

## Two new linearized equations derived from the pseudo-second-order kinetic model

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### ABSTRACT

There are six different linearized models of the pseudo-second-order kinetic model found in the literature. The pseudo-second-order kinetic model's linearized model count was expanded to eight in this study by deriving two newly linearized models. This study used experimental data from the literature for creating plots of these two new models. In the type 7 model, the slope of the line obtained by plotting  $1/(q_e - q_t)$  vs.  $t$  graph gives  $1/k_2$ , and its shift gives  $[-1/k_2q_e]$ . In the type 8 model, the slope of the line obtained by plotting  $t$  vs.  $t/q_t$  graph gives  $q_e$ , and its shift gives  $[-1/k_2q_e]$ . Regression analysis was performed based on  $R^2$  values, which revealed that the concordance of the kinetic data's degree was type 3 = type 4 < type 2 = type 5 < type 1 = type 7 < type 6 = type 8. It was discovered that the regression coefficients of type 6 and newly derived type 8 models are equal and have the highest value. It was determined that the highest  $q_e$  value belonged to type 6 with  $12.594 \text{ mg}\cdot\text{g}^{-1}$ , and the highest  $k_2$  value belongs to type 2 as  $0.0175 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ . It was also understood that the  $k_2$  and  $q_e$  constants are close in the six models. On the other hand, the constants of types 1 and 7 are almost half the value of the constants in other models. Different constants offer alternatives in adsorption affinity, uptake in equilibrium, and degree of coherence. Since the  $k_2$  constants are also used in the Arrhenius equation, it is understood that different  $k_2$  constants will provide a wide range of alternatives for calculating the activation energy.

**Keywords:** Pseudo-second kinetic rate order; Adsorption kinetics; Linearized kinetic model; Linear regression; Nickel(II); Clay

### 1. Introduction

The increase in production that came with industrial development leads to numerous primary and secondary problems worldwide. The two most important of these are environmental and health problems. Today's developing technology and increasing population results in adverse effects on nature by increasing the use of heavy metals. While this pollution directly penetrates living organisms, it also indirectly threatens living organisms that try to survive through the food chain. Scientists who want to find

solutions to such problems are now researching how to protect living organisms from toxic substances with carcinogenic effects [1].

One of the solution methods is the removal of heavy metals from the solutions found in wastewater by adsorption. In this study, clay was used as an adsorbent. It can be easily obtained from nature at a low cost [2]. Kostoglou and Karapantsios [3] examined why the linear form of pseudo-second-order was so successful in adsorption utilizing experimental data. High efficiency can be achieved if the adsorption process is well designed. Additionally, it

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is possible to obtain high quality recycled water after the treatment process [4,5]. Adsorption is a phenomenon that expresses the interaction between two different phases that form an interface layer as a result of the transfer of a molecule from a liquid or gas mass to a solid surface [6]. The adsorption process involves the solid interface's deposition of matter by mass transfer from a liquid or gas. On the other hand, adsorption kinetics helps determine the amount of time that the adsorbent is in contact with the adsorber, where adsorption can take place. Furthermore, it also enables us to understand adsorption's nature, mechanism, pathway, affinity, and activation energy.

Studies on adsorption kinetics are carried out worldwide, and experimental data are modeled. The most prevalent kinetic models are the intraparticle diffusion model, also known as the Weber–Morris model, the Elovich kinetic model, the Lagergren pseudo-first-order kinetic model, and the pseudo-second-order kinetic model.

### 1.1. Intraparticle diffusion model

According to this model, the boundary layer resistance influences the rate of solution adsorption, the equilibrium, and, as a result, the contact time. Adsorbed material is removed from the surface of the adsorbent by intraparticle diffusion [7].

The model's linear form is given in Eq. (1) [8]:

$$q_t = k_{WB}t^{1/2} \quad (1)$$

where  $q_t$  is the amount of material absorbed per gram of adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ );  $k_{WB}$ : kinetic rate constant ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ );  $t$ : contact time ( $\text{min}^{1/2}$ ).

