

Research Article

Kinetic Model for pH Variation Resulted from Interaction of Aqueous Solution Contaminated with Nickel Ions and Cement Kiln Dust

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Reaction term in the transport equation which described the migration of metal ions in the porous medium is frequently represented by conventional kinetic models such as pseudo-first order, pseudo-second order, and others. Unfortunately, these models are applicable for the constant value of solution pH, and they cannot simulate the real situation in the field scale where this pH may be changed with time. Accordingly, the present study is a good attempt to derive the kinetic model that can simulate the change in the pH of the solution through solute transport. This was achieved by modifying the adsorption capacity and reaction constant to be functions in terms of solution pH by using semianalytical analysis and numerical approximation. The results proved that the kinetic model based on the numerical approximation (using exponential functions for adsorption capacity and reaction constant) symbolised as model 2 was more representative from other models applied for the description of interaction of nickel ions (with initial concentration of 400 mg/L) and cement kiln dust with sum of squared error ≤ 1.54913 and determination coefficient ≥ 0.889 . Also, the developed models had high ability for recognizing between pure precipitation and pure adsorption.

1. Introduction

Contamination of groundwater and surface water resources due to leakage of heavy metals such as cadmium, lead, mercury, chromium, nickel, zinc, and others from natural and anthropogenic activities are considered serious environmental problem [1–5]. Unlike the organic compounds, the heavy metals cannot be degraded, and the contaminated streams can be treated by separating these metals using conventional methods such as ion exchange [6, 7], precipitation, air flotation, and adsorption [8–12]. Natural pollution with nickel is occurred due to pumped of groundwater from chalk aquifer where nickel is present within the pyrite nodules as in the southwestern Sweden and Denmark [13, 14].

The production of cement material is accompanied with the generation of large quantities of byproduct named cement kiln dust (CKD). It is a heterogeneous fine-grained solid of highly alkaline constituent due to the presence of a greatest percentage of limestone [15, 16]. Discarding this byproduct to the ecosystem can associate with many problems that have negative impacts on the living and nonliving elements of the environment. So, reuse of CKD as reactive material in the remediation of wastewater streams is very valuable in the application of sustainability concepts, especially many agencies classified this material as nonhazardous solid waste [17, 18].

The major mechanisms responsible of the contaminant transfer during the treatment process due to the interaction of cement kiln dust (CKD) and aqueous solution

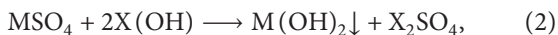
contaminated with heavy metals have been proved in the previous studies. These studies clarified that the mechanisms include adsorption/desorption and precipitation/dissolution; unfortunately, the distinguishing between the mentioned mechanisms is not declared in the evidence approach. Many studies illustrated that the removal of heavy metals onto CKD is governed by pure adsorption within the specific range of initial pH, and this can be attributed to the fine texture of this sorbent and presence of the metal oxide in its composition [19, 20]. Actually, the pH of the contaminated water can be increased dramatically with the presence of CKD due to the high lime content and, consequently, metal hydroxide can be formed [21–23]. So, there is another mechanism rather than the pure adsorption which governed the treatment process which known as “pure precipitation.” In addition, the last group of these studies is considered the treatment process as just interaction between contaminant and reactive material regardless which mechanism governed the removal of contaminant or what the contribution and adsorption when occurred together [24–26].

The interaction of CKD and water can cause a potential increase in the pH of aqueous solution as a function of the contact time, and this may be attributed to the gradual dissolution of calcium oxide. Kinetic models are mostly utilized to describe the kinetic data at certain value of pH. Thus, when the pH varied with time (as for interaction of CKD and water), the kinetic model can be modified to take this situation into account by deriving the relationships related between kinetic constants and pH of the solution. Accordingly, the derivation and development of kinetic model as a function of solution pH will be more attractive for characterization between adsorption and precipitation when occurred together in the treatment process, and this is the significant point of this study. In the future, the present model can be incorporated with solute transport equation to reflect the effect of pH variation (which is the common state in the field scale) on the extent of the contaminant plume. Experimental outputs resulted from interaction of CKD and aqueous solution contaminated with nickel ions are used to verify the derived model.

2. Derivation of Kinetic Model for CKD-Metal Ions Interaction

Stepwise approach must be applied to represent the adsorption and precipitation mechanisms that resulted from interaction of aqueous solution of heavy metal and CKD as described previously. This approach is required to formulate each mechanism alone, and then the final results are collected together as follows [24, 27–29]:

(1) Metal (M) removal by precipitation:



where M: Ni; X: K, Na.

