Comparative studies of linear and nonlinear methods of pseudo-second-order kinetic in Ni(II) removal from aqueous solution onto calcium alginate

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ABSTRACT

In this study, a comparison between linear and nonlinear methods of estimating the kinetic parameters of Nickel(II) removal onto calcium alginate was examined. The kinetic data were analyzed using the four different type of pseudo-second-order linear kinetic model. The coefficient of determination r^2 and chi-square test χ^2 was employed as methods of error analysis for determining the best-fitting equation. The type 3 pseudo-second-order kinetic model accurately represented the kinetic uptake of Ni(II) by Ca-alginate. Further, the non-linear method of pseudo-second-order was suitable in estimating biosorption parameters. In addition, the χ^2 test was found to be a better method for determination of the best-fitting model. EDX analysis of Ca-alginate biosorbent before and after Ni(II) sorption revealed that the ion-exchange mechanism was the principal sorption process.

Keywords: Adsorption; Nickel(II); Calcium alginate; Kinetics; Regression analysis

1. Introduction

Adsorption processes have been investigated as an effective method for the sorption of heavy metal ions from aqueous environments [1]. Heavy metals such as Ni(II) tend to accumulate in organisms. They can be accomplished by a variety of methods, which lead to numerous health problems [2]. Ni(II) ions are carcinogen and their effects are varying from skin irritation to damage the lungs and nervous system. Therefore, the removing of excess Ni(II) ions from wastewater is necessary to protect human health [3]. One of the promising techniques for the metal ions removal is the use of biopolymers as sorbents [4]. The capability of Ca-alginate to form stable biodegradable gels in the presence of divalent cations has been known and studied extensively since the seventies [5]. The major component of the alginate is alginic acid, a polymer composed of unbranched chains of 1,4-linked α-L-guluronate (G), and α-D-mannuronic acid (M) [6]. The prediction of the adsorption kinetics is important for the effective sorption system design. Chemical kinetics investigates the uptake rate of adsorbate and also the factors affecting the reaction rate [6]. The most commonly used kinetic expressions to predict the mechanism involved in the solid/liquid adsorption processes are the pseudo-first-order kinetic, pseudo-second-order kinetic model, intraparticle diffusion,

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and external mass transfer model [6–8]. Pseudo-second-order expression as proposed by Ho accurately represents the experimental kinetic data for the entire range of the heavy metal sorption systems [9]. In the recent years, linear regression is most commonly used to determine the best-fitting kinetic equations [10]. The nonlinear method for analyzing the experimental data provides a more complex mathematical analysis for determining kinetic parameters [11]. However, during the last few years, a development interest in the utilization of nonlinear optimization modeling has been noted. This is mainly due to such transformation of nonlinear equations to linear forms implicitly alters their error structure and may also violate the normality assumptions of standard least squares and the error variance [12]. Little information is available on comparative analysis of linear and nonlinear of pseudo-second-order kinetic for Ni(II) removal from aqueous solution onto Ca-alginate. Linear regression method has been used commonly to determine the most fitted sorption kinetic parameters of Ni(II) removal onto ca-alginate. Al-Rub et al. [13] carried out a study on Ni(II) biosorption using ca-alginate. They investigated the analysis of linear method of estimating the pseudo-first- and pseudo-second-order kinetic parameters. Vijaya et al. [14] studied the equilibrium and kinetic of Ni(II) removal onto Ca-alginate in column and batch methods. In their research, linear methods were applied for obtaining the kinetic parameters of Ni(II). The results of the kinetic studies showed that the sorption of Ni(II) ions followed pseudo-second-order kinetics. A kinetic and equilibrium research was performed by Bayramoglu and Yakup Arica [15] on Cu(II), Zn(II), and Ni(II) biosorption from aqueous solution using Ca-alginate beds. They study the Ho pseudo-second-order expression to describe the biosorption phenomenon by Ca-alginate. The pseudo-first-order and pseudo-second-order kinetic models have been widely used in most

biosorption kinetic studies. A number of experiments fitted using these two models are given in Table 1.

From Table 1, the results showed that for the pseudo-second-order model, the correlation coefficients were higher than 0.98 in most studies. Further, the calculated equilibrium uptake values agreed very well with the experimental data. Therefore, in comparison to pseudo-first-order kinetics, this model is considered more appropriate to predict the kinetic data in biosorption systems. The main objectives of the present study are:

(1) Characterizing the biosorbent structure through scanning electron microscopy (SEM) and EDX analysis.
(2) To make a comparative study of linear and nonlinear regression analysis of pseudo-second-order expression using the experimental kinetic data of Ni(II) biosorption onto Ca-alginate for estimating and optimum kinetics.
(3) To discuss the problems associated with linearization.
(4) Employing the coefficient of determination r^2 and chi-square test χ^2 as methods of error analysis for determining the best-fitting equation of Ni(II) biosorption onto Ca-alginate.

