Türk Biyokimya Dergisi [Turkish Journal of Biochemistry–Turk J Biochem] 2011; 36 (2) ; 93–101.

Research Article [Araştırma Makalesi]

Caulerpa scalpelliformis as an antibiotic carrier

[Antibiyotik Taşıyıcısı olarak *Caulerpa scalpelliformis*]

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Registered: 10 May 2010; Accepted: 31 January 2011

[Kayıt Tarihi : 10 Mayıs 2010; Kabul Tarihi : 31 Ocak 2011]

ABSTRACT

Aim: Excreted tetracycline via urine and feces of animals is an important ecological problem since microorganisms in soils can change their genetic structures to be resistant against tetracycline. Therefore, uncontrolled release of this antibiotic to environment should be prevented. Biosorption of tetracycline by *Caulerpa scalpelliformis,* alien seaweed for Turkish coastlines, was studied in the present study.

Methods: Kinetics (pseudo first order, pseudo second order), isotherm (Langmuir, Freundlich and Dubinin- Radushkevich) and thermodynamics models were applied to the biosorption data.

Results: Pseudo-second-order model was fitted well with the sorption data compared to pseudo-first-order model. Langmuir, Freundlich and Dubinin-Radushkevich (DR) isotherm models were also investigated. The energy values related to DR at 293, 308 and 323 K were found as 0.224, 0.845 and 1.291 kj/mol, respectively. These values revealed that biosorption process is in physical nature. According to DR model, the maximum adsorption capacity was found as 3.171 mg/g at 308 K. Thermodynamic parameters such as entropy, enthalpy and free energy values showed that biosorption process was endothermic and was not spontaneous.

Conclusion: *C.scalpelliformis* could be used as a low-cost biomaterial for biosorption of tetracycline from aqueous solutions and also its tetracycline immobilised form could be evaluated as an animal food.

Conflict of Interest: Authors did not declare any conflict of interest.

Keywords: Antibiotics, biosorption, *Caulerpa scalpelliformis,* tetracycline, waste water treatment.

ÖZET

Amaç: Hayvan dışkı ve idrarları yoluyla çevreye salınan tetrasiklin, topraktaki mikroorganizmaların bu antibiyotiğe dirençli hale gelmeleri için genetik yapılarını değiştirebileceğinden ötürü ekolojik bir problemdir. Bu nedenle, bu antibiyotiğin çevreye kontrolsüz salınımı önlenmelidir. Bu çalışmada, Türk kıyıları için yabancı bir deniz yosunu olan *Caulerpa scalpelliformis* üzerine tetrasiklin biyosorpsiyonu çalışılmıştır.

Metod: Kinetik (yalancı birinci ve ikinci mertebe), izoterm (Langmuir, Freundlich ve Dubinin- Radushkevich) ve termodinamik modeller biyosorpsiyon verileri üzerine uygulanmıştır.

Bulgular: Yalancı ikinci mertebe modeli, yalancı birinci mertebe modeline kıyasla sorpsiyon verileri ile daha iyi uyum göstermiştir. Aynı zamanda Langmuir, Freundlich ve Dubinin-Radushkevich (DR) izoterm modelleri de incelenmiştir. DR ile ilgili 293, 308 ve 323 K'deki enerji değerleri sırasıyla 0.224, 0.845 ve 1.291 kj/mol olarak bulunmuştur. DR modeline göre maksimum adsorpsiyon kapasitesi 308 K'de 3.171 mg/g olarak bulunmuştur. Entropi, entalpi ve serbest enerji gibi termodinamik parametrelere ait değerler biyosorpsiyon işleminin endotermik ve istemsiz olduğunu göstermiştir.

Sonuç: *C.scalpelliformis*, sulu çözeltilerden tetrasiklin biyosorpsiyonu için düşük maliyetli biyomateryal olarak kullanılabilir ve ayrıca tetrasiklin immobilize edilmiş formu hayvan yemi olarak değerlendirilebilir.

Anahtar Kelimeler: Antibiyotikler; biyosorpsiyon; *Caulerpa scalpelliformis;* tetrasiklin; atık su arıtımı.

Introduction

Tetracycline is one of the most widely used antibiotics in human and animals all around the world. Its unabsorbed version or so called excreted tetracycline can be released to the environment via feces and urines of animals. Uncontrolled release of tetracycline can cause deleterious effects on human or ecosystem health since the soil microorganisms can develop resistance against this antibiotic if they are exposed to tetracycline in their environment [1]. Therefore, the uncontrolled release of tetracycline to environment especially soil should be prevented or novel strategies should be developed to remove it from waste waters to protect ecosystem health. Within five years, many different materials to solve this environmental problem have been reported in scientific literature. These are activated carbon, silica, clays, iron oxide, oxide-rich soils, iron oxides-coated quartz, rectorite, palygorskite, biosolids, La-impregnated MCM-41 materials, carbon nanotubes, aluminium oxide, cinnamon soil and mesoporous Fe/carbon composites [1-13].

