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Adsorption of nickel ions from seawater by modified chitosan

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ABSTRACT

Chitosan (CS) was modified by using sodium chloride as the porogen agent to remove nickel ions in seawater. The modified CS was characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, and pH_{pzc} analysis. The influence of pH, background electrolyte concentrations on nickel ions adsorption by CS and modified CS was investigated. The results showed that nickel ions adsorption capacity by CS and modified CS are greatly improve when background electrolyte concentration increase from 0 to 0.8556 mol/L, indicating the modified CS could be an excellent adsorbent to remove nickel ions from seawater. Langmuir, Freundlich, Redlich–Peterson, and Langmuir–Freundlich models were used to illustrate the isotherms of the adsorption process. The mechanism of the adsorption was a combination of electrostatic interaction and chemical adsorption. The nickel species distribution was predicted by Visual MINTEQ program, and the total content of Ni^{2+}, $NiOH^{+}$, and $NiCl^{+}$ cation species increased with the increase of ion strength in aqueous, which could demonstrate the adsorption mechanism is dominantly an electrostatic interaction as well. The modified CS could be a potential material to remove nickel ions in pretreatment of seawater for mariculture or industrial applications.

Keywords: Nickel ions; Seawater; Adsorption; Modified chitosan; Isotherm; Kinetic

1. Introduction

Due to the readily assimilation and bioaccumulation in organisms, toxic heavy metals are recognized as one of the most hazardous pollutants in ecosystems, determining a potential risk to human beings from waters and contaminated foods [1,2]. Especially, toxic metals could be taken by the marine organisms, entering the food chain and remained for years, which could significantly accumulate in the seafood and eventually result in adverse effects to human beings due to the consumption of these contaminated seafood [3,4]. For example, nickel concentration in bivalves in China is generally less than 5 mg/kg. However, higher concentrations are reported in green mussels *Psychotria viridis* (~33 mg/kg) from Shantou port shelter and in clam *Ruditapes philippinarum* (~10 mg/kg) from Bohai Bay [3]. Though nickel is a moderately toxic element, it is known that excessive accumulation of nickel might bring about serious lung and kidney problems [5]. Metal ions release into the sea through lots of routes, most notably via river input, atmospheric deposition, and industrial waste disposal [6–8], some emergencies, such as oil spill, earthquakes, etc. [9,10].

Dalian city is surrounded by the seawaters of the Yellow Sea to the east and the Bohai Sea to the west and south. The Bohai Sea has attracted significantly

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attentions due to the high input of anthropogenic pollutants from adjacent terrestrial areas. Bohai Sea is recognized as one of the most contaminated coastal areas and its fishery resources has declined dramatically because contamination, overexploitation, and suffering from poor water exchange conditions [3]. In addition, seawater was widely used in coastal cities, like Dalian, to reduce the consumption of freshwater recently, for example, as the source of cooling water system in power plant, nuclear power station, and petrochemical industries. The salt drift and blowdown returns brought lots of problems including corrosion caused by the high content of salts in the seawater, thermal pollution, and environmental impacts [11]. The use of seawater is widespread for cooling purpose, particularly for cooling the condensers in the electrical generating plants. These cooling systems could change temperature, turbidity, chemical constituents, and concentrations of heavy metal of receiving waters [12,13], while the contents of nickel ions and iron ions. As more and more attention paid to human health and food safety, it is urgently potential to explore an effective approach to remove heavy metals in the pretreatment of mariculture or industrial applications.

The most popular technologies for nickel ions removal from aqueous solutions include chemical precipitation, ion exchange, electrodialysis, solvent extraction, coagulation, evaporation, flotation, membrane, and adsorption [14–17]. Adsorption as a physicochemical treatment process is effective in removing nickel ions from aqueous solutions. And low-cost adsorbents requiring little processing, abundant in nature, or obtained by products and waste materials from other industries are available [18–22]. Adsorbents prepared by polymer chitosan (CS) have attracted wide concerns in environmental field for the removal of heavy metal ions [23–26]. CS is a heteropolymer with high content of amine (–NH_2) functional group and remarkable availability [23]. In order to increase the porous of the CS adsorbents, sodium chloride has been reported widely as the porogen reagent. However, to the best of our knowledge, there are few literatures found to study the removal of nickel ions by modified CS from seawater.

The objectives of this study are to modify CS by using sodium chloride as the porogen agent with the purpose for application in seawater system; to predict nickel species distributions at various background electrolyte NaCl concentrations and the effect of nickel species on the adsorption process; to investigate the nickel ions adsorption performance in seawater; to discuss the adsorption mechanism of nickel ions by the modified CS from seawater.

