



Sorption of boron by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*

Elif Ant Bursali, Levent Cavas, Yoldas Seki*, Serap Seyhan Bozkurt, Muruvvet Yurdakoc

Dokuz Eylul University, Faculty of Arts & Sciences, Department of Chemistry, 35160 Kaynaklar Campus, Izmir, Turkey

ARTICLE INFO

Article history:

Received 21 September 2008
Received in revised form 6 January 2009
Accepted 10 January 2009

Keywords:

Caulerpa racemosa var. *cylindracea*
Boron
Sorption
Biological invasion

ABSTRACT

The sorption of boron from aqueous solution onto *Caulerpa racemosa* var. *cylindracea* (CRC), collected from Seferihisar/Izmir region in Turkey, was investigated as a function of pH, temperature, initial boron concentration, adsorbent dosage, contact time and ionic strength. Optimum conditions for the sorption of boron were obtained at pH 7.5, 318 K, 8 mg L⁻¹ initial boron concentration, 0.2 g of CRC, 2.5 h contact time and greater ionic strength (10⁻¹ M NaCl). As the temperature was increased the boron removal took place with higher percentages. In experiments conducted at optimum conditions, maximum boron sorption was determined to be about 63%. The experimental data were analyzed by Freundlich, Langmuir and Dubinin–Radusckevich (DR) equations. Freundlich and DR models provide best conformity with the experimental data. In order to describe kinetics of boron sorption onto CRC, first-order Lagergren equation, pseudo-second-order kinetic model and intraparticle diffusion model were used. It was seen that the first order Lagergren equation was better described than the pseudo-second-order kinetic model. Thermodynamic parameters of sorption process were also calculated. It was obtained that sorption process was not spontaneous. The characterization of CRC was carried out by Fourier transform infrared spectroscopy (FTIR) analysis.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Caulerpa racemosa var. *cylindracea* (CRC) is an invasive marine green alga which has been negatively affecting sublittoral ecosystem of Mediterranean Sea since 1991 [1,2]. Most of Turkish Aegean and the Mediterranean coastlines have been also invaded by this invasive species [3–5]. This species at the moment is a reason of biological pollution in the twelve Mediterranean countries and in some big islands in the Mediterranean Sea [1,2]. Members of *Caulerpa* genus are candidate marine products for industrial usage since not only their high growth properties, low cost and easiness in cultivation but also higher adsorption capacities for some metal and some dyes [6–11]. Moreover, it is recently reported that *Caulerpa lentillifera* has higher adsorption capacity for methylene blue compared to a widely used commercial activated carbon [12].

Boron is a naturally occurring element that is widely distributed at low concentrations in the environment. Boron is rare, being found in dry regions of the world such as Turkey, which has the largest boron reserves in the world. Although boron is essential for plant life and small amounts of boron are even claimed to be beneficial for human, high levels may be toxic [13]. The concentration range of boron in drinking water is judged to be between 0.1 and 0.3 mg L⁻¹ [14]. Boron compounds find extensive use in a wide range of industrial applications and may be introduced into the environment in the form of hazardous materials [15].

trial applications and may be introduced into the environment in the form of hazardous materials [15].

Boron removal can be achieved by several methods including ion exchange [16], precipitation–coagulation [17], membrane filtration [18], removal by clays [19], boron specific resins [20], reverse osmosis [21], fly-ash [22], solvent-extraction [23], ultrafiltration [24] and also using aquatic plants [25].

The main goal of the present study is to investigate boron removal efficiency of the invasive marine alga *Caulerpa racemosa* var. *cylindracea* as a cost effective biosorbent.

2. Materials and methods

2.1. Materials

CRC used as sorbent in this study, was hand-picked by SCUBA diving from Izmir–Seferihisar region in Turkey. It was washed with distilled water several times to remove some impurities then oven-dried at 353 K for 12 h. Dried CRC was grinded and used without any treatment. To characterize CRC, Fourier transform infrared spectroscopy (FTIR) analysis was conducted with PerkinElmer Spectrum BX-II Model FTIR spectrophotometer. KBr pellets were recorded in the range of 4000 and 400 cm⁻¹. The possible functional groups available in dried CRC were presented in Table 1.

Boric acid was purchased from Merck Company. Boric acid stock solution (100 ppm) was prepared by dissolving boric acid in ultra pure water. Working solutions were freshly prepared from stock

* Corresponding author. Tel.: +90 232 4128694; fax: +90 232 4534188.
E-mail address: yoldas.seki@deu.edu.tr (Y. Seki).

Table 1
Functional Groups in dried *Caulerpa racemosa* var. *cylindracea*.

| Functional group | Wavenumber (cm ⁻¹) |
|------------------------|---|
| Hydroxyl-H | 3200–3400 (max: 3409 cm ⁻¹) |
| Amine; NH ₂ | 3300–3500 |
| Alkyl; C–H | 2923 |
| Carbonyl; C=O | 1646 |
| S=O | 1245 |
| C–O | 1028 |
| S–O | 602 |

solution. The pH values of the solutions were determined by WTW model pH meter.

