Sorption Properties of Ion-imprinted Seaweed-Chitosan Composite Adsorbents for Nickel Ions

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Abstract. A granulated biosorbent-Ni-SC (Ni²⁺ ions imprinted seaweed-chitosan) was made by seaweed powder encapsulated with cross-linked chitosan and ion-imprint technology in this study. Ni-SC and granulated SC biosorbent (without ion-imprint technology) were investigated for nickel ions removal. The maximum nickel adsorption capacity of Ni-SC and SC were both achieved at pH 7.0 and the capacity of Ni-SC was higher than that of SC. The diffusion-controlled model and pseudo-second-order model were used to fit the adsorption kinetics data. The adsorption capacity of Ni-SC was higher than that of SC during the whole kinetics process. Also the adsorption isotherm study showed that the maximum adsorption capacity of Ni-SC (0.99 mmol·g⁻¹) was higher than that of SC (0.41 mmol·g⁻¹). The Thomas model can well describe the dynamic adsorption observations and the maximum column adsorption capacity qmax was 0.24 mmol·g⁻¹.

1. Introduction
Heavy metal waste water is one kind of industrial waste water which poses the most harmful threat to human health and ecological environment. The main technologies to treat heavy metal wastewater include chemical method, physicochemical method and biochemical method. The biosorption has a good application prospects for heavy metal waste water treatment owning to its low cost, high adsorption capacity for metal ions especially for waste water with low concentration metal) and their wide availabilities [1].

Seaweed as a new type of biosorbent has attracted great attention. Results showed that maximum metal uptake by seaweed ranged from 0.09 to 3.08 mmol·g⁻¹ biosorbent [1,2]. Chitosan is a derivative obtained by the deacetylation treatment of chitin, and contains carboxyl groups, amino groups and some n-acetyl amino groups, which show excellent adsorption capacity for heavy metals.

In this study, the granular adsorbent SC (seaweed-chitosan) was prepared by the relatively inexpensive seaweed powder wrapped in crosslinked chitosan. However, because the crosslinking reaction reduces the amount of active groups in chitosan, this study used ion imprinting technology to combine heavy metal ions with the active group in chitosan first, and then copolymerization under the action of crosslinking agent, and finally to elute the metal ions in the cavity network of the polymer[3]. Thus, a large number of active hole sites which completely matched with metal ions in spatial structure morphology were retained. This imprinted nickel-ion seaweed chitosan composite granular adsorbent was named Ni-SC. In this study, the optimum pH value, adsorption kinetics and isotherm process of this two kinds of adsorbent SC, Ni-SC for nickel ions removal were investigated, and the dynamic adsorption behavior of Ni-SC adsorbent was also investigated.
2. Materials and Methods

2.1. Materials

The raw biomass of brown seaweed was reaped from the seafront of Tianjin. The biomass was first cleaned with ultra pure water, and then dried in an oven at 50 °C for 8h. The dried seaweed was ground into fine powder with particle diameter below 120 μm. Chitosan (90% deacetylation), acetic acid, epichlorohydrin (ECH), nickel nitrate, sodium pyrophosphate, potassium oxalate and sodium nitrate were provided by Tianjin Fuchen Chemical Reagent Company (China). All the chemicals were of analytical grade.

2.2. Seaweed-Chitosan biosorbent preparation

0.01 g NiNO₃·6H₂O was dissolved into 30 mL acetic acid (0.6 mol·L⁻¹), and then 0.5 g chitosan were added into the solution. 0.05 mL ECH was added to the viscous liquid for cross-linking of chitosan for 24 h at 25 °C. 1.5 g seaweed powder was then added into the mixture and the suspension was stirred homogeneously by a blender. The uniformly mixture was then injected drop-wise into the mixed solution with 0.07 mol·L⁻¹ sodium pyrophosphate and 0.22 mol·L⁻¹ potassium oxalate to form the small pellets. The pellets were soaked in the solution for 30 min to strengthen their mechanical stabilities, and then washed with ultra pure water till neutral pH. Finally, the pellets were eluded by 7 mmol·L⁻¹ EDTA for 24 h and then regenerated by 0.03 mol·L⁻¹ NaOH for 2 h to remove the chelated Ni(II) on the biosorbents. The Ni-SC composite sorbent was washed by ultra pure water till neutral pH and dried at 50 °C. In order to find out the elevated effect of imprinted nickel ion biosorbent for nickel removal, non-imprinted seaweed-chitosan sorbents (SC) were prepared. The SC sorbent was made in light of the above method except that the nickel ion was not added.

