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Characteristics of calcium adsorption by Ca-Selectivity zeolite in fixed-pH and in a range of pH

Chenghuan Qin, Ren Wang, Wei Ma*

Research Centre of Seawater Desalination and Multipurpose Utilization, Department of Chemistry, Dalian University of Technology, Dalian 116023, PR China

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ABSTRACT

Ca-Selectivity zeolite was synthesized and the structure morphology, the physical and chemical performances were characterized by SEM, XRD and FT-IR. It was used as adsorbents of calcium in batch system for this study. The Ca^{2+} adsorption performances in the fixed-pH 9.18 and in pH ranges from 2 to 12.5 were tested. The Langmuir and Freundlich isotherms were adopted to evaluate the experimental data in fixed-pH and the competitive adsorption models were fitted to data in the condition which the pH values are without any control during adsorption process, respectively. The results noted that the Ca-Selectivity zeolite presented good adsorption capacity with about 105 mg/g and electrostatic adsorption, ion-exchange and hydroxyl complex are major mechanism of calcium adsorption. It indicated that the Ca-Selectivity zeolite has potential application value in zero discharge of seawater desalination.

1. Introduction

The traditional seawater desalination technologies, such as reverse osmosis, thermal distillation, and electrodialysis [1–3], are not environmental friendly due to always produce harmful brine [4]. However, the existing desalination methods are impossible to receive brines with such a high concentration level, because of the so-called "calcium barrier". So, all the modern seawater processing technologies require preliminary steps to remove calcium from concentration seawater for decreasing scale trend [5,6], in order to achieve "seawater desalination zero discharge" purpose by reverse osmosis following thermal distillation.

Various methods including precipitation [7] and adsorption have been used for calcium removal. Adsorption is considered as an attractive one when the effective, low-cost materials are used as adsorbents. Several adsorbents, such as clay minerals [8], resins [9], and zeolite [10], have been used to remove calcium. Among these adsorbents, zeolite is recognized to be an attractive one for its high ion-exchange capacity, selectivity and compatibility with the natural environment. Zeolites are hydrated aluminosilicates that possess a three-dimensional framework structure, which is formed by AlO_4 and SiO_4 tetrahedron connected by sharing an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge which is neutralized by the exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) [11] appears.

The adsorption of calcium on Ca-Selectivity zeolite achieved equilibrium within 70 min. The sorption could be well described by pseudo-second-order kinetic model. However, the influence of pH on sorption was also an important aspect for actual applications [12]. The effect of pH on the sorption, in fact, could be simulated as a binary sorption where hydrogen ion was considered as an additional sorbate, and there was competition between hydrogen ion and metal ions in the sorption medium. Wang et al. [13] reported that an increase of pH tended to increase sorption capacity of Cu^{2+} and Pb^{2+} by natural zeolite, but tended to decrease sorption capacity of humic acid. Bektaş et al. [14] indicated that the sorption capacity of Pb^{2+} by natural sepiolite increased with pH. In summary, pH is a key parameter, along with metal concentration and solution composition, in determining sorption levels. However, there were relatively fewer studies of effects of pH on calcium adsorption. Accordingly the objectives of this work are: (i) to evaluate the sorption of calcium by Ca-Selectivity zeolite from aqueous solution and determine the effects of pH values in the range of 2–12.5; (ii) to study equilibrium isotherms on the calcium adsorption in a fixed-pH 9.18; (iii) to evaluate the application isotherms and analyze adsorption mechanism of the effect of pH on calcium ions uptake.

2. Materials and methods

2.1. Materials and characteristic

Ca-Selectivity zeolite samples were synthesized in hydrothermal synthesis method. Prior to adsorption experiments, it was washed with distilled water until pH < 8 dried at 105 °C. The chemical composition of Ca-Selectivity zeolite is shown in Table 1. The

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* Corresponding author. Tel.: +86 0411 847076303; fax: +86 0411 84707416.
E-mail address: chmawv@yahoo.com (W. Ma).

