



## A Novel Technique: Conceived Predictive Diagonal (CPD) Graphical Nonlinear Regression Modeling and Simulation

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### Abstract

The present work predicts a novel technique for treating workable results. It aims to more professional data treating with less numbers of experiments. A Conceived Predictive Diagonal (CPD) technique is suggested for this target. For the latter a non-linear regression procedure is applied using MATLAB software. Four published examples are employed and treated. By remodeling rate of reaction -Arrhenius combination for studying a pair of factors simultaneously the simulated results are very closed to that reported. It also successfully applied for lab scale uranium removal from nitrate solution by Amberlite IR 120 at Nuclear Materials Authority, Egypt. This work demands skillful in matrices, nonlinear regression modeling, MATLAB, and kinetics- thermodynamics relation.

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### 1-Introduction

Effective persons continually do their best to achieve workable accuracy results via innovative easy and time-saving methodologies. In this manner, the suggestion of an inventive technique Conceived Predictive Diagonal (CPD) is a trial effort for such aim. The very less number of experiments, the more professional analysis is the goal of CPD technique. This technique does not depend on the matrix diagonally dominant techniques or the eigenvalue principle, at the same time is differing from Design of Experiment DOE and Taguchi techniques.

CPD technique supposes that: if the factors distribution covers the task range skillfully in sequence to achieve the response homogeneity, the diagonal of the Conceived Predictive matrix is enough to represent this case.

The study which re/models two factors simultaneously to achieve workable accuracy results is to be considered as an important step within a great achievement. It goes without saying, the other points won't be performed, and the saved time might be employed to study another several pairs of factors simultaneously.

This work demands skillful in matrices, nonlinear regression modeling, MATLAB, and kinetics-thermodynamics relation. And for prospective proceeding, the simulated models can be optimized using MATLAB or any available software.

Software such as MATLAB is able to simulate this link graphically after constructing proper m-files. Herein, "cftool", "ezyfit", and some functions which are suitable for achieving this target.

Non-linear models nowadays are the effect choice not only for accuracy demands but the further dealing to enlarge the model's beneficitation as well. Emphasis on the accuracy when simulating the model -itself and its chain rings- gives a good realizing the system criteria. This is in

general can aid many workers who look forward to a quick effect modeling and simulation as a front end of many advanced processes or for saving a lot of effort, time and financial burdens.

With growing computational power, advances in numerical computers, and the dropping prices of computational resources, MATLAB has become the language of engineering. With challenges posed from open source alternatives like Scilab, Octave, and Python, it now needs to innovate in new dimensions to remain relevant, both commercially and academically.[1]

Other programs e.g. Minitab, Inc., AS, S-Plus, Inc., Design-Expert are used to treat the experimental results for deep dealt more results and saving time.[2]

Non-linear relations are graphically relied. Linear fitting is often used to estimate the characteristics of many systems owing to the simplicity of the relation. Various linear models lead to certain offset of the estimated values. This fact is being assured by statistical calculations. Thus, it is much reliable to find the coefficients by non-linear method. On applying linear models, it is recommended to take into consideration the approximate values rather than the exact data set. [3] The careful non- linear formulation or reformulation is an important step to ease the model simulation.

After referring to internet and available data bases and within the limits of my knowledge there are no similar efforts except those deploying DOE or Taguchi techniques. There are many millions of works using DOE and Taguchi! - After referring to internet-. These valuable efforts covered a wide range of different branches of science. For examples, from aerospace, to PVC production fields many researchers have done their best. [4-10]

The researcher appears a multitude of respect for both general DOE and Taguchi methods. Although that, through a long journey of separation processes, the results from such were far from reality despite statistical assurances. Other researchers have also noted the heterogeneity or limitations in other areas. [11-15]

Undoubtedly, to be convenient it is preferred to study any factor analytically or graphically with a range of  $\geq 4$  points. Traditionally, if two factors are to be studied simultaneously, as much as  $\geq 4 \times 4$  points are required to analyze the response. For example; to determine the activation energy for any reaction through the range of time (t) and absolute Temperature (T), [t,T]={[15 to 40 min],[(273+15)to(273+70)] °K} it is required a matrix A that will be explained soon.