The slip term has been introduced to the formula throughout time [9] The equation's ultimate state is given Eq. (2) [10]:

$$q_t = k_{WB}t^{1/2} + C \quad (2)$$

The  $C$  term is defined as the intersection point that can be reached based on the thickness of the produced boundary layer [11], or a constant related to diffusion resistance [12].

### 1.2. Elovich model

Elovich model expressed as [13]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (3)$$

where  $\alpha$  ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ ) is the initial sorption rate, and  $\beta$  ( $\text{g}\cdot\text{mg}^{-1}$ ) is related to the activation energy of chemical adsorption and surface coverage.  $1/\beta$  represents free adsorption sites.

Researchers widely use Lagergren's first-order rate equation [14–16].

This model, published by the study of Lagergren [17]:

$$\frac{dq}{dt} = k(X - x) \quad (4)$$

Ho rearranged the equation as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

The equation has been referred to as the 'pseudo-first-order rate' since 1998 [18]. Ho, derived the linear form of the pseudo-first-order rate:

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (6)$$

The pseudo-second-order model is widely used by researchers. Also, many studies have been conducted particularly on the pseudo-second-order kinetic model [19–22]. Blanchard proposed a second-order rate equation to remove the divalent metallic ions from an aqueous solution by using  $\text{NH}_4^+$  fixed zeolite particles [Eq. (7)] [23]:

$$\frac{dn}{dt} = K(n_0 - n)^2 \quad (7)$$

Ho rearranged Blanchard's 'second-order rate equation', non-linearly and created 4 linearized forms. The term 'pseudo-second-order rate' has been used to describe the equation since 1995 [24]. The differential form of the derived pseudo-second-order equation can be written as follows [25,26]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

Ho created a linear form of this equation [27]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

In Eqs. (1)–(6)  $X$ ,  $q_e$ , and  $n_0$ : the amount of substance adsorbed per gram by the adsorbent at equilibrium ( $\text{mg}\cdot\text{g}^{-1}$ );  $x$ ,  $q_t$ , and  $n$ : the amount of substance adsorbed per gram by the adsorbent at time  $t$  ( $\text{mg}\cdot\text{g}^{-1}$ );  $k$ ,  $k_1$ ,  $K$ , and  $k_2$ : kinetic rate constants of the first-rate, pseudo-first-order, second order, and pseudo-second-order ( $\text{min}^{-1}$ );  $t$ : contact time.

For the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of Eq. (8) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (10)$$

where, Ho has presented Eq. (10) not as a linear form, but rather as an integrated form [25].

If Eq. (7) were to be rearranged, then Eq. (8) would be obtained:

$$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t \quad (11)$$

In the same year, Khambhaty et al. [28] presented four pseudo-second-order rates. Later on, Oboh et al. [29], Ghaedi et al. [30], Etim [31] provided four types. Five types were presented by Vasanth Kumar [32], Adnan and Thanasupsin [33]. Finally, six types were presented by

Hamdaoui [23], Huang and Shih [34], Huang et al. [35], Vasanth Kumar [32], Onursal and Dal [36], and Onursal [37].

The six types of equations in the literature for pseudo-second kinetic order are given in Table 1.

Kinetic models help us understand the adsorption process. However, only a few adsorption kinetic models are available. Each model and its equations serve as a window into the realm of adsorption. As a result, a new equation provides a new opportunity, because each equation has the potential to be more compatible with experimental data. The equations' constants provide information on the affinity between the adsorbent and the adsorbed. The  $k_2$  constants from the pseudo-second-order model are also used in the Arrhenius equation to calculate the activation energy. The activation energy and adsorption rate have an inverse relationship. Only substances which have high adsorption energies, such as atoms, molecules, ions, or radicals, will react.

## 2. Materials and methods

This study uses both theoretical, yet newly found equations, as well as old ones. Experimental data shall be compared with each other. The experimental data employed within this study was gathered from the literature [38]. In their study, Siirt Koçpınar mixed type clay (SKMTC) was used as the adsorbent, and  $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was used as the adsorbate, and the study was conducted at 298 K. The experimental data for  $\text{Ni}^{2+}$  adsorbed onto the surface of SKMTC were fitted to the six different linearized versions of the pseudo-second-order equation. Then, the two new equations were derived from the pseudo-second-order equation. These two equations were likewise subjected to the aforementioned experimental data. The  $q_e$ ,  $k_2$  and  $R^2$  values were obtained from the information shown in the graphics. The least squares method was used for the regression analysis, and the degree of suitability of linear equations

was compared on this basis. Microsoft Excel 2010 program was used for calculations.

