equation B and solved by least squares method. Also, the lowest q_e (2.1763) came from linear regression B solved by least squares method. The highest value of q_e (3.0668) came from equation A solved with the Microsoft excel solver method. These results indicated that the values of K_2 and q_e are functions of the adsorbates, adsorbents, linear equations and methods used. These different observations in the values of K_2 and q_e by these linear methods show the complexities in predicting the optimum adsorption kinetics parameters (K_2 and q_e) These different outcomes show the real

Table 4. Statistical evaluation of the Linear equations and methods.

Statistical Methods	Evaluation technique	Least Squared	Microsoft excel solver	Elimination	Graphical	Iteration	Overall Average of linearized equation
Linear regression A $\left(\frac{t}{q_t}\right) = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e}t$	MSC	4.1929	4.1933	4.1930	4.1925	4.1927	4.19288
	CD	0.9849	0.9849	0.9849	0.9849	0.9849	0.98490
	Total error	0.0104	0.0104	0.0104	0.0104	0.0104	0.01040
	R	0.9924	0.9924	0.9924	0.9924	0.9924	0.99240
	Mean Error	0.0337	0.0337	0.0337	0.0337	0.0337	0.03370
Linear regression B $\left.\frac{1}{q_t}\right) = \frac{1}{k_2(q_e)^2}\left(\frac{1}{t}\right) + \frac{1}{q_e}$	MSC	3.0362	3.2051	3.1583	3.1651	3.1583	3.14460
	CD	0.9522	0.9595	0.9576	0.9595	0.9576	0.95728
	Total error	0.0332	0.0280	0.0294	0.0292	0.0294	0.02984
	R	0.9758	0.9795	0.9786	0.9787	0.9786	0.97824
	Mean Error	0.0472	0.0439	0.0446	0.0445	0.0446	0.04496
Linear regression C $q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$	MSC	3.7385	3.6002	3.5712	3.5702	3.5713	3.61028
	CD	0.9762	0.9727	0.9719	0.9719	0.9719	0.97292
	Total error	0.0164	0.0189	0.0194	0.0195	0.0194	0.01872
	R	0.9880	0.9862	0.9858	0.9858	0.9858	0.98632
	Mean Error	0.0377	0.0406	0.0392	0.0392	0.0392	0.03918
Linear regression D $\left.\frac{{}_t}{}\right) = k_2(q_e)^2 - k_2(q_e)q_t$	MSC	3.3364	3.9539	4.0822	4.0942	3.9523	3.88380
	CD	0.9649	0.9808	0.9831	0.9833	0.9808	0.97858
	Total error	0.0246	0.0133	0.0117	0.0115	0.0133	0.01488
	R	0.9823	0.9904	0.9915	0.9916	0.9903	0.98922
	Mean Error	0.0449	0.0358	0.0346	0.0345	0.0359	0.03714
Linear regression E $\left(\frac{1}{t}\right) = -k_2(q_e) + k_2(q_e)^2\frac{1}{q_t}$	MSC	3.1809	3.2473	3.2366	3.2460	3.1741	3.21698
	CD	0.9586	0.9612	0.9608	0.9612	0.9583	0.96002
	Total error	0.0287	0.0269	0.0272	0.0269	0.0289	0.02772
	R	0.9791	0.9882	0.9802	0.9804	0.9876	0.98310
	Mean Error	0.0441	0.0378	0.0429	0.0427	0.0381	0.04112
Linear regression F $t = q_e\frac{t}{q_t} - \frac{1}{k_2(q_e)}$	MSC	3.7495	3.7508	3.7507	3.7495	3.7344	3.74698
	CD	0.9765	0.9765	0.9765	0.9765	0.9761	0.97642
	Total error	0.0163	0.0162	0.0162	0.0163	0.0165	0.01630
	R	0.9882	0.9882	0.9882	0.9882	0.9880	0.98816
	Mean Error	0.0377	0.0378	0.0376	0.0377	0.0378	0.03772
Overall Average of the methods in solving linearized equations	MSC	3.5391	3.6584	3.6653	3.6696	3.6305	
	CD	0.9689	0.9726	0.9725	0.9729	0.9716	
	Total error	0.0216	0.0190	0.0191	0.0190	0.0197	
	R	0.9843	0.9875	0.9861	0.9862	0.9871	
	Mean Error	0.0409	0.0383	0.0388	0.0387	0.0382	

complexities and problems in estimating the kinetic parameters by linearization technique. Various outcomes for the six linearized equations are also due to the different axis settings that would alter the result of linear regression and influence the determination process (Kumar 2006). This indicates that the linear method does not check whether the process or the kinetic trend is linear or not, instead it assumes the experimental data or the transformed experimental data are linear. The linear method just reports the slope and intercept for a linear trend line that best predicts the Y value for a given X. This makes the reason for the better or worse fit of pseudo second-order kinetics due to the various axis settings due to the transformation of non-linear kinetic expression to various linear expressions (A to F). The various outcomes due to linearization clearly indicate that, for linear method, all the uncertainty is in Y, while X is known precisely. In addition, the different outcomes for the different linearized forms of pseudo second-order models are due to the variation in the error structure. This indicates that error structure that will be obtained will vary upon linearizing the non-linear equation. The error distribution may vary better or worse, depending on the way the kinetic model is linearized. This means that the linear method can cause some problems because the assumptions behind linear regression get violated. The

Table 5a: Analysis of Variance between statistical Evaluations methods and methods of solving .