A somewhat less accurate method for determining the activation energy involves integration of the following equations (1, and 2)

$$\frac{d(\ln(k_1))}{d\left(\frac{1}{T}\right)} = -\frac{E}{R} \dots \dots \dots (1)$$

Over the interval between two data points, assuming that E is constant:

**I.2. Tools and Verification**

In fact, this idea demands a powerful software and at the same time practical data to verify it. We can employ MATLAB as trusted software.

**I.2.1. Using MATLAB  $\geq$  2014a**

For any square matrix A, for example (4, 4)  
 $A = \text{sym}('x\_ \%d\_ \%d', 4)$

$$A = \begin{bmatrix} x_{1_1} & x_{1_2} & x_{1_3} & x_{1_4} \\ x_{2_1} & x_{2_2} & x_{2_3} & x_{2_4} \\ x_{3_1} & x_{3_2} & x_{3_3} & x_{3_4} \\ x_{4_1} & x_{4_2} & x_{4_3} & x_{4_4} \end{bmatrix}$$

$$dA = \text{diag}(A)$$

$$dA = [x_{1_1}, x_{2_2}, x_{3_3}, x_{4_4}]^T$$

**I.2.2. Verification This Technique to Be Modus Operandi**

**I.2.2.1. Declared Aspects**

To employ the **Conceived Predictive Diagonal (CPD)** technique

1. Gather some practical data suitable for whether suggested or/and traditional methods
2. Add the initial point (x<sub>0</sub>,y<sub>0</sub>,z<sub>0</sub>) to every vector
3. Simulate the suggested models easily using "cftool(x, y, and z)" in MATLAB and customize the obtained graph. (in some cases, ezyfit is useful tool also)
4. Compare the calculated results with the practical values using r, R<sup>2</sup> and adj R<sup>2</sup> or any available tool.
5. Use simple interactive simulation tool (Data Cursor) presented in the "cftool interface" to compare the remained values in the table

**I.2.2.2. Numerical Examples**

**CPD** was applied in some arbitrary examples.  
 Example: 1

$$\ln\left(\frac{k_1}{k_2}\right) = \left(-\frac{E}{R}\right)\left(\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right) \dots \dots \dots (2)$$

When more than two data points are available, the graphical method is much better to use than common averaging techniques. It gives one a visual picture of the fit of the data to equation (1) [16]. Complementing to save time, the MATLAB "**cftool**" will be employed to achieve the fast modeling and simulation.

In fact, this work depends upon combination of four published and experimental works.

**2-Procedure**

The procedure of the suggested technique CPD can be clarified as follow:

1. Split the factors affecting the process into interlock pairs
2. Conceive a square matrix, every element varies in sequence through the interlock pairs
3. Study every pairs through at least 4 points as the case demand
4. Represent the diagonal of the conceived matrix
5. This diagonal declares the gained responses of the corresponding studied points
6. The pair of factors are X, and Y while the response is Z
7. Cftool(X,Y,Z)

This application was built upon J. Zhao et al: Rapid and Efficient Catalytic Oxidation of As(III) with Oxygen over a Pt Catalyst at Increased Temperature [17]. The deployed matrix "CAS" representing concentration of formed As (V) was selected from their "Fig. 10 Effect of temperature on the oxidation of As (III) over 1 wt%-Pt/ZrO<sub>2</sub>".

The temperature range TAS=273+[20 40 60 80] °K.

The time range was tAS=[0 10 20 30 60 90 120] min.

CAS = concentration of converted As (III) to As (V) in ppm is Non square matrix.