2. Materials and methods

2.1. Materials

CS with ⩾90% deacetylation degree was provided by Weifang Haizhiyuan Bio-products Co., Ltd. (China). Nickel sulfate hexahydrate, supplied by Kermel, Tianjin, was used to prepare the nickel ions solution in the adsorption experiments. Sodium hydroxide was supplied by Shenyang (China), and glutaraldehyde, acetic acid, sodium chloride, and sulfuric acid were purchased from Dalian (China). Seawater obtained from Dalian sea area was used to prepare the nickel ions solution. All the reagents were analytical grade.

2.2. Synthesis and characterization

CS acetic acid solution was obtained by dissolving 10 g CS powder in 1 L 2% acetic acid solution stirred by a magnetic stirrer for 1 h, and 15 g sodium chloride was added into the solution stirring for 3 h. And then, the solution was dropwise added into 1 L of 2 mol/L NaOH solution and keeps stirring for 4 h. The obtained beads were then filtered and washed exhaustively with deionized water until neutral. Finally, the obtained beads were cross-linked by 200 mL 0.25% glutaraldehyde solution and dried naturally at room temperature.

The pH of the solution was measured by an acidimeter (PHS-2 Model, Hangzhou, China). The structure and morphology of the modified CS were examined by scanning electron microscopy (SEM) (JEOL JMS-5600LV). X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos XSAM-800 spectrometer with Mg Kα radiator. The concentrations of nickel ions were determined by atomic absorption spectrophotometer (Solan 969 USA) method. Nickel species distribution at various NaCl concentrations were predicted by Visual MINTEQ software.

2.3. Adsorption experiments

The effect of background electrolyte and pH on the nickel ions adsorption was investigated initially. About 50 mL nickel sulfate solutions with 0, 8.556, 85.56, 171.1, 513.3, and 855.6 mM/L NaCl mixed with 0.1 g CS/modified CS adsorbent stirred continuously for 24 h. The removal of nickel ions from seawater by the modified CS was carried out. The isotherm study of the adsorption process was conducted by varying the initial concentration of nickel ions in seawater ranging from 5 to 200 mg/L. 0.1 g modified CS was stirred in 50 mL nickel ions solution for 24 h at room temperature. Adsorption kinetics study was carried out with initial nickel ions concentration of 50 mg/L. A container with 2 g modified CS and 1 L nickel ions seawater solution was stirred at room temperature. And 1 mL of the solution was taken from the solution to measure the nickel ions concentrations in a certain time intervals. The nickel ions adsorption capacity (mg/g) was determined by the equation as follows:

$$q = \frac{(c_0 - c) \times V}{m} \tag{1}$$

3. Results and discussion

3.1. Characterization

Fig. 1 shows SEM analysis of CS and modified CS. The surface of the modified CS before nickel ions adsorption shows irregular and uneven compared with the CS beads (Fig. 1(a) and (b)).

XPS analysis is useful to characterize ligand effect in transition metal complexes (electron-donating ligand will lower the binding energy [BE] of the core-level electrons and electron withdrawing ligands will rise their BE) and is also used to identify the existence of a particular element in material and distinguish the different oxidation states of the same element [27]. XPS analysis of the modified CS before and after nickel ions adsorption, BE profiles of nickel (Ni 2*p*), carbon (C 1*s*), oxygen (O 1*s*), and nitrogen (N 1*s*) are presented in Fig. 2. As can be seen from the spectra, the two peaks at 856.8 and 872.7 eV of nickel (Ni 2*p*) spectrum can be observed, indicating the existence of nickel in the modified CS after adsorption. And there is no oxidation states change of nickel ions in the adsorption process. Fig. 2 illustrates that the nitrogen (N 1*s*) band increased from 399.3 to 399.5 eV, indicating that complexes CS and nickel ions was formed, in which a pair of lone electrons from nitrogen atoms were shared with nickel ions, giving rise to the decrease in electron cloud density of nitrogen atoms and resulting in a higher BE peak observed [28,29]. The carbon (C 1*s*) at 284.6 eV does not change, indicating that the carbon atoms in the modified CS did not participate in the adsorption process.

The specific BET surface areas of commercial CS and modified CS were 29.57 and 58.17 m^2/g, respectively, that is, the modified process improved markedly the specific surface of CS. Furthermore, the average pore diameter of CS was 12.82 nm compared wih 21.46 nm of modified CS.pH drift method was used to measure the pH_{pzc} of the modified CS in this study [30]. pH_{pzc} of the modified CS is obtained from the ΔpH ($pH_{final} - pH_{initial}$) vs. $pH_{initial}$ curves at different electrolyte concentrations and the pH_{pzc} is 7.2 as revealed by the point of $\Delta pH = 0$ (Fig. 3).