The quantity of metal ions that captured by CKD particles (q_p) due to pure precipitation may be

determined by dividing the difference between initial concentration (C_o) and remaining concentration (C_p) after precipitation onto the CKD dosage (m) for volume of sample (V) as follows [30, 31]:

$$q_p = \frac{V(C_o - C_p)}{m}. \quad (3)$$

(2) Metal sorbed onto CKD particles:



The quantity of metal ions that captured by CKD particles (q_{sr}) due to pure adsorption may be determined by dividing the difference between initial concentration and remaining concentration (C_{sr}) after pure adsorption onto the CKD dosage (m) as follows [31, 32]:

$$q_{sr} = \frac{V(C_o - C_{sr})}{m}. \quad (5)$$

Adsorption in combination with precipitation can cause total removal quantity of metal ions (q) calculated based on the remaining concentration of these ions at time (t) as follows [26]:

$$q = \frac{V(C_o - C_t)}{m}. \quad (6)$$

Consequently,

$$q = q_{sr} + q_p, \quad (7)$$

$$\frac{V(C_o - C_t)}{m} = \frac{V(C_o - C_{sr})}{m} + \frac{V(C_o - C_p)}{m}, \quad (8)$$

$$(C_o - C_{sr}) = (C_o - C_p) - (C_o - C_t), \quad (9)$$

$$C_{sr} = C_o - C_t + C_p. \quad (10)$$

By substituting equation (10) into equation (5), the result will be

$$q_{sr} = \frac{V(C_t - C_p)}{m}. \quad (11)$$

(3) Kinetic models: these are very important in the prediction of the transfer rate of the metal ions from the liquid phase to the solid phase in the remediation process [33]. Previous studies are mainly based on the pseudo-first and pseudo-second order kinetic models in the description of this transfer rate [34]; however, more general expression named pseudo- n^{th} order kinetic model was derived to simulate the kinetic adsorption measurements as listed in Table 1. For kinetic precipitation measurements, theory on the kinetics of solid state chemical reaction was developed by Melvin Avrami (between 1939 and 1941) in the Columbia University, and the derived

TABLE 1: Kinetic models used to describe the mechanisms governed the interaction of nickel ions and cement kiln dust.

Mechanism	Model	Expression
Sorption	Pseudo-first order n^{th} order	$q_t = q_e (1 - e^{-k_1 t})$ $q_{t1} = q_{c1} - ((n_1 - 1)k_n t^a + q_{c1}^{1-n_1})^{(1/1-n_1)}$
Precipitation	Avrami	$q_t = q_e (1 - e^{-k_1 t^a})$

q_t and q_e are the quantities of solute removed from the aqueous solution at time t and at equilibrium, respectively, in (mg/g), k_1 is the pseudo-first order reaction constant (1/min), and k_n is the pseudo- n^{th} order reaction constant (g/mg min).

equation (Table 1) can be utilized to describe the results of precipitation process [35–37].

- (4) Modification of sorption kinetics model: derivation of the simultaneous sorption kinetic model for simulated pH effect must be introduced. Modification of reaction constant and adsorption capacity based on the effects of pH can be achieved either by semianalytical model or numerical model as follows:

- (1) Semianalytical model: the nickel sorption phenomena are based on the following equation:



So, the reaction constant of sorption process will be

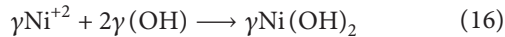
$$k_1 = \frac{[\text{CKD} - \text{Ni}]^c}{[\text{CKD}]^b [\text{Ni}]^a} \quad (13)$$

On the contrary, the sorption of the nickel hydroxide can be described by the following equations:

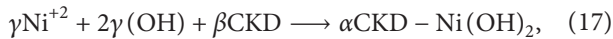


$$k_2 = \frac{[\text{CKD} - \text{Ni}(\text{OH})_2]^\alpha}{[\text{CKD}]^\beta [\text{Ni}(\text{OH})_2]^\gamma} \quad (15)$$

The nickel hydroxide transformation is governed by the following equation:



To find the relationship between the reaction constant and pH, the summation of equations (14) and (16) may result in



$$k_3 = \frac{[\text{CKD} - \text{Ni}(\text{OH})_2]^\alpha}{[\text{CKD}]^\beta [\text{Ni}]^\gamma [\text{OH}]^\gamma} = k_3 = \frac{K}{[\text{OH}]^\gamma} = K[\text{OH}]^{-\gamma}. \quad (18)$$

For more simplification,

$$k_3 = K * 10^{-\gamma(\text{pH}-14)} \quad (19)$$

or $k_3 = K * 10^{-(A\text{pH}-B)}$.