2.2. Sorption experiments

Batch adsorption technique was used for sorption of boron from aqueous solutions at different temperatures (298, 308 and 318 K). 0.1 g CRC was mixed with 25 mL boric acid solution at different concentrations. From contact time experiments, it was obtained that 2.5 h was adequate to reach the equilibrium concentration. The suspensions were shaken at 150 rpm by using GFL 1086 model shaker. After equilibrium was reached the samples were centrifuged and equilibrium boron concentration in supernatant was measured by newly developed azomethine-H-fluorimetric method in Varian Cary Eclipse model spectrofluorometer [26]. The influence of pH on the sorption of boron was examined. The pH values of the solutions were adjusted by using dilute HCl and NaOH solutions. Also, temperature effect on the sorption has been investigated at 298, 308 and 318 K. Optimum adsorbent dosage was determined by using various amounts of adsorbents (0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g CRC). 1×10^{-1} , 10^{-2} and 10^{-3} M NaCl solutions were used to identify the effect of ionic strength. The optimum conditions for all parameters were applied to the sorption of boron with CRC.

The amount of adsorbed boron was calculated as follows:

$$C_s = \frac{(C_0 - C_t)V}{m_s} \quad (1)$$

where C_s is the amount of adsorbed boron (mg g⁻¹), C_0 is the initial boron concentration (mg L⁻¹) and C_t is boron concentration at time t . V is the volume of the solution (L) and m_s is the mass of the adsorbent (g).

The % boron removal from aqueous solution was obtained by the following equation:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

3. Results and discussion

3.1. Effect of adsorbent dosage

To investigate the effect of adsorbent dosage on boron removal, different amounts (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 g) of CRC were subjected to fixed boron concentration of 10 mg L⁻¹. As demonstrated in Fig. 1, boron removal increases up to 0.2 g of adsorbent dosage due to the increase in boron sorption sites. Beyond 0.2 g of adsorbent dosage, boron removal remains constant at 50%.

3.2. Adsorption isotherm

Adsorption isotherm can be demonstrated graphically by plotting the amount of adsorbed boron per 1 g CRC against equilibrium concentration of boron (Fig. 2). The shape of the isotherm corresponds to S type isotherm which is mostly considered as indicative of physical adsorption [27]. Clustering of adsorbate molecules at the surface is favored because they bond more strongly with one

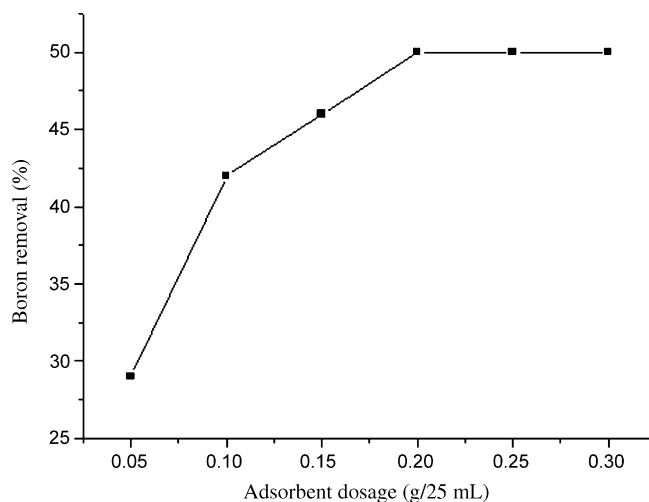


Fig. 1. Effect of adsorbent dosage on the removal of boron ($T=298$ K, initial boron concentration: 10 mg L⁻¹).

another than with the surface [28]. The amount of adsorbed boron increased with the rise of temperature. This is due to increase in the possibility of interaction between boron and CRC.

The experimental data were analyzed by most common isotherm equations such as Freundlich, Langmuir and Dubinin–Radoskevich (DR) to search for the best model which provides better fit with the data. It is possible to find the sorption capacity values by using the equation which has high correlation coefficient. Also, some information related to nature of sorption such as monolayer and multilayer coverage can be obtained. Contrary to Freundlich equation, Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface [7,8]. Linear forms of Langmuir and Freundlich equations are represented in (3) and (4), respectively:

$$\frac{C_e}{C_s} = \frac{1}{C_m L} + \frac{C_e}{C_m} \quad (3)$$

$$\ln C_s = \ln K_f + n_f \ln C_e \quad (4)$$

where C_e is the equilibrium concentration (mg L⁻¹), C_s is the amount of adsorbed (mg g⁻¹), C_m is the monolayer adsorption capacity, L is a constant related to adsorption energy. K_f and n_f are known as relative adsorption capacity (mg g⁻¹) and adsorption intensity, respectively. These parameters were computed from the