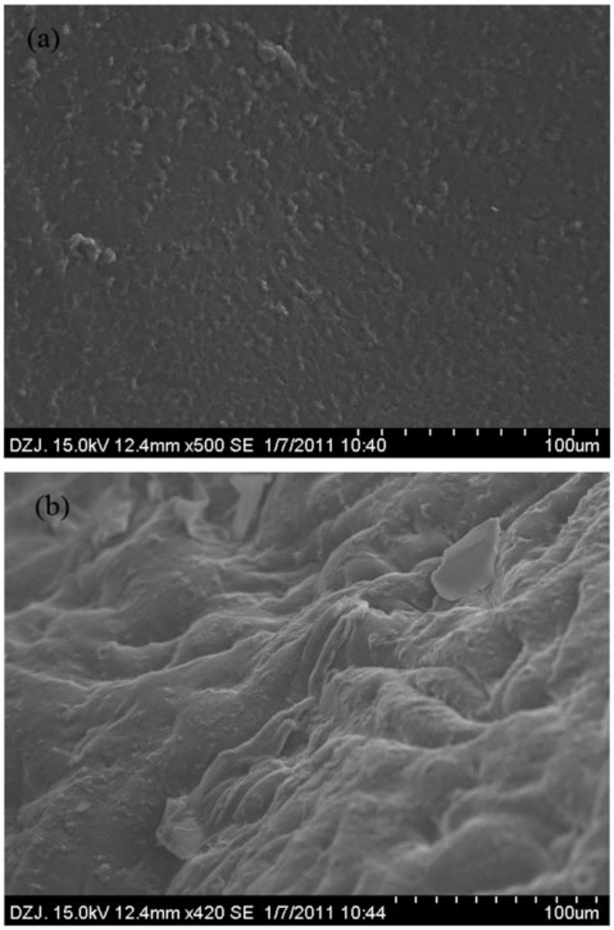

Fig. 1. SEM analysis of CS (a) and modified CS (b).

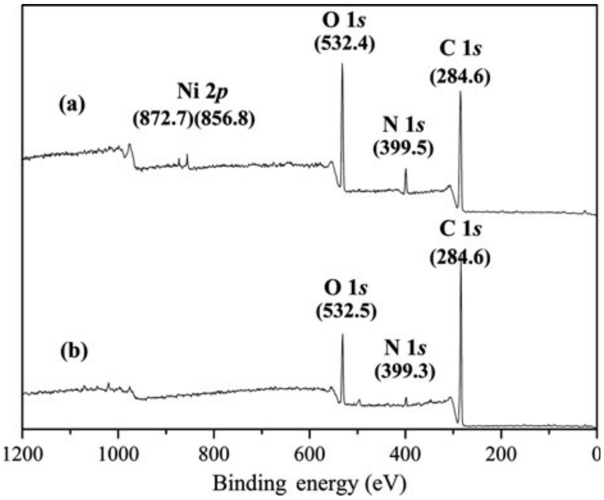

Fig. 2. XPS spectra of modified CS before (b) and after (a) nickel ions adsorption.

3.2. Effect of background electrolyte concentration on nickel ions adsorption by CS and modified CS

The distribution of nickel species at pH ranged from 2.0 to 14.0 at different NaCl background electrolyte concentrations were predicted using the Visual MINTEQ software (Version 3.0) for Windows. As can be seen in Fig. 4, Ni^{2+} specie content decreases slightly as the pH ranged from 2.0 to 8.0, while decreases dramatically when pH above 9.0. On the other hand, the total Ni^{2+}, $NiOH^{+}$, and $NiCl^{+}$ species content increases with the addition of NaCl concentration in the solution at fixed pH.

The effect of background electrolyte sodium chloride concentration on the adsorption of nickel ions by CS and modified CS is presented in Fig. 5. The nickel ions uptake by the CS and modified CS is increased significantly when the NaCl concentrations ranged from 0 to 855.6 mM/L, and the modification of CS by sodium chloride could improve the adsorption capacity of nickel ions. It was reported that adsorption process was sensitive to concentration changes of the supporting electrolyte if electrostatic attraction was the significant mechanism for metal ions removal [31].

Ghaee and Verbych [31,32] reported that the zeta potential (ζ) of the biopolymer varied from positive to negative as the pH increased. It was assumed that a high concentration of Cl^{-} in the electrolyte causes adsorption of these anions by polymer and decreases the positive value of the zeta potential. From the prediction of nickel species distribution at different NaCl concentrations, the $NiCl^{+}$ species content is dramatically increased with the increase in the NaCl concentration as shown in Fig. 4, which is consistent with the results reported above.