2.3. Batch biosorption studies

All experiments were conducted at 25±0.1°C. All the nickel solution has the ionic strength of 0.01 mol·L⁻¹ (NaNO₃). The experiments for pH effect, sorption kinetic experiment and sorption isotherm were conducted.

The effect of pH on the biosorption was studied at the initial nickel concentration of 0.92 mmol·L⁻¹ between pH 2.0 to pH 8.0 with the sorbent dosage of 3 g·L⁻¹. All the solutions were shaken at 130 rpm for 24 h. The solution pH was measured and adjusted to their original values during the experiments by diluted HCl or diluted NaOH. The Ni(II) concentration of the solution was determined using the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin-Elmer Optima 2000, USA). In the sorption kinetic experiments, 2 g Ni-SC and SC sorbent were respectively added into 400 mL of 1.17 mmol·L⁻¹ nickel solution with an ionic strength of 0.01 mol·L⁻¹ NaNO₃ at pH 7.0, and then the solution was agitated with a blender at 130 rpm for 24 h. The samples were taken at different times and analyzed for the nickel concentrations by the ICP-OES.

The biosorption dynamics data of Ni-SC or SC for nickel ions were modeled with an intraparticle diffusion-controlled model[4]. The diffusion-controlled model can be formulated as follows:

\[
D_s \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t}, \quad 0 \leq r \leq a_p, t > 0
\]  

(1)

The boundary conditions may be specified as

\[
D_s \frac{\partial q}{\partial r} |_{r=a_p} = k_f (C - C^*), \quad r = a_p
\]  

(2)

where C is the concentrations of the metal ions in solution (mmol·L⁻¹), q is the sorption capacity of sorbent (mmol·g⁻¹), C* is the metal concentration of aqueous phase at the surface of sorbent (mmol·L⁻¹), Ds is the surface diffusion rate related with the properties of the sorbent (m²·s⁻¹), ρp is the density of sorbent (g·L⁻¹), k_f is the external mass transfer coefficient related with stirring speed and adsorbent size (m·s⁻¹).
The pseudo-second-order model assumes that adsorption rate is controlled by chemical adsorption mechanism which involves electronic sharing or transfer between adsorbent and adsorbate. The pseudo-second-order model can be formulated as follows:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t + \frac{1}{q_e}v_0 \]

where \( k_2 \) and \( v_0 \) are the adsorption rate constant of the pseudo-second-order \((g \cdot mmol^{-1} \cdot min^{-1})\) and initial adsorption rate \((mg \cdot g^{-1} \cdot min^{-1})\), respectively.

For the sorption isotherm experiments, 0.15 g of Ni-SC or SC was respectively added into a 50 mL nickel solution with different initial concentrations \((0.12 \text{ to } 2.0 \text{ mmol} \cdot L^{-1})\). The solution pH and ionic strength were controlled at 7.0 and 0.01 mol \cdot L^{-1} NaNO₃, respectively. Other procedures were the same as those in the above pH effect experiment. The Langmuir and Freundlich equations were used for fitting sorption isotherm data of biosorbents for nickel ions.

The Langmuir equation can be expressed as:

\[ q_e = \frac{q_{\text{max}}bC_e}{1+bC_e} \]

where \( q_{\text{max}} \) \((mmol \cdot g^{-1})\) is the maximum sorption capacity, \( C_e \) is the nickel concentration in the solution when sorption reaches equilibrium \((mmol \cdot L^{-1})\), \( q_e \) is the sorption capacity of the sorbent when adsorption reaches equilibrium \((mmol \cdot g^{-1})\), and \( b \) is the sorption affinity constant related to the binding energy of sorption \((L \cdot mmol^{-1})\).