Due to the change of pH with time, numerical relationship between pH and time can be suggested as follows:

$$\text{pH} = \log_{10}(at^b). \quad (20)$$

So,

$$k_3 = K * 10^{-B} * (a^{-A} t^{-bA})$$

or $k_3 = K * a^{-A} * 10^{-B} * t^{-bA}$. (21)

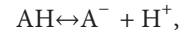
Let $\xi = K * a^{-A} * 10^{-B}$ and $\psi = -bA$, then

$$k_3 = \xi t^\psi. \quad (22)$$

By assuming that the one weakly acid functional group is responsible of sorption process, the sorption capacity (q_c) can be written as follows [32, 38, 39]:

$$q_c = \frac{Q_1 + (Q_2 * 10^{\text{pH}-\text{pKa}})}{1 + 10^{\text{pH}-\text{pKa}}}, \quad (23)$$

where k_a is the apparent equilibrium constant and Q_2 and Q_1 are the adsorption capacities for deprotonated (A^-) and protonated (AH) forms of functional group, and the reaction of equilibrium may be explained as



$$\text{pH} = \log_{10}(at^b), \quad (24)$$

$$q_c = \frac{Q_1 + (Q_2 * 10^{\log_{10}(at^b) - \text{pKa}})}{1 + 10^{\log_{10}(at^b) - \text{pKa}}}.$$

For more simplification,

$$q_c = \frac{Q_1 + (Q_2 * 10^{-\text{pKa}} * a * t^b)}{1 + 10^{-\text{pKa}} * a * t^b}, \quad (25)$$

$$\text{or } q_c = \frac{Q_1 + (Q_2 * a * 10^{-\text{pKa}} * t^b)}{1 + 10^{-\text{pKa}} * a * t^b}.$$

Let $\phi = Q_2 * a * 10^{-\text{pKa}}$ and $\Theta = 10^{-\text{pKa}} * a$, then

$$q_c = \frac{Q_1 + (\phi t^b)}{1 + \Theta t^b}. \quad (26)$$

- (2) Numerical kinetic model: the sorption process is mainly based on the pH of aqueous solution; so, the heavy metal with very acidic solution can be reacted easily with the protonated site. Hence, the identification of the operating mechanism depends on the presence of affinity series in agreement with the constant of hydrolysis. The complexity of this

phenomenon may be due to the presence of various mechanisms of sorption that operated at different pH [40]. However, further investigations must be achieved to explore the behaviour of affinity series and sorbent selectivity under the pH effect. In the affinity series of systems with single metal, this metal with the highest affinity may rarely be affected by the existence of other heavy metals in solution [40, 41]. Due to the complexity of the phenomenon under consideration and to express of the sorption performance, the numerical model was utilized to simulate the influence of pH. The kinetic model derived previously can be completed by using different numerical simulation functions that are based on the exponential model for representing of (q_e) and (k_1) (Table 2).

3. Materials and Methods

3.1. Mediums and Contaminant. Factory of Al-Kufa cement, Al-Najaf, Iraq was the source for CKD utilized as reactive material in the batch tests. This material has high percentage of Calcium oxide (approximately 46%), and the dissolution of this constituent may be the primary cause for changing the acidity of the solution. For this reason, the CKD is chosen in the present study to recognize between adsorption and precipitation because they related with variation of solution pH.

The nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) manufactured by SD Fine-Chem Limited, India was dissolved in one liter of distilled water to prepare the stock solution with the initial concentration of 1000 mg/L. To obtain the required concentration, stock solution must be diluted, and the pH of solution can be modified by adding base or acid as required.

3.2. Batch Experiments. The batch experiments are as follows:

- (1) Total sorption (adsorption and precipitation): kinetic experiments are carried out at room temperature with initial pH = 3 where 50 mL volumes of aqueous solution contaminated with specific concentration of nickel ions must be distributed on the set of 250 mL flasks and 0.5 ± 0.01 g of CKD added to each flask. Orbital shaker was used to agitate all flasks at a speed of 200 rpm for duration not exceeding 180 min; however, the filter paper can be utilized to separate the soil particles from aqueous solution after the end of agitation process. Certain volume (≈ 10 mL) of clear solution resulted after filtration from each flask was adopted to measure the residual concentration of nickel ions in the solution using the Shimadzu AA-6300 flame atomic absorption spectrophotometer at a wavelength equal to 232.2 nm. Mass balance

equation can be applied to find the quantity of metal ions sorbed to the CKD material.