2. Materials and methods

2.1. Reagents and equipment

Ni(II) concentration in solution were determined by atomic absorption spectrophotometer (Varian-AA 240, Australia) with Nickel hollow cathode lamp at wavelength of 341.5 nm after biosorption. Samples of biosorbents were coated under vacuum with a thin layer of gold and examined by SEM (∑ IGMA/VP-ZEISS, Germany) to study the surface texture morphology of the biomass before and after the biosorp-

Table 1
Kinetic parameters for the sorption of Nickel(II) ions by different biosorbents

| Sorbent | $q_{e,exp}$ (mg g^{-1}) | First-order kinetic | | | Second-order kinetic | | | References |
		q_e (mg g^{-1})	k_1 (L min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	
Cystoseria indica	42.00	34.91	0.044	0.968	47.61	0.002	0.996	[16]
Orange peel	29.04	19.85	2.602	0.940	29.16	0.165	0.999	[17]
Litchi chinensis seed	32.81	30.83	1.339	0.973	35.80	0.050	0.990	[18]
Talinum triangular (water leaf)	3.020	4.820	0.824	0.975	3.020	0.460	0.999	[19]
Immobilized *Aspergillus awamori*	6.80	3.77	0.019	0.888	7.25	0.009	0.997	[20]

tion. Further confirmation of the adsorption of Ni(II) ions onto ca-alginate was done by energy dispersive X-ray (EDX, Oxford instruments) analysis.

2.2. Synthesis of Ca-alginate

The stock solution of Ni(II) (500 mg L^{-1}) was prepared by dissolving 0.24 g analytical reagent grade of NiSO$_4$·7H$_2$O (Merck, Germany) in 100 mL deionized distilled water. All working solutions of desired concentrations were prepared by diluting the stock solution with suitable volume of distilled water. Ca-alginate beads were prepared by dropping of 2% sodium alginate (Merck, Germany) solution into a 2% calcium chloride (Merck, Germany) solution. Alginate beds were stored in a 2% calcium chloride solution at 4°C for at least 60 min to complete the process, then collected and washed with deionized water for several times to remove calcium chloride from the bead surface. The structure of ca-alginate is given by Fig. 1.

2.3. Batch studies of adsorption

Sorption kinetic experiments were carried out using the batch method for different initial Ni(II) concentrations. The initial pH value of each experiment was adjusted to desires value by the addition of 0.1 M HCl (Merck, Germany) and 0.01 M NaOH (Merck, Germany) at the beginning of each experiment. The process was performed in 250 mL erlenmeyer flasks containing 100 mL of Ni(II) solution using a fixed amount (0.5 g) of Ca-alginate at pH 6. The flasks were agitated at a constant speed of 150 rpm in an incubator shaker (JalTajhiz, Iran). The shaking time was varied from 5 to 180 min in different concentration (25, 35, 50, and 75) of Ni(II) solution. The results showed that maximum Ni(II) removal with Ca-alginate was reached at 120 min, beyond which there was no fur-

ther increase in Ni(II) removal. The residual amount of Ni(II) in each flask was investigated using a flame atomic absorption spectrometer (Varian-AA240, Australia) at λ_{max} of 341.5 nm. Metal uptake by biosorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e is the equilibrium uptake (mg g^{-1}), C_0 and C_e are the initial and the equilibrium metal ion concentration mg L^{-1}, respectively, V is the volume of the solution in contact with the biosorbent in mL, and m is the mass of the added biosorbent in g [22].

3. Results and discussion

3.1. SEM and EDX analysis of ca-alginate

The SEM micrographs of the Ca-alginate were compared before and after biosorption of Ni(II) with a thin layer of gold to improve electron conductivity and image quality and examined by SEM ($\sum$ IGMA/ VP-ZEISS, Germany) in Figs. 2a and 2b. The biosorbent structure was in the constant conditions as 0.5 g of the biosorbent, pH 6, and 100 mL of Ni(II) with initial concentration of 25 mg L^{-1}, constant temperature (25°C), a constant speed of 150 rpm, and 120 min for contact time. The results obviously show the difference between before and after loading of Ni(II) on the biomass surface in Ca-alginate biomatrix. By comparing the two micrographs, it was found that the biosorbent before sorption of Ni(II) ions indicates a smooth regular spherical structure of the Ca-alginate surface (Fig. 2a). Moreover, following metal loading on Ca-alginate, some deformation and appearance of cavities and pores onto the Ca-alginate surface were observed. This morphology may contribute to the relatively high surface area of the biomaterial (Fig. 2b). Further confirmation of the adsorption of Ni(II) ions onto Ca-alginate was done by EDX analysis. Figs. 2c and 2d show the typical EDX (Oxford instruments) pattern for Ca-alginate before and after the sorption of Ni(II), respectively. The EDX pattern for Ca-alginate before adsorption did not show the characteristic signal of Ni (II), whereas after sorption a clear signal of Ni(II) was observed. The EDX spectra depict the peaks of C, O, Cl, Na, and Ca, which are the main constituents of Ca-alginate. These peaks point out the polymer types representing available functionalities on the biomass, i.e. –COOH and –OH. A complete elimination peak for Cl after biosorption of Ni(II) indicates chemical transformation or variations in polymer chains.
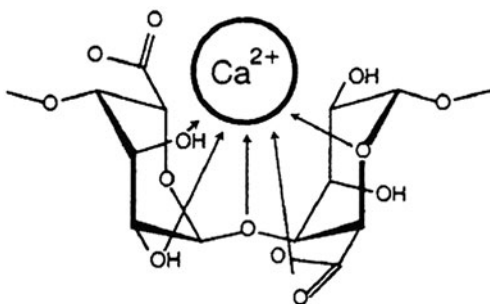