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Nomenclature

C_0	initial metal concentration (mg/L)
C_e	final metal concentration (mg/L)
V	volume of solution (mL)
w	mass of sorbent (g)
Q_i	observation from the batch experiment
q_i	estimate from the isotherm for corresponding Q_i
m	number of observations in the experimental data
E_i	error at point
q_m	maximum amount of adsorption (mg/g)
b	Langmuir constant (L/mg)
K_c	Freundlich constant related to adsorption capacity ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
n	Freundlich isotherm constant related to adsorption intensity
C_f	equilibrium metal ion concentration (mmol/L)
K_h	equilibrium constant for the binding of proton (mmol/L)
K_{Ca}	equilibrium constant for the binding of metal (mmol/L)
q_{max}	maximum amount of adsorption (mmol/g)
q	amount of metal bound to the Ca-Selectivity zeolite (mmol/g)

Table 1
Chemical composition of Ca-Selectivity zeolite.

Constituents	Values (%, w/w)
SiO_2	34 ± 1
Al_2O_3	28 ± 1
Na_2O	18 ± 1
Others	20 ± 1

structure and morphology of the zeolite are examined through scanning electron microscopy (SEM, JELO JSM-5600LV). Fourier transform spectrometry (FT-IR) was obtained on a Bruker TENSOR 27 FT-IR spectrometer with the KBr method. X-ray diffraction (XRD) analysis for the zeolite is carried out on a Shimadazu XRD-6000 X-ray diffractometer with the Cu Kα ray source ($\lambda = 1.54 \times 10^{-10}$ m (1.54 Å)). Scanning diffraction angle range is set as 0–90° and the spectra are recorded at 40 kV and 30 mA. XRD pattern in Fig. 1 suggested that the zeolite sample was A-type. Fig. 2 showed the FT-IR spectra of zeolite sample. The peak at about 1641 cm^{-1} belongs to flexing vibrations of free water at the edge of zeolite and in zeolite holes. The peak at about 1001 cm^{-1} belongs to Si–O stretching vibrations. The band at about 556 cm^{-1} is attributed to Si–O–Si flexing vibration and the band at about 3440 cm^{-1} belongs to the stretching vibrations of hydroxyl. The SEM image in Fig. 3 showed zeolite particle in a square shape, the particle size distribution was from 1.5 μm to 3 μm.

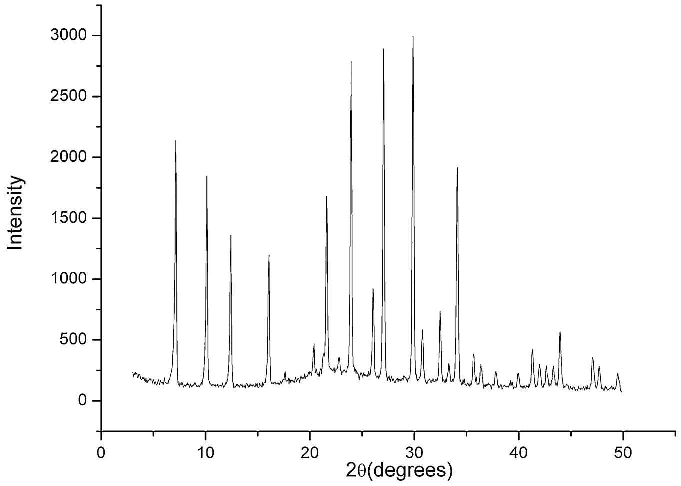

Fig. 1. XRD diffractogram of Ca-Selectivity zeolite.

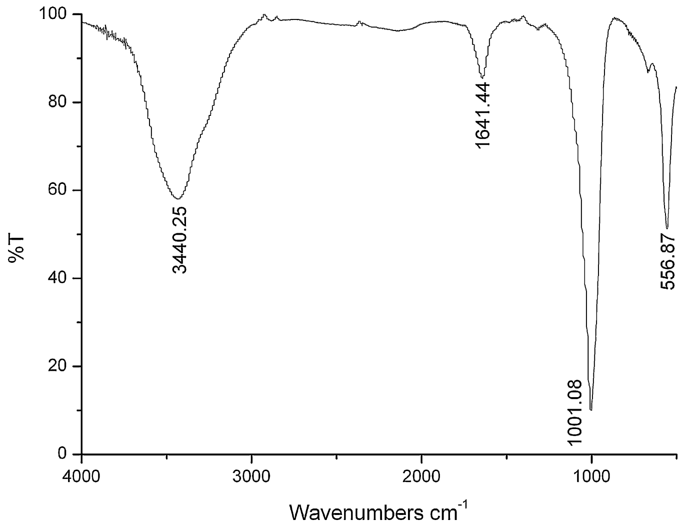

Fig. 2. FT-IR spectra of Ca-Selectivity zeolite.