- (2) Pure precipitation: the procedure adopted in the present study to find the quantity of metal ions that precipitated due to the raise of solution pH is similar to the "tea-bag" experiment published in the previous studies [42]. 50 mL of uncontaminated water with pH of 3 was distributed into the set of 250 mL flasks, and a specific quantity of CKD ($=0.5 \pm 0.01$ g/50 mL) must be added to each flask, and all mixtures were continuously agitated using a shaker for a period equal to 200 rpm at room temperature. Thereafter, the solutions were filtered using the Whatman 6900-2504 PVDF GD/X 25 Sterile Syringe Filter (25 mm, $0.45 \mu\text{m}$) to obtain the clear solution, and they have been mixed with the solution contaminated with nickel ions. The aim of this approach is to take the effect of CKD on the solution pH and, then, study the behavior of metal ions under the effect of this value of pH after separating the solid phase. However, the mixtures are agitated for equilibrium time, and then the precipitates are separated by filtration. The Shimadzu AA-6300 flame atomic absorption spectrophotometer can be used to measure the concentration of nickel ions still staying in these solutions; so, the precipitated concentration may be obtained by mass balance. The pH meter (type WTW pH 330i) was adopted to monitor the values of pH for solutions in all conducted tests.

4. Results and Discussion

Direct contact between the nickel ions and CKD sorbent during the experiments concerned the total sorption can increase the possibility of metal attachment on the particle surfaces. This is may be the main reason for the removal of metal ions without any delay, and conversely, remarkable lag can be observed in the removal of these ions by pure precipitation. For the interaction of nickel ions and CKD, pure adsorption must be determined as a complementary portion for precipitation share within the total sorption by using the developed previous equation (equation (10)) as plotted in Figure 1. Increasing the initial concentrations of metal ions according to this figure can cause a significant decrease in the total sorption, and this will associate with the increase of precipitation share while decreasing the adsorption share. The high reactivity of CKD in the change of solution pH will enhance the formation of nickel hydroxide, and it is considered the main cause for increasing the portion of precipitation process. Accordingly, reaching the adsorption capacity requires longer time because of the slow adsorption process in comparison with precipitation. Figure 2 and Table 3 show the trends and constants of the kinetic models which described the pure adsorption and

TABLE 2: Selected approximations for constants of kinetic models for numerical approach.

Model	Equation	Type of model for	
		k	q_c
Model 1	$Q = q_{c1} (1 - e^{-at^b+c})$	Exponential	Without modification
Model 2	$Q = (q_c t^\alpha + \beta) (1 - e^{-at^b+c})$	Exponential	Exponential
Model 3	$Q = q_c \exp(\mu t) (1 - e^{-at^b+c})$	Exponential	Exponential based on (e) constant
Model 4	$Q = q_{c1} (1 - e^{-z \exp(st)})$	Exponential based on (e) constant	Without modification
Model 5	$Q = (q_c t^\alpha + \beta) (1 - e^{-z \exp(st)})$	Exponential based on (e) constant	Exponential
Model 6	$Q = (q_c \exp(\mu t)) (1 - e^{-z \exp(st)})$	Exponential based on (e) constant	Exponential based on (e) constant

Q is the quantity of solute removed from the aqueous solution at time t (mg/g), q_{c1} is the numerical constant (mg/g min ^{α}), and q_c is the quantity of solute removed from the aqueous solution at equilibrium (mg/g); $b, c, z,$ and α are numerical constants (-), μ and s are also numerical constants (1/min), and a is the numerical constant (1/min ^{b}).

