

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

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ABSTRACT

In the present study, the potential of *Cystoseira indicia* (*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 methemoglobinaemia 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 indicia* is very plentiful marine brown algae (Davis *et al.*, 2003).

In the present study, the potential of brown alga (*Cystoseira indicia*) 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

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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:

$$q_e = \frac{(C_0 - C_e)V}{1000M} \quad (1)$$

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.

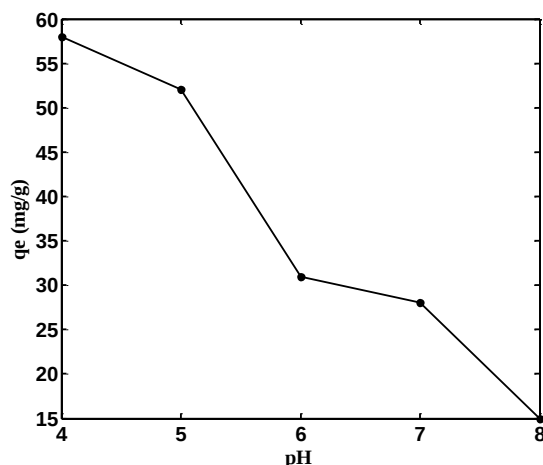


Figure 1: Effect of pH on the Nitrate Sorption Using *C. Indica*

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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-particle sites. After 1 h, almost all of the internal and external active sites were saturated and the system reached the sorption equilibrium.

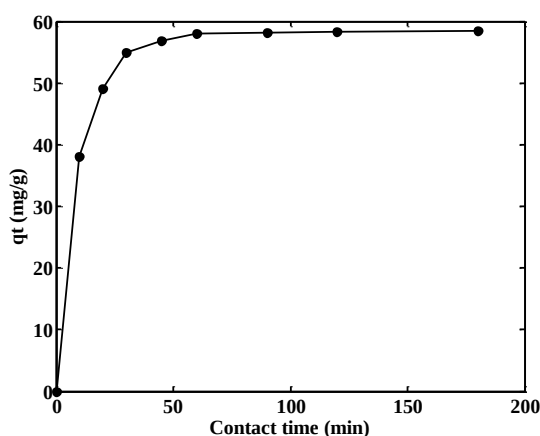


Figure 2: Effect of Contact Time on the Nitrate Removal Using *C. Indica*

Effect of Initial Concentration of Nitrate on the Nitrate Sorption

The effect of the initial concentration of nitrate (50-500mg 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.

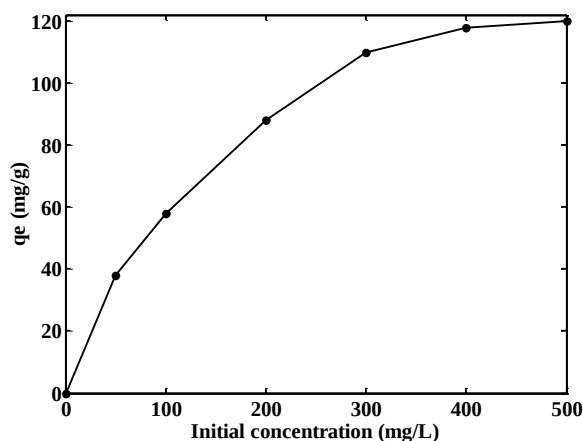


Figure 3: Effect of Initial Concentration of Nitrate on the Nitrate Sorption Using *C. Indica*

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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):

$$q_t = q_e (1 - \exp(-k_1 t)) \quad (2)$$

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

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

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 ($\text{g mg}^{-1} \text{min}^{-1}$) 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.