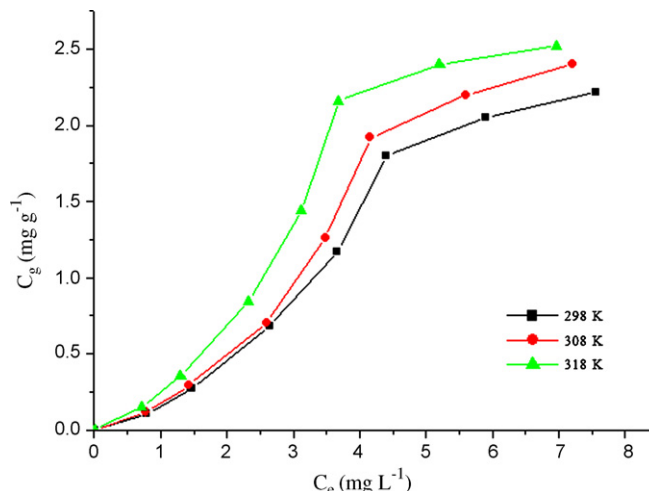


Fig. 2. Isotherms for boron sorption onto CRC at different temperatures.

Table 2
Adsorption isotherm parameters for boron biosorption onto CRC.

| | 298 K | 308 K | 318 K |
|--|-------|-------|-------|
| Linear form of Langmuir | | | |
| C_m (mg g ⁻¹) | -1.12 | -1.16 | -1.61 |
| L (L mg ⁻¹) | -0.13 | -0.13 | -0.14 |
| R^2 | 0.77 | 0.80 | 0.73 |
| Linear form of Freundlich | | | |
| K_f (mg g ⁻¹) | 0.15 | 0.17 | 0.25 |
| n_f | 1.55 | 1.56 | 1.50 |
| R^2 | 0.99 | 0.99 | 0.99 |
| DR Model | | | |
| R^2 | 0.99 | 0.99 | 0.99 |
| $X_m \times 10$ (mol g ⁻¹) | 0.35 | 0.38 | 0.41 |
| E (kJ mol ⁻¹) | 5.81 | 6.04 | 6.35 |

linear plots of C_e/C_s against C_e and $\ln C_s$ against $\ln C_e$. The calculated parameters were listed in Table 2. Considering the correlation coefficients obtained from the linear plots, Freundlich equation ($R^2 = 0.99$ for each temp.) fitted better than Langmuir equation ($R^2 = 0.73$ – 0.80 in the range 298–308 K). The better fit of equilibrium data to the Freundlich equation refers the multilayer sorption of boron onto CRC. The relative sorption capacity was obtained to be 0.15 mg g⁻¹ at 298 K and increased with the rise in temperature. A comparison was made in terms of the relative adsorption capacity values (K_f) for boron adsorption between CRC and other adsorbents and presented in Table 3. It was observed that CRC has greater K_f value than those of cotton cellulose, calcined alunite, Siral 5, Çamlıca Bentonite 1 [26,29–33]. One can realize that n_f values are greater than 1, expressing S type isotherm. This confirms physical adsorption and multilayer adsorption [19].

The experimental data further evaluated by Dubinin–Radusckevich equation which is expressed with the following equations:

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (5)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

where q_e is the amount of adsorbed boron (mol g⁻¹), X_m is defined as maximum adsorption capacity (mol g⁻¹), β is a constant related to sorption energy (mol² kJ⁻²), C_e is equilibrium concentration (mol L⁻¹) and ε is Polanyi sorption potential (the amount of energy required to pull a sorbed molecule from its sorption site to infinity) [34–36]. The results were summarized in Table 2. β value is a constant related to energy (E) with below expression:

$$E = \frac{\beta^{-1/2}}{\sqrt{2}} \quad (7)$$

Table 3
Comparisons of the relative adsorption capacities (K_f) for sorption of boron by different adsorbents.

| Type of adsorbent | (K_f) (mg/g) | Temp. (°C) | pH | Refs. |
|-----------------------------------|------------------------|------------|-----|---------------|
| Dowex 2 × 8, anion exchange resin | 1.43 ($R^2 = 0.90$) | 25 | 9 | [29] |
| CRC | 0.25 ($R^2 = 0.99$) | 45 | 5.7 | Present study |
| Cotton cellulose | 0.16 ($R^2 = 0.75$) | Room temp. | 7 | [30] |
| Calcined alunite | 0.033 ($R^2 = 0.99$) | 25 | 10 | [31] |
| Siral 5 | 0.12 ($R^2 = 0.995$) | 25 | – | [32] |
| Çamlıca Bentonite 1 | 0.05 ($R^2 = 0.997$) | 45 | 10 | [26] |
| Non-activated waste sepiolite | 8.34 ($R^2 = 0.865$) | 20 | 10 | [33] |