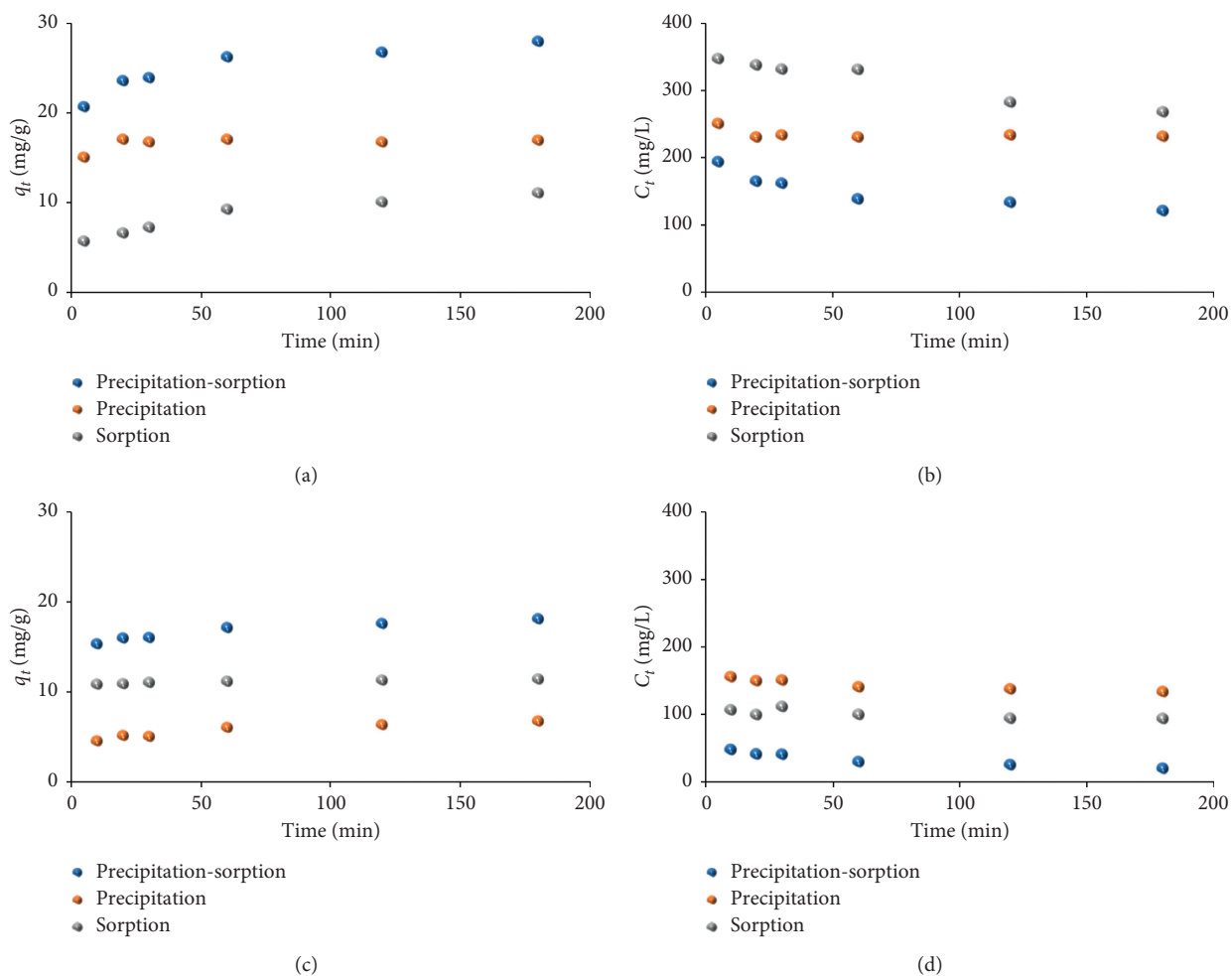


FIGURE 1: Variation of uptake capacities and remaining concentrations versus time for total sorption, sorption, and precipitation mechanisms at different values of initial nickel metal concentrations. (a) $C_o = 400$ mg/L. (b) $C_o = 400$ mg/L. (c) $C_o = 200$ mg/L. (d) $C_o = 200$ mg/L.

total sorption for interaction of nickel ions and CKD sorbent; however, poor matching can be recognized between the predicted and experimental results due to variation of pH versus the time.

