KINETIC AND EQUILIBRIUM STUDIES OF NITRATE REDUCTION FROM AQUEOUS SOLUTIONS USING BROWN ALGAE C. INDICA

Mohsen Hojjatyfar and *Reza Mohsen Beygi
Department of Chemical Engineering, Payam Noor University, North Tehran, Iran
*Author for Correspondence

ABSTRACT
In the present study, the potential of Cystoseira indica (C. indica) bio adsorbent was investigated as a function of initial pH, contact time and initial nitrate concentration in a batch system. Kinetic models including pseudo-first order and pseudo-second order were used to describe the experimental data of nitrate removal. The results indicated that kinetic data of nitrate sorption were well fitted using pseudo-first-order kinetic model. The equilibrium data were analyzed using known Langmuir and Freundlich isotherm models. Results showed that equilibrium data of nitrate sorption were well described by Langmuir isotherm model. The maximum monolayer adsorption capacity of C. indica for nitrate sorption was found to be 135 mg g⁻¹ at an optimum pH of 4 and equilibrium time of 60 min. The obtained results revealed that the C. indica have high potential for removal of nitrate from wastewaters in practical processes.

Keywords: C. Indica, Nitrate, Adsorption, Kinetic, Isotherm

INTRODUCTION
Nitrate is a major nutrient required for plant growth and nitrogenous fertilizers. The excessive use of nitrogenous fertilizers nitrate, presence of nitrate in industrial wastewaters and disposal of untreated wastes leads to high risk to environment and public health (Pennington, 1998; Canter, 1997; Camargo and Alonso, 2006; Chiu et al., 2007).

The nitrate concentration limit recommended by World Health Organization (2011) and the European Union is 50 mg L⁻¹. The increase in nitrate – levels in waters can be lead to several health problems in people such as blue-baby syndrome or methemoglobinemia in infants and stomach cancer in adults. Therefore, the nitrate reduction from wastes of those industries with respect to the environmental and public health issues is necessary.

Several methods including ion exchange, chemical and biological methods, reverse osmosis and adsorption have been used for nitrate removal for aqueous solutions (Bhatnagar and Sillanpaa, 2011; Zhan et al., 2011; Abou-Shady et al., 2003; Schoeman and Steyn, 2003). Among techniques, adsorption process due to its simplicity, moderate operational conditions and economic feasibility is preferred. In adsorption process, the functional groups and surface area of adsorbent as well as cost of adsorbent is very important.

Several adsorbents including activated carbon, biosorbents, ion exchange resins, and other synthetic organic and inorganic compounds have been used to remove nitrate from water (Khan et al., 2011; Afkhami et al., 2007; Chabani et al., 2007; Hamoudi et al., 2007; Jaafari et al., 2001). Biomass adsorbents include marine algae, bacteria, and fungi. Large nitrate adsorption capacity, high nitrate selectivity in the presence of other ions, low cost, capable of efficient regeneration for multiple reuse of the adsorbent should be considered in nitrate sorption (Pahlavanzadeh et al., 2010).

Among biosorbent materials, brown algae have been proved to have desirable properties such as availability in large quantities, regeneration and nitrate recovery potentials, less volume sludge disposal, high efficiency in dilute effluents and high surface area to volume ratio (Pahlavanzadeh et al., 2010). Cystoseira indica is very plentiful marine brown algae (Davis et al., 2003).

In the present study, the potential of brown algae (Cystoseira indica) was investigated for nitrate removal from aqueous solutions. The effect of sorption parameters in a batch system including pH, contact time and initial concentration of nitrate on the nitrate removal was evaluated. Kinetic data were fitted by...
pseudo-first-order and pseudo-second-order models and known isotherm models including Freundlich and Langmuir models were used to describe the equilibrium data of nitrate sorption.

MATERIALS AND METHODS

Materials

The brown algae, C. indicia, obtained from coast of Kish, Iran was used through this work. The samples were washed three times with distilled water and on the beach and then were dried in an oven at 60°C for 24 h. Finally, the dried biomass was crushed in a laboratory blender in the range of 1.0–5.0 mm particle size.