The Freundlich model of metal biosorption is expressed by the equation:

\[ q_e = K_F C_e^{1/n} \]

while \( K_F \) is the Freundlich constant related to sorption capacity of biomass and \( 1/n \) is sorption intensity indicator.

2.4. Dynamic adsorption experiment

The 15.5g Ni-SC biosorbent was loaded into a glass column with a diameter of 2.1cm, and the adsorption bed height was 20.3cm. At room temperature 25°C, the 0.32 mmol \cdot L^{-1} NiNO₃ solution with a flow rate of 4.5ml \cdot min^{-1} at pH 7 flowed through the adsorption column at down flow mode. The samples were taken at the bottom of the column at different time intervals until the effluent concentration was equal to the inlet concentration, and analyzed for the nickel concentrations by the ICP-OES. The adsorption process of Ni-SC for Ni²⁺ in adsorption column was simulated by Thomas Model [5].

The Thomas model of dynamic adsorption is expressed by the equation:

\[ \ln \left( \frac{C_t}{C_0} - 1 \right) = \frac{k_{TH}q_{\text{max}}m_a}{Q} - k_{TH}C_0 t \]

where \( C_t \) is the concentration of effluent adsorbate \((mmol \cdot L^{-1})\), \( C_0 \) is the concentration of adsorbate at column inlet \((mmol \cdot L^{-1})\), \( k_{TH} \) is the rate constant \((ml \cdot min^{-1} \cdot mmol^{-1})\), \( Q \) is flow rate \((ml \cdot min^{-1})\), \( q_{\text{max}} \) is the maximum column adsorption capacity \((mmol \cdot g^{-1})\), \( m_a \) is adsorbent quality \((g)\), \( t \) is the adsorption column run time \((min)\).

3. Results and Discussion

3.1. Effect of pH on nickel sorption

At higher pH (>8.3) nickel ions \((≥2.0 \text{ mmol} \cdot L^{-1})\) will precipitate as metal oxides or hydroxides, and not bind with the biosorbent [6]. In order that the nickel ions retain in their ionic states during biosorption, the pH effect experiment was carried out between pH 2.0 to pH 8.0.

Figure 1 illustrates that the absorptive capacity of SC and Ni-SC for nickel increased remarkably from pH 2.0 to pH 7.0. It is generally known that the cell wall and intracellular ligands of seaweed consist of carboxyl, hydroxyl and amino groups [1]. These functional groups on the seaweed can be protonated in low pH solution, which induced an electrostatic repulsion of nickel ion. At higher pH values \((pH ≥ 7)\) the amino groups in chitosan and deprotonated hydroxyl groups have greater availability for metal ions, so pH 7.0 was the optimum for nickel ions sorption on SC sorbent [7].
3.2. Sorption kinetics

Figure 2 shows the kinetics of nickel biosorption onto Ni-SC and SC. The nickel sorption on Ni-SC and SC progressed rapidly within 260 min, followed by a relatively slow process. The kinetics data of Ni-SC showed in Figure 2 indicate that nearly 80% of total nickel sorption rapidly progressed with 7.5 h. While only 53% of total nickel sorption on SC were achieved within 6 h, and only 61% of total nickel sorption on SC occurred in 22.5 h. As shown in Figure 2, the diffusion controlled model well describes the experimental observations. As the sorbents size and stirring speed in kinetic experiment were used the same, the $k_f$ values of Ni-SC and SC kinetics models were kept the same as $6.4 \times 10^{-5}$ m·s$^{-1}$. The $D_s$ values of Ni-SC ($1.0 \times 10^{-9}$ m$^2$·s$^{-1}$) obtained from the modeling were higher than that of SC ($9.5 \times 10^{-13}$ m$^2$·s$^{-1}$). The pseudo-second-order model can also well fit the biosorption kinetics observations. The above two models’ constants were summarized in Table 1.