1	1	2	3	5	6
1	3	4	7	9	11
3	5	7	11	14	16
5	8	11	16	18	19

But the **CPD** demands a square matrix so, suppose it CAS<sub>m</sub>. The time and temperature were tAS<sub>m</sub>=[10 30 60 120] min, TAS<sub>m</sub>=273+ [20 40 60 80] °K respectively.

CAS<sub>m</sub>= concentration of converted As (III) to As (V) in ppm is square matrix.

1	2	3	6
1	4	7	11
3	7	11	16
5	11	16	19

Using MATLAB to determine the diagonal of CAS<sub>m</sub> and subsequently using "cftool" function for instantaneously graphical modeling and simulation via Transition and Arrhenius theorems as show in Figs. (1.ex.1 and 2.ex.1).

The diagonal of concentration matrix  
 DC<sub>m</sub>=diag(CAS<sub>m</sub>) = [ 1 4 11 19]

Notable: cftool (tAS<sub>m</sub>,TAS<sub>m</sub>,DC<sub>m</sub>) represents instantaneously graphical modeling and simulation of time ,temperature, and the diagonal of concentration matrix Fig. (ex.1.1).

While cftool(tASm, TASm, CASm) represents instantaneously graphical modeling and simulation of time, temperature, and the matrix itself Fig. (ex.1.2).

DE represents activation energy instead of  $\Delta E$  as a result of Latin alphabet isn't accepted in graphical MATLAB

simulation.  $k_0$ : frequency (pre-exponential) factor;  $m: 0 \leq m \leq 1$  exponent in collision (transition) theory,  $n$ : pseudo order of the reaction.

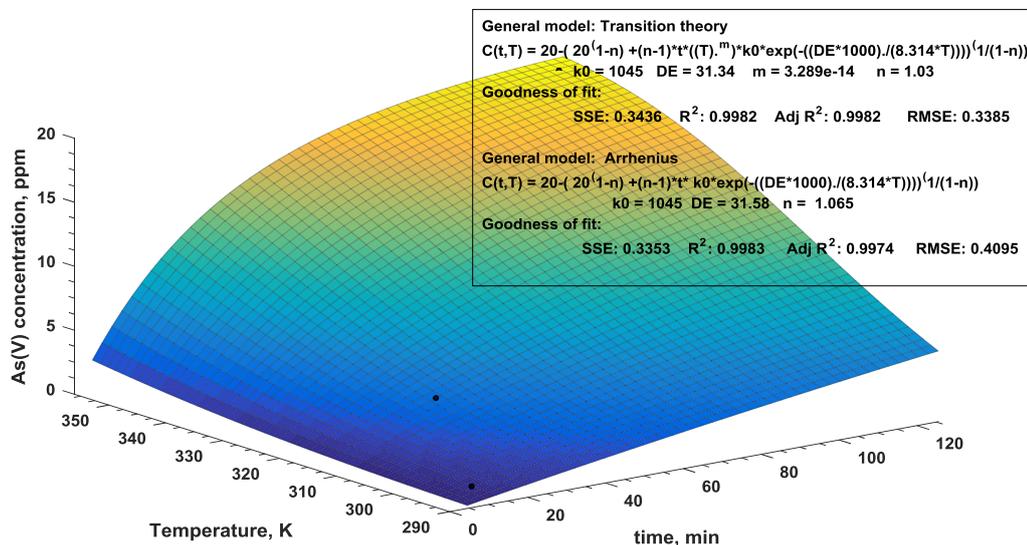


Fig (ex.1.1): Pseudo-first-order kinetic model diagonal representation of As (III) conversion