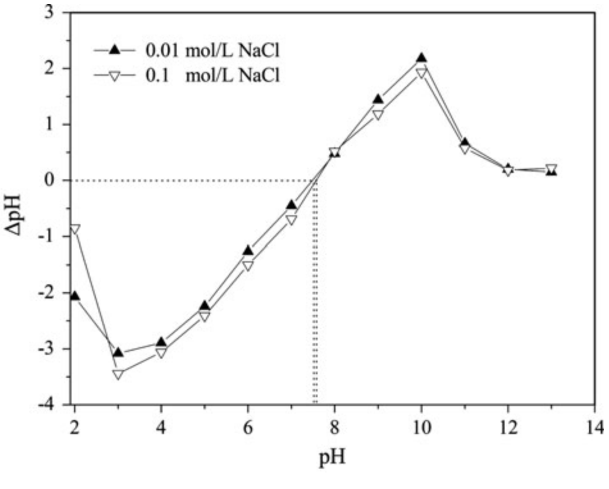

Fig. 3. pH_{pzc} of the modified CS.

3.3. Effect of pH on nickel ions adsorption by modified CS

It is known that pH is an important parameter affecting the removal of heavy metal ions by adsorption. The influence of pH on the adsorption of nickel ions in seawater by modified CS was investigated by adjusting the solution pH from 2.0 to 8.0. As mentioned above, there would be predominantly Ni^{2+} and $NiCl^{+}$ species presented in solution at pH ranged from 2.0 to 8.0. From Fig. 6, the adsorption capacity of nickel ions by the modified CS from seawater is significantly increased from 2.497 to 14.97 mg/g when the pH increased from 2.0 to 4.0, and the adsorption capacity increased slightly when the pH of the seawater increased from 4.0 to 8.0. It could be explained that the competition between nickel species and proton played an important role at lower pH. And the adsorption pH in all experiments is the original pH (7.8) of the seawater which could simple the operation and decreases the cost.

3.4. Isotherm study

Adsorption isotherm study is a very important expression for the adsorption process. Langmuir, Freundlich, Redlich–Peterson, and Langmuir–Freundlich isotherm models are the most commonly employed isotherms to describe the experimental data of the adsorption process. Langmuir isotherm model assumes that monolayer adsorption onto a surface with a finite number of uniform adsorption sites [33].

$$q = \frac{q_{\max} b c_e}{1 + b c_e} \tag{2}$$

Freundlich isotherm model is an empirical equation based on the adsorption on a heterogeneous surface [34].

$$q = k_F c_e^{1/n} \tag{3}$$

Redlich–Peterson model and Langmuir–Freundlich model are derived from the combination of above models [1,35–37]. Redlich–Peterson model could be expressed as:

$$q = \frac{k_R c_e}{1 + a_R C_e^{b_R}} \tag{4}$$

Langmuir–Freundlich model:

$$q = \frac{q_m (k_{LF} c_e) b_{LF}}{1 + (k_{LF} c_e) b_{LF}} \tag{5}$$

Fig. 7 illustrates isotherm model of the adsorption process and the related parameters are presented in Table 1. The maximum adsorption capacity of nickel ions was 42.41 mg/g obtained from Langmuir isotherm model, which shows modified CS could be an effective adsorbent to remove nickel ions from seawater. Redlich–Peterson isotherm model shows better fit to the experimental data, which confirmed that nickel ions adsorption from seawater is dominantly an electrostatic adsorption process combined with some extent chemsorption [1].

3.5. Adsorption free energy

Dubinbin–Radushkevich (D–R) isotherm model [38] is used to estimate the adsorption free energy. It is shown in the following equations:

$$Q = Q_{\max} e^{\beta \varepsilon^2} \tag{6}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

D–R isotherm model is plotted by ln$Q$ vs. ε^2 according to the experimental data. The parameters of R^2, χ^2, and adsorption free energy (E) are presented in Table 2. The adsorption free energy E is 3.452 kJ/mol, which is lower than the energy of ion exchange reactions with 8–16 kJ/mol [39,40].

3.6. Kinetic study

In order to investigate the mechanism of the adsorption process, external mass transfer model, Weber and Morris intraparticle diffusion model, pseudo-first-order model and pseudo-second-order model were used to fit the experimental data. Pseudo-first-order model [41] is one of the most popular reaction kinetics models. For the liquid/solid adsorption system, it is summarized as follows:

$$q = q_e(1 - e^{-k_1 t}) \tag{9}$$

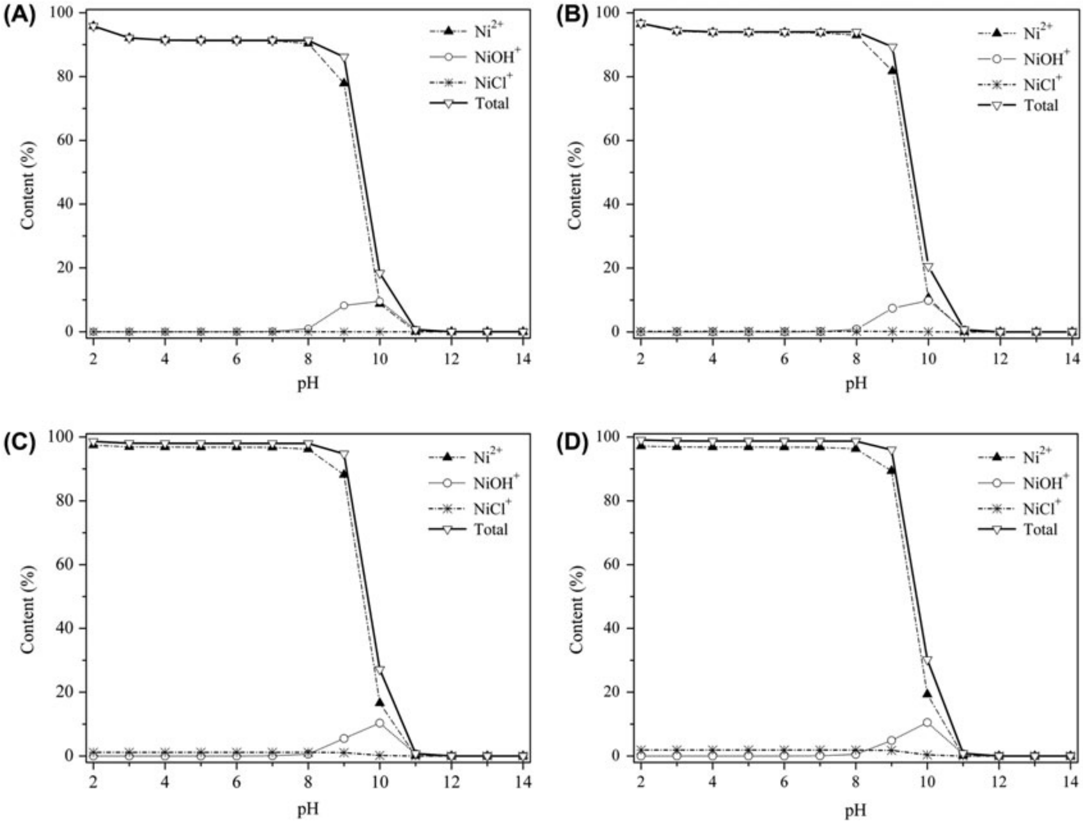

Fig. 4. Distributions of nickel species and total Ni^{2+}, NiOH$^+$, NiCl$^+$ cation species as a function of pH at different electrolyte concentration predicted by Visual MINTEQ (NaCl of 0 mM/L (A), 8.556 mM/L (B), 85.56 mM/L (C), 177.1 mM/L (D), 513.3 mM/L (E), 855.6 mM/L (F), total Ni^{2+}, NiOH$^+$, NiCl$^+$ cation species (G)).