## 3. Results and discussion

### 3.1. Plots created from six linearized versions of the pseudo-second-order equations

Following are the plots of six linearized versions of the pseudo-second-order equation: For the linearized type 1,  $t$  is on the X-axis and  $1/(q_e - q_t)$  is on the Y-axis in Fig. 1. For the linearized type 2 in Fig. 2,  $1/t$  is on the X-axis and  $1/q_t$  is on the Y different axis. For the linearized type 3, Fig. 3 shows  $q_t/t$  on the X-axis and  $q_t$  on the Y-axis. The linearized type 4 is represented in Fig. 4 by  $q_t$  on the X-axis and  $q_t/t$  on the Y-axis. For the linearized type 5, Fig. 5 has  $1/q_t$  on the X-axis and  $1/t$  on the Y-axis. For the linearized type 6, Fig. 6 has  $t$  on the X-axis and  $t/q_t$  on the Y-axis.

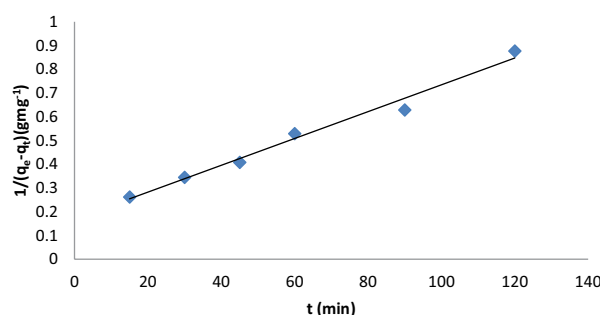


Fig. 1. Type 1 plot for  $\text{Ni}^{2+}$  on SKMTC in 298 K temperature.

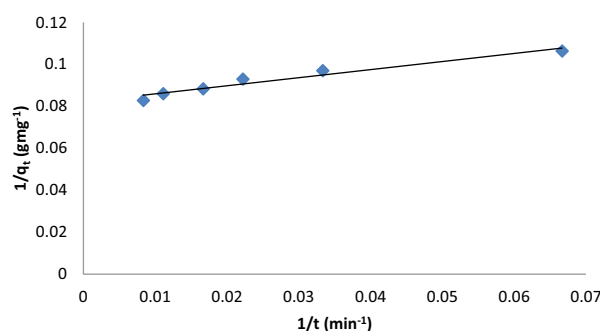


Fig. 2. Type 2 plot for  $\text{Ni}^{2+}$  on SKMTC in 298 K temperature.

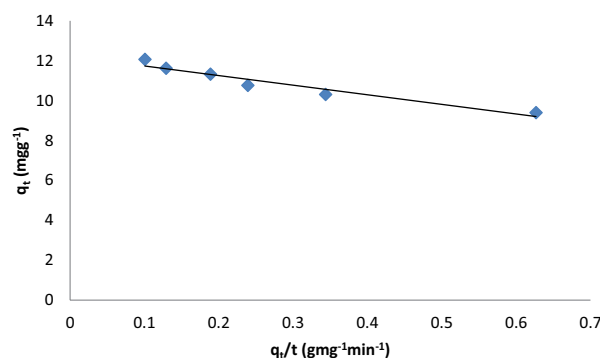


Fig. 3. Type 3 plot for  $\text{Ni}^{2+}$  on SKMTC in 298 K temperature.