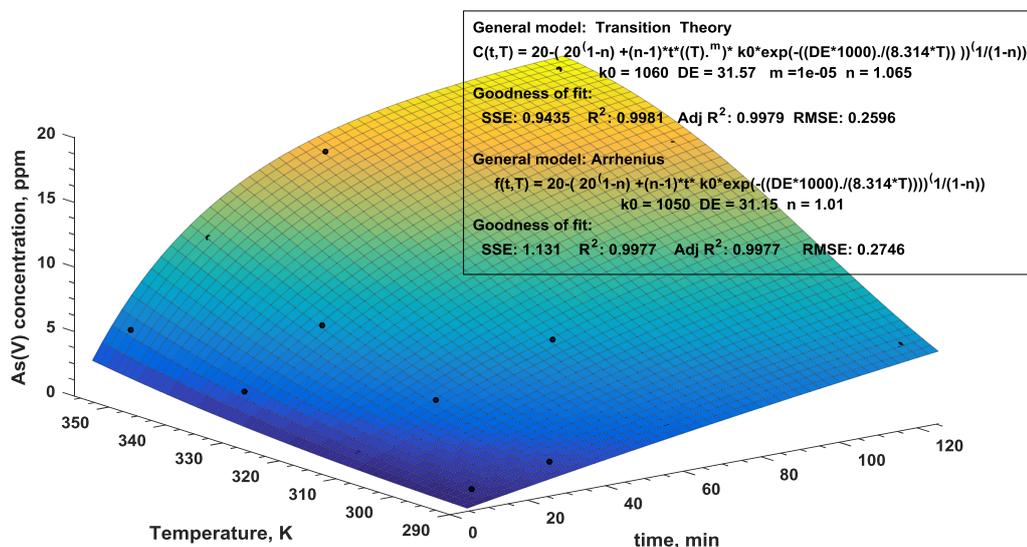


Fig. (ex.1.2): Pseudo-first-order kinetic model matrix representation of As (III) conversion

The simulated results of pre-exponential factor  $k_0$  and activation energy in the Figs. (ex.1.1 and ex.1.2)  $\approx 1.05 \times 10^3$  and 31.6 are closed to the reported  $1.05 \times 10^3 \text{ mol}^{-0.5} \cdot \text{L}^{0.5}$  and  $31.1 \text{ kJ mol}^{-1}$ , respectively. It is clearly that the only diagonal 4 points are capable to represent this system well as supposed.

**Example: 2**

This application was built upon Sarawalee Thanasilp et al: One-pot oxydehydration of glycerol to value-added compounds over metal-doped SiW/HZSM-5 catalysts: Effect of metal type and loading [18]. The deployed matrix "X" representing glycerol conversion was selected from their "Fig. 10 Glycerol conversion as a function of reaction time at different temperatures for kinetic study.

The temperature range TX=273+[60 70 80 90] °K.

The time range was tAS= t= [0 10 20 30 40 50 60 70 80] min.

X= glycerol conversion (non-square matrix). Xmax= maximum conversion.

**Glycerol conversion=X =**

0	23	35	43	47	49	51	52	63
0	33	51	59	64	67	68	69	70
0	45	65	84	77	79	80	81	82
0	60	81	87	88	89	90	91	92

As mentioned above the CPD demands a square matrix so, in this example, we represented diagonals of “selected two square matrices” from X as follow:

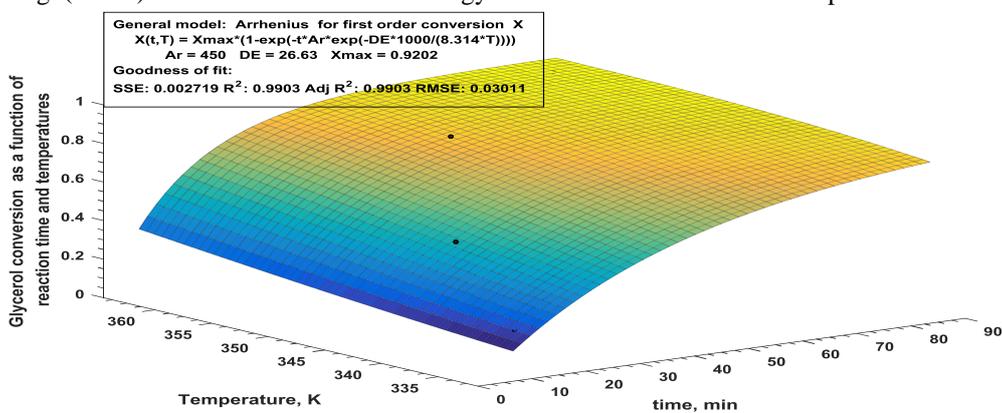
**Example: 2.a.**

The time and temperature vectors were tASm1= [10 20 30 40] min, TXm1=273+ [60 70 80 90] °K respectively and Xs1= glycerol conversion (square matrix).

**Xs1=**

23	35	43	47
33	51	59	64
45	65	84	77
60	81	87	88

As shown in Fig. (ex.2.a) the simulated activation energy DE= ΔE is 26.63 kJ mol<sup>-1</sup> as reported.



**Fig. (ex.2.a): Pseudo-first-order kinetic model diagonal representation of glycerol conversion**

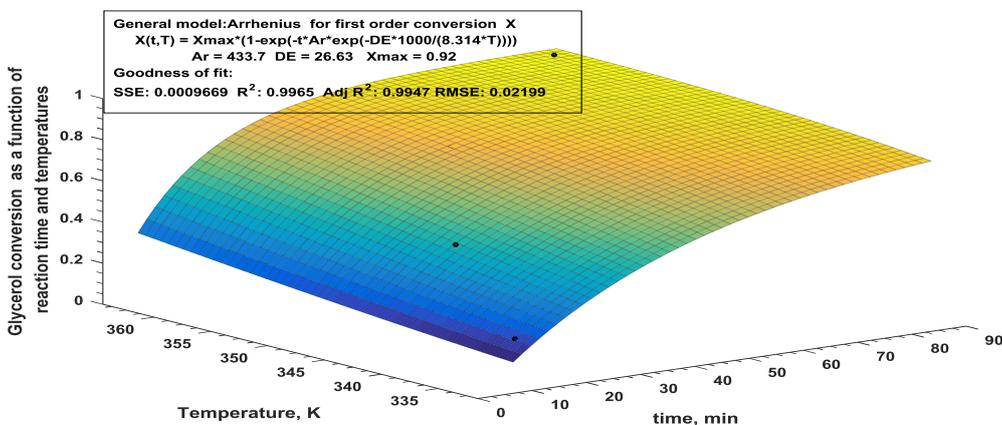
**Example: 2.b.**

The time and temperature vectors were tASm2= [10 20 40 80] min, TXm2=273+ [60 70 80 90] °K respectively and Xs2= glycerol conversion (square matrix).

**Xs2=**

23	35	47	63
33	51	64	70
45	65	77	82
60	81	88	92

As shown in Fig. (ex.2.b) the simulated activation energy DE= ΔE is 26.63 kJ mol<sup>-1</sup> as reported.



**Fig. (ex.2.b): Pseudo-first-order kinetic model diagonal representation of glycerol conversion**  
It is clearly that as mentioned above the only diagonal 4 points are capable to represent this system well as supposed.

**Example: 3**

This application was built upon Suelen M. Amorim et al: Lithium orthosilicate for CO2 capture with high regeneration capacity: Kinetic study and modeling of carbonation and decarbonation reactions [20]. The deployed matrix "XL" was selected from their "Fig. 7. Conversion vs. time for the isothermal decarbonation analysis of the carbonated Li4SiO4 (pure N2). The temperature range was TXL=273+[550 600 650 700] °K. The time range was tXL = [15 30 60 65] min. XL= isothermal decarbonation conversion (square matrix).