In comparison with conventional models, the predictions of the modified kinetic models using semianalytical approximation presented a satisfactory agreement for the measured results of the pure adsorption as in Figure 3;

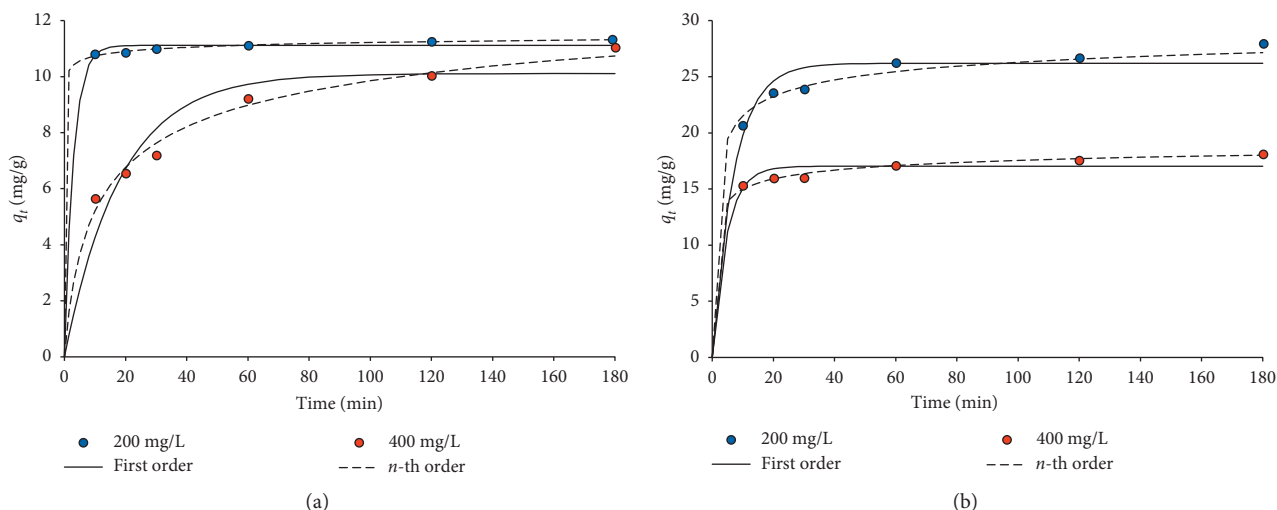


FIGURE 2: Kinetic model for nickel ions onto CKD particles as a result of total sorption and pure adsorption. (a) Sorption. (b) Adsorption-precipitation.

TABLE 3: Simulation of predominant mechanisms by different kinetic models.

Mechanism	Name of model	Parameter	C_o (mg/L)	
			200	400
<i>Precipitation-sorption</i>	First order	q_c	17.03	26.19
		k_1	0.215	0.141
		R^2	0.460	0.620
		SSE	13.99	8.92
	n^{th} order	q_c	21.280	32.436
		k_n	6.931×10^{-6}	1.883×10^{-6}
		N	5.397	4.967
		R^2	0.961	0.854
		SSE	0.271	2.067
		<i>Sorption</i>	First order	q_c
k_1	0.347			0.055
R^2	0.370			0.854
SSE	0.160			4.040
n^{th} order	q_c		12.520	15.67
	k_n		202×10^{-6}	6×10^{-6}
	n		8.320	4.489
	R^2		0.973	0.974
	SSE		0.007	0.595
	<i>Precipitation</i>		Avrami	q_c
k_l		0.166		0.319
a		1.606		0.197
R^2		0.969		0.964
SSE		0.092		0.132

especially, the n^{th} order model may be more representative than first order model. The constants (Table 4) of these models are calculated by the nonlinear regression analysis using “Solver” option within the Excel (2016).

For numerical kinetic models mentioned in Table 2, the nonlinear regression method with the first tentative values

for the parameters of these models as determined by Excel were utilized to fit the experimental measurements at different periods of time. The fitted values for parameters of all numerical kinetic models are listed in Table 5; however, the scatter diagram for selected values of models under consideration is shown in Figure 4. Table 5 in combination with