Table 1  
Linear equations of the pseudo-second-order model

Type name	Formula
Type 1	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$ (10)
Type 2	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{K_2 q_e^2} \frac{1}{t}$ (12)
Type 3	$q_t = q_e - \frac{1}{K_2 q_e} \frac{q_t}{t}$ (13)
Type 4	$\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$ (11)
Type 5	$\frac{1}{t} = -k_2 q_e + k_2 q_e^2 \frac{1}{q_t}$ (14)
Type 6	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$ (9)

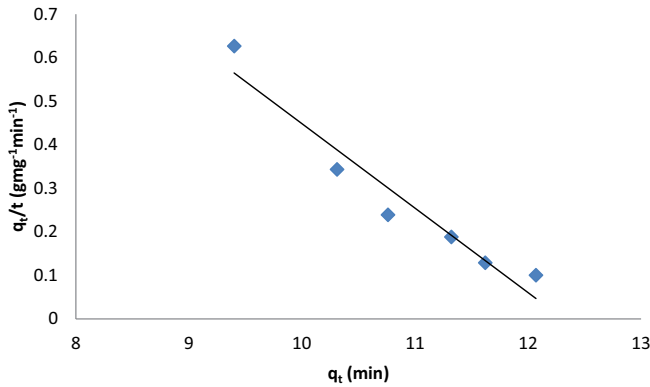


Fig. 4. Type 4 plot for Ni<sup>2+</sup> on SKMTC in 298 K temperature.

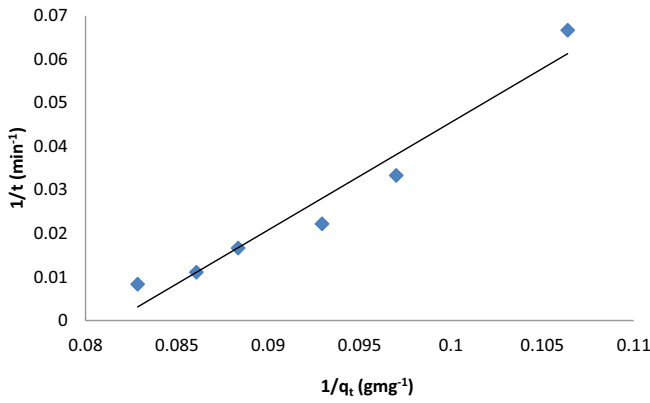


Fig. 5. Type 5 plot for Ni<sup>2+</sup> on SKMTC in 298 K temperature.

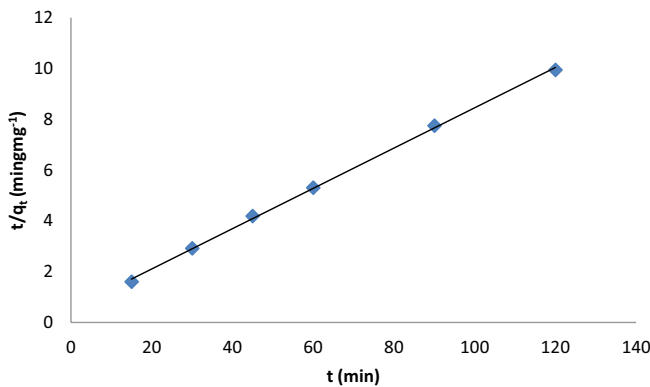


Fig. 6. Type 6 plot for Ni<sup>2+</sup> on SKMTC in 298 K temperature.

3.2. Derivation process of types 7 and 8 linear equations

The derivation stages of type 7 linear equation followed the steps:

Non-linear pseudo-second-order equation [39,40]

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{15}$$

When the term  $q_t$  is multiplied by the denominator:

$$q_t (1 + q_e k_2 t) = q_e^2 k_2 t \tag{16}$$

$$q_t + q_t q_e k_2 t = q_e^2 k_2 t \tag{17}$$

When the terms are taken to the same side of the equation:

$$q_e^2 k_2 t - q_t - q_t q_e k_2 t = 0 \tag{18}$$

When the term  $q_e$  is added to both sides of Eq. (15):

$$q_e + q_e^2 k_2 t - q_t - q_t q_e k_2 t = q_e \tag{19}$$

When the terms are in common brackets:

$$(q_e - q_t)(1 + q_e k_2 t) = q_e \tag{20}$$

When Eq. (17) is rearranged:

$$\frac{1}{q_e - q_t} = \frac{1 + q_e k_2 t}{q_e} \tag{21}$$

$$\frac{q_e}{q_e - q_t} - 1 = q_e k_2 t \tag{22}$$

When  $t$  is left alone in Eq. (19):

$$t = \frac{q_e}{q_e - q_t} \frac{1}{k_2 q_e} - \frac{1}{k_2 q_e} \tag{23}$$

When necessary, simplifications are made and type 7 equation is obtained as follows:

$$t = \frac{1}{k_2} \frac{1}{q_e - q_t} - \frac{1}{k_2 q_e} \tag{24}$$

The derivation stages of type 8 linear equation followed the steps:

Non-linear pseudo-second-order equation.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{15}$$

When both sides of Eq. (12) are reversed.

$$\frac{1}{q_t} = \frac{1}{q_e^2 k_2 t} + \frac{q_e k_2 t}{q_e^2 k_2 t} \tag{25}$$

When necessary, simplifications are made:

$$\frac{1}{q_t} = \frac{1}{q_e^2 k_2} \frac{1}{t} + \frac{1}{q_e} \tag{12}$$

$$\frac{1}{q_t} - \frac{1}{q_e} = \frac{1}{q_e^2 k_2} \frac{1}{t} \tag{26}$$

When the  $1/t$  term is left alone.

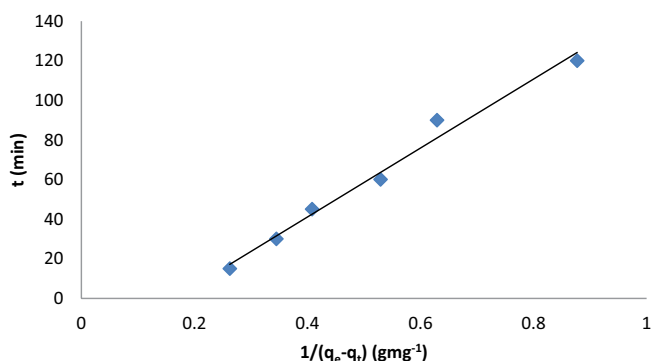


Fig. 7. Type 7 plot for Ni<sup>2+</sup> on SKMTC in 298 K temperature.

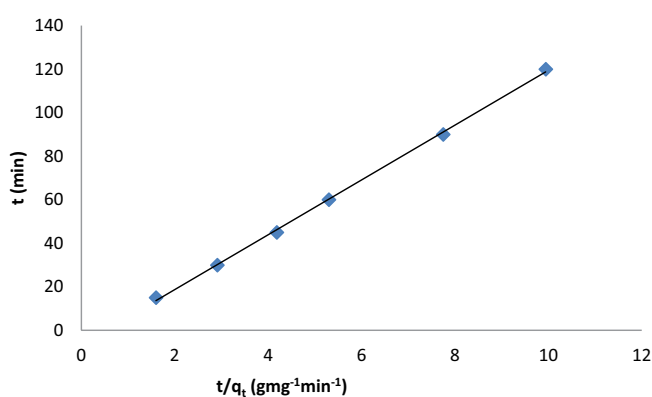


Fig. 8. Type 8 plot for Ni<sup>2+</sup> on SKMTC in 298 K temperature.

$$\frac{q_e^2 k_2}{q_t} - \frac{q_e^2 k_2}{q_e} = \frac{1}{t} \tag{27}$$

When necessary, simplifications are made.

$$q_e^2 k_2 \frac{1}{q_t} - q_e k_2 = \frac{1}{t} \tag{28}$$

When both sides of the equation are multiplied by the *t* term.

$$q_e^2 k_2 \frac{t}{q_t} - q_e k_2 t = 1 \tag{29}$$

$$q_e^2 k_2 \frac{t}{q_t} - 1 = q_e k_2 t \tag{30}$$

If the *t* term on the right in Eq. (28) is left alone:

$$t = \frac{q_e^2 k_2}{q_e k_2 q_t} \frac{t}{q_e k_2} - \frac{1}{q_e k_2} \tag{31}$$