XL=	0.01	0.01	0.02	0.30
	0.02	0.04	0.09	0.14
	0.15	0.25	0.61	0.79
	0.30	0.85	0.98	0.98

Before proceeding we should regard to the great difference between the first two elements and the last two in the diagonal vector. This careful notice encourages us to expect shifted pseudo order. In general, shifted pseudo order representation may demand more than 4 points, therefore, we represent the diagonal in 2D to determine the unchangeable parameter "maximum conversion X" in Fig. (ex.3.a) to employ it in the 3D representation.

By the same above manner, dgXL=diag(XL); cftool(tL,dgXL); and cftool(tL,TL,dgXL).

As shown in Fig. (ex.3.b) the simulated results of apparent activation energy of pseudo zero order DEz= ΔE is 56.62 kcal/mol as reported. ( effects of pseudo first order ΔE1 and frequency factor k01 are negligible).

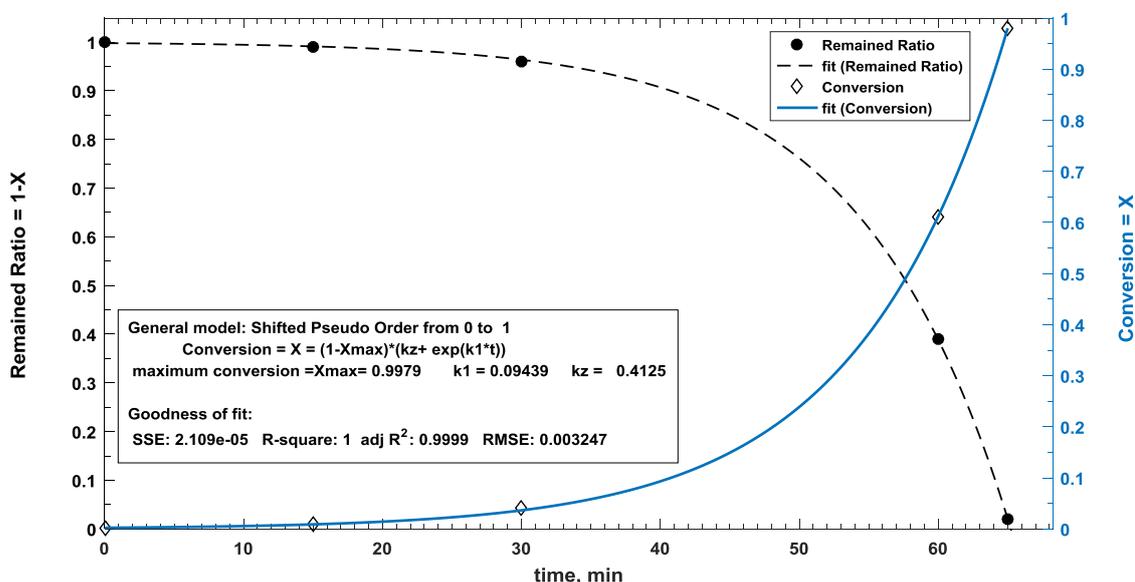


Fig. (ex.3.a): Shifted Pseudo Order from 0 to 1 kinetic model diagonal representing the conversion of isothermal decarbonation of Li4SiO4 (pure CO2)