2.2. Batch adsorption experiments

Calcium solution was prepared from CaC1$_2$. In all experiments, 150 mL conical flasks containing 0.1 g of adsorbent in a 50.00 mL of desired solution were placed in a horizontal shaker, at room temperature (20 °C). The initial and final metal concentrations were determined by atomic absorption spectrophotometer (solan 969 USA). The wavelength used for the analysis of Ca^{2+} was 422.7 nm.

The following equation was used to compute sorbent uptake capacity at equilibrium (q_e) in mg/g:

$$q_e = \frac{(C_0 - C_e) \times V}{w} \quad (1)$$

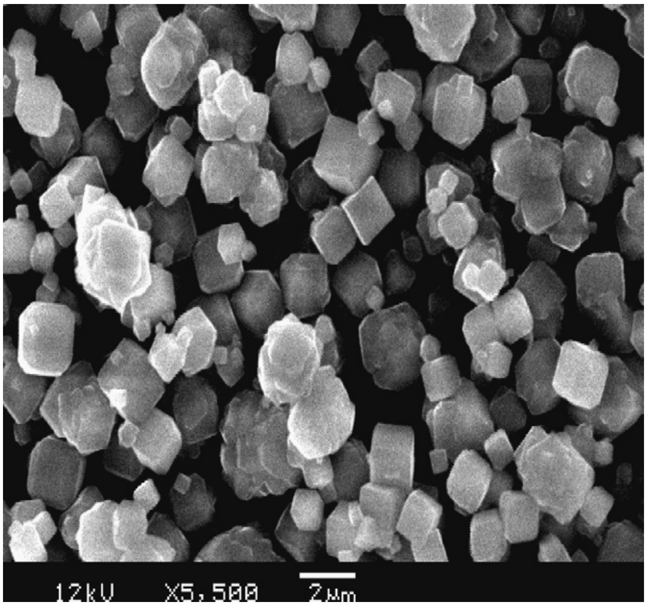

Fig. 3. SEM image of Ca-Selectivity zeolite.

where C_0 is the initial metal concentration in mg/L, C_e is the final metal concentration in mg/L, V is the volume of solution in mL and w is the mass of sorbent in g.

2.3. Nonlinear regression analysis

In this study all the model parameters were evaluated by nonlinear regression by Matlab 6.1. The optimization procedure required an error function to be defined in order to evaluate the fit of the equation to the experimental data. Not only the determination coefficient (R^2) but also the residual root mean square error (*RMSE*) and average of percentage error (Average of Error (%)) were used to measure the goodness-of-fit. *RMSE* [15] can be represented as follows:

$$RMSE = \sqrt{\frac{1}{m-2}\sum_{i=1}^{m}(Q_i - q_i)^2} \tag{2}$$

Average of Error (%) can be represented as follows:

$$E_i = \left|\frac{Q_i - q_i}{Q_i}\right| \tag{3}$$

$$\text{Average of Error (\%)} = \frac{100 \times \sum_{i=1}^{m} E_i}{m} \tag{4}$$

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i, m is the number of observations in the experimental data, E_i is the error at point. If data from model are similar to the experimental data, *RMSE* and Average of Error (%) will be a small number.

2.4. Sorption isotherms

The Langmuir and Freundlich isotherms were used for fitting sorption equilibrium data taking no account of the changes of pH. In this experiment the sorption was studied in a fixed-pH (pH 9.18).

The Langmuir isotherm assumes monolayer coverage of sorption. Each molecule onto the surface has equal sorption activation energy. It has traditionally been used to quantify and contrast the performance of different sorbents and it can be expressed as follows [16]:

$$q_e = \frac{q_m C_e}{1/b + C_e} \tag{5}$$

where q_m is the maximum amount of adsorption (mg/g), b is the Langmuir constant (L/mg) and C_e is the equilibrium concentration of the calcium ion in solution (mg/L).

The Freundlich isothermal equation is also used to describe adsorption from solution as a multilayer sorption and the adsorption process takes place on a nonuniform surface. It is given by

$$q_e = K_c C_e^{1/n} \tag{6}$$

where K_c is the Freundlich constant related to adsorption capacity ($\mathrm{mg}^{1-1/n}\,\mathrm{L}^{1/n}\,\mathrm{g}^{-1}$) and n is the Freundlich isotherm constant related to adsorption intensity.