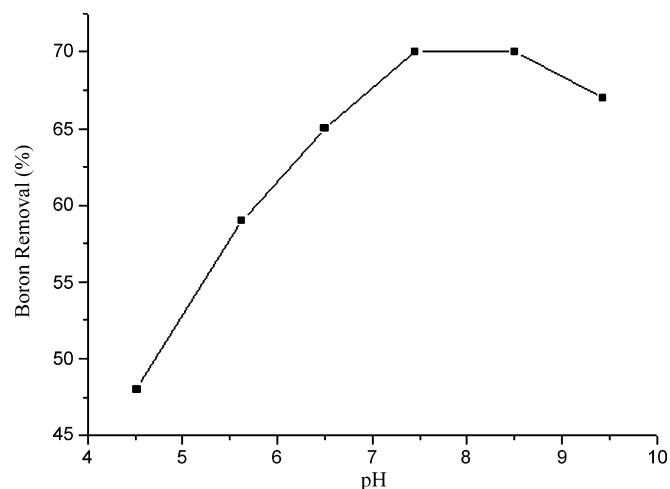


Fig. 3. The effect of pH on removal of boron from aqueous solution. (Initial boron concentration: 10 mg L⁻¹ (25 mL), adsorbent dosage: 0.1 g, $T = 298$ K.)

The calculated E values were smaller than 8 kJ mol⁻¹ corresponding to physical adsorption. This result is compatible with the previous result which claims physical adsorption as type of adsorption. Maximum adsorption capacity values, X_m are increasing with the rise of temperature.

3.3. Influence of pH

Fig. 3 exhibits the effect of pH on the removal of boron from aqueous solution. The amount of adsorbed boron was investigated in the pH range 4.5–9.5. The pH of the solution influences the degree of ionization of the adsorbate. At pH values around 9.0, the $B(OH)_3$ and $B(OH)_4^-$ concentrations are practically the same, while at higher pH values (11.0), $B(OH)_4^-$ is the predominant species ($pK_a = 9.2$) [37]. The amount of adsorbed boron and also the species of $B(OH)_4^-$ increase with the rise of pH from 4.5 to 7.5. Between the pH values 7.5 and 8.5 which can be also accepted as the optimum pH values, boron removal was at maximum and remains constant. As the pH increases from 8.5 to 9.5, boron removal reduces. There may be a competition between OH^- and $B(OH)_4^-$ for the sorption sites and thus adsorption of anions is not favorable.

3.4. Influence of ionic strength

The influence of ionic strength for boron sorption onto CRC is given in Fig. 4. The amount of adsorbed boron increased with the increase in ionic strength. The higher concentration of mobile ions outside CRC, decrease the CRC–water interactions. Probably mobile ions prevent adsorption of water and this will reduce the competition between water and boron species.

3.5. Optimum conditions

Sorption experiments were performed at optimum conditions for two cases. These were 318 K, pH 7.5, initial boron concentration: 8 mg L⁻¹, NaCl: 10⁻¹ M and 318 K, pH 7.5, initial boron concentration: 8 mg L⁻¹, in the absence of NaCl. Maximum boron sorption was attained about 63% for the first case. Approximately 3% difference was observed between the first and second case.

3.6. Adsorption kinetics

Kinetic studies involve effect of major parameters such as contact time, adsorbent dosage and concentration of the adsorbate solution on the uptake of boron by CRC [7,8]. In order to describe

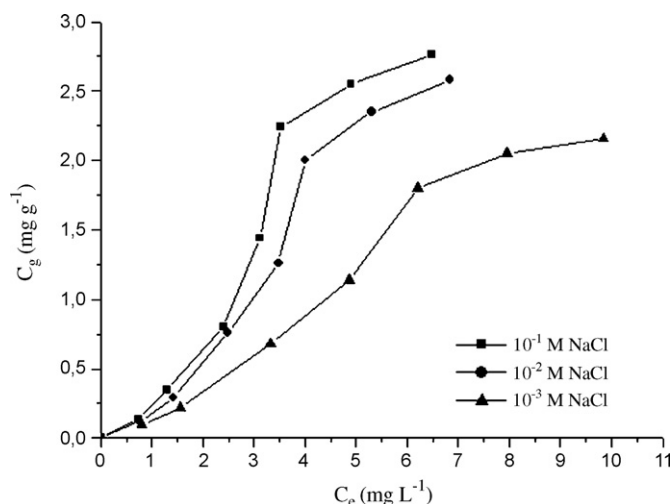


Fig. 4. The effect of ionic strength on boron removal.

kinetics of boron sorption onto CRC, some models such as first order rate equation and pseudo-second-order kinetic model were applied to experimental data. The first-order Lagergren equation is given by Eq. (8) [38]:

$$\log(q_{e\text{exp}} - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

where t is time (h), q_t (mg g^{-1}) is the amount of adsorbed boron at time t , k_1 is rate constant. The $q_{e\text{exp}}$ (mg g^{-1}) and q_e (mg g^{-1}) are expressed as the amount of boron adsorbed at equilibrium-experimental data equilibrium-calculated data, respectively. The first-order Lagergren plots for boron sorption onto CRC at different temperatures were given in Fig. 5. Results obtained by applying the first-order Lagergren model to the experimental data were given in Table 4.