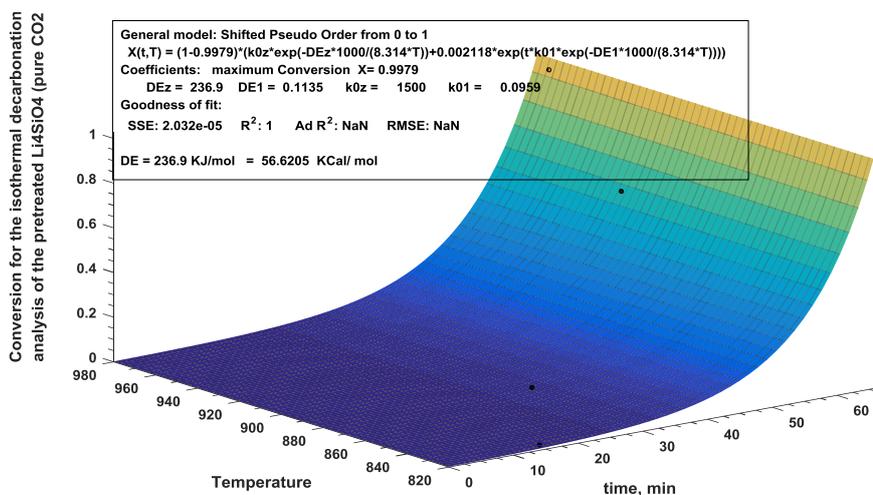


Fig. (ex.3.b): Shifted Pseudo Order from 0 to 1 kinetic model diagonal representing the conversion of isothermal decarbonation of Li4SiO4 (pure CO2)

By the same manner in fast note, we can simulate their Fig. 6. Conversion vs. time for the isothermal carbonation analysis of the pretreated Li4SiO4 (pure CO2). The simulated results of apparent activation energy DE= ΔE is 40.2486 kcal/mol ( reported 40.97)

By deploying MATLAB capability, we can make a fast-shrinking core test using the deployed model in the original issue; Xf: film diffusion controlled, XD: solid diffusion controlled, Xc: chemical reaction controlled. Only the previous diagonal 4 points can declare the type of this reaction.

$$XS = [Xf^2 \quad XD^2 \quad Xc^2]$$

$$XS = \begin{bmatrix} 0.0101 & 0.0000 & 0.0034 \\ 0.0404 & 0.0006 & 0.0137 \\ 0.6162 & 0.1832 & 0.2733 \\ 0.9899 & 0.8800 & 0.7838 \end{bmatrix}$$

$$S = tL \backslash XS$$

S = [0.011473 0.0076212 0.0075762]; solid diffusion and chemical controlled are slow but the chemical is the slowest means chemically controlled system.

This example is a good proof for the CPD concept.

**Example: 4**

This application was built upon Ebrahim .A. Gawad: Uranium removal from nitrate solution by cation exchange resin (Amberlite IR 120), adsorption and kinetic characteristics.[20] The deployed matrix "qt" was selected

from his Figs. (9-10): uptake – (time and temperature) dependency (general pseudo order system) and pseudo first order.

$$T = [273 \ 288 \ 293 \ 298 \ 303 \ 308 \ 313];$$

$$t1 = [0 \ 5 \ 10 \ 15 \ 20 \ 25 \ 30];$$

The uptake matrix (square matrix 7\*7)

$$qt = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 6.4000 & 5.2000 & 5.0000 & 4.8000 & 4.6000 & 4.4000 \\ 0 & 8.4000 & 8.8000 & 8.4000 & 8.2000 & 8.0000 & 7.6000 \\ 0 & 12.8000 & 11.2000 & 10.8000 & 10.6000 & 10.2000 & 10.0000 \\ 0 & 14.0000 & 12.8000 & 12.4000 & 12.2000 & 12.0000 & 11.6000 \\ 0 & 14.6000 & 13.8000 & 13.6000 & 13.4000 & 13.2000 & 13.0000 \\ 0 & 15.0000 & 14.6000 & 14.4000 & 14.2000 & 14.0000 & 13.8000 \end{bmatrix};$$

Although qt is a square matrix but the CPD aims to reduce the number of experiments, therefore demand 4 points can be calculated from a selected square matrix qt4.

$$T4 = [273 \ 288 \ 293 \ 308 \ 313]; \quad t4 = [0 \ 5 \ 10 \ 25 \ 30];$$

$$qt4 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 6.4000 & 5.2000 & 4.6000 & 4.4000 \\ 0 & 8.4000 & 8.8000 & 8.0000 & 7.6000 \\ 0 & 14.600 & 13.800 & 13.2000 & 13.0000 \\ 0 & 15.000 & 14.600 & 14.0000 & 13.8000 \end{bmatrix};$$

$$dig4 = \text{diag}(qt4);$$

$$cftool(t4, T4, dig4)$$

As shown in Figs. (ex.4.a-b) the simulated results of activation energy E = -6.698 kJ mol<sup>-1</sup>, frequency factor Ar = 0.00498, order of reaction n = 1.01, and equilibrium uptake qe = 16.04 mg/g are very closed to the reported values -6.698, 0.00498, 0.9935, and 16.03 respectively same as ex4.a results.