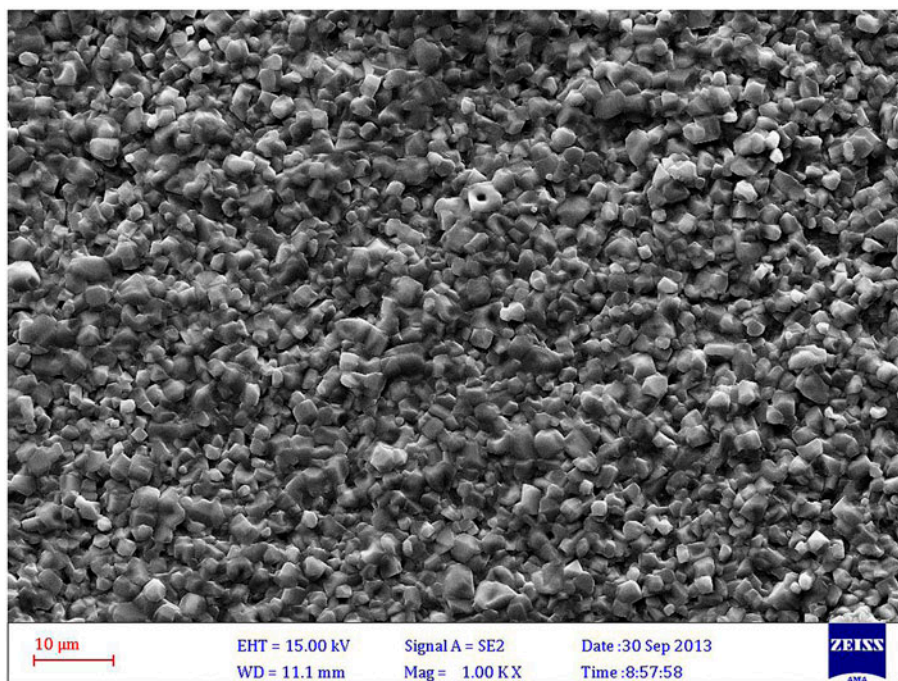Fig. 1. Chemical structure of Ca-alginate [21].

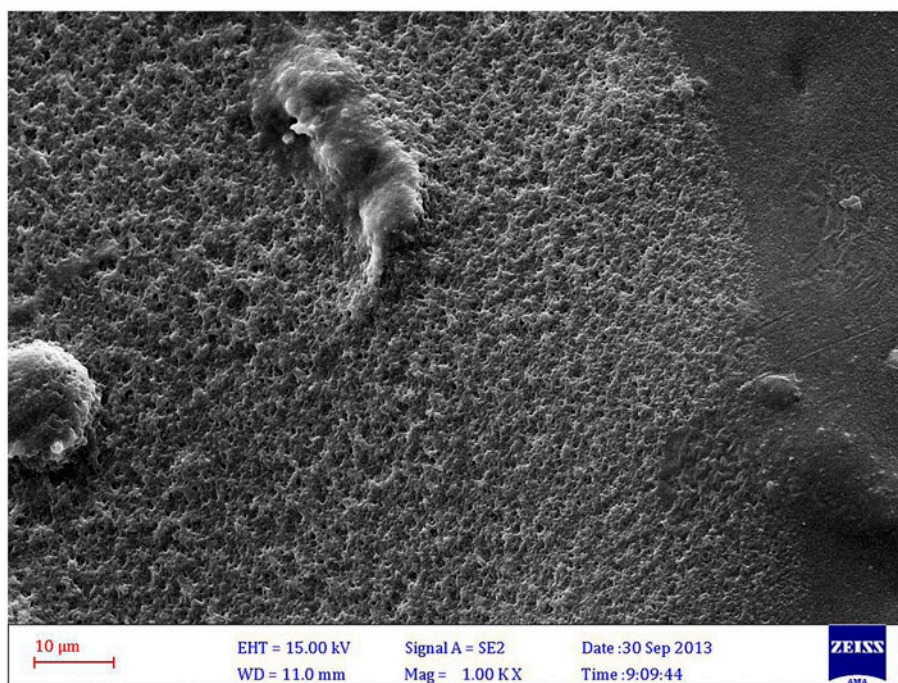Fig. 2a. Micrograph of Ca-alginate before biosorption of Nickel(II).

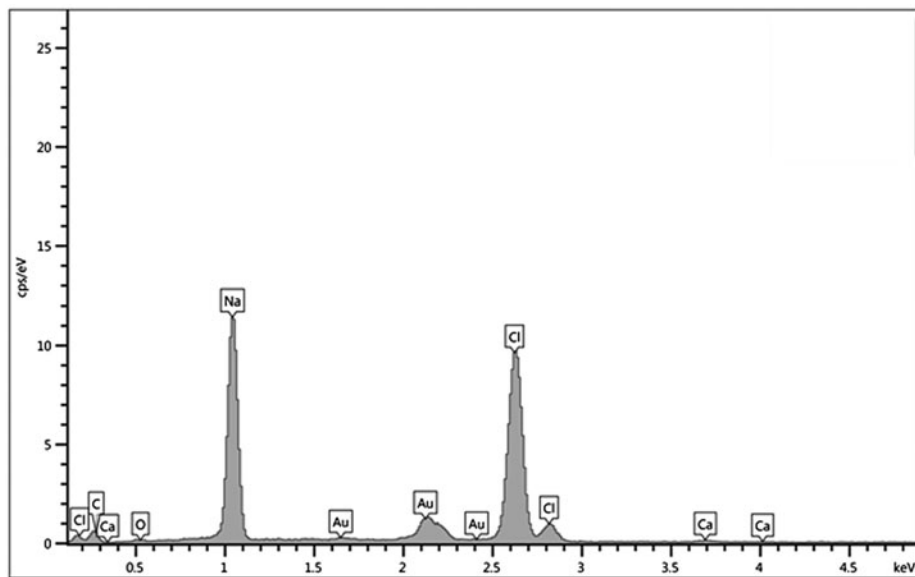Fig. 2b. Micrograph of Ca-alginate after biosorption of Nickel(II).