Members of *Caulerpa* genus are of important inasmuch as their possible potential uses related to industrial areas have been reported in many scientific papers. So far, *Caulerpa* species have been used in many biosorption studies as biosorbents [14-16]. Due to their high biosorptive capacities of dried and modified forms of *Caulerpales* on some metals and dyes, over-produced biomass of invasive members of *Caulerpales* could be utilized in the biosorption of various hazardous materials from environment which includes tetracycline. *Caulerpa scalpelliformis* (Brown ex Turner) C. Agardh (Caulerpaceae, Chlorophyceae) is an alien seaweed for Turkish coastline and it has been recently re-observed in Antalya coastlines.

The below research questions are answered in the present paper: Can dried biomass of *C.scalpelliformis* be used in the removal of tetracycline from aqueous solutions? What are the possible advantages of tetracycline immobilized *C.scalpelliformis* biomass compared to other published adsorbent agents for tetracyline?

Materials and Methods

Biosorbent and its preparation

Caulerpa scalpelliformis (Brown ex Turner) C. Agardh (Caulerpaceae, Chlorophyceae) was collected from Antalya harbor by SCUBA diving. The algae material was put into plastic barrel with fresh sea water. After collecting algal samples from the sea, it was firstly washed with seawater then with distilled water several times to remove some impurities and salty water, respectively. The washed material was dried at 65°C for 16 hours. Then dried material was ground by mortar and pestle followed by mechanical blender. 500 µm particle sized material was used for adsorption studies. In order to prevent possible interference substances from *C. scalpelliformis*, the dried materials were shaken in distilled water at 65°C until no substance was observed at 276 nm since the determination of tetracycline was based on the absorbance measurement at 276 nm.

Preparation of tetracycline solution

Tetracycline hydrochloride from Sigma (T-3383) was used without purification. Stock solution of tetracycline was prepared by using distilled water and its concentration was adjusted as 200 mg/l. Four different antibiotic concentration (2.4 mg/l, 4.8 mg/l, 9.6 mg/l, and 19.2 mg/l) were prepared from stock solution by using distilled water for proper dilution.

Biosorption experiments

Biosorption studies were carried out to obtain the equilibrium data. The experiments were performed at different temperatures (293, 308 and 323 K). Adsorbent dosage was 0.2 g and pH was 7.0 in the experiments at 308 K. Polyethylene vessels were filled with 30 ml of various concentrations of tetracycline solutions and 0.2 g dried and pre-treated *C. scalpelliformis* was added. The solutions were agitated at 170 rpm, in a temperature controlling shaker (GFL 1092) for three hours. The samples were centrifuged at 10000 rpm for 10 minutes. Tetracycline concentrations in supernatants were measured by using Shimadzu UV-Visible 1601 model spectrophotometer at 276 nm. The amount of tetracycline adsorbed onto *C. scalpelliformis* at equilibrium was calculated by using the equation as shown below:

$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of tetracycline (mg/l), respectively. q is the amount of tetracycline biosorbed onto *C. scalpelliformis* at equilibrium (mg/g), V is the volume of the tetracycline solution (L) and m is the amount of the adsorbent used (g).

Results and Discussion

Effect of pH on the biosorption of tetracycline onto C. scalpelliformis

The effect of pH on the biosorption of tetracycline onto *C. scalpelliformis* was shown in Figure 1. As can be seen from Figure 1, although there was an increasing trend starting from pH 3.0 to pH 9.0, the values were not remarkably different. No strong effect of pH was observed for biosorption of tetracycline on biomass of *C. scalpelliformis.* On the other hand, strong effect of pH was reported by Turku et al. [2] for silica and tetracycline interaction. Tetracycline is composed of different functional groups: tricarbonylamide (pKa: 3.3), phenolic diketone (pKa: 7.68) and dimethylamine (pKa: 9.69) [9]. Higher biosorption values observed around pH 7.0 could be explained with the existence of zwitterionic form of tetracycline at this pH. Therefore, weak physical interactions such as van der Waals could be considered for the biosorption process for tetracycline - *C. scalpelliformis*.