Source of Variation	Sum of Squared	Df	Mean Squared	F-value	P-value
Between statistical evaluation Methods	265.97	29	9.17138	2521	5.00 x 10^{-149}
Between method of solving Linearized equations	0.014484	4	0.003621	0.9953	0.413101
Error	0.422007	116	0.003638		
Total	266.4065	149			

Table 5b. Analysis of Variance between linearized equations and Methods of solving (using MSC values).

Source of Variation	Sum of Squared	Df	Mean Squared	F-value	P-value
Between Linearized equations	4.0074	5	0.80148	43.96305	4.1. x 10^{-10}
Between Method of solving	0.071157	4	0.017789	0.975775	0.442781
Error	0.364615	20	0.018231		
Total	4.443172	29			

Df is the degree of Freedom.

transformations of non-linear pseudo second-order expression to linear regressions also have some errors which fall within the experimental error of linear regression (less than 5 %). These results were in agreement with observations made in literature such as (Kumar, 2006; Ho, 2006; Yen and Chen, 2009, Ho, 2014) on relationship between non-linear regression and linear regression equations. This error and variations may be due to the possibility of the violation of the normality assumptions behind the linear regression method.

Statistical evaluations

Table 4 presents statistical evaluation of the linear regression equations and linear regression methods. Detail of these computations are as presented at the appendices (Appendices A and B). From the Table, the higher CD values for linear regression A solved by Microsoft excel solver and graphical methods. These values suggest that the equations and methods can be used to represent and solve the kinetics of lead onto PCC. Values of MSC were in the range of 3.0362 to 4.1933 (Table 4). The lowest value of MSC (3.0362) was from linear regression B solved by least squares method and the highest value (4.933) was from linear regression A solved by Microsoft excel solver. The table revealed that the theory behind the linear pseudo second-order model was getting valid for a linear regression A pseudo second-order expression solved by Microsoft excel solver. The theory of linear pseudo second-order kinetics and the adsorption theory were founded on getting violated by linear regression B pseudo second-order expression for the same experimental data of lead onto PCC. These two observations based on linear regression A and linear regression B expressions suggest that the linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption kinetics. The values for total error, mean error and correlation coefficient (R) were in the same trend as MSC and CD. The observation for the statistical values and parameters were the same as MSC and CD. The observations also show that the order of accuracy of the methods was in Graphical greater than (>) Elimination > Microsoft excel solver > Iteration > Least Squared method based on the value of MSC; Microsoft excel solver > Elimination > Graphical > Iteration > Least Squared based on CD and Microsoft excel solver equal to Graphical > Elimination > Iteration > Least Squared based on error value.. Analysis of variance (ANOVA) of the statistical evaluations and errors revealed that there is a significant difference between the statistical evaluation methods at 95 % confidence level (Table 5a; $F = 2521$ and $p < 0.05$), but there is no significant difference between the linearized equations at 95 % confidence level ($F = 0.9953$; $p > 0.05$). Table 5b revealed that there is significant difference between linearized equations ($F = 43.96305$; $p < 0.05$) at 95 % confidence level.

CONCLUSION

This study investigated adsorption capacities of Pb^{2+} onto absorbents, and linear regressions of pseudo second order kinetics as well as linear methods were evaluated statistically. The study concluded that linear pseudo second-order kinetics and the adsorption theory was found of getting violated by linear regression B pseudo second-order expression for the same experimental data of lead onto PCC. These two observations based on linear regression A and linear regression B expressions suggest that the linear method just verify the hypothesis of linear regression instead of verifying the theory of adsorption kinetics. The observation also shows that the order of accuracy of the methods was in Graphical greater than (>) Elimination > Microsoft excel solver > Iteration > Least Squared method based on the value of MSC; Microsoft excel solver > Elimination > Graphical >

Iteration > Least Squared based on CD and Microsoft excel solver equal to Graphical > Elimination > Iteration > Least Squared based on error value. The equation

$$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} - k_2 t$$

which has been in use by many researchers is wrong.