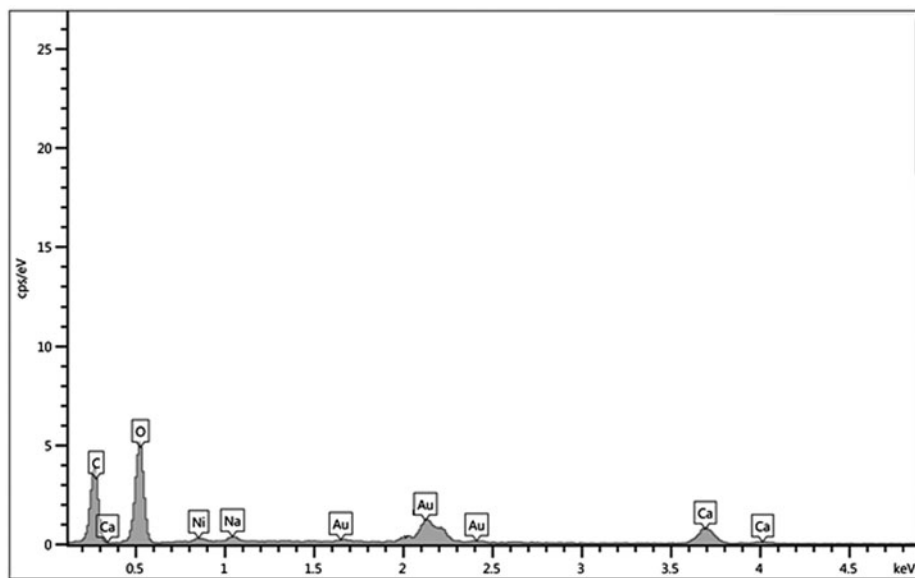Fig. 2c. EDX spectra of Ca-alginate before Ni(II) biosorption.

Fig. 2d. EDX spectra of Ca-alginate after Ni (II) biosorption.

Further, Cl could be removed during Ni(II) biosorption via an ion-exchange mechanism.

3.2. Pseudo-second-order kinetic model

The experimental data were used for pseudo-first- and pseudo-second-order kinetic models and it was observed that the correlation coefficient factor, R^2, alculated from pseudo-second-order model fits the experimental data very well with amount of 0.99 (figures not shown). As such, pseudo-second-order kinetic could represent the kinetic data better than the pseudo-first-order expression. The differential form of the model is expressed as [23]:

Table 2
Four different linearized forms of the pseudo-second-order equation

Type	Linear form	Plot
Type 1 pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e} t$	t/q_t vs. t
Type 2 pseudo-second-order	$\dfrac{1}{q_t} = \dfrac{1}{q_e} + \dfrac{1}{k_2 q_e^2} \dfrac{1}{t}$	$1/q_t$ vs. $1/t$
Type 3 pseudo-second-order	$q_t = q_e - \dfrac{1}{k_2 q_e} \dfrac{q_t}{t}$	q_t vs. q_t/t
Type 4 pseudo-second-order	$\dfrac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t$	q_t/t vs. q_t

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where (k_2 mg^{-1} min^{-1}) is the pseudo-second-order rate constant of sorption, q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amount of Ni(II) adsorbed onto Ca-alginate at any time and equilibrium time, respectively. Applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (2) becomes:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where k_2 (mg^{-1} min^{-1}) is the pseudo-second-order rate constant of sorption, q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amount of Ni(II) adsorbed onto Ca-alginate at any time and equilibrium time, respectively [24]. The different linearized forms of the pseudo-second-order Eq. (3) are given in Table 2. The most popular form used is type 1 [25,26].

3.3. Error analysis

To evaluate the fit of the equations to the experimental results, error functions are required. In the present research, the coefficient of determination r^2 and the chi-square test χ^2 was used in order to investigate and compare the applicability of each model quantitatively [13, 26–28]:
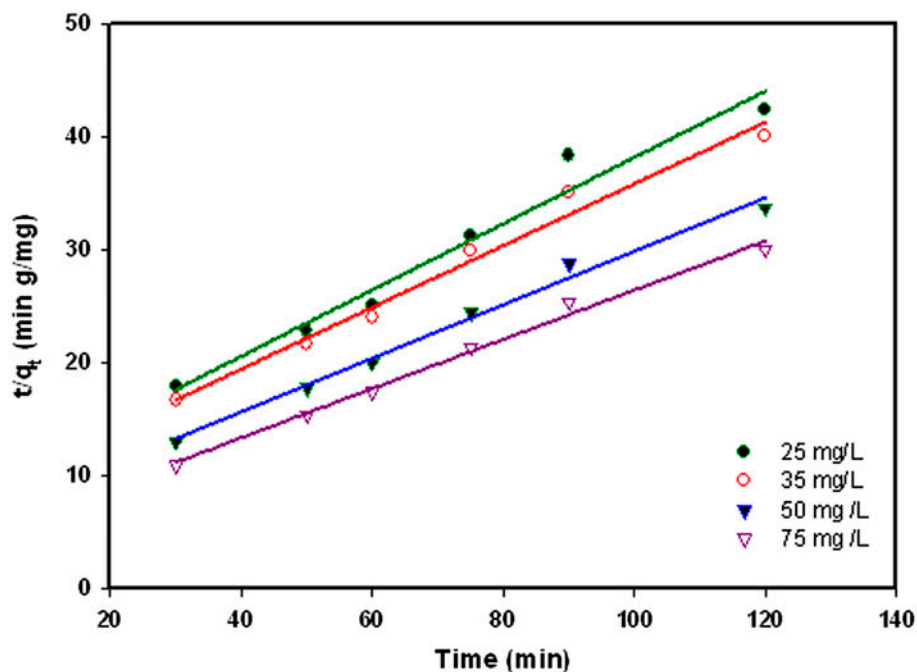