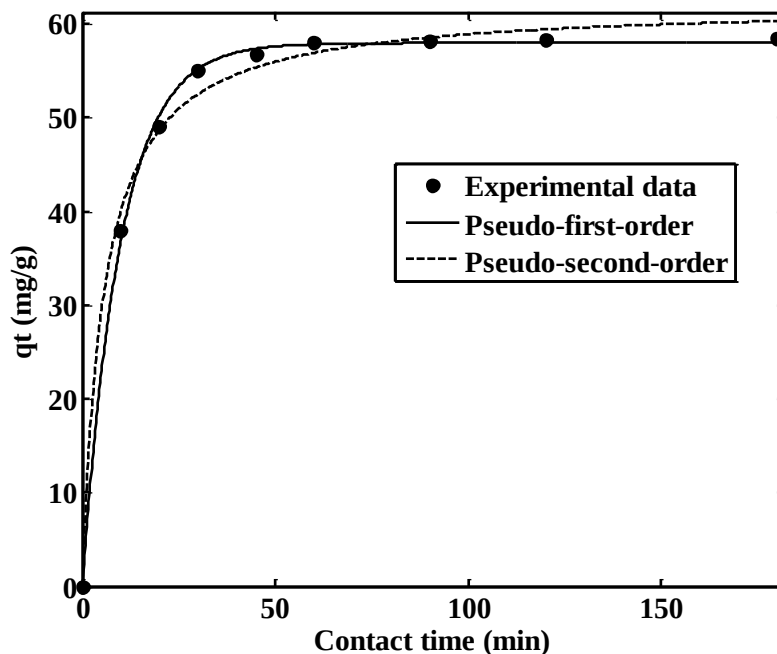


Figure 4: Pseudo-First-Order and Pseudo-Second-Order Kinetic Plots for Nitrate Sorption Using *C. Indica*

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

Pseudo-First-Order Model			Pseudo-Second-Order Model		
q_{eq} (mg/g)	K_1 (min^{-1})	R^2	q_{eq}	K_2 (g/mg.min)	R^2
57.99	0.0101	0.998	62.18	0.00291	0.992

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):

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$$q_e = k_F C_e^{\frac{1}{n}} \quad (4)$$

The Langmuir isotherm model is expressed as follows (Langmuir, 1916):

$$q_e = q_m \frac{bC_e}{1+bC_e} \quad (5)$$

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

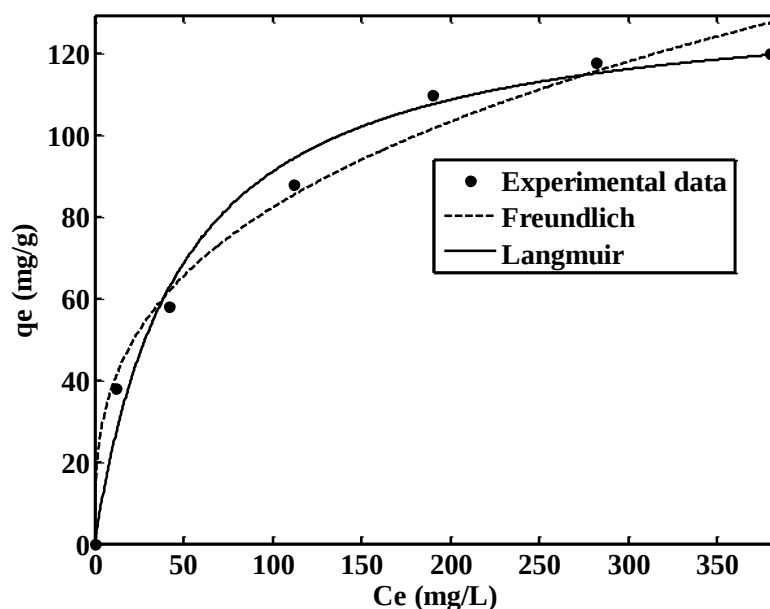


Figure 5: Freundlich and Langmuir Isotherm Plots for Nitrate Sorption Using *C. Indica*

Table 3: Isotherm Parameters for Nitrate Sorption Using *C. Indica* Particles

Freundlich Isotherm			Langmuir Isotherm		
K_F (mg/g)	n	R^2	$q_{\max}(\text{mg/g})$	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} .