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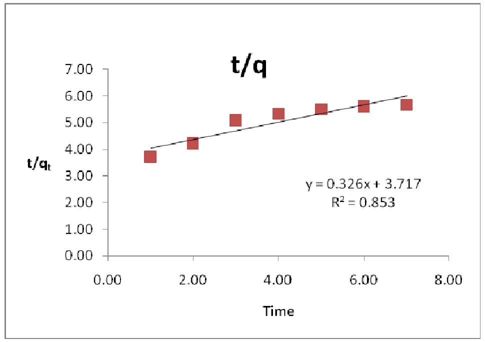

Figure A: Graphical Solution to Equation (11)

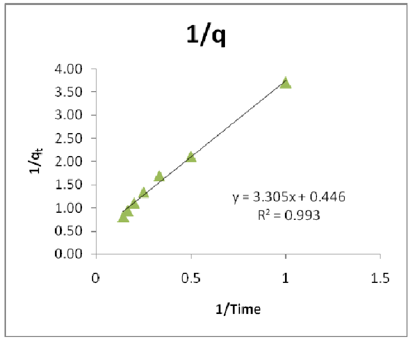

Figure B: Graphical Solution to Equation (9)

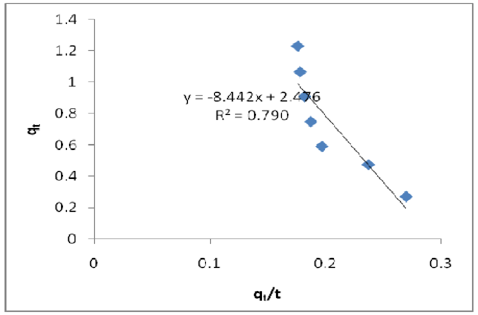

Figure C: Graphical Solution to Equation (15)

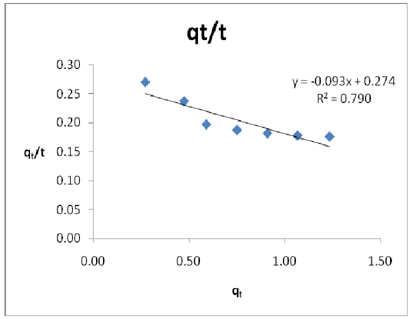

Figure D: Graphical Solution to Equation (16)

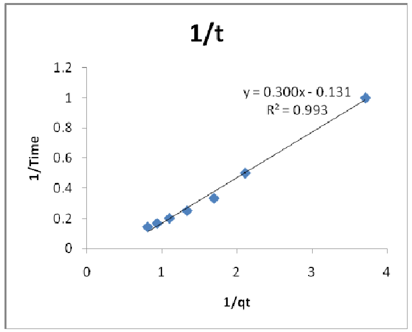

Figure E: Graphical Solution to Equation (17)

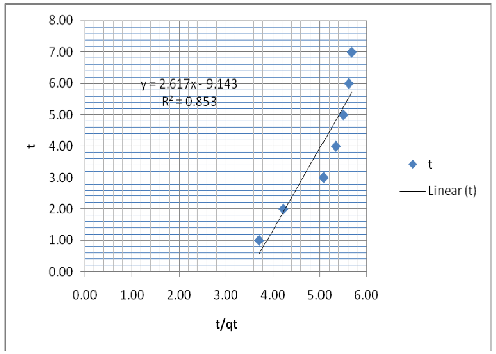

Figure f: Graphical Solution to Equation (16)

Appendix B: Detailed Statistical Evaluation.

Using Iteration	**Qe = 3.0668127**			$\left(\frac{t}{q_t}\right)$	$= \frac{1}{k_2 (q_e)^2}$	$+$	$\frac{1}{q_e} t$	**Equation 2 Using Iteration**	**qe**	**2.2400749**	$\left(\frac{1}{q_t}\right) =$	$\frac{1}{k_2 (q_e)^2}$	$\left(\frac{1}{t}\right)$	$+ \frac{1}{q_e}$	
	k2	0.0286033							k2	0.060283					
Time	Actual qt	Cal qt	Error	Sq Error	Act - Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act - Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2473	0.0222	0.0005	0.2367	0.2377		1	0.2695	0.2665	0.0030	0.0000	0.2367	0.2198	
2	0.4739	0.4577	0.0162	0.0003	0.0796	0.0802		2	0.4739	0.4763	0.0024	0.0000	0.0796	0.0699	
3	0.5906	0.6389	0.0484	0.0023	0.0274	0.0277		3	0.5906	0.6458	0.0553	0.0031	0.0274	0.0218	
4	0.7491	0.7966	0.0475	0.0023	0.0000	0.0001		4	0.7491	0.7856	0.0366	0.0013	0.0000	0.0001	
5	0.9091	0.9350	0.0259	0.0007	0.0234	0.0231		5	0.9091	0.9029	0.0062	0.0000	0.0234	0.0292	
6	1.0676	1.0575	0.0101	0.0001	0.0971	0.0964		6	1.0676	1.0026	0.0650	0.0042	0.0971	0.1084	
7	1.2324	1.1667	0.0657	0.0043	0.2269	0.2259		7	1.2324	1.0885	0.1439	0.0207	0.2269	0.2441	
Average	0.7560	0.7571	0.0337	0.0015	0.0987	0.0987		Average	0.7560	0.7383	0.0446	0.0042	0.0987	0.0990	
Total	5.2922	5.2999	0.2360	0.0104	0.6911	0.6911		Total	5.2922	5.1683	0.3124	0.0294	0.6911	0.6933	
				MSC	4.1927	0.9849	CD					MSC	3.1583	0.9576	CD
						0.9924	R							0.9786	R
Using Elimination	qe	3.0668						Using Elimination	qe	2.2400749					
	k2	0.02859							k2	0.060283					
Time	Actual qt	Cal qt	Error	Sq Error	Act - Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act - Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2472	0.0223	0.0005	0.2367	0.2375		1	0.2695	0.2665	0.0030	0.0000	0.2367	0.2198	
2	0.4739	0.4576	0.0164	0.0003	0.0796	0.0801		2	0.4739	0.4763	0.0024	0.0000	0.0796	0.0699	
3	0.5906	0.6387	0.0481	0.0023	0.0274	0.0277		3	0.5906	0.6458	0.0553	0.0031	0.0274	0.0218	
4	0.7491	0.7963	0.0472	0.0022	0.0000	0.0001		4	0.7491	0.7856	0.0366	0.0013	0.0000	0.0001	
5	0.9091	0.9347	0.0256	0.0007	0.0234	0.0232		5	0.9091	0.9029	0.0062	0.0000	0.0234	0.0292	