Fig. 3. Type 1 pseudo-second-order kinetics by linear method and experimental kinetics for the sorption of Nickel(II) onto Ca-alginate (pH 6; agitation speed: 150 rpm).
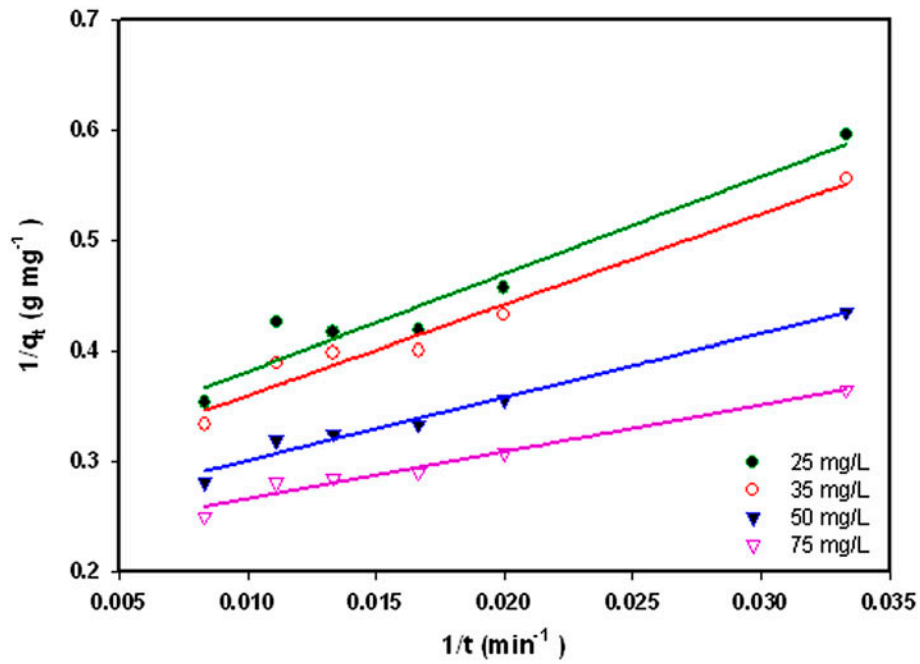
Fig. 4. Type 2 pseudo-second-order kinetics by linear method and experimental kinetics for the sorption of Nickel(II) onto Ca-alginate (pH 6; agitation speed: 150 rpm).

Fig. 5. Type 3 pseudo-second-order kinetics by linear method and experimental kinetics for the sorption of Nickel(II) onto Ca-alginate (pH 6; agitation speed: 150 rpm).

Fig. 6. Type 4 pseudo-second-order kinetics by linear method and experimental kinetics for the sorption of Nickel(II) onto Ca-alginate (pH 6; agitation speed: 150 rpm).
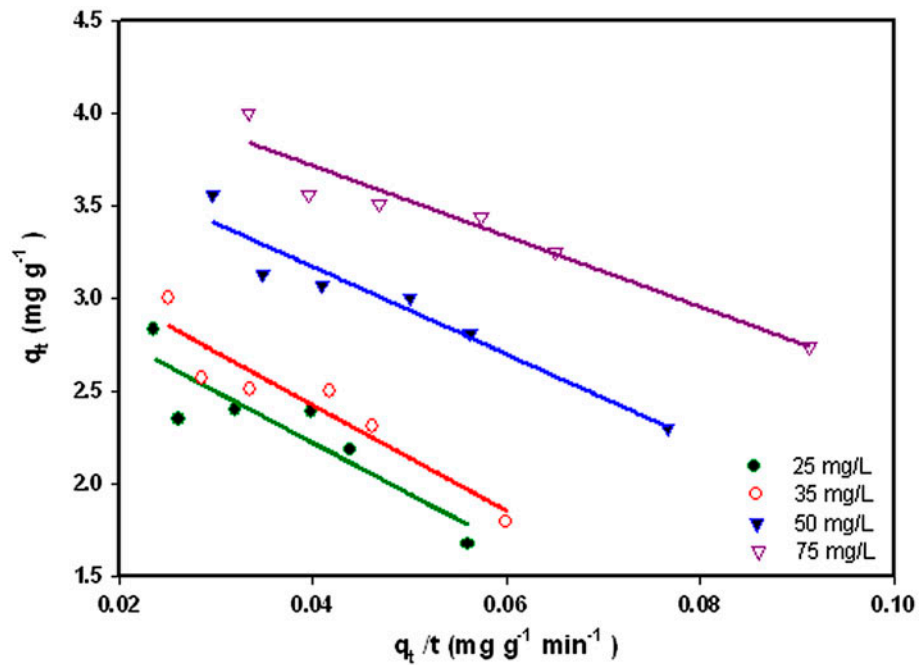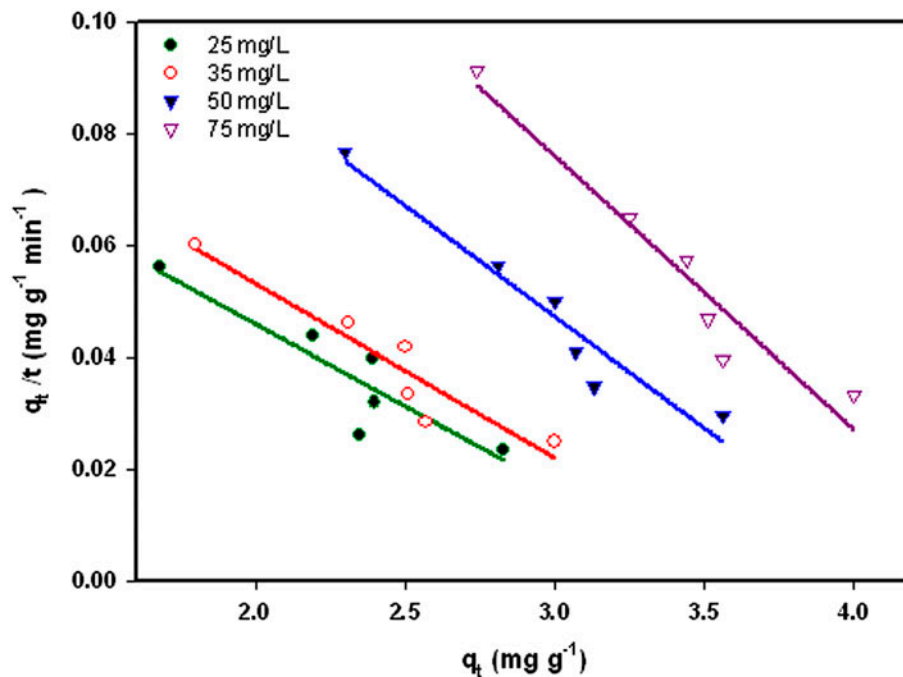
$$r^2 = \frac{(q_{e,meas} - \overline{q_{e,cal}})^2}{\sum (q_{e,meas} - \overline{q_{e,cal}})^2 + (q_{e,meas} - q_{e,cal})^2} \quad (4)$$