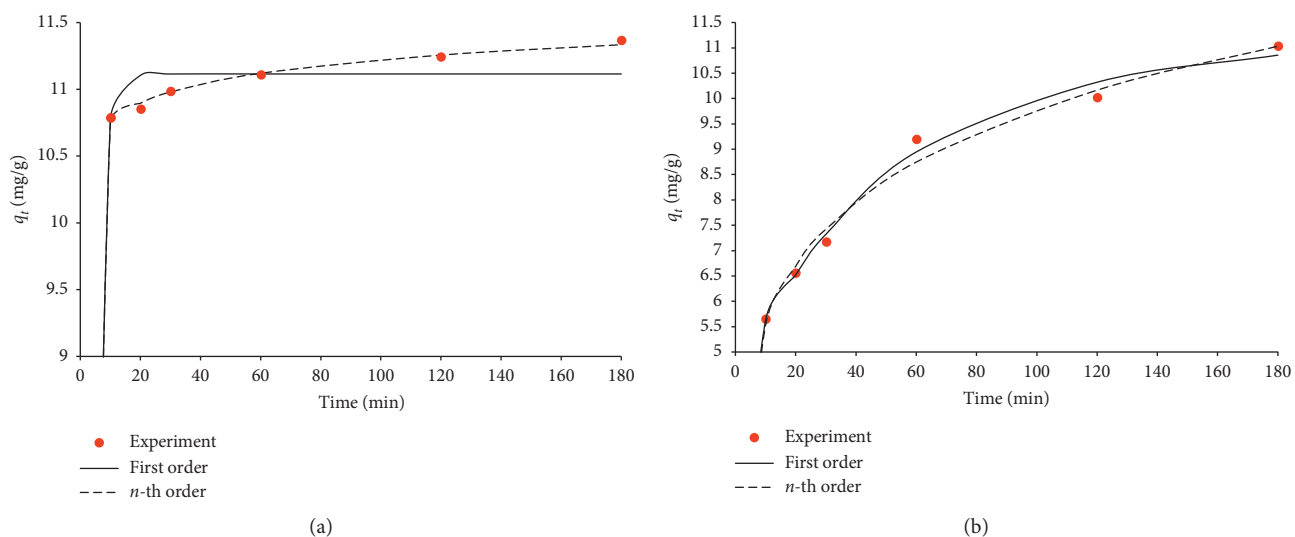


FIGURE 3: Semianalytical approximation for kinetic model to simulate the sorption kinetic data for initial concentration of (a) 200 and (b) 400 mg/L.

TABLE 4: Parameters of different semianalytical models for sorption kinetic data of nickel ions-CKD interaction.

Model	Parameter	C_o (mg/L)	
		200	400
<i>First order</i>	Γ	0.266	0.143
	Ψ	-0.137	2.345
	Q_I	30.71	52.093
	Θ	1.800	2.638
	B	0.052	-0.089
	Φ	3.498	-20.470
	R^2	0.894	0.881
	SSE	0.114	1.65
<i>nth order</i>	Ξ	$1.293 * 10^{-6}$	0.143
	Ψ	-1.202	0.940
	Q_I	23.546	1117.499
	Θ	429.145	109.981
	B	-3.350	-0.078
	Φ	4409.536	-16.058
	N	1.020	8.203
	SSE	0.114	1.681

TABLE 5: Parameters of different numerical kinetic models for sorption kinetic data of nickel ions-CKD interaction.

Model	Parameter	C_o (mg/L)	
		200	400
<i>Model 1</i>	q_{c1}	10.791	17.74725
	a	0.080	4.477
	b	1.440	0.054
	c	-0.189	4.149
	R^2	0.731	0.850
	SSE	0.290	2.092

TABLE 5: Continued.

Model	Parameter	C_o (mg/L)	
		200	400
Model 2	q_c	12.334	9.462
	α	-0.031	0.085
	β	0.001	0.001
	a	0.00001	0.00002
	b	3.860	4.416
	c	-1.826	-1.751
	R^2	0.922	0.889
	SSE	0.084	1.549
Model 3	q_c	11.108	13.153
	μ	-0.00031	0.00155
	a	0.00001	0.00070
	b	3.938	0.796
	c	-2.057	-2.073
	R^2	0.864	0.733
	SSE	0.147	3.716
Model 4	q_{c1}	10.787	14.892
	z	0.044	1.327
	s	0.400	0.008
	R^2	0.732	0.761
	SSE	0.289	3.320
Model 5	q_c	11.582	9.461
	α	0.001	0.001
	β	-0.017	0.085
	z	0.044	0.101
	s	0.389	0.311
	R^2	0.900	0.889
	SSE	0.170	1.549
Model 6	q_c	10.991	12.147
	μ	-0.0002	-0.002
	z	0.044	0.099
	s	0.393	0.400
	R^2	0.833	0.742
	SSE	0.180	73.713