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REFERENCES

- Abou-Shady A, Peng C, Bi J, Xu H and Juan Almeria O (2003).** Recovery of Pb (II) and removal of NO_3^- from aqueous solutions using integrated electrodialysis, electrolysis, and adsorption process. *Desalination* **286** 304-315.
- Afkhami A, Madrakian T and Karimi Z (2007).** The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions. *Journal of Hazardous Materials* **144** 427- 431.
- Bhatnagar A and Sillanpää M (2011).** A review of emerging adsorbents for nitrate removal from water. *Chemical Engineering Journal* **168** 493-504.
- Camargo JA and Alonso Á (2006).** Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. *Environment International* **32** 831-849.
- Canter LW (1997).** *Nitrates in Groundwater*, (CRC Press, Inc., Lewis Publishers, New
- Chabani M, Amrane A and Bensmaili A (2007).** Kinetics of nitrate adsorption on Amberlite IRA 400 resin. *Desalination* **206** 560-567.
- Chiu H, Tsai S and Yang C (2007).** Nitrate in drinking water and risk of death from bladder cancer: an ecological case control study in Taiwan. *Journal of Toxicology and Environmental Health, Part A: Current Issues* **70** 1000-1004.
- Davis TA, Volesky B and Mucci A (2003).** A review of the biochemistry of heavy metal biosorption by brown algae. *Water Research* **37**(18) 4311–4330.
- Freundlich HMF (1906).** Über die adsorption in losungen. *Zeitschrift für Physikalische Chemie* **57** 385–471.
- Hamoudi S, Saad R and Belkacemi K (2007).** Adsorptive removal of phosphate and nitrate anions from aqueous solutions using ammonium-functionalized mesoporous silica. *Industrial & Engineering Chemistry Research* **46** 8806-8812.
- Ho YS and McKay G (1999).** Pseudo-second-order model for sorption processes. *Process Biochemistry* **34** 451–465.
- Irani M, Keshtkar AR and Moosavian MA (2012).** Preparation of poly (vinyl alcohol)/ tetraethyl orthosilicate hybrid membranes modified with TMPTMS by sol–gel method for removal of lead from aqueous solutions. *Korean Journal of Chemical Engineering* **29** 1459-1465.
- Jaafari K, Ruiz T, Elmaleh S, Coma J and Benkhoulja K (2001).** Equilibrium and kinetics of nitrate removal by protonated cross-linked chitosan. *Water SA* **27** 9-13.
- Khan AM, Ahn Y, Kumar M, Lee W, Min B, Kim G, Cho D, Park WB and Jeon B (2011).** Adsorption studies for the removal of nitrate using modified lignite granular activated carbon. *Separation Science and Technology* **46** 2575-2584.
- Lagergren S (1898).** Zur theorie der sogenannten adsorption gel ster stoffe, Kungliga svenska vetenskapsakademiens. *Handlingar* **24**(4) 1–39.
- Langmuir I (1916).** The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society* **38** 2221–2295.
- Pahlavanzadeh H, Keshtkar AR, Safdari J and Abadi Z (2010).** Biosorption of nickel (II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies. *Journal of Hazardous Materials* **175** 304–310.
- Pennington JAT (1998).** Dietary exposure models for nitrates and nitrites. *Food Control* **9** 385-395.
- Schoeman JJ and Steyn A (2003).** Nitrate removal with reverse osmosis in a rural area in South Africa. *Desalination* **155** 15-26.
- WHO (2011).** *Guidelines for Drinking-Water Quality*, fourth edition, (Geneva: World Health Organization).
York, USA).
- Zhan Y, Lin J and Zhu Z (2011).** Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent. *Journal of Hazardous Materials* **186** 1972-1978.