6	1.0676	1.0572	0.0104	0.0001	0.0971	0.0966		6	1.0676	1.0026	0.0650	0.0042	0.0971	0.1084	
7	1.2324	1.1664	0.0660	0.0044	0.2269	0.2261		7	1.2324	1.0885	0.1439	0.0207	0.2269	0.2441	
Average	0.7560	0.7569	0.0337	0.0015	0.0987	0.0987		Average	0.7560	0.7383	0.0446	0.0042	0.0987	0.0990	
|Total	5.2922	5.2981	0.2361	0.0104	0.6911	0.6911		Total	5.2922	5.1683	0.3124	0.0294	0.6911	0.6933	
				MSC	4.1930	0.9849	CD					MSC	3.1583	0.9576	CD
						0.9924	R							0.9786	R
Using Least Squared	qe	3.0665						Using Least Squared	qe	2.1762786					
	k2	0.028586							k2	0.06449					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2471	0.0224	0.0005	0.2367	0.2373		1	0.2695	0.2678	0.0017	0.0000	0.2367	0.2164	
2	0.4739	0.4574	0.0165	0.0003	0.0796	0.0799		2	0.4739	0.4770	0.0031	0.0000	0.0796	0.0680	
3	0.5906	0.6385	0.0480	0.0023	0.0274	0.0276		3	0.5906	0.6448	0.0543	0.0029	0.0274	0.0208	
4	0.7491	0.7961	0.0470	0.0022	0.0000	0.0001		4	0.7491	0.7825	0.0334	0.0011	0.0000	0.0002	
5	0.9091	0.9345	0.0254	0.0006	0.0234	0.0232		5	0.9091	0.8974	0.0117	0.0001	0.0234	0.0304	
6	1.0676	1.0569	0.0107	0.0001	0.0971	0.0967		6	1.0676	0.9949	0.0728	0.0053	0.0971	0.1108	
7	1.2324	1.1661	0.0663	0.0044	0.2269	0.2263		7	1.2324	1.0785	0.1539	0.0237	0.2269	0.2477	
Average	0.7560	0.7567	0.0337	0.0015	0.0987	0.0987		Average	0.7560	0.7347	0.0472	0.0047	0.0987	0.0992	
|Total	5.2922	5.2967	0.2362	0.0104	0.6911	0.6911		|Total	5.2922	5.1429	0.3307	0.0332	0.6911	0.6943	
				MSC	4.1929	0.9849	CD					MSC	3.0362	0.9522	CD
						0.9924	R							0.9758	R