Adsorption Experiments

The performance of prepared C. indicia particles for nitrate sorption was investigated as a function of pH (4–8), contact time (0–180 min) and initial concentration of nitrate (50–500 mg L⁻¹) in a batch system. The nitrate test solution was prepared from solid NaNO₃. For this, 0.1 g of particles were placed in a flask containing 100 mL of nitrate solution on a rotary shaker at 200 rpm for 3 h. pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH. Each experiment was repeated triplicate and the results were given as averages. The final nitrate concentrations could be analyzed by ion chromatography (Metrohm 761 Compact IC). The amount of nitrate adsorbed was calculated as follows:

\[
q_e = \frac{(C_0 - C_e)V}{1000M}
\]

Where, \(q_e\) is the adsorption capacity in mg g⁻¹, \(C_0\) and \(C_e\) are the initial, and equilibrium concentrations of nitrate solution in mg L⁻¹, \(V\) is the volume of the solution in mL and \(M\) is the weight of the dry absorbents in g.

RESULTS AND DISCUSSION

Effect of pH on the Nitrate Sorption

The effect of pH on the nitrate sorption by C. indicia in the pH range of 4-8 at 25 °C for the initial metal concentration of 100 mg L⁻¹ nitrate solution is illustrated in Figure 1. As shown, the optimal pH value for nitrate sorption was found to be 4 for C. indicia particles. Nitrate (NO₃⁻) ions are also negative and repulsion forces also exist between ions and adsorbent in alkaline conditions. The poor removal efficiency of ions in alkaline conditions could be attribute to the increasing competition for sites between OH⁻ ions and nitrate ions for chelating with available sites of adsorbent. Nitrate can be reduced to nitrite (NO₂⁻) by microbial action under reducing conditions. However, nitrite is unstable and can be oxidized back to nitrate. Therefore, the increases the electrostatic adsorption of anions in acidic conditions resulted in optimal pH value of 4 for nitrate adsorption in studied condition.

![Figure 1: Effect of pH on the Nitrate Sorption Using C. Indica](image-url)
Effect of Contact Time on the Nitrate Sorption

The contact time is an important issue in modeling and designing adsorption process in industry. The adsorption capacity increases with time. When the adsorption sites saturate during the adsorption process, the adsorption capacity does not change any more with time, which is known as equilibrium time (Irani et al., 2012). The nitrate adsorption using C. indica was investigated as a function of adsorption time (10-180 min) with an optimum pH of 4 and initial concentration of 100 mg L\(^{-1}\). The result is illustrated in Figure 2. As shown, the nitrate removal efficiency increased by increasing adsorption time and reached the equilibrium time after 60 min. More than 90% of total nitrate adsorption occurred within first 30 min. The fast sorption at the first 30 min could be attributed to the large number of vacant surface sites of C. indica. After that, the active external sites were saturated, and the adsorption process needed more time to be performed by active intra-particular sites. After 1 h, almost all of the internal and external active sites were saturated and the system reached the sorption equilibrium.

Effect of Initial Concentration of Nitrate on the Nitrate Sorption

The effect of the initial concentration of nitrate (50-500 mg L\(^{-1}\)) on the adsorption capacity of C. indica with an optimum pH of 4 and equilibrium time of 60 min is illustrated in Figure 3. As shown, the nitrate adsorption capacity by C. indica was increased by enhancement in nitrate concentration and then approached a fixed value at higher concentrations of nitrate. The increasing adsorption capacity could be attributed to the increase of the driving force gradient for mass transfer created by increasing initial concentration. The fixed value of the adsorption capacity could be attributed to the saturation of the active adsorption sites of C. indica adsorbent.
Kinetic Models

Kinetic models, namely pseudo-first-order and pseudo-second-order models were used to describe the adsorption kinetics of nitrate using C. indica adsorbent.

The pseudo-first-order kinetic model is given as follows (Lagergren, 1898):

\[ q_t = q_e (1 - \exp(-k_1 t)) \]  

(2)

The pseudo-second-order kinetic model is given as follows (Ho and McKay, 1999):

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \]  

(3)

Where \( q_t \) and \( q_e \) (mg g\(^{-1}\)) are the adsorption capacity at time \( t \) and equilibrium time. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the pseudo-first-order and pseudo-second-order models constants. The results are presented in Figure 4 and the kinetic parameters are listed in Table 1. By contrasting the determination coefficient \( (R^2) \) values for pseudo-first-order \( (R^2=0.999) \) and pseudo-second-order \( (R^2=0.992) \), it was found that the pseudo-first-order model fitted better than the pseudo-second-order model with kinetic data.