$$\chi^2 = \sum \frac{(q_{e,meas} - q_{e,cal})^2}{q_{e,cal}} \quad (5)$$

where $q_{e,meas}$ (mg g^{-1}) and $q_{e,cal}$ (mg g^{-1}) are the measured and calculated adsorbate capacity at equilibrium, and $\overline{q_{e,cal}}$ (mg g^{-1}) is the average of $q_{e,cal}$. The (χ^2) will be a small number if the experimental data and data from the model are similar and vice versa. Therefore, the isotherm model that gives the smallest chi-square value is considered the best-fit isotherm [29].

3.4. Linear method

In the present study, the experimental kinetic data for Ni(II) onto ca-alginate were fitted to the four different linearized forms of pseudo-second-order expression, and the least square method is used for finding the parameters of the kinetic models. The best-fit kinetic equation is selected based on the error functions that produce minimum error distribution between the predicted and experimental values.

The pseudo-second-order kinetics constant, the theoretical q_e and k_2 by a type 1 pseudo-second-order expression were obtained from the plot of t/q_t vs. t as shown in Fig. 3.

Similarly the pseudo-second-order kinetics constant, q_e and k_2 were calculated from the plot of $1/q_t$

Table 3
Pseudo-second-order rate constants by linear method for the sorption of Nickel(II) onto Ca-alginate (C_0 mg L^{-1}, q_e mg g^{-1}, k_2 g mg^{-1} min^{-1})

| C_0	q_e (exp)	Type 1				Type 2				Type 3				Type 4			
		k_2	q_e	r^2	χ^2	k_2	q_e	r^2	χ^2	k_2	q_e	r^2	χ^2	k_2	q_e	r^2	χ^2
25	2.83	0.0097	3.41	0.967	0.098	0.0071	3.56	0.922	0.149	0.011	3.29	0.815	0.064	0.0084	3.53	0.829	0.138
35	3.00	0.0087	3.66	0.981	0.119	0.0080	3.70	0.930	0.132	0.009	3.51	0.865	0.074	0.0090	3.60	0.832	0.100
50	3.56	0.0091	4.42	0.989	0.167	0.0084	4.26	0.968	0.115	0.007	4.12	0.898	0.076	0.0120	4.28	0.790	0.121
75	4.00	0.0101	4.59	0.991	0.075	0.0075	4.66	0.966	0.093	0.006	4.55	0.894	0.066	0.0156	4.78	0.860	0.127
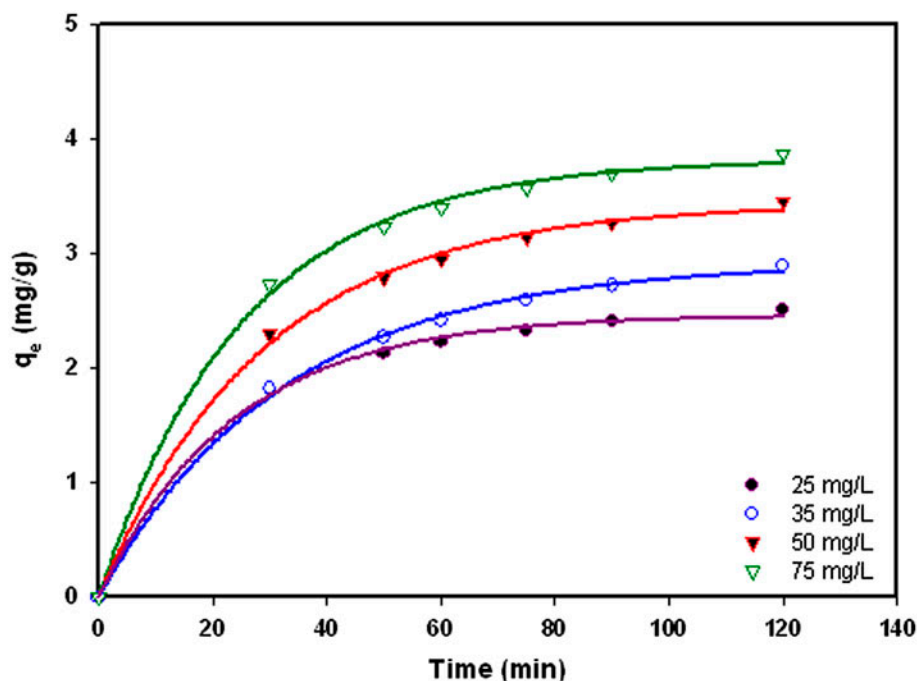
Fig. 7. Pseudo-second-order kinetics by nonlinear method and experimental kinetics for the sorption of Nickel(II) onto Ca-alginate (pH 6; agitation speed: 150 rpm).