If Eq. (29) is simplified, the type 8 equation is obtained:

$$t = q_e \frac{t}{q_t} - \frac{1}{q_e k_2} \tag{32}$$

Table 2  
Constants are obtained from the graphs

Linearized types	<i>k</i> <sub>2</sub> (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	<i>q</i> <sub>e</sub> (mg·g <sup>-1</sup> )	<i>R</i> <sup>2</sup>
Tip 1	0.0056	5.899	0.984
Tip 2	0.0175	12.180	0.952
Tip 3	0.0170	12.219	0.933
Tip 4	0.0158	12.313	0.933
Tip 5	0.0165	12.257	0.952
Tip 6	0.0122	12.594	0.999
Tip 7	0.0057	6.104	0.984
Tip 8	0.0123	12.592	0.999

The experimental data for Ni<sup>2+</sup> adsorbed onto the surface of SKMTC were fitted to these two linearized versions of the pseudo-second-order equation. For the linearized type 7, Fig. 7 shows *t* on the X-axis and 1/(*q*<sub>e</sub> - *q*<sub>t</sub>) on the Y-axis. For the linearized type 8, Fig. 8 has *t*/*q*<sub>t</sub> on the X-axis and *t* on the Y-axis (Table 2).

The *R*<sup>2</sup> values acquired from the visuals were compared in order to carry out the regression analysis of the equations. When the table is examined, the newly found type 7 exhibited an equal degree of conformity with type 1. Again, the newly found type 8 was equally compatible with the most well-known type of pseudo-second-order rate and the highest conformity, type 6.

#### 4. Conclusion

Adsorption kinetics helps us to understand the nature and mechanism of adsorption. Among kinetic models, the pseudo-second-order rate is the most important one.

The model's fit to the experimental data has a significant impact. The model is widely applied, particularly in the adsorption kinetics of divalent heavy metals.

In this study, two new linearized types of pseudo-second-order rate, types 7 and 8 were derived, and, together with the 6 existing linearized types in the literature, the model's number of linearized equations went up to eight.

In the type 7 model, the slope of the line obtained by plotting 1/(*q*<sub>e</sub> - *q*<sub>t</sub>) vs. *t* plot gives 1/*k*<sub>2</sub>, and its shift gives [-1/*k*<sub>2</sub>*q*<sub>e</sub>]. In type 8 model, the slope of the line obtained by plotting *t* vs. *t*/*q*<sub>t</sub> plot gives *q*<sub>e</sub>, and its shift gives [-1/*k*<sub>2</sub>*q*<sub>e</sub>].

To compare the new equations with the old ones, experimental data were gathered from literature. The materials and methods section specifies the information regarding the literature and how to obtain the data. Regression analysis was performed based on *R*<sup>2</sup> values. Finally, eight plots were created from the eight types of linearized equations. Afterwards, *q*<sub>e</sub>, *k*<sub>2</sub>, and *R*<sup>2</sup> values and the results were compared. When these eight types are sorted in ascending order based on their *k*<sub>2</sub> values, it can be seen that type 1 < type 7 < type 6 < type 8 < type 4 < type 5 < type 3 < type 2. When these models are written according to their *k*<sub>2</sub> values, the values are as follows: 0.0056 < 0.0057 < 0.0122 < 0.0123 < 0.0158 < 0.0165 < 0.0170 < 0.0175. It was observed that the *k*<sub>2</sub> values of types 1 and 7 were almost half the *k*<sub>2</sub> values of the other types. When the 8 models are sorted in an ascending order based on their *q*<sub>e</sub> values, it can be seen that typ

e 1 < type 7 < type 2 < type 3 < type 5 < type 4 < type 8 < type 6. Based on the  $q_e$  values for these models, the values were calculated as 5.899 < 6.104 < 12.180 < 12.219 < 12.257 < 12.313 < 12.592 < 12.594. In parallel with the  $k_2$  values, it was determined that the  $q_e$  values of types 1 and 7 were approximately half of the  $q_e$  values of the other types. In addition to these findings, it was understood that the type e 3 = type 4 < type 1 = type 7 < type 2 = type 5 < type 6 = type 8, and the most crucial criteria, the  $R^2$  values, which determine the degree of conformity of the linear equations with the experimental data. Plots demonstrate that the  $R^2$  values listed above are, 0.933 = 0.933 < 0.952 = 0.952 < 0.984 = 0.984 < 0.999 = 0.999, respectively.

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