The values of calculated adsorption capacity (q_e) are 1.6, 1.4 and 1.5 mg g^{-1} for 298, 308 and 318 K, respectively. There is not so much difference between the q_e values obtained at different temperatures. The greatest rate constant value was obtained at 298 K ($k = 1.07 \text{ h}^{-1}$).

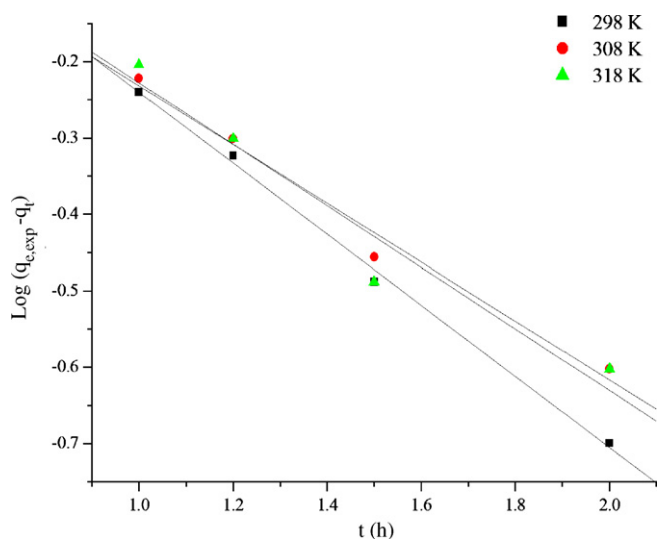


Fig. 5. The first-order Lagergren plots for boron sorption onto CRC at different temperatures.

Table 4
Kinetic parameters for boron biosorption onto CRC.

| | 298 K | 308 K | 318 K |
|---|-------|-------|-------|
| Lagergren equation | | | |
| $q_{e\text{exp}}$ (mg g^{-1}) | 1.0 | 1.1 | 1.2 |
| q_e (mg g^{-1}) | 1.6 | 1.4 | 1.5 |
| k_1 (h^{-1}) | 1.07 | 0.89 | 0.92 |
| R^2 | 0.99 | 0.98 | 0.95 |
| Pseudo-second-order | | | |
| q_2 (mg g^{-1}) | 4.8 | 2.6 | 2.6 |
| $k_2 \times 10^2$ ($\text{g mg}^{-1} \text{ h}^{-1}$) | 2.3 | 9.9 | 11.3 |
| R^2 | 0.53 | 0.83 | 0.73 |
| Intraparticle | | | |
| k_p ($\text{mg g}^{-1} \text{ h}^{-1/2}$) | 0.95 | 0.97 | 1.00 |
| R^2 | 0.99 | 0.98 | 0.97 |

Pseudo-second-order kinetic model can be represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (9)$$

where k_2 ($\text{g mg}^{-1} \text{ h}^{-1}$) is the rate constant of adsorption, q_2 is maximum adsorption capacity (mg g^{-1}) [39]. The values of k_1 , q_e and k_2 , q_2 were obtained from the slopes and intercepts of plots of $\log(q_e - q)$ versus t and t/q_t versus t at different temperatures. The calculated parameters were given in Table 4. When the correlation coefficients of models were compared, first order equation has a greater R^2 values. Then, it is inferred that first order Lagergren equation is better described than the pseudo-second-order kinetic model. Besides, as given in Table 4, the amount of boron adsorbed at equilibrium-calculated data, q_e (mg g^{-1}) obtained from Lagergren equation are closer to the amount of boron adsorbed at equilibrium-experimental data, $q_{e\text{exp}}$. Therefore, Lagergren equation was more suitable than pseudo-second-order kinetic model to describe the adsorption kinetics.

Sorption kinetic was also evaluated by Intraparticle diffusion model (the amount of uptake varies linearly with \sqrt{t}) which can be defined by Eq. (10):

$$q_t = k_p \sqrt{t} \quad (10)$$

where q_t is the amount of adsorbed at time t (mg g^{-1}), k_p is intraparticle rate constant ($\text{mg g}^{-1} \text{ h}^{-1/2}$). Intra-particle diffusion constants (k_p) at different temperatures were obtained from the slopes of the linear portions of the plots and are listed in Table 4. Correlation coefficients were high, indicating that the above model demonstrates a good fit to the experimental data. As can be seen from Fig. 6, there was a linear relationship for short t values between $t^{0.5}$ and q_t values. Intraparticle diffusion rate constant (k_p) values were obtained to be 0.95, 0.97 and $1 \text{ mg g}^{-1} \text{ h}^{-1/2}$ for 298, 308 and 318 K, respectively. Generally, if the adsorption steps are independent of one another, the plot of q_t versus $t^{1/2}$ usually shows two or more intersecting lines depending upon the exact mechanism [40]. As can be seen from Fig. 6, multi-linearity which is composed of three steps was observed for boron sorption onto CRC (the fourth one is beyond the equilibrium time and constant, therefore it is not shown in Fig. 6). It can be said that multiple nature for the relationship shows that intra-particle diffusion is not a fully operative mechanism for sorption of boron onto CRC. The first linear portion is attributed to rapid external surface adsorption. The second portion may show a gradual adsorption. The third portion is sharper than the second portion. Namely, the rate of uptake boron in the third region is greater than that in the second region.