vs. t (Fig. 4), $1/t$ vs. q_t (Fig. 5) q_t/t vs. q_t (Fig. 6) for a type 2, type 3, and type 4 pseudo-second-order expressions, respectively. The amount of Ni(II) adsorbed at equilibrium q_e (mg/g) was calculated as explained in Table 2. The obtained kinetics constants, their corresponding coefficient r^2, and the predicted q_e values by linear and nonlinear analysis were given in Tables 2 and 3, respectively. From Table 3, the theoretically predicted q_e values increases with increasing initial Ni(II) concentration. However, in the actual adsorption process, which is a surface phenomenon, the amount of sorbed Ni(II) should increase with increasing initial Ni(II) concentration. Further, from Table 3, it is clear that, if the r^2 values were used for selecting the best-fit kinetic equation and the type 1 pseudo-second-order model would be most suitable for the experimental results. If the χ^2 values were used for comparison, the type 3 pseudo-second-order model would be most suitable, followed by the type 1 pseudo-second-order model. However, compared with the predicted q_e value of the type 3 model, the predicted q_e value of the type 1 model was deviated from the experimental value. Therefore, the type 3 pseudo-second-order equation was the best representative of the experimental data of Ni(II) onto Ca-alginate in the linear system for all the range of initial concentrations studied. These findings also suggest that error analysis using the chi-square test χ^2 may be a better method

than using r^2 determines the best-fit equation. The type 3 pseudo-second-order kinetics well represents the multi-step sorption process that include initial rapid phase and the later slower phase, which proceeds toward saturation [13].

These different observations and predictions for the same experimental data by linear method show the real complexities in predicting the optimum sorption kinetics and in estimating the kinetics parameters. The linear method assumes that the scatter of points around a line follows a Gaussian distribution and the standard deviation is the same at any given value of X. The linear regression just reports the intercept and slope for a linear trend line that best predicts the Y value for a given X. The various results clearly indicate that for linear method, all the uncertainty is in Y,

Table 4
Pseudo-second-order rate constants by nonlinear method for the sorption of Nickel (II) onto ca-alginate (C_0 mg L^{-1}, q_e mg g^{-1}, k_2 g mg^{-1} min^{-1})

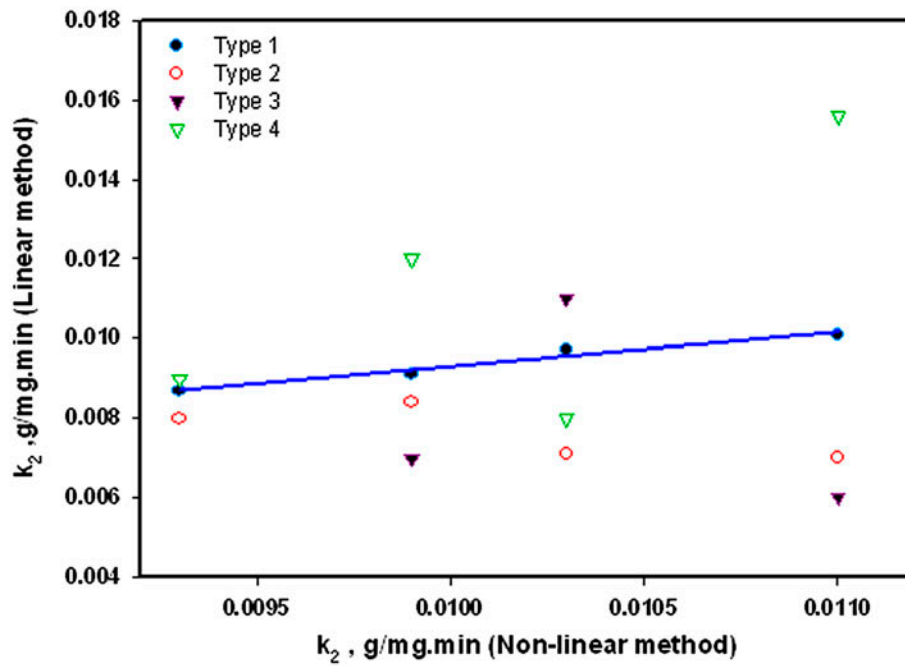|		(Non-linear expression)			
C_0	$q_{e\ (exp)}$	k_2	q_e	r^2	χ^2
25	2.83	0.0102	3.37	0.997	0.0046
35	3.00	0.0093	3.60	0.998	0.0039
50	3.56	0.0099	4.14	0.998	0.0037
75	4.00	0.0112	4.50	0.997	0.0041

Fig. 8. Effects of linearization on pseudo-second-order rate constant, K_2.

while X is known precisely [6]. The error distribution may depend on the linearized kinetics model. This confirms the possibility of the violation of the normality assumptions of standard least squares.