Using Graphical	qe	3.06654						Using Graphical	qe	2.2421525					
	k2	0.028609							k2	0.0601864					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2473	0.0222	0.0005	0.2367	0.2377		1	0.2695	0.2666	0.0029	0.0000	0.2367	0.2201	
2	0.4739	0.4577	0.0162	0.0003	0.0796	0.0802		2	0.4739	0.4765	0.0026	0.0000	0.0796	0.0701	
3	0.5906	0.6389	0.0484	0.0023	0.0274	0.0277		3	0.5906	0.6461	0.0556	0.0031	0.0274	0.0219	
4	0.7491	0.7966	0.0475	0.0023	0.0000	0.0001		4	0.7491	0.7860	0.0369	0.0014	0.0000	0.0001	
5	0.9091	0.9350	0.0259	0.0007	0.0234	0.0231		5	0.9091	0.9033	0.0057	0.0000	0.0234	0.0290	
6	1.0676	1.0575	0.0101	0.0001	0.0971	0.0964		6	1.0676	1.0032	0.0644	0.0042	0.0971	0.1082	
7	1.2324	1.1667	0.0657	0.0043	0.2269	0.2259		7	1.2324	1.0892	0.1432	0.0205	0.2269	0.2437	
Average	0.7560	0.7571	0.0337	0.0015	0.0987	0.0987		Average	0.7560	0.7387	0.0445	0.0042	0.0987	0.0990	
Total	5.2922	5.2998	0.2360	0.0104	0.6911	0.6911		Total	5.2922	5.1709	0.3115	0.0292	0.6911	0.6932	
				MSC	4.1925	0.9849	CD					MSC	3.1651	0.9579	CD
						0.9924	R							0.9787	R
Using Solver	qe	3.0668127						Using Solver	qe	2.2400749					
	k2	0.0285533							k2	0.060883					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2469	0.0226	0.0005	0.2367	0.2368		1	0.2695	0.2688	0.0007	0.0000	0.2367	0.2241	
2	0.4739	0.4571	0.0169	0.0003	0.0796	0.0797		2	0.4739	0.4801	0.0061	0.0000	0.0796	0.0724	
3	0.5906	0.6380	0.0475	0.0023	0.0274	0.0274		3	0.5906	0.6504	0.0599	0.0036	0.0274	0.0232	
4	0.7491	0.7956	0.0465	0.0022	0.0000	0.0001		4	0.7491	0.7907	0.0416	0.0017	0.0000	0.0000	
5	0.9091	0.9339	0.0248	0.0006	0.0234	0.0234		5	0.9091	0.9082	0.0009	0.0000	0.0234	0.0276	
6	1.0676	1.0563	0.0113	0.0001	0.0971	0.0970		6	1.0676	1.0081	0.0595	0.0035	0.0971	0.1054	
7	1.2324	1.1655	0.0669	0.0045	0.2269	0.2268		7	1.2324	1.0941	0.1383	0.0191	0.2269	0.2396	

Average	0.7560	0.7562	0.0338	0.0015	0.0987	0.0987		Average	0.7560	0.7429	0.0439	0.0040	0.0987	0.0989	
|Total	5.2922	5.2933	0.2365	0.0104	0.6911	0.6911		Total	5.2922	5.2004	0.3070	0.0280	0.6911	0.6923	
				MSC	4.1933	0.9849	CD					MSC	3.2051	0.9595	CD
						0.9924	R							0.9795	R
Using Iteration	qe	2.4763492	$q_t = q_e - \frac{1}{k_2(q_e)}\left(\frac{q_t}{t}\right)$					Using Iteration	qe	2.7932041					
	k2	0.0478335							k2	0.0358366					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2623	0.0073	0.0001	0.2367	0.2314		1	0.2695	0.2542	0.0154	0.0002	0.2367	0.2370	
2	0.4739	0.4743	0.0004	0.0000	0.0796	0.0766		2	0.4739	0.4659	0.0080	0.0001	0.0796	0.0798	
3	0.5906	0.6493	0.0587	0.0034	0.0274	0.0256		3	0.5906	0.6451	0.0545	0.0030	0.0274	0.0275	
4	0.7491	0.7961	0.0470	0.0022	0.0000	0.0000		4	0.7491	0.7986	0.0496	0.0025	0.0000	0.0001	
5	0.9091	0.9211	0.0120	0.0001	0.0234	0.0251		5	0.9091	0.9317	0.0226	0.0005	0.0234	0.0233	
6	1.0676	1.0288	0.0388	0.0015	0.0971	0.1005		6	1.0676	1.0481	0.0195	0.0004	0.0971	0.0969	
7	1.2324	1.1225	0.1099	0.0121	0.2269	0.2321		7	1.2324	1.1508	0.0816	0.0067	0.2269	0.2266	
Average	0.7560	0.7506	0.0392	0.0028	0.0987	0.0988		Average	0.7560	0.7563	0.0359	0.0019	0.0987	0.0987	
Total	5.2922	5.2544	0.2741	0.0194	0.6911	0.6913		|Total	5.2922	5.2944	0.2512	0.0133	0.6911	0.6911	
				MSC	3.5713	0.9719	CD					MSC	3.9523	0.9808	CD