Table 1. Diffusion controlled model and pseudo-second-order model coefficients for nickel adsorption on Ni-SC and SC adsorbents ($m = 5$ g·L$^{-1}$, pH = 7.0).

| Adsorbent | Diffusion controlled model | Pseudo-second-order model |
|-----------|----------------------------|---------------------------|
|           | $D_s$ (m$^2$·s$^{-1}$) | $k_f$ (m·s$^{-1}$) | $q_e$ (mmol·g$^{-1}$) | $k_2$ (g·mmol$^{-1}$·min$^{-1}$) | $r^2$ |
| SC        | $9.5 \times 10^{-13}$ | $6.4 \times 10^{-5}$ | $0.14$ | $0.34$ | $0.93$ |
| Ni-SC     | $1.0 \times 10^{-9}$  | $6.4 \times 10^{-5}$ | $0.21$ | $0.11$ | $0.98$ |

3.3. Sorption isotherms

The isotherm experiments were conducted at the optimal pH 7.0. The initial nickel concentrations of isotherm experiments were controlled at 0.12-2.0 mmol·L$^{-1}$ in order to prevent hydroxyl complexes formation. Sorption isotherms data of SC and Ni-SC for nickel were presented in Figure 3.

The Langmuir and Freundlich coefficients from the data fitting were listed in Table 2. The $q_{max}$ of SC and Ni-SC for nickel were 0.41 mmol·g$^{-1}$ and 0.99 mmol·g$^{-1}$, respectively. $q_{max}$ of Ni-SC increased by 140% due to ion-imprint modification which retained more sorption groups on the Ni-SC than that of SC. The nickel adsorption capacities on Alginate/Fucus vesiculosus/PEI sorbent and red seaweed Kappaphycus alvarezii powder were 1.03 and 0.38 mmol·g$^{-1}$, respectively[7, 8]. Therefore, the ion-imprinted composite sorbent Ni-SC in this study possesses higher adsorption capacity compared with most of the above biosorbents.
Table 2. Langmuir and Freundlich coefficients of Ni-SC and SC adsorbents for nickel (m = 3 g·L⁻¹, pH = 7.0).

| Adsorbent | Freundlich model | Langmuir model |
|-----------|-----------------|----------------|
|           | $K_F$          | $n$           | $r^2$ | $q_{max}$ (mmol·g⁻¹) | $b$ (L·mmol⁻¹) | $r^2$ |
| SC        | 0.34           | 1.77          | 0.99  | 0.41                  | 3.19          | 0.94  |
| Ni-SC     | 0.28           | 2.29          | 0.99  | 0.99                  | 1.99          | 0.99  |

3.4. Dynamic adsorption performance

It can be seen that the dynamic adsorption of Ni-SC for Ni²⁺ is penetrating at 1110 min (18.5 h), and the nickel concentration at penetration time is 0.06 mmol·L⁻¹ ($C_t/C_0=0.2$) (figure 4). When the concentration of effluent pollutants reaches more than 95%-98% of the inlet concentration the corresponding time is called exhaustion time, so exhaustion time approximately occurred in 4500-4740 min. The Thomas model can well fit the dynamic adsorption observations and the $R^2$ was 0.92. The $k_{TH}$ value was 0.073 ml·min⁻¹·mmol⁻¹ and the maximum column adsorption capacity $q_{max}$ was 0.24 mmol·g⁻¹.

4. Conclusion

Nickel ion imprinted crosslinked chitosan wrapped inexpensive seaweed powder composite biosorbent-Ni-SC and SC sorbent without ion imprinting technology were made and studied for the elimination of nickel from aqueous solutions. The maximum nickel uptake capacities on Ni-SC and SC were achieved at pH 7. The diffusivity coefficient $D_s$ of Ni-SC is slightly higher than that of seaweed and SC, possibly due to the application of ion-imprint technology. Sorption isotherm results indicated that the $q_{max}$ of Ni-SC and SC for nickel were 0.99 mmol·g⁻¹ and 0.41 mmol·g⁻¹, respectively. Because of ion imprinting technology much more functional groups were retained in Ni-SC, so the nickel sorption capacity of Ni-SC were higher than that of SC when initial nickel concentration, solution pH and other experimental condition were the same. The Thomas model can well fit the dynamic adsorption observations and the maximum column adsorption capacity $q_{max}$ was 0.24 mmol·g⁻¹. Ion-imprinted seaweed-chitosan composite adsorbents-Ni-SC has good sorption capacity for nickel ions and great prospect for application due to its good mechanical strength, easy solid-liquid separation and low cost.

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