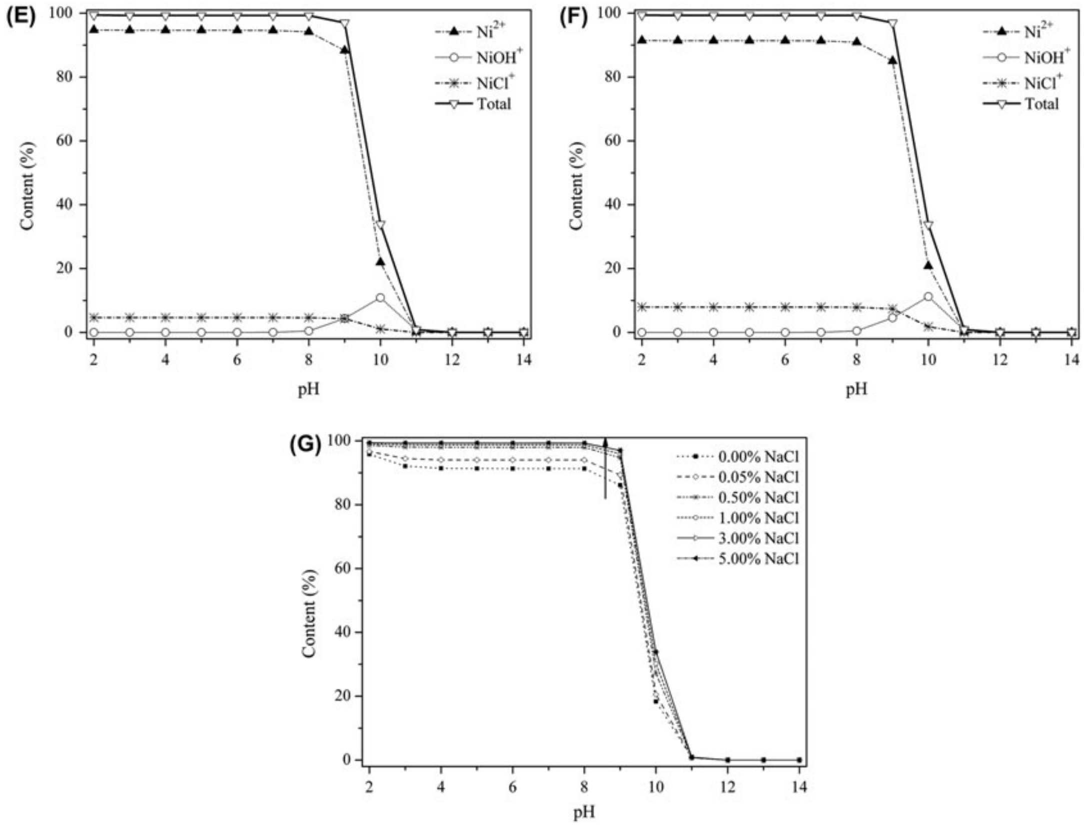

Fig. 4. (*Continued*)

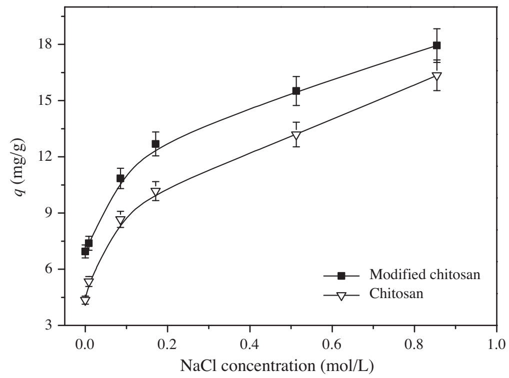

Fig. 5. Effect of background electrolyte NaCl concentration on nickel ions adsorption by CS and modified CS adsorbents ($T = 20$℃; $m = 0.1$ g; $V = 50$ mL; $C_0 = 50$ mg/L; pH = 7.8).

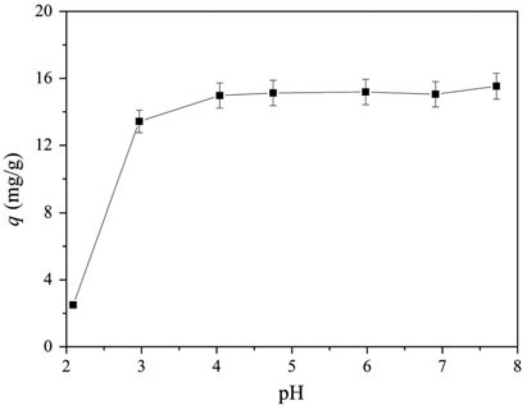

Fig. 6. Effect of pH on nickel ions adsorption by modified CS adsorbents from seawater ($T = 20$℃; $m = 0.1$ g; $V = 50$ mL; $C_0 = 50$ mg/L; pH = 2.0–8.0).

Pseudo-second-order model [42,43] is based on the sorption capacity on the solid phase. It is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{10}$$

Table 1
Isotherm constants of nickel ions adsorption from seawater by modified CS

Langmuir	$q_{\max}$	mg/g	42.41
	b	L/mg	0.02772
	R^2		0.9965
	χ^2		0.4502
Freundlich	k_F	(mg/g)(L/mg)$^{1/n}$	3.014
	n		1.973
	R^2		0.9762
	χ^2		3.095
Redlich–Peterson	k_R	L/g	1.342
	a_R	(L/mg)$^{-bR}$	0.05455
	b_R		0.8914
	R^2		0.9977
	χ^2		0.3756
Langmuir–Freundlich	q_m	mg/g	45.83
	k_{LF}	L/mg	0.02275
	b_{LF}		0.9213
	R^2		0.9966
	χ^2		0.4390

Intraparticle diffusion model proposed by Weber and Morris [44,45] is determined by the linear equation:

$$q = k_{WM}t^{1/2} + C \tag{11}$$

External mass transfer model [46] describes the solution concentration changes with time, and it is expressed as:

$$\ln\frac{c_0 - c_s}{c - c_s} = k_f a_m t \tag{12}$$

The parameters of these models are presented in Table 3. The results obtained from the experiments show that external mass transfer model, Weber and Morris intra particle diffusion model and pseudo-second-order model well described the experimental data (Fig. 8). According to Weber and Morris model, the plot of q_t vs. $t^{1/2}$ should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin, then the intraparticle diffusion is the rate-controlling step [47]. When the plot does not pass through the origin, this is indicative of boundary layer control to some extent, and this further indicates that intra particle diffusion process is not the sole rate controlling step, and other kinetics models may also control the rate of the adsorption process. The plot did not pass through the origin: the initial curved region corresponds to the external mass transfer process, the second stage relates the intra-particle diffusion as the rate-limiting step and the final plateau region indicates the equilibrium process [48]. The mechanism of nickel ions adsorption from seawater is dominantly an electrostatic adsorption combined with chemisorption to some extent.