						0.9858	R							0.9903	R
Using Elimination	qe	2.4763243						Using Elimination	qe	2.932299					
	k2	0.0478347							k2	0.0319325					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2623	0.0073	0.0001	0.2367	0.2314		1	0.2695	0.2511	0.0185	0.0003	0.2367	0.2387	
2	0.4739	0.4743	0.0004	0.0000	0.0796	0.0766		2	0.4739	0.4625	0.0114	0.0001	0.0796	0.0807	
3	0.5906	0.6493	0.0587	0.0034	0.0274	0.0256		3	0.5906	0.6431	0.0525	0.0028	0.0274	0.0281	
4	0.7491	0.7961	0.0470	0.0022	0.0000	0.0000		4	0.7491	0.7990	0.0499	0.0025	0.0000	0.0001	
5	0.9091	0.9211	0.0120	0.0001	0.0234	0.0251		5	0.9091	0.9351	0.0260	0.0007	0.0234	0.0228	
6	1.0676	1.0288	0.0388	0.0015	0.0971	0.1005		6	1.0676	1.0548	0.0128	0.0002	0.0971	0.0958	
7	1.2324	1.1225	0.1099	0.0121	0.2269	0.2321		7	1.2324	1.1610	0.0714	0.0051	0.2269	0.2250	
Average	0.7560	0.7506	0.0392	0.0028	0.0987	0.0988		Average	0.7560	0.7581	0.0346	0.0017	0.0987	0.0987	
Total	5.2922	5.2544	0.2741	0.0194	0.6911	0.6913		Total	5.2922	5.3065	0.2425	0.0117	0.6911	0.6911	
				MSC	3.5712	0.9719	CD					MSC	4.0822	0.9831	CD
						0.9858	R							0.9915	R
Using Least Squared	qe	2.6007						Using Least Squared	qe	2.8403602					
	k2	0.0425811							k2	0.0319325					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2593	0.0103	0.0001	0.2367	0.2348		1	0.2695	0.2362	0.0333	0.0011	0.2367	0.2011	
2	0.4739	0.4716	0.0024	0.0000	0.0796	0.0785		2	0.4739	0.4361	0.0378	0.0014	0.0796	0.0596	
3	0.5906	0.6485	0.0580	0.0034	0.0274	0.0267		3	0.5906	0.6075	0.0170	0.0003	0.0274	0.0163	

4	0.7491	0.7984	0.0493	0.0024	0.0000	0.0000		4	0.7491	0.7561	0.0071	0.0001	0.0000	0.0010	
5	0.9091	0.9268	0.0177	0.0003	0.0234	0.0240		5	0.9091	0.8862	0.0229	0.0005	0.0234	0.0365	
6	1.0676	1.0382	0.0294	0.0009	0.0971	0.0983		6	1.0676	1.0010	0.0666	0.0044	0.0971	0.1222	
7	1.2324	1.1357	0.0967	0.0094	0.2269	0.2288		7	1.2324	1.1030	0.1294	0.0167	0.2269	0.2646	
Average	0.7560	0.7541	0.0377	0.0023	0.0987	0.0987		Average	0.7560	0.7180	0.0449	0.0035	0.0987	0.1002	
|Total	5.2922	5.2785	0.2638	0.0164	0.6911	0.6911		Total	5.2922	5.0262	0.3141	0.0246	0.6911	0.7012	
				MSC	3.7385	0.9762	CD					MSC	3.3364	0.9649	CD
						0.9880	R							0.9823	R
Using Graphical	qe	2.476						Using Graphical	qe	2.9462366					
	k2	0.0478414							k2	0.0315657					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2622	0.0073	0.0001	0.2367	0.2314		1	0.2695	0.2507	0.0189	0.0004	0.2367	0.2386	
2	0.4739	0.4742	0.0003	0.0000	0.0796	0.0765		2	0.4739	0.4621	0.0119	0.0001	0.0796	0.0807	
3	0.5906	0.6492	0.0586	0.0034	0.0274	0.0256		3	0.5906	0.6427	0.0521	0.0027	0.0274	0.0281	
4	0.7491	0.7960	0.0469	0.0022	0.0000	0.0000		4	0.7491	0.7988	0.0498	0.0025	0.0000	0.0001	
5	0.9091	0.9210	0.0119	0.0001	0.0234	0.0251		5	0.9091	0.9352	0.0261	0.0007	0.0234	0.0228	
6	1.0676	1.0287	0.0389	0.0015	0.0971	0.1005		6	1.0676	1.0552	0.0124	0.0002	0.0971	0.0958	
7	1.2324	1.1224	0.1100	0.0121	0.2269	0.2322		7	1.2324	1.1617	0.0707	0.0050	0.2269	0.2250	
Average	0.7560	0.7505	0.0392	0.0028	0.0987	0.0988		Average	0.7560	0.7580	0.0345	0.0016	0.0987	0.0987	
Total	5.2922	5.2537	0.2741	0.0195	0.6911	0.6913		Total	5.2922	5.3063	0.2418	0.0115	0.6911	0.6911	
				MSC	3.5702	0.9719	CD					MSC	4.0942	0.9833	CD
						0.9858	R							0.9916	R