Effect of biosorbent dosage on biosorption of tetracycline onto C. scalpelliformis

In order to observe the effect of biosorbent dosage on the tetracycline biosorption by *C. scalpelliformis*, different amounts of biomass (0.05, 0.1, 0.2, 0.5, 1 g) were added to 30 mL tetracycline (9.6 mg/L) containing polyethylene vessels. The results were depicted in Figure 2. While tetracycline biosorbed amount increased dependent on the adsorbent dosage, the tetracycline concentration at equilibrium decreased with increasing biosorbent dosage.

Effect of the contact time and temperature on the biosorption of tetracycline onto C. scalpelliformis

The effect of contact time at 308 K was investigated in the present study. The results were given in Figure 3. The different initial tetracycline concentrations were agitated at 170 rpm for three hours at 293 and 323 K. The results showed that biosorption reached equilibrium after 90 minutes for all concentrations. A slight increase was observed for q values at 90 min as 1.049 mg/g, 1.179 mg/g, 1.216 mg/g for 293, 308 and 323 K (9.6 mg/L initial concentration), respectively. When the equilibrium time was considered, lower equilibrium time was observed for *C. scalpelliformis* compared to other published adsorbents for tetracycline [1-13]. Lower equilibrium time can be considered as an important property for *C.scalpelliformis* compared to other materials.

Biosorption kinetics

The determination of adsorption kinetics is of importance because the kinetic approaches provide information about adsorption capacity and rate of the reaction. Two kinetic models (pseudo-first-order kinetic model and pseudo-second-order kinetic model) were used to evaluate the experimental data.

Linear form of pseudo-first-order model is expressed as:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

where q_e and q are the amount of tetracycline adsorbed at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant (1/min) (17). The linear plot of log (q_e-q) versus t was composed and the values of q_e and k_1 were determined from the intercept and the slope of the plot, respectively (Figure 4). Pseudo-first-order parameters were given in Table 1.

The widely used linear form of pseudo-second-order equation is expressed as:

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

where k_2 is the pseudo-second-order rate constant (g/mg.min). This model expresses the chemisorption behavior of the reaction [18].

To find the q_e and k_2 values of pseudo-second-order equation, the slope and the intercept of the linear plot of t/q *versus* t were calculated, respectively (Figure 5). The results related to pseudo second order kinetics were given in Table 2.

As it is shown in Table 1 and 2, the highest R^2 values were found in pseudo-second-order kinetic model. On the other hand, the R^2 values of pseudo-first-order model at 323 K were also higher than those of other temperature values (Table 1). The interaction between tetracycline and *C.scalpelliformis* could be explained with the pseudo-second order kinetic model because of high R^2 values. On the other hand, pseudo-second order model supports chemisorption. However, since heterogeneous functional groups of *C.scalpelliformis* are existed on the surface of this seaweed, more support was needed for biosorption mechanisms between *C.scalpelliformis* and tetracycline. In following parts of this paper, energy values obtained from Dubinin-Radusckevich equation were also studied for this problem.

Adsorption isotherms

Three adsorption models, Langmuir, Freudlich and Dubinin-Radusckevich were applied to biosorption data to obtain maximum biosorption capacities.

Langmuir isotherm

A monolayer adsorption characteristic can be explained by the Langmuir isotherm. The linear form of the Langmuir model is given by the following equation ([19].

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m} \cdot \frac{1}{C_e} \qquad (4)$$

where q_m shows the monolayer adsorption capacity (mg/g), b Langmuir constant (L/mg), C_e equilibrium concentration of adsorbate in the solution (mg/l) and q the solid phase concentration of adsorbate at equilibrium (mg/g). Since R^2 values were lower than those of other isotherm models and also negative values of q_m calculated we considered as the Langmuir model as it is not appropriate to express the biosorption data (Table 3).

Freundlich isotherm

The Freundlich equation suggests a multilayer adsorption. Expressions of the non-linear and linear versions of the model can be written as follows [20]:

$$q = K_f C_e^{1/n} \qquad (5)$$

$$\log q = \log K_f + \frac{1}{n} \log C_e \qquad (6)$$

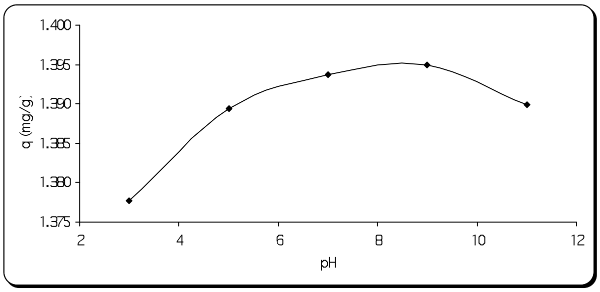

Fig. 1. Effect of pH on tetracycline biosorption by *C. scalpelliformis* at 308 K (initial tetracycline concentration: 9.6 mg/L).