Table 2
D–K model constants of nickel ions adsorption from seawater by modified CS

Dubinin–Radushkevich model	β	mol^2/kJ^2	−0.04197
	E	kJ/mol	3.452
	R^2		0.9745
	χ^2		0.1487

Table 3
Parameters of kinetics models studied

External mass transfer model	c_0	mg/L	47.52
	c_s	mg/L	19.97
	k_f	m/h	0.1467
	R^2		0.9813
	χ^2		1.677
Intraparticle diffusion model	C	mg/g	1.021
	k_{WM}	h$^{-1/2}$	3.489
	R^2		0.9923
	χ^2		0.3296
Pseudo-first-order model	q	mg/g	14.87
	k_1	h^{-1}	0.1904
	R^2		0.9657
	χ^2		0.7673
Pseudo-second-order model	q	mg/g	17.92
	k_2	g h/mg	0.01216
	R^2		0.9865
	χ^2		0.3021

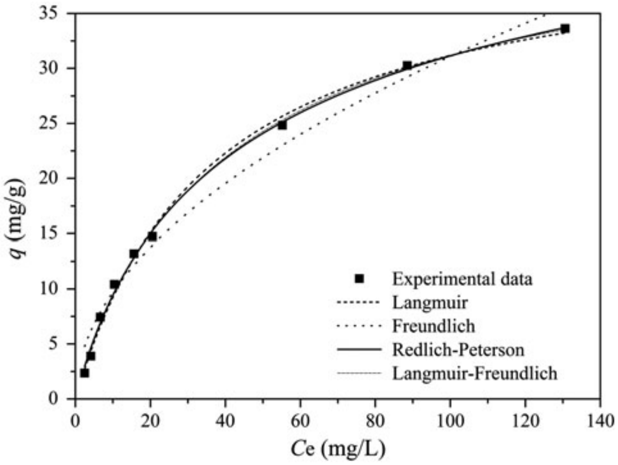

Fig. 7. Plots of isotherm model of nickel ions adsorption ($T = 20^\circ$C; $m = 0.1$ g; $V = 50$ mL; $C_0 = 5$–200 mg/L; pH = 7.8).

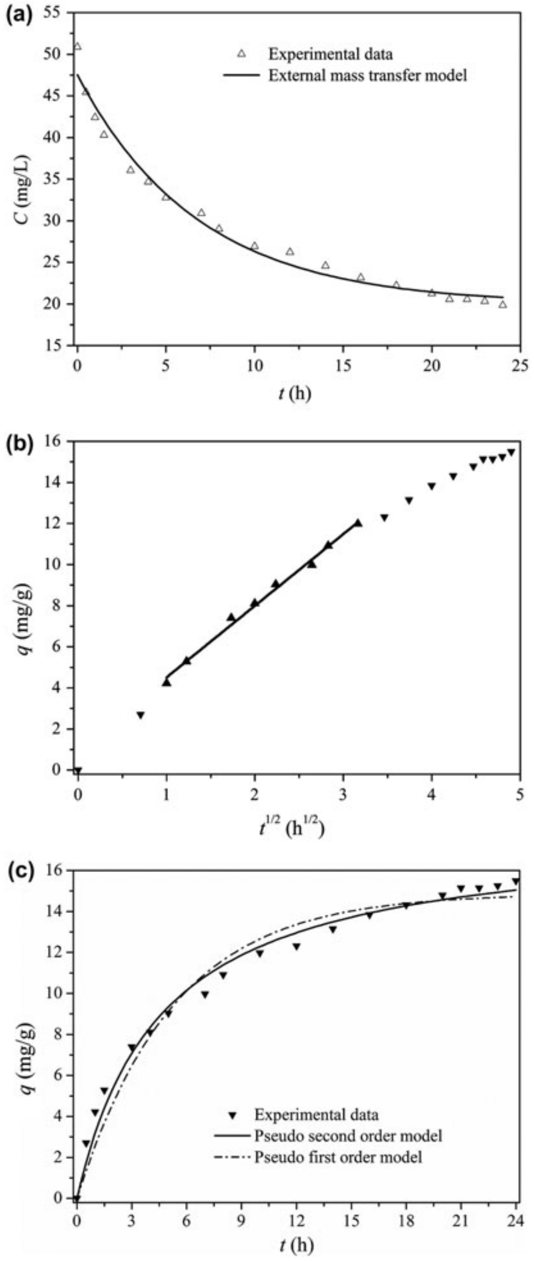

Fig. 8. External mass transfer model (a), Webber and Morris intraparticle diffusion model (b), pseudo-first-order model and pseudo second order model (c) of nickel ions adsorption by modified CS from seawater ($T = 20$°C; $m = 0.1$ g; $V = 50$ mL; $C_0 = 50$ mg/L; pH = 6.74; $t = 0$–24 h).