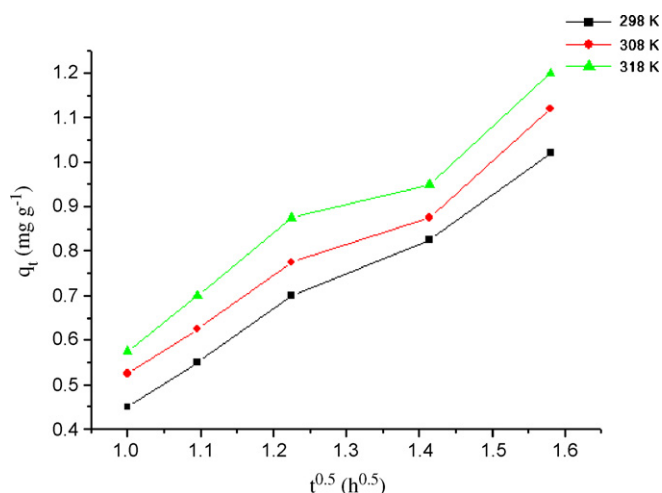


Fig. 6. The intraparticle diffusion plots for boron biosorption onto CRC at different temperatures.

3.7. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were also found out to give more information about the nature of sorption process. The thermodynamic parameters were calculated by the following equations:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{ (van't Hoff equation)} \quad (11)$$

$$\Delta G^\circ = -RT \ln K_c \quad (12)$$

where $K_c (=C_s/C_e)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is gas constant. When $\ln K_c$ versus $1/T$ is plotted, ΔH° and ΔS° values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters were given in Table 5. The Gibbs free energy change values were obtained to be 4.75, 4.66 and 3.76 kJ mol⁻¹ for 298, 308 and 318 K, respectively. This suggests that sorption process is not spontaneous and as the temperature increases ΔG° values get lower. A positive value of enthalpy change shows the endothermic nature of sorption process. In addition to this, enthalpy change is used to identify type of adsorption. Sorption of boron onto CRC may be considered as the possibility of physical process on account of the fact that enthalpy change is lower than 40 kJ mol⁻¹ [41]. This conclusion supports the findings (about the type of adsorption) by Dubinin–Ruduskevich equation. Positive value of entropy change implies increased randomness at the solid-solution interface during the sorption of boron onto CRC.

3.8. FTIR analysis

The FTIR spectra of CRC and boron loaded CRC were given in Fig. 7. OH stretching vibration at 3409 cm⁻¹ reduces to 3403 cm⁻¹ as a result of sorption of boron. Aliphatic CH stretching vibrations was observed at 2923 cm⁻¹ and did not almost change. The band at 1646 cm⁻¹ which is due to C=O groups increased 1653 cm⁻¹ after

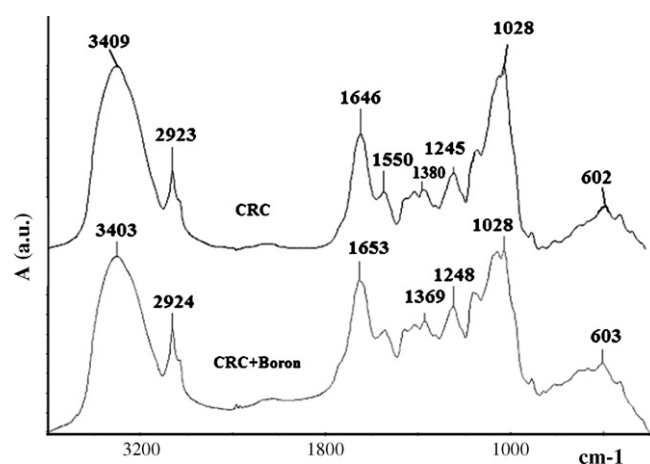


Fig. 7. The FTIR spectra of CRC and boron loaded CRC.

boron adsorption on CRC. The band located at 1380 cm⁻¹ is probably corresponding to CH bending vibrations which shifted to 1369 cm⁻¹ when boron is adsorbed. In the spectrum of CRC there is a band at 1245 cm⁻¹ which can be attributed to S=O group and significant change was not observed. The band centered at 1028 cm⁻¹ in the spectrum of CRC was similar in spite of sorption of boron. It can be claimed that adsorption of boron onto CRC was confirmed by FTIR analysis. The low difference between wavenumber changes in the functional groups before and after adsorption supports that adsorption takes place as physically process.