Using Solver	qe	2.4763492						Using Solver	qe	2.7938041					
	k2	0.0487315							k2	0.0359256					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2667	0.0029	0.0000	0.2367	0.2403		1	0.2695	0.2548	0.0147	0.0002	0.2367	0.2385	
2	0.4739	0.4815	0.0075	0.0001	0.0796	0.0817		2	0.4739	0.4671	0.0069	0.0000	0.0796	0.0806	
3	0.5906	0.6582	0.0677	0.0046	0.0274	0.0286		3	0.5906	0.6466	0.0560	0.0031	0.0274	0.0280	
4	0.7491	0.8062	0.0571	0.0033	0.0000	0.0001		4	0.7491	0.8003	0.0513	0.0026	0.0000	0.0001	
5	0.9091	0.9319	0.0228	0.0005	0.0234	0.0223		5	0.9091	0.9336	0.0245	0.0006	0.0234	0.0229	
6	1.0676	1.0400	0.0276	0.0008	0.0971	0.0948		6	1.0676	1.0501	0.0175	0.0003	0.0971	0.0959	
7	1.2324	1.1340	0.0984	0.0097	0.2269	0.2234		7	1.2324	1.1529	0.0795	0.0063	0.2269	0.2251	
Average	0.7560	0.7598	0.0406	0.0027	0.0987	0.0987		Average	0.7560	0.7579	0.0358	0.0019	0.0987	0.0987	
Total	5.2922	5.3184	0.2841	0.0189	0.6911	0.6912		Total	5.2922	5.3053	0.2503	0.0133	0.6911	0.6911	
				MSC	3.6002	0.9727	CD					MSC	3.9539	0.9808	CD
						0.9862	R							0.9904	R
Using Iteration	qe	2.6034627	$\left(\frac{1}{t}\right) = \frac{k_2(q_e)^2}{q_t} - k_2(q_e)$					Using Iteration	qe	2.6037327	$t = q_e \frac{t}{q_t} - \frac{1}{k_2(q_e)}$				
	k2	0.0419775							k2	0.0423275					

Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2565	0.0130	0.0002	0.2367	0.2291		1	0.2695	0.2585	0.0111	0.0001	0.2367	0.2333	
2	0.4739	0.4670	0.0070	0.0000	0.0796	0.0752		2	0.4739	0.4703	0.0037	0.0000	0.0796	0.0776	
3	0.5906	0.6428	0.0523	0.0027	0.0274	0.0249		3	0.5906	0.6470	0.0564	0.0032	0.0274	0.0262	
4	0.7491	0.7919	0.0428	0.0018	0.0000	0.0000		4	0.7491	0.7966	0.0476	0.0023	0.0000	0.0000	
5	0.9091	0.9199	0.0108	0.0001	0.0234	0.0259		5	0.9091	0.9250	0.0159	0.0003	0.0234	0.0245	
6	1.0676	1.0311	0.0366	0.0013	0.0971	0.1020		6	1.0676	1.0364	0.0312	0.0010	0.0971	0.0993	
7	1.2324	1.1284	0.1040	0.0108	0.2269	0.2344		7	1.2324	1.1339	0.0985	0.0097	0.2269	0.2303	
Average	0.7560	0.7482	0.0381	0.0024	0.0987	0.0988		Average	0.7560	0.7525	0.0378	0.0024	0.0987	0.0987	
Total	5.2922	5.2376	0.2665	0.0171	0.6911	0.6915		Total	5.2922	5.2677	0.2644	0.0165	0.6911	0.6912	
				MSC	3.7021	0.9753	CD					MSC	3.7344	0.9761	CD
						0.9876	R							0.9880	R
Using Elimination	qe	2.283761						Using Elimination	qe	2.6174815					
	k2	0.0575971							k2	0.0417834					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2655	0.0041	0.0000	0.2367	0.2217		1	0.2695	0.2580	0.0115	0.0001	0.2367	0.2334	
2	0.4739	0.4757	0.0017	0.0000	0.0796	0.0710		2	0.4739	0.4698	0.0042	0.0000	0.0796	0.0777	
3	0.5906	0.6462	0.0557	0.0031	0.0274	0.0225		3	0.5906	0.6466	0.0561	0.0031	0.0274	0.0263	
4	0.7491	0.7873	0.0383	0.0015	0.0000	0.0001		4	0.7491	0.7966	0.0475	0.0023	0.0000	0.0000	
5	0.9091	0.9061	0.0030	0.0000	0.0234	0.0285		5	0.9091	0.9253	0.0162	0.0003	0.0234	0.0245	
6	1.0676	1.0074	0.0602	0.0036	0.0971	0.1071		6	1.0676	1.0371	0.0305	0.0009	0.0971	0.0992	
7	1.2324	1.0948	0.1376	0.0189	0.2269	0.2420		7	1.2324	1.1350	0.0974	0.0095	0.2269	0.2302	
Average	0.7560	0.7404	0.0429	0.0039	0.0987	0.0990		Average	0.7560	0.7526	0.0376	0.0023	0.0987	0.0987	
|Total	5.2922	5.1829	0.3006	0.0272	0.6911	0.6928		|Total	5.2922	5.2684	0.2635	0.0162	0.6911	0.6912	
				MSC	3.2366	0.9608	CD					MSC	3.7507	0.9765	CD
						0.9802	R							0.9882	R