2.5. Competitive adsorption models

Some researchers have been developed competitive adsorption isotherms in order to take into account the sorption of H^+ [17–20], such as following Eq. (7) (denoted Model A) and Eq. (8) (denoted Model B).

$$q = \frac{(q_{\max}/K_{Ca})C_f[\mathrm{Ca}]}{1 + (1/K_{Ca})C_f[\mathrm{Ca}] + (1/K_h)C_f[\mathrm{H}]} \tag{7}$$

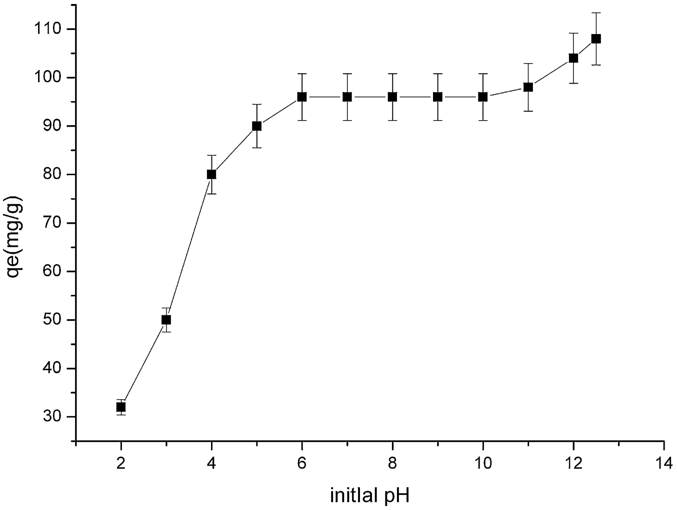

Fig. 4. Effects of initial pH on sorption of calcium (initial calcium concentration: 800 mg/L; contact time: 70 min; sorbent dose: 0.1 g/50 mL).

$$q = \frac{q_{\max}\left\{(1/K_{Ca})C_f[\mathrm{Ca}]\right\}^{1/2}}{1 + ((1/K_{Ca})C_f[\mathrm{Ca}])^{1/2} + ((1/K_h)C_f[\mathrm{H}])} \tag{8}$$

where C_f is the equilibrium metal ion concentration (mmol/L), K_h is the equilibrium constant for the binding of proton (mmol/L), K_{Ca} is the equilibrium constant for the binding of metal (mmol/L), $q_{\max}$ is the maximum amount of adsorption (mmol/g), q is the amount of metal bound to the Ca-Selectivity zeolite (mmol/g).

Among this, there assuming that sorption equilibrium can be expressed as

Zeolite + $Ca^{2+} \leftrightarrow$ Zeolite-Ca, Zeolite + $H^+ \leftrightarrow$ Zeolite-H in Model A and
Zeolite + $Ca^{2+} \leftrightarrow$ Zeolite-$Ca_{0.5}$, Zeolite + $H^+ \leftrightarrow$ Zeolite-H in Model B.

3. Results and discussion

3.1. pH effect on the adsorption amount

The initial pH of working solution was controlled by adding diluted HNO_3/NaOH solution. The adsorption of calcium onto Ca-Selectivity zeolite was examined at pH varying in the range from 2 to 12.5 and the results were presented in Fig. 4. The removal of calcium from aqueous solution increased remarkably with the increase of pH when pH lower than 6, and then remained until pH increasing to 10, but a second increase was observed when increasing pH continually. It suggested that pH had significant influences on the uptake of Ca^{2+}. The maximum uptake capacity for calcium is 105 mg/g at pH 12.5. Compare to other types of adsorption materials, such as lyocell fibres [21], which was observed at a calcium binding capacity of 18–20 mmol/kg at pH 9. Ca-Selectivity zeolite showed better adsorption capability.

4. Time dependence study at different pH

In order to investigate the effect and variation of pH on Ca^{2+} uptake in detail, time dependence studies at different pH were carried out. Because it was difficult to track the quick variation of solution pH and adsorption capacity of Ca^{2+}, the solution volume was enlarged to 500 mL which can clearly reflect the variation of pH and the process of Ca^{2+} uptake without other negative influence. The pH evolution of Ca^{2+} as function of time was illustrated in Fig. 5(a) at pH values 2, 4, 6, 8, 10. From Fig. 5(a), we can see that