4. Conclusions

Sorption of boron onto *Caulerpa racemosa* var. *cylindracea* was studied in this study as a function of contact time, adsorbent dosage, temperature, pH and ionic strength. Contact time studies showed that the sorption process reached equilibrium around 2.5 h. Optimum adsorbent dosage was obtained to be 0.2 g for boron sorption onto CRC. The amount of adsorbed boron increases with the rise of pH from 4.5 to 7.5. From 7.5 to 8.5, boron removal was at maximum and remains constant. Ionic strength studies showed that the amount of adsorbed boron increased with the increase in ionic strength. Boron removal at optimum conditions ($T=318$ K, pH 7.5, initial boron concentration: 8 ppm, 0.1 M NaCl) was about 63%. Sorption kinetic was also investigated and it was merged that first-order Lagergren model provided better fit than pseudo-second-order kinetic model. Sorption isotherm studies indicate that sorption data fitted Freundlich equation ($R^2=0.99$ for each temp.) better than Langmuir equation ($R^2=0.73-0.80$ in the range of 298–308 K). From thermodynamic studies it was obtained that positive value of enthalpy change shows the endothermic nature of sorption process. Positive values of Gibbs free energy change (ΔG°) imply that sorption process is not spontaneous. It is very important to note that since *Caulerpa racemosa* var. *cylindracea* is an invasive seaweed, the present study does not recommend the cultivation of this species in non-invaded areas. The paper presents an alternative usage of the biomass of *Caulerpa racemosa* var. *cylindracea* after a possible eradication method which will be based on manual uprooting. In conclusion, *Caulerpa racemosa* var. *cylindracea* as a low cost biomaterial could be used for the removal of boron species from aqueous solution.

Acknowledgement

The authors are grateful to Research Foundation of Dokuz Eylul University (Project 05-KB-FEN-052) for the financial support.

Table 5

Thermodynamic parameters for boron biosorption onto CRC.

| T (K) | K_c | ΔG° (kJ mol ⁻¹) | ΔS° (J mol ⁻¹ K ⁻¹) | ΔH° (kJ mol ⁻¹) |
|-------|-------|--|---|--|
| 298 | 0.15 | 4.75 | 46.38 | 18.67 |
| 308 | 0.16 | 4.66 | | |
| 318 | 0.24 | 3.76 | | |