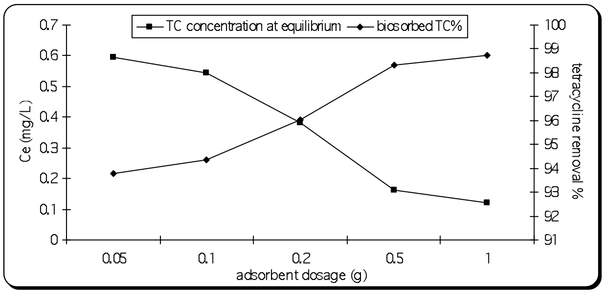

Fig. 2. Effect of adsorbent dosage on tetracycline biosorption by *C. scalpelliformis* at 308 K (initial tetracycline concentration: 9.6 mg/L).

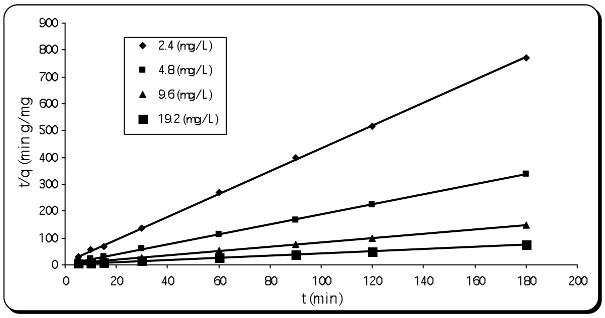

Fig. 5. Pseudo-second-order kinetics of tetracycline biosorption by *C.scalpelliformis* at various tetracycline concentrations at 308 K (Adsorbent dose = 0.2 g).

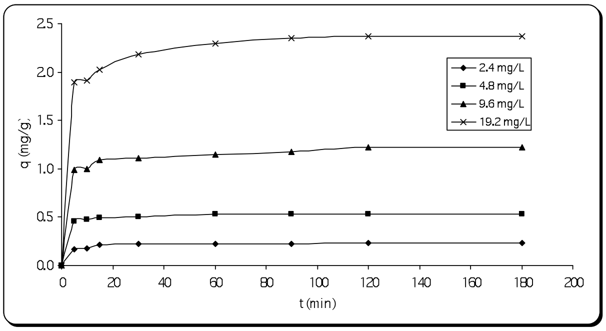

Fig. 3. Time and concentration dependent biosorption of tetracycline by *C. scalpelliformis* at 308 K. The values are the mean of three separate experiments.

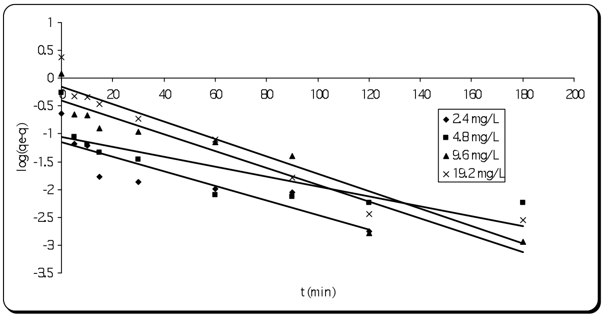

Fig. 4. Pseudo-first order kinetics of tetracycline biosorption by *C. scalpelliformis* at different initial tetracycline concentrations at 308 K (Adsorbent dose = 0.2 g).

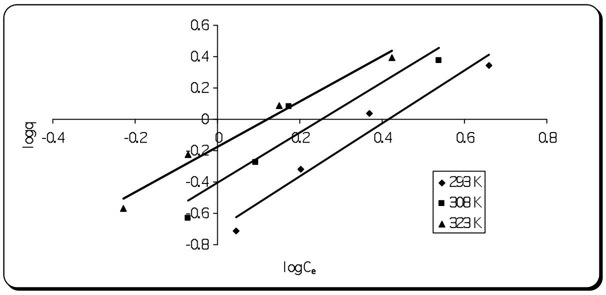

Fig. 6. Freundlich isotherm plots for the biosorption of tetracycline by *C.scalpelliformis*.

Table 1. Pseudo-first-order kinetic parameters for the biosorption of tetracycline by *C. scalpelliformis* at 293, 308 and 323 K.