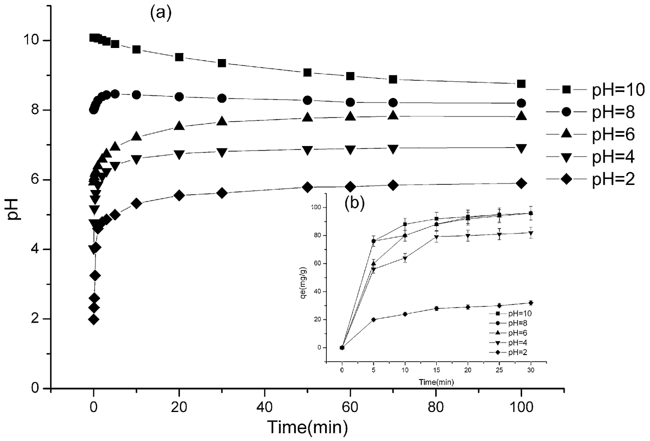

Fig. 5. (a) Change of solution pH as function of contact time; (b) variation of Ca^{2+} uptake as a function of time with initial pH of the solution (initial calcium concentration: 800 mg/L; sorbent dose: 1 g/500 mL).

the solution pH had a significant increase within 30 min at pH 2, 4, 6, from 2 to 5.62, from 4 to 6.81, and from 6 to 7.60, respectively, these pH values were all about 94% of the equilibrium pH. Simultaneity, the sorption amount of Ca^{2+} was increased from 32 mg/g, to 80 mg/g, and 96 mg/g as the pH from 2 to 6 as shown in Fig. 5(b). But at pH 8, 10, the solution pH decreased appreciably. In order to investigate the effect of pH on Ca^{2+} uptake, two three-dimensional models was used to model the process of adsorption.

4.1. Equilibrium studies fixed-pH 9.18

In addition, borax buffer solution (fixed-pH 9.18) was applied in equilibrium studies in order to avoid the effect of pH on Ca^{2+} uptake. It was found from Fig. 6 and Table 2 that the Langmuir isotherm could be fitted to the experimental results reasonably well compared to Freundlich isotherm, giving the R^2 value of 0.994 and the *RMSE* value of 2.06. The values of q_m and b were found to be 92.50 mg/g and 0.247 L/mg, respectively. It noted that the calcium adsorption onto the zeolite may occur by monolayer adsorption.

4.2. Competitive adsorption studies

The results of experimental data and the nonlinear regression analysis for Model A and Model B to the calcium uptake data were shown in Fig. 7(a) and Fig. 8(a). The parameters for model verification were also shown in Table 3. The accuracy of the models was plotted in Fig. 7(b) and Fig. 8(b), the point should close to the diagonal line if the model could predict the sorption performance well. The method to describe the accuracy was also used by Apiratikul et al. Low *RMSE* and average of percentage error (Average

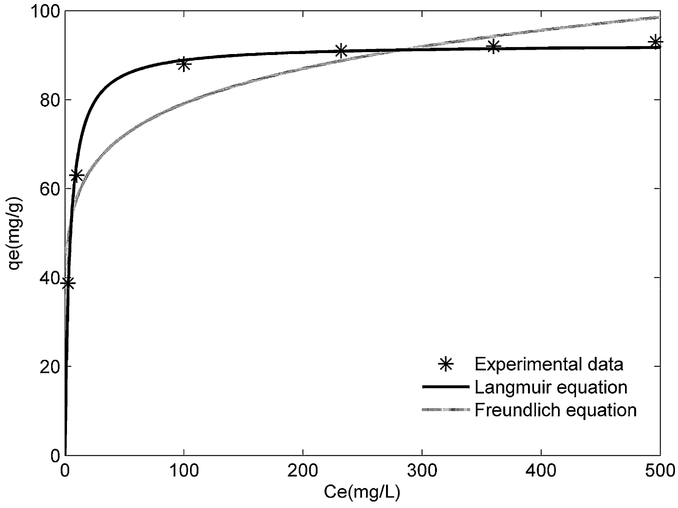

Fig. 6. The adsorption experimental data and isotherms (fixed-pH 9.18; contact time: 70 min; sorbent dose: 0.1 g/50 mL).

Table 2
Calculated equilibrium constants and thermodynamic parameters.