References

- [1] M. Verlaque, C. Durand, J.M. Huisman, C.F. Boudouresque, Y. Parco, On the identity and origin of the Mediterranean invasive *Caulerpa racemosa* (*Caulerpales*, *Chlorophyta*), *Eur. J. Phycol.* 38 (2003) 325–339.
- [2] J. Klein, M. Verlaque, The *Caulerpa racemosa* invasion: a critical review, *Mar. Pollut. Bull.* 56 (2) (2008) 205–225.
- [3] B. Akcali, Ege Denizi kiyilarındaki yabancı ve yayilimci deniz bitkileri üzerine bir araştırma, Ph.D. Thesis, Dokuz Eylül University, Graduate School of Natural and Applied Sciences, Izmir, Turkey, 2006.
- [4] L. Cavas, K. Yurdakoc, A comparative study: assessment of the antioxidant system in the invasive green alga *Caulerpa racemosa* and some macrophytes from the Mediterranean, *J. Exp. Mar. Biol. Ecol.* 321 (2005) 35–41.
- [5] L. Cavas, K. Yurdakoc, An investigation on the antioxidant status of the invasive marina alga: *Caulerpa racemosa*, *J. Exp. Mar. Biol. Ecol.* 325 (2005) 189–200.
- [6] S. Cengiz, L. Cavas, Removal of methylene blue by using an invasive marine alga *Caulerpa racemosa* var. *cylindracea*, *Biores. Technol.* 99 (2008) 2357–2363.
- [7] R. Aravindhan, N.N. Fathima, J.R. Rao, B.U. Nair, Equilibrium and thermodynamic studies on the removal of basic black dye using calcium alginate beads, *Colloids Surfaces A* 299 (2007) 232–238.
- [8] R. Aravindhan, J.R. Rao, B.U. Nair, Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*, *J. Hazard. Mater.* 142 (2007) 68–76.
- [9] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, *Biores. Technol.* 97 (2006) 2321–2329.
- [10] R. Apiratikul, P. Pavasant, Sorption isotherm model for binary component sorption of copper, cadmium, and lead ions using dried green macroalga, *Caulerpa lentillifera*, *Chem. Eng. J.* 119 (2006) 135–145.
- [11] K. Marungrueng, P. Pavasant, Removal of basic dye (Astrazon Blue FGRL) using macroalga *Caulerpa lentillifera*, *J. Environ. Manag.* 78 (2006) 268–274.
- [12] K. Marungrueng, P. Pavasant, High performance biosorbent (*Caulerpa lentillifera*) for basic dye removal, *Biores. Technol.* 98 (2007) 1567–1572.
- [13] J.Q. Jiang, Y. Xu, J. Simon, K. Quill, K. Shettle, Removal of boron (B) from waste liquors, *Water Sci. Technol.* 53 (2006) 73–79.
- [14] World Health Organization, Guidelines for Drinking-water Quality, Vol. 1, third ed., World Health Organization, Geneva, 2004, Chapter 8.
- [15] N. Bektaş, S. Oncel, H. Akbulut, A. Dimoglo, Removal of boron by electrocoagulation, *Environ. Chem. Lett.* 2 (2004) 51–54.
- [16] M.O. Simonnot, C. Castel, M. Nicolai, C. Rosin, M. Sardin, H. Jauffret, Boron removal from drinking water with a boron selective resin: is the treatment really selective? *Water Res.* 34 (2004) 109–116.
- [17] I. Rodionov, O.M. Voytova, N.Y. Romanov, Recent problems in treating boron wastewater, *Uspekhi Khimii* 60 (1991) 2448–2462.
- [18] Y. Magara, A. Tabaka, M. Kohki, M. Kawasaki, M. Hirose, Development of boron reduction system for seawater desalination, *Desalination* 118 (1998) 25–34.
- [19] S. Karahan, M. Yurdakoc, Y. Seki, K. Yurdakoc, Removal of boron from aqueous solution by clays and modified clays, *J. Colloid Interface Sci.* 293 (2006) 36.
- [20] S. Sahin, A mathematical relationship for explanation of ion exchange for the boron adsorption, *Desalination* 143 (2002) 35–43.
- [21] N. Nadav, Boron removal from seawater reverseosmosis permeate utilizing selective ion exchangeresin, *Desalination* 124 (1999) 131–135.
- [22] H. Polat, A. Vengosh, I. Pankratov, M. Polat, A new methodology for removal of boron from water by coal and fly ash, *Desalination* 164 (2004) 173–188.
- [23] M. Matsumoto, K. Kondo, M.S. Hirata, T.K. Hano, T. Takada, *Sep. Sci. Technol.* 32 (1997) 983.
- [24] B.M. Smith, P. Todd, C.N. Bowman, Boron removal by polymer-assisted ultra filtration, *Sep. Sci. Technol.* 30 (1995) 3849–3859.
- [25] S.M. Davis, K.D. Drake, K.J. Maier, Toxicity of boron to the duckweed, *Spirodella polyrrhiza*, *Chemosphere* 48 (2002) 615–620.
- [26] S. Seyhan, Y. Seki, M. Yurdakoc, M. Merdivan, Application of iron-rich natural clays in Çamlica, Turkey for boron sorption from water and its determination by fluorimetric-azomethine-H method, *J. Hazard. Mater.* 146 (2007) 180–185.
- [27] C.H. Giles, T.H. Mac Evan, S.N. Nakhwa, D. Smith, Studies in adsorption. XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and measurement of specific surface areas of solids, *J. Chem. Soc.* 786 (1960) 3973–3993.
- [28] H. Bradl, *Encyclopedia of Surface and Colloid Science*, Dekker, New York, 2002, pp. 373–384.
- [29] N. Ozturk, T. Ennil Köse, Boron removal from aqueous solutions by ion-exchange resin: batch studies, *Desalination* 227 (2008) 233–240.
- [30] R. Liu, W. Ma, C. Jia, L. Wang, H. Li, Effect of pH on biosorption of boron onto cotton cellulose, *Desalination* 207 (2007) 257–267.
- [31] D. Kavak, Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design, *J. Hazard. Mater.*, 2008, doi:10.1016/j.jhazmat.2008.06.093.
- [32] M. Yurdakoc, Y. Seki, S. Karahan, K. Yurdakoc, Removal of boron from aqueous solution by clays and modified clays, *J. Colloid Interface Sci.* 286 (2005) 440–446.
- [33] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption on waste sepiolite and activated waste sepiolite using full factorial design, *Adsorption* 10 (2004) 245–257.
- [34] S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London and New York, 1967, pp. 195–223.
- [35] S.M. Hasany, M.H. Chaudhary, Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution, *Appl. Rad. Iso.* 47 (1996) 467–471.
- [36] J.P. Hobson, Physical adsorption isotherms extending from ultra high vacuum to vapor pressure, *J. Phys. Chem.* 73 (1969) 2720–2727.
- [37] J. Lou, G.L. Foutch, W.N. Jung, The sorption capacity of boron on anionic-exchange resin, *Sep. Sci. Technol.* 34 (1999) 2923–2941.
- [38] S. Lagergren, About the theory of so-called adsorption of soluble substances, *H. Band* 24 (1898) 1–39.
- [39] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process. Biochem.* 34 (1999) 451–465.
- [40] K. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder, *Dyes Pigments* 65 (2005) 51–59.
- [41] G. McKay, V.J.P. Poots, Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent, *J. Chem. Technol. Biotechnol.* 30 (1980) 279–292.