Pseudo first order parameters												
Ci (mg/L)	qe, exp (mg/g)			k^1 (1/min)			qe, cal (mg/g)			R^2		
	293 K	308 K	323 K	293 K	308 K	323 K	293 K	308 K	323 K	293 K	308 K	323 K
2.4	0.234	0.072	0.185	0.018	0.030	0.061	0.194	0.233	0.271	0.895	0.785	0.965
4.8	0.438	0.089	0.398	0.120	0.021	0.056	0.482	0.535	0.592	0.895	0.676	0.993
9.6	0.887	0.397	0.920	0.083	0.035	0.050	1.092	1.219	1.232	0.944	0.890	0.949
19.2	1.769	0.698	2.549	0.145	0.036	0.036	2.200	2.367	2.487	0.913	0.914	0.921

Table 2. Pseudo-second-order kinetic parameters for the biosorption of tetracycline by *C. scalpelliformis* at 293, 308 and 323 K.

Pseudo second order parameters												
Ci (mg/L)	qe, exp (mg/g)			k_2 (g/mg.min)			h (mg/g.min)			R^2		
	293 K	308 K	323 K	293 K	308 K	323 K	293 K	308 K	323 K	293 K	308 K	323 K
2.4	0.235	0.236	0.283	0.141	1.661	0.464	0.008	0.092	0.037	0.987	0.999	0.999
4.8	0.526	0.539	0.615	0.143	1.488	0.289	0.039	0.433	0.109	0.998	1.000	1.000
9.6	1.182	1.232	1.272	0.066	0.317	0.159	0.093	0.480	0.258	0.998	0.999	1.000
19.2	2.389	2.402	2.613	0.034	0.176	0.051	0.195	1.017	0.351	0.998	0.999	1.000

Table 3. The calculated equations for adsorption isotherms.

	293 K	308 K	323 K
Langmuir-Linear Form $\frac{1}{q}=\frac{1}{bq_m}\cdot\frac{1}{C_e}+\frac{1}{q_m}$	y = 6.9357x - 1.6231 R^2 = 0.9095	y = 4.4198x - 1.3983 R^2 = 0.8703	y = 2.4781x - 0.803 R^2 = 0.944
Freundlich-Linear Form $\log q=\frac{1}{n}\log C_e+\log K_f$	y = 1.6909x - 0.7015 R^2 = 0.9548	y = 1.592x - 0.4049 R^2 = 0.8860	y = 1.4453x - 0.176 R^2 = 0.9797
Freundlich-Nonlinear Form $q=K_fC_e^{1/n}$	$y = 0.1989x^{1.6909}$ R^2 = 0.9548	$y = 0.3936x^{1.592}$ R^2 = 0.8860	$y = 0.6666x^{1.4453}$ R^2 = 0.9797
Dubinin-Radushkevich-Linear Form $\ln q_e=-B\varepsilon^2+\ln q_m$	$y = -1.10^{-6}x + 0.9472$ R^2 = 0.9891	$y = -7.10^{-7}x+ 1.1542$ R^2 = 0.9668	$y = -3.10^{-7} + 1.0337$ R^2 = 0.9848
Dubinin-Radushkevich-Nonlinear Form $q_e=q_m\exp^{-B\varepsilon^2}$	$y = 2.5785e-1.10^{-6}x$ R^2 = 0.9891	$y = 3.1714e-7.10^{-7}x$ R^2 = 0.9668	$y = 2.8115e-3.10^{-7}x$ R^2 = 0.9848

Table 4. Freundlich isotherm constants for the biosorption of tetracycline by *C. scalpelliformis* at 293, 308 and 323 K.

Freundlich constants				
Temperature (K)	K_f	n	1/n	R^2
293	0.199	0.591	1.691	0.9548
308	0.394	0.628	1.592	0.8860
323	0.667	0.692	1.445	0.9797

where K_f shows the relative adsorption capacity, 1/n is a constant related to adsorption intensity. These values were obtained from plotting logq versus $\log C_e$. The calculated equations were shown in Table 3 and the Freundlich plot and the related values were shown in Figure 6 and Table 4, respectively. According to results, the K_f values tented to be increase depending on temperature values. If 1/n value is lower than 1, it can be considered as the existence of a strong interaction between adsorbent and adsorbate [21, 22].

Dubinin-Radushkevich (DR) isotherm

One of the important and widely used isotherms is DR model and it is shown as follows [23-25]:

$$q_e = q_m \exp^{-B\varepsilon^2} \tag{7}$$

$$\ln q_e = \ln q_m - B\varepsilon^2 \tag{8}$$

where q_e is the amount of adsorbed tetracycline onto *C. scalpelliformis* per unit weight (mg/g); q_m represents the adsorption capacity; B is the constant related to the adsorption energy (mol^2/kj^2); ε the Polanyi potential which can be obtained as follow:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{9}$$

where C_e is the equilibrium concentration of tetracycline (mg/L), R is ideal gas constant (8.314 J/mol K) and T is the temperature (K). The linear and nonlinear plots of DR equations were shown in Figure 7 and 8. The DR equations at different temperatures were also shown in Table 3. DR model parameters, q_m, B and R^2 were shown in Table 5. The mean free energy can be calculated from the constant B by using the following equation [25-27]:

$$E = \frac{B^{-1/2}}{\sqrt{2}} \tag{10}$$

B values are obtained from the slope of the plot between $\ln q_e$ and ε^2 (for linear equation of DR). The energy values related to equation 10 were presented in Table 5. According to literature, energy value lower than 8 kj/mol is considered to be obeyed van Der Waals forces [28-30]. Energy values in the present study were found in the range of 0.224-1.291 kj/mol and therefore this range showed the weak physical forces between *C. scalpelliformis* biomass and tetracycline. Weak physical forces between tetracycline and *C. scalpelliformis* can provide advantage in the digestive tract for easy release if *C.scalpelliformis* is considered as a tetracycline carrier.

Thermodynamic Parameters

Thermodynamic parameters related to biosorption of tetracycline onto *C. scalpelliformis* were calculated by using below equations:

$$\ln K_d = \frac{-\ H}{R}\frac{1}{T} + \frac{S}{R} \tag{11}$$

$$K_d = \frac{C_s}{C_e} \tag{12}$$

To calculate the ΔG value, two different equations [13-14] were used:

$$\Delta G \ = \Delta H \ - T\Delta S \tag{13}$$

$$G = -RT\ln K_d \tag{14}$$

where K_d is equilibrium constant for adsorption, C_s the amount of the tetracycline adsorbed at equilibrium (mg/g), C_e equilibrium concentration of tetracycline (mg/L), R is ideal gas constant (8.314 J/mol K), T temperature (K). The value of $\ln K_d$ was plotted versus 1/T (Figure 9). The values of enthalpy and entropy changes were calculated from the graph and the results were summarized in Table 6. The positive values of enthalpy (ΔH) agree the endothermic nature of adsorption and the positive values of entropy (ΔS) present the increased randomness. Additionally, the negative values of free energy (ΔG) imply that the biosorption occurs spontaneously. However, we have found positive free energy values that mean biosorption does not occur spontaneously. On the other hand, the free energy values decreased dependent on both increases in the temperature and initial tetracycline concentrations. The free energy values at the initial tetracycline concentration at 19.2 mg/L for 323 K were obtained as 0.292 kj/mol and 0.183 kj/mol and these values were so close to negative. *C.scalpelliformis* is an alien species for Turkish coastlines. Observation of this species in the Antalya coastlines with small groups about 5x5 m^2 covered areas motivated us to find an evaluation method for this alien species instead of collecting and burning it. Release of antibiotics without treatment to environment is of great problem in recent years and damage microorganisms of the soil and also increases the resistance of pathogenic microorganisms. *C.scalpelliformis* like other members of *Caulerpa* genus has important vitamins and trace metals for animal health and antibiotic loaded biomass of *Caulerpa scalpelliformis* could be used as an antibiotic carrier because of its biodegradable property. Although Gokoglu et al (2010) have observed this species in wider areas compared to previous invasion, the distribution of this species should be followed seasonally [31]. To compare the sorption capacity of *C. scalpelliformis* with other published adsorbents developed for tetracycline, Table 7 was created. Although biosorption capacity of the present biomass was lower than those of the published materials, *C. scalpelliformis* may have advantages in the view of biodegradability, lower equilibrium time and being a natural adsorbent. DR equation was applied to biosorption data to understand the behavior of sorption. The energy values related to Dubinin-Radushkevich equation at 293 K, 308 K and 323 K were found as 0.224, 0.845 and 1.291 kj/mol, respectively. These values revealed that biosorption process was in physical nature. According to DR model, the maximum adsorption capacity was found as 3.171 mg/g at 308 K. Thermodynamic parameters such as entropy, enthalpy and Gibbs free energy values showed that the biosorption process was endothermic and unspontaneous.

There have been growing interests on the adsorption of tetracycline from aqueous solution for last five years. Reason of this recent attention is that up to 80% unabsorbed tetracycline by digestive tract of animals can be excreted easily via urine and feces to the environment. This excreted tetracycline can result in deleterious effects in especially microorganisms and plants [12]. Therefore, the recent published papers were reviewed and results of published papers were also compared with the results of present study (Table 7).

Choi et al (2008) have studied the removal of tetracycline and sulfonamide from deionized and DOC wa-

Table 5. Dubinin-Radushkevich (DR) isotherm constants for the biosorption of tetracycline by *C. scalpelliformis* at 293, 308 and 323 K.