1. Langmuir isotherm constants	Values
q_m (mg/g)	92.50
b (L/mg)	0.247
R^2	0.994
RMSE	2.06
2. Freundlich isotherm constants	
K_c ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)	42.20
n	7.33
R^2	0.905
RMSE	7.64

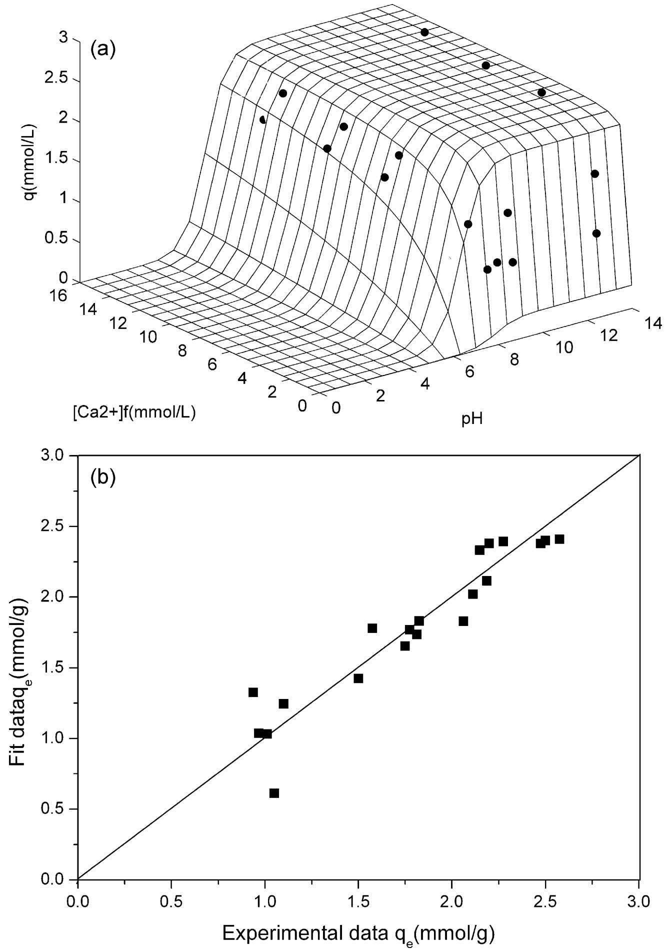

Fig. 7. (a) Three-dimensional sorption surfaces showing model prediction (Model A) and experimental data points; (b) accuracy of the models prediction (Model A).

Table 3
Parameters of the pH prediction model.

	K_m ($\times 10^{-2}$)	K_n ($\times 10^{-5}$)	q_{max} (mmol/L)	*RMSE*	Average of Error (%)
Model A	7.82	1.13	2.43	0.186	9.43
Model B	4.01	4.62	2.38	0.229	12.3

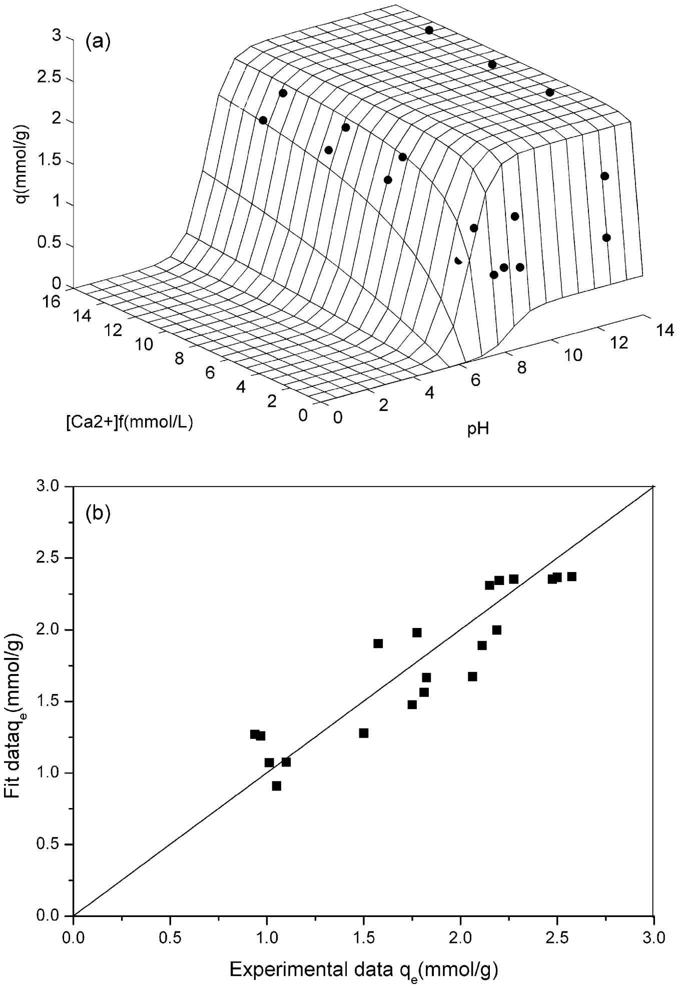

Fig. 8. (a) Three-dimensional sorption surfaces showing model prediction (Model B) and experimental data points; (b) accuracy of the models prediction (Model B).