It is clearly that as mentioned above the only diagonal 4 points are capable to represent this system well as supposed.

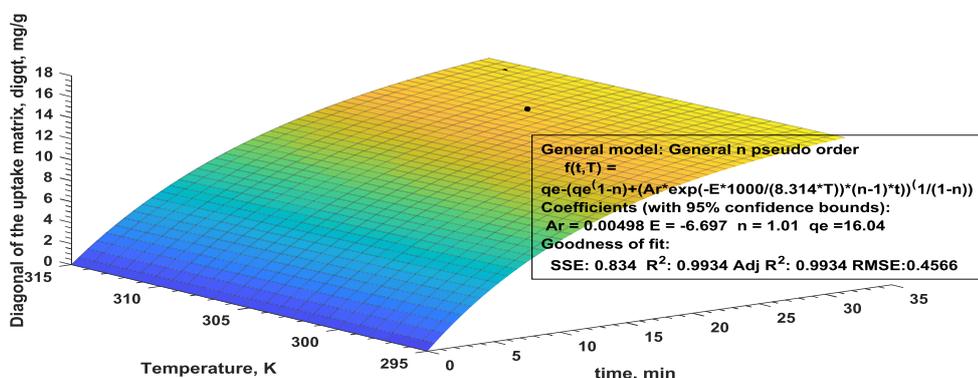


Fig (4-a): uptake – (time and temperature) dependency (pseudo n order system)

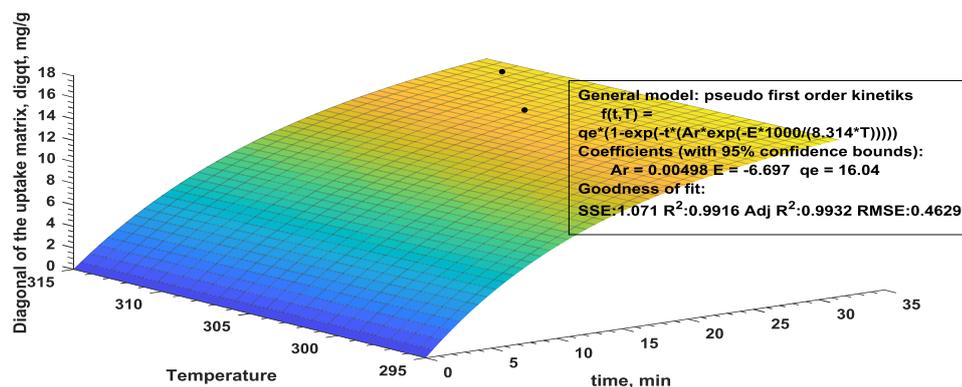


Fig (4-b): uptake – (time and temperature) dependency (pseudo n order system)

## V. Conclusion

The studying of two factors simultaneously by deploying rate of reaction -Arrhenius combination is capable to proof the suggested conceived predictive diagonal CPD technique through 4examples. In fact, this technique enabled us to study also Van't Hoff accompanying isotherms, and other prospective graphical simulations that will be appeared in other works in future!

The CPD is a benefit technique that enabled us to understand the complicated sub-systems in easy manner.

This work is dedicated to the souls of the professors Drs. Abdul Karim Abul Hassan, Nabil El Hazek, Ahmed Khazbak, and Mohamed Abdel Hakam Mahdy. Great thanks for all whom support of their own good will and special mention of Nuclear Materials Authority NMA,

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