3.7. Adsorption of other metal ions

The adsorption of Co(II), Cr(VI), and Ca(II) were illustrated in Fig. 9. As can be seen in Fig. 9, the adsorption capacity of Cr ions increased slightly with the addition of other heavy metal ions, oppositely, that of Co decreased obviously. Meanwhile, the adsorption capacity of Ni ions was always high, and Ca barely removed.

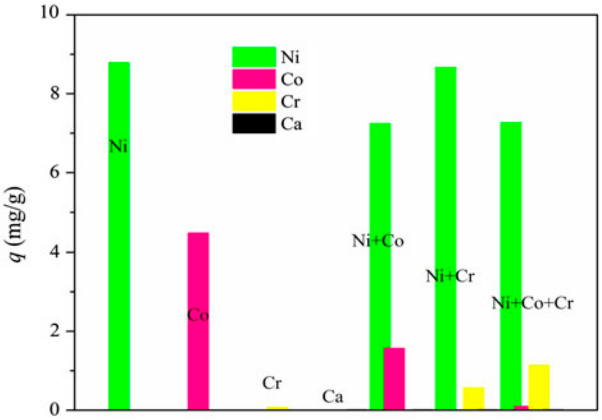

Fig. 9. Adsorption of Ni(II), Co(II), Cr(VI), and Ca(II) ions by the modified CS ($T = 20$°C; $m = 0.1$ g; $V = 50$ mL; $C_0 = 50$ mg/L).

4. Conclusion

CS was modified by using sodium chloride as the porogen agent to remove nickel ions from seawater system. SEM analysis indicates that the modified CS had irregular and uneven surface. The results obtained from the nickel ions adsorption experiments indicate that the modification of CS could improve nickel ions adsorption performance, and nickel ions adsorption capacity increased with the increase of background electrolyte concentration. The results obtained from nickel ions adsorption from seawater proved the point, and the maximum adsorption capacity is 42.41 mg/g from seawater at pH 7.8. The mechanism of the adsorption is an electrostatic interaction combined with chemisorption. Thus, the removal of nickel ions from seawater by the modified CS in pretreatment of mariculture or other industrial applications has a hopeful application prospect.

Acknowledgment

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List of symbols

a_R	—	is the Redlich–Peterson isotherm constants ($(L/mg)^{-bR}$)
b	—	is Langmuir constant (L/mg)
b_{LF}	—	is the Langmuir–Freundlich isotherm constants
b_R	—	is the Redlich–Peterson isotherm constants
c	—	is the concentration of nickel ions after adsorption (mg/L)
c_0	—	is the initial concentration of nickel ions before adsorption (mg/L)

c_e — is the equilibrium concentrations of nickel ions in solutions (mg/L)

c_s — is the solute concentration at the surface of adsorbent (mg/L)

C — is the intercept (mg/g)

C_e — is the equilibrium concentration (mol/m^3)

k_1 — is the rate constant of the pseudo-first-order model (h^{-1})

k_2 — is the rate constant of the pseudo-second-order equation (g h/mg)

k_f — is the mass transfer coefficient between the solution and the surface (m/h)

k_F — is Freundlich constants

k_{LF} — is the Langmuir–Freundlich isotherm constants (L/mg)

k_R — is the Redlich–Peterson isotherm constants (L/g)

k_{WM} — is the intraparticle diffusion rate constant (h$^{-1/2}$)

m — is the mass of adsorbent added (g)

n — is Freundlich constants, being indicative of the extent of adsorption and the adsorption intensity

q — is the nickel ions adsorption amount per mass adsorbent (mg/g)

q_e — is the amount of nickel ions adsorbed by modified CS (mg/g)

q_{max} — is the maximum adsorption capacity of nickel ions (mg/g)

Q — is the adsorption capacity at equilibrium (mol/kg)

Q_{max} — is the maximum amount per unit mass (mol/kg)

R — is the universal gas constant (8.314×10^{-3} kJ/(mol K))

t — is adsorption time (h)

T — is temperature in Kelvin (K)

V — is the volume of solution (L)

B — is the activity coefficient (mol^2/kJ^2)

ε — is Polanyi potential (J^2/mol^2)

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