of Error (%)) indicated high accuracy of the model in the prediction of sorption characteristics [22]. Model A gives good predictions for the maximum uptake $q_{\max}$ 96.8 mg/g (2.42 mmol/g) and can predict the sorption performance better than Model B.

Model A is based on the assumptions that in a Ca^{2+}–H^+ binary system, sorbent binding sites form complexes denoted Zeolite-Ca when Ca^{2+} binding occurs and complexes denoted Zeolite-H when protons are bound. Model B assumes that each ion binds to monovalent sites in the sorbent equal in number to its valence the overall charge balance is maintained. Accordingly divalent ions bind to form two complexes denoted Zeolite-$Ca_{0.5,}$ while protons are viewed as monovalent species and bind to form Zeolite-H complexes.

4.3. Mechanism discussion

Metal removal was significantly affected by the initial pH of the metal solution due to cation ions competition with the hydrogen ions (H^+). As showed in Fig. 5, at lower pH of 2, solution pH increased remarkably within the initial 10 min, while Ca^{2+} adsorption amount was not very high, this indicated that more H^+ absorb onto the zeolite than Ca^{2+} which made the solution pH increased rapidly. H^+ adsorption was the dominant process in the sorption. At pH 4, solution pH still increased rapidly in the initial 10 min, but Ca^{2+} adsorption amount increased to 60 mg/g. This revealed that more and more calcium ions were absorbed onto the zeolite, H^+ sorption and the calcium sorption took place coequally in the whole adsorption process. The pHzpc of the zeolite was found at 9, at lower pH the zeolite carried positive electrical charge, it made lower Ca^{2+} adsorption amount. When pH increased to 6 and 8, there was no obvious increase of the solution pH, while the maximum calcium adsorption amount increased to 96 mg/g compared with 32.5 mg/g at pH 2. This could be explained that at pH 6 and 8, the dominant adsorption process changed from H^+ sorption to calcium sorption and the adsorption mechanism was ion-exchange. When solution pH increased to 10, the solution pH decreased in the sorption process. This was because that when the solution pH was greater than 9.5, $Ca(OH)^+$ was another form of calcium ions, and the adsorption mechanism changed from ion-exchange to hydroxyl complexing. The hydroxyl complexation made the solution pH decreased slightly from 10 to 8.76. From Fig. 4, the second sorption increase at pH >10 suggested calcium strongly hydrolyzed and started to precipitate in the form of insoluble $Ca(OH)_2$. Therefore, the adsorption mechanism of calcium onto the zeolite changed at different pH, including ion electrostatic adsorption, ion-exchange, hydroxyl complexing. and $Ca(OH)_2$ precipitation when pH greater than 12.

Moreover, the effect of ion strength on uptake of calcium by the models is still being studied in our laboratory.

5. Conclusions

In this study, a Ca-Selectivity zeolite was synthesized and the effects of pH on calcium adsorption were studied. The results are summarized as follows:

- The obtained results strongly demonstrate that pH affects calcium uptake capacity of Ca-Selectivity zeolite; the maximum uptake capacity for calcium is 105 mg/g at pH 12.5 with initial concentration 800 mg/L.
- The best isotherm model describes the experimental data with high R^2 and low values of *RMSE*. The suitable sorption isotherm model for the sorption of calcium is Langmuir isotherm at pH 9.18 in a fixed-pH aqueous phase.
- Model A assumes direct competition between metal and H^+ ions for binding sites and has been shown to fit the experimental data well. Three-dimensional sorption surfaces using parameters derived from this model can be used to predict the effects of pH on calcium uptake over a continuum of pH values. All model predictions were within 9.43% of the experimental calcium uptake values.
- The adsorption of calcium onto the Ca-Selectivity zeolite was affected by the solution pH remarkably, therefore, the adsorption mechanism was changed at different pH, i.e., ions electrostatic adsorption at lower pH, ion-exchange at pH about 6–8 and hydroxyl complexing at pH about 10.

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