![Figure 4: Pseudo-First-Order and Pseudo-Second-Order Kinetic Plots for Nitrate Sorption Using C. Indica](image)

Table 1: Kinetic Parameters of Nitrate Sorption Using C. Indica

<table>
<thead>
<tr>
<th>Pseudo-First-Order Model</th>
<th>Pseudo-Second-Order Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_{eq} ) (mg/g)</td>
<td>( K_1 ) (min(^{-1}))</td>
</tr>
<tr>
<td>57.99</td>
<td>0.0101</td>
</tr>
</tbody>
</table>

Isotherm Models

Known Freundlich and Langmuir isotherm models were used to describe the equilibrium data of nitrate sorption using C. indica particles. The Freundlich isotherm equation is expressed as follows (Freundlich, 1906):

\[ q = \frac{K q^F}{1 + q^F} \]  

Where:
- \( q \) is the amount of adsorbed solute per unit mass of adsorbent (mg/g).
- \( K \) is the Freundlich constant (L/mg).
- \( n \) is the Freundlich exponent.

\[ q = \frac{K q^F}{1 + q^F} \]  

(4)

And the Langmuir isotherm equation is expressed as follows (Langmuir, 1918):

\[ q = \frac{q_m K C}{1 + K C} \]  

(5)

Where:
- \( q \) is the amount of adsorbed solute per unit mass of adsorbent (mg/g).
- \( q_m \) is the maximum amount of adsorbed solute per unit mass of adsorbent (mg/g).
- \( K \) is the Langmuir constant (L/mg).

These models help in understanding the interaction between the adsorbent and the adsorbate and in predicting the adsorption capacity under different conditions.
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The Langmuir isotherm model is expressed as follows (Langmuir, 1916):

\[ q_e = \frac{1}{n} \frac{k_F C_e}{1 + b C_e} \tag{4} \]

Where \( k_F \) (mg g\(^{-1}\)) and \( n \) are Freundlich parameters related to the sorption capacity and intensity of the sorbent, respectively. \( q_{\text{max}} \) (mg g\(^{-1}\)) and \( b \) (mg\(^{-1}\)) are the Langmuir model constants.

The parameters of isotherm models were calculated by nonlinear regression of \( q_e \) versus \( C_e \) using MATLAB software. The results are shown in Figure 5 and are listed Table 2. As shown, the maximum adsorption capacity of \( C. \) indica for nitrate sorption was found to be 135 mg g\(^{-1}\). By comparing the determination coefficient \( (R^2) \) values, it was found that the equilibrium data was best described by Langmuir isotherm model \((R^2 > 0.976)\) compared with Freundlich \((R^2 > 0.952)\) isotherm model. This behavior indicated the monolayer sorption of nitrate by \( C. \) indica particles.

![Figure 5: Freundlich and Langmuir Isotherm Plots for Nitrate Sorption Using \( C. \) Indica](image)

| Table 3: Isotherm Parameters for Nitrate Sorption Using \( C. \) Indica Particles |
|-----------------|-----------------|-----------------|
| **Freundlich Isotherm** | **Langmuir Isotherm** |          |
| \( K_F \) (mg g\(^{-1}\)) | \( n \) | \( R^2 \) | \( q_{\text{max}} \) (mg g\(^{-1}\)) | \( K_L \) (L/mg) | \( R^2 \) |
| 18.07 | 3039 | 0.980 | 135.0 | 0.0207 | 0.990 |

Conclusion

The performance of \( C. \) indica as a bio adsorbent was investigated for the removal of nitrate from aqueous solutions. The kinetic data of nitrate sorption were best described by pseudo-first-order kinetic model at equilibrium time of 60 min and optimum pH value of 4. The equilibrium data of nitrate sorption followed well the Langmuir isotherm model with maximum monolayer sorption capacity of 135 mg g\(^{-1}\).
REFERENCES