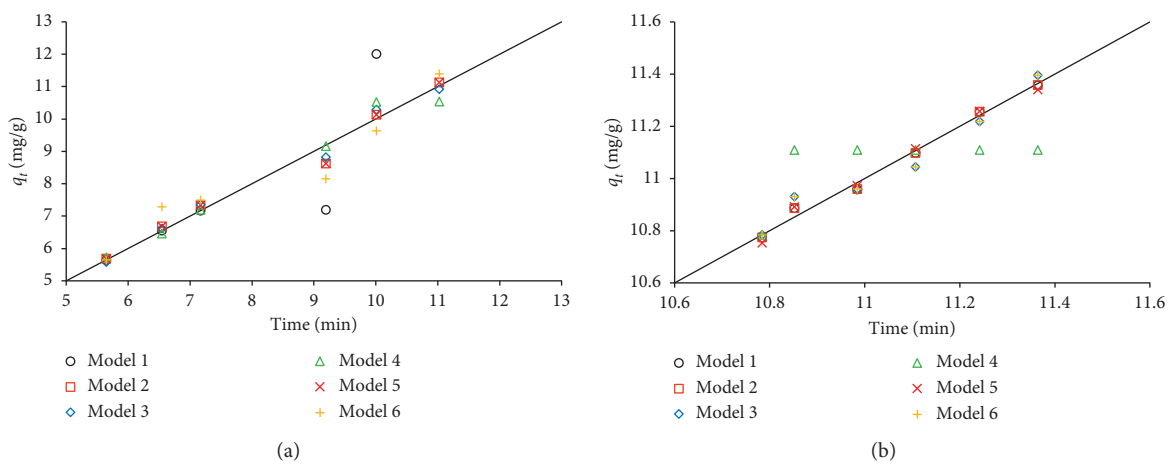


FIGURE 4: Continued.

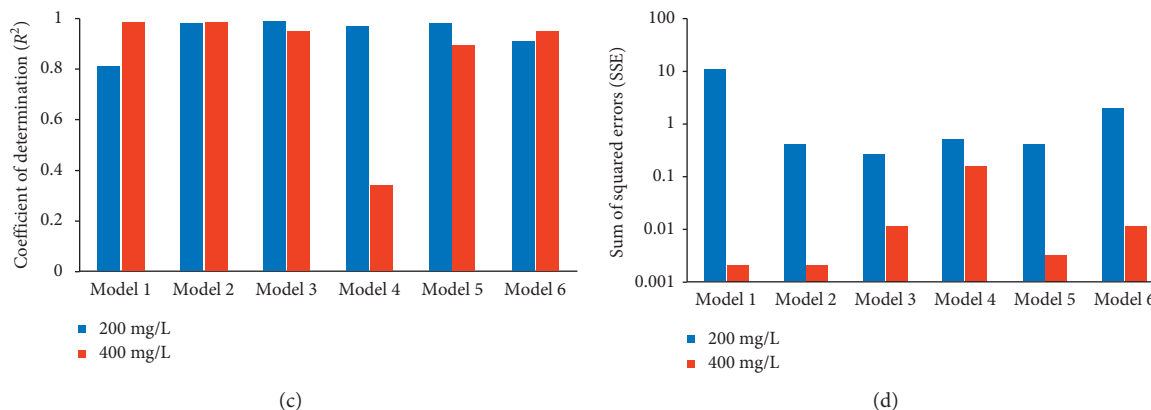


FIGURE 4: Scatter diagram with related statistical measures of numerical kinetic models for sorption kinetic data of nickel ions-CKD interaction. (a) $C_o = 200$ mg/L. (b) $C_o = 400$ mg/L. (c) R^2 . (d) SSE.

Figure 4 signified that the model 2 is more dependent in the description of the kinetic experimental measurements for CKD-nickel ions interaction under the variation of the solution pH with sum of squared errors (SSE) ≤ 0.54913 and coefficient of determination (R^2) ≥ 0.88862 .

5. Conclusions

The common situation in the real-field scale problems for propagation of metal ions in the subsurface medium is the variation of water pH versus the time and this definitely can influence the mechanism which governed the transport process. Accordingly, the finding of more suitable kinetic model that has high ability in the description of the transport process based on the set of kinetic measurements for interaction of nickel ions and CKD was developed. The present analysis was implemented to distinguish between the predominant mechanisms (i.e., total sorption, pure adsorption, and pure precipitation) by using traditional kinetic models. Then, modifications are achieved on the adsorption capacity (q_c) and reaction constant (k_1) of the kinetic model by applying semianalytical approximation as well as numerical models. Results proved that model 2 utilized the exponential approximation for q_c and (k_1) can lead to suitable representation for kinetic data under consideration with $SSE \leq 1.54913$ and $R^2 \geq 0.88862$. This model is valuable and can be integrated with solute transport in the future to find the effect of variation of solution pH on the distribution of metal ions in the porous medium.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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