Dubinin-Radushkevich constants				
Temperature (K)	qm (mg/g)	Bx10^{-7} (mol^2/j^2)	E (kj/mol)	R^2
293	2.578	10.0	0.224	0.9891
308	3.171	7.0	0.845	0.9668
323	2.811	3.0	1.291	0.9848

Table 6. Thermodynamic parameters of tetracycline biosorption by *C. scalpelliformis* at 293, 308 and 323 K.

			ΔG (kJ/mol)		
Concentration of tetracycline (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	293 K	308 K	323 K
2.4	25.275	0.072	4.179[1]	3.099[1]	2.019[1]
			4.238[2]	3.303[2]	2.089[2]
4.8	21.638	0.064	2.886[1]	1.926[1]	0.966[1]
			2.906[2]	2.151[2]	0.980[2]
9.6	16.693	0.051	1.750[1]	0.985[1]	0.220[1]
			1.859[2]	0.520[2]	0.360[2]
19.2	17.411	0.053	1.882[1]	1.087[1]	0.292[1]
			1.783[2]	0.973[2]	0.183[2]

[1,2] ΔG values were determined by ΔG = ΔH–TΔS and ΔG = -RT lnK, respectively.

Table 7. Comparison of maximum adsorption capacities of various materials for tetracycline

Adsorbent	Temperature	pH	Equilibrium contact time	qm	Isotherm type	References
Palygorskite	313	8.7	24 hours	99 mg/g	Langmuir	Chang et al (2009)
Rectorite		4-5	24 hours	140 mg/g	Langmuir	Chang et al (2009)
Iron-oxides-coats quarts	333	5.5±0.2	800 min	4 (mmol/m^2)	Langmuir	Tanis et al (2008)
Silica	296	4.0		16.5 (mol/L)	Langmuir	Turku et al (2007)
Powdered activated carbon	298	7.0	24 hours	7.8 µg/L (at 1 mg/L carbon dosage)	---	Choi et al (2008)
Aerobically digested biosolid	296	6.9 (biosolid)	24 hours	3982±751 µg^{1-n}. mL^n .g^{-1}	Freundlich	Wu et al (2009)
La-impregnated MCM-41	298	7.0	36 hours	303.3 mg/g	Langmuir	Vu et al (2010)
Carbon nanotubes (KOH activated SWNT)	298	6.0	72 hours	1400±300 mmol^{1-n}.L^n .kg^{-1}	Freundlich	Ji et al (2010)
Aluminum oxide	295	5.0	24 hours	~40% of initial tetracycline (20-110 µM)	---	Chen and Huang (2010)
Cinnamon soil	298	5-7	24 hours	1095±154.4 L/kg	Freundlich	Wan et al (2010)
Sediment clay	298	8.91	24 hours	0.860 L/g	Freundlich	Wang et al (2010)
Fe/carbon composite (Fe/OMC-100)	310	---	24 hours	428 mg/g	---	Yuan et al (2009)
C. scalpelliformis	308	6.8	90 min	3.2 mg/g	D-R	Present study

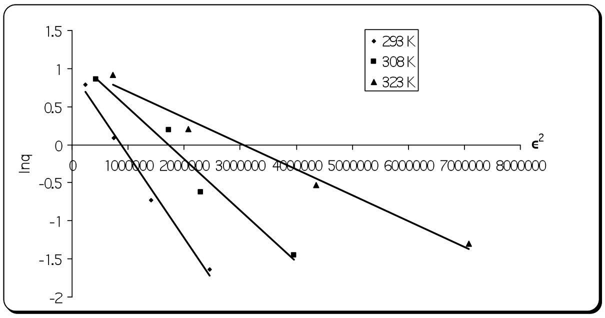

Fig. 7. Plots of Linear version of Dubinin-Radushkevich isotherm for the biosorption of tetracycline by *C.scalpelliformis*.

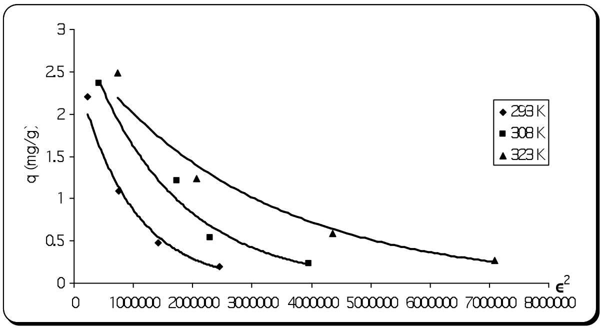

Fig. 8. Non-linear form of Dubinin-Radushkevich isotherm for the biosorption of tetracycline by *C. scalpelliformis*.