3.5. Nonlinear method

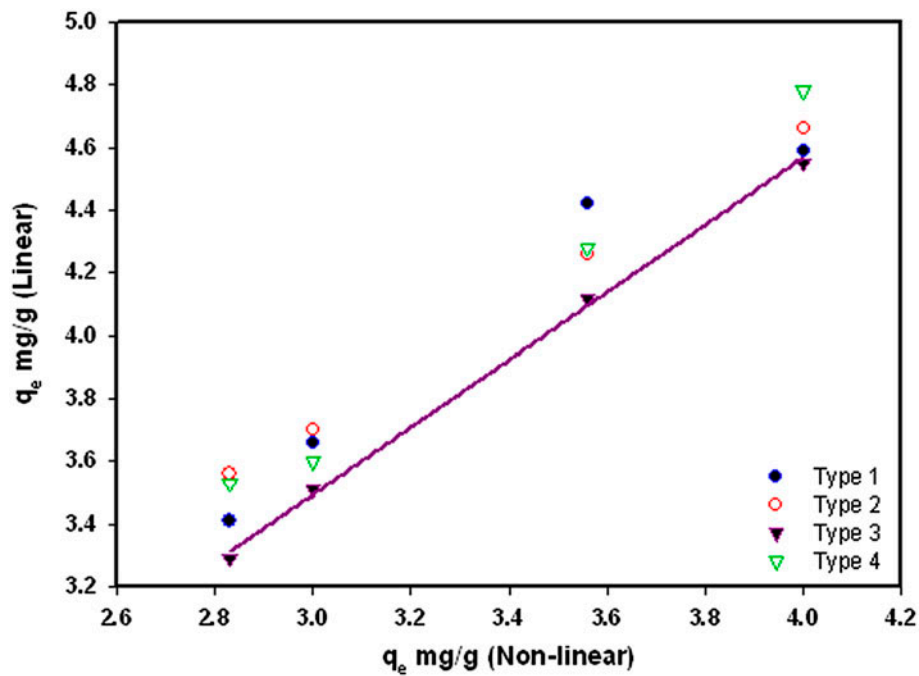For nonlinear method, a trial and error procedure was developed to determine the kinetic parameters by

Fig. 9. Effects of linearization on the amount of Nickel(II) adsorbed (predicted q_e).

minimizing the respective coefficient of determination between experimental data and predicted values using the solver add-in with Microsoft Excel.

Fig. 7 shows experimental data and the predicted pseudo-second-order kinetics using the nonlinear method. The values of the pseudo-second-order kinetic model constant k_2, and the amount of Ni(II) adsorbed at equilibrium, q_e along with the error function values are enlisted in Table 4. For linear models, category 3 expression gave the best fit among others. From Table 4, the very higher r^2 (0.997) and lower χ^2 (0.0046) values for a pseudo second-order kinetics suggests nonlinear method can be used to represent the kinetic uptake of Ni(II) onto Ca-alginate. While the q_e values of pseudo-second-order kinetics obtained by linear method (Table 2) and nonlinear method (Table 3), it can be observed that the nonlinear and linear method of type 3 method of second-order would attain first and second position in estimating q_e values, respectively. Using nonlinear method all the kinetics parameters are fixed in the same axis. There are no problems with transformations of nonlinear pseudo-second-order equation to linear forms and the error distribution does not get altered as in linear technique [30]. Thus, it will be more appropriate to use nonlinear method to estimate the kinetics equation and the parameters involved in them.

Best-fit linear expression not only depends on how it best represents the experimental data but also it should be accurate in predicting the rate kinetic parameters, which actually play an essential role in adsorbent design [6]. The effect of linearization on the kinetic parameters was estimated by plotting the k_2 and predicted q_e values calculated by linear method against these constants predicted by nonlinear method as shown in Figs. 8 and 9, respectively.

Figs. 8 and 9 demonstrate that it is appropriate to use the type 1 (Ho pseudo-second-order) expression instead of the other three linear forms of pseudo-second-order expressions, which show consistency in predicting the rate constant k_2. However, from Fig. 9, it was clear that type 3 pseudo-second-order expressions provides good correlation with nonlinear method in predicting q_e (mg/g), the amount of Ni(II) adsorbed at equilibrium condition.

4. Conclusions

In this research, a comparison between linear and nonlinear methods of estimating the kinetic parameters of Ni(II) removal using calcium alginate was investigated. Nonlinear method was found as a suitable method for predicting the optimum kinetics and the parameters involved in them for all the range of initial Ni(II) concentration. By linear method the type 3 expression very well represented the kinetic uptake of Ni(II) onto Ca-alginate. The type 1 pseudo-second-order expression produced similar second-order kinetic constant to that of nonlinear pseudo-second-order kinetics. The chi-square test (χ^2) or error analysis was better to determine the best-fitting model in this case.

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