Using Least Squared	qe	2.2544476						Using Least Squared	qe	2.617					
	k2	0.0593405							k2	0.0417934					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2660	0.0035	0.0000	0.2367	0.2201		1	0.2695	0.2580	0.0115	0.0001	0.2367	0.2333	
2	0.4739	0.4759	0.0019	0.0000	0.0796	0.0701		2	0.4739	0.4697	0.0042	0.0000	0.0796	0.0776	
3	0.5906	0.6457	0.0551	0.0030	0.0274	0.0220		3	0.5906	0.6465	0.0560	0.0031	0.0274	0.0262	
4	0.7491	0.7859	0.0368	0.0014	0.0000	0.0001		4	0.7491	0.7965	0.0474	0.0022	0.0000	0.0000	
5	0.9091	0.9036	0.0055	0.0000	0.0234	0.0290		5	0.9091	0.9252	0.0161	0.0003	0.0234	0.0245	
6	1.0676	1.0038	0.0638	0.0041	0.0971	0.1082		6	1.0676	1.0369	0.0307	0.0009	0.0971	0.0993	
7	1.2324	1.0902	0.1422	0.0202	0.2269	0.2437		7	1.2324	1.1348	0.0976	0.0095	0.2269	0.2303	
Average	0.7560	0.7387	0.0441	0.0041	0.0987	0.0990		Average	0.7560	0.7525	0.0377	0.0023	0.0987	0.0987	
Total	5.2922	5.1711	0.3088	0.0287	0.6911	0.6932		Total	5.2922	5.2676	0.2636	0.0163	0.6911	0.6912	
				MSC	3.1809	0.9586	CD					MSC	3.7495	0.9765	CD
						0.9791	R							0.9882	R

Using Graphical	qe	2.2900763						Using Graphical	qe	2.617					
	k2	0.0572033							k2	0.0417934					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2653	0.0043	0.0000	0.2367	0.2218		1	0.2695	0.2580	0.0115	0.0001	0.2367	0.2333	
2	0.4739	0.4754	0.0015	0.0000	0.0796	0.0711		2	0.4739	0.4697	0.0042	0.0000	0.0796	0.0776	
3	0.5906	0.6461	0.0555	0.0031	0.0274	0.0225		3	0.5906	0.6465	0.0560	0.0031	0.0274	0.0262	
4	0.7491	0.7874	0.0383	0.0015	0.0000	0.0001		4	0.7491	0.7965	0.0474	0.0022	0.0000	0.0000	
5	0.9091	0.9063	0.0027	0.0000	0.0234	0.0284		5	0.9091	0.9252	0.0161	0.0003	0.0234	0.0245	
6	1.0676	1.0078	0.0598	0.0036	0.0971	0.1070		6	1.0676	1.0369	0.0307	0.0009	0.0971	0.0993	
7	1.2324	1.0955	0.1369	0.0188	0.2269	0.2419		7	1.2324	1.1348	0.0976	0.0095	0.2269	0.2303	
Average	0.7560	0.7405	0.0427	0.0038	0.0987	0.0990		Average	0.7560	0.7525	0.0377	0.0023	0.0987	0.0987	
Total	5.2922	5.1838	0.2991	0.0269	0.6911	0.6928		Total	5.2922	5.2676	0.2636	0.0163	0.6911	0.6912	
				MSC	3.2460	0.9612	CD					MSC	3.7495	0.9765	CD
						0.9804	R							0.9882	R
Using Solver	qe	2.6037627						Using Solver	qe	2.6037627					
	k2	0.0429575							k2	0.0429575					
Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal		Time	Actual qt	Cal qt	Error	Sq Error	Act -Mean Ac	Ac qt- Mean Cal	
1	0.2695	0.2619	0.0076	0.0001	0.2367	0.2405		1	0.2695	0.2619	0.0076	0.0001	0.2367	0.2405	
2	0.4739	0.4760	0.0021	0.0000	0.0796	0.0818		2	0.4739	0.4760	0.0021	0.0000	0.0796	0.0818	
3	0.5906	0.6542	0.0636	0.0040	0.0274	0.0287		3	0.5906	0.6542	0.0636	0.0040	0.0274	0.0287	
4	0.7491	0.8048	0.0558	0.0031	0.0000	0.0001		4	0.7491	0.8048	0.0558	0.0031	0.0000	0.0001	

5	0.9091	0.9339	0.0248	0.0006	0.0234	0.0222		5	0.9091	0.9339	0.0248	0.0006	0.0234	0.0222	
6	1.0676	1.0457	0.0220	0.0005	0.0971	0.0946		6	1.0676	1.0457	0.0220	0.0005	0.0971	0.0946	
7	1.2324	1.1434	0.0890	0.0079	0.2269	0.2232		7	1.2324	1.1434	0.0890	0.0079	0.2269	0.2232	
Average	0.7560	0.7600	0.0378	0.0023	0.0987	0.0987		Average	0.7560	0.7600	0.0378	0.0023	0.0987	0.0987	
|Total	5.2922	5.3199	0.2648	0.0162	0.6911	0.6912		|Total	5.2922	5.3199	0.2648	0.0162	0.6911	0.6912	
				MSC	3.7508	0.9765	CD					MSC	3.7508	0.9765	CD
						0.9882	R							0.9882	R