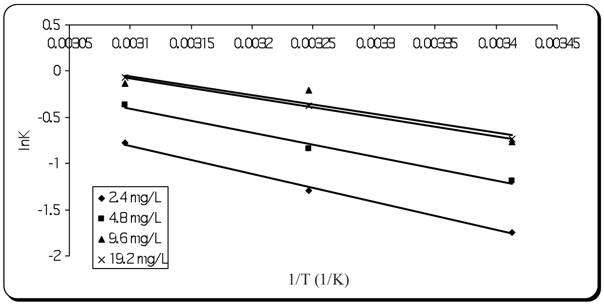

Fig. 9. Plots of $\ln K_d$ versus 1/T for the biosorption of tetracycline by *C. scalpelliformis* at different tetracycline concentrations.

ter by powdered activated carbon. Removal efficiency of tetracycline from deionized water was higher than sulfonamide's. Removal percentage of tetracycline at 0.3 mg/L coal carbon addition was in the range of 78-97% [1]. Wu et al (2009) have investigated the sorption and degradation of six antibiotics including tetracycline by an aerobically digested biosolid. Adsorption and desorption isotherms were fitted well with experimental data by using Freundlich and linear equations. Wu et al (2009) have reported that sorption of TC onto biosolid was strong according to K_d values [8]. Vu et al (2010) have studied the adsorption of tetracycline onto La-impregnated MCM-41 support material. Adsorption capacity of support material was increased by La impregnation compared to raw material and increasing loading amount. From the Langmuir isotherm data, maximum adsorption capacity for tetracycline was found as 303.3 mg/g [9]. Ji et al (2010) have investigated the adsorption of model monoaromatic compounds and pharmaceutical antibiotics including tetracycline onto activated carbon nanotubes which were prepared by KOH dry etching. According to results of Ji et al (2010)'s study, adsorption data was well in line with Freundlich isotherm. Adsorptions of test solutes onto activated carbon nanotubes were higher than that of pristine carbon nanotubes due to high K_d values [10]. Wang et al (2010) have studied the sorption of tetracycline onto clay and marine sediment at different pHs, salinities and temperatures. Freundlich isotherms for different sorbents were fitted well with experimental data. Results of Wang et al (2010)'s study were showed that tetracycline sorption was decreased with increasing pH and salinity [32]. In another study on the removal of tetracycline from aqueous solutions [12], Wan et al (2010) have investigated the adsorptive property of cinnamon soil. Cinnamon soil was in this study was collected from forest park in the Tianjin Economic-Technological Development Area (TEDA) in northern China where no antibiotic application or contamination was reported. It was very interesting to note that the while K_f values of tetracycline biosorption was 1095, it is increased to 1305 in presence of Cd [12]. Yuan et al (2009) have recommended Fe/carbon composites (Fe/OMC-100) as a possible tetracycline carrier because of their high adsorption capacity [13].

Conclusion

In order to remove tetracycline from aqueous solutions, dried biomass of *C. scalpelliformis* was used in the present study. According to results, tetracycline has a weak affinity to bind biomass of *C. scalpelliformis* therefore van der Waals interaction can be considered between biosorbent and tetracycline. Although it seems that *C.scalpelliformis* is not a strong adsorbent for tetracycline when compared to other developed adsorbents for this purpose, this weak interaction can be important for desorption of tetracycline from *C.scalpelliformis* in animal metabolism for easy release. Another advantage of *C.scalpelliformis* can be its biodegradable structure compared to other published materials for tetracycline adsorption. In addition, as a member of *Caulerpa* genus, *C.scalpelliformis* has important trace elements and minerals which could be necessary for animal growth and health [16]. For example, caulerpenyne, a secondary metabolite of *Caulerpa* genus, has many functional properties on metabolism [16]. Therefore, antibiotic loaded *C.scalpelliformis* could be a food supplement for animals, since the tetracycline can be desorbed easily from biomass because of the physical nature of biosorption. So far, seven *Caulerpa* taxa have been reported from Turkish coastlines. Among them, *C.racemosa* var.*cylindracea* and *C.taxifolia* are invasive members of *Caulerpa* genus in Turkey as well as *C.scalpelliformis*. Since their high productions, proliferations and also ecological side effects under the water have been reported many scientific papers [16], they can also be considered as tetracycline adsorbents after a possible and a valid manual uprooting based eradication method on invasive *Caulerpa* strains. To the best of our knowledge, this is the first scientific contribution on the biosorption of tetracycline by using an eco-friendly material, *C.scalpelliformis*. In conclusion, *C.scalpelliformis* could be used as a low-cost material for biosorption of tetracycline from aqueous solutions and this research could be model for other possible over produced seaweed biomass.

Conflict of Interest

Authors did not declare any conflict of interest.

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