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PROOF RESEARCH PAPER

Artificial Neural Network Modeling of Tetracycline Biosorption by Pre-treated *Posidonia oceanica*

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Abstract

Importance of the artificial intelligence in the chemical processes has been increased in the recent studies. Although biosorption is widely studied topic in chemistry, modelling of biosorption data is based on very old equations. However, use of artificial intelligence in the biosorption based studies can give important clues to researchers. For this purpose, the biosorption of tetracycline by using *Posidonia oceanica* from the Mediterranean Sea was studied in this study. According to classical evaluation, the data were well in line with pseudo-second order kinetic and Langmuir's isotherm. In the artificial neural network modelling, the best back propagation algorithm, optimum number of hidden neuron and optimum training:validation:testing ratio were found as Bayesian Regulation, 16 and 70:10:20, respectively. In conclusion, *P. oceanica* based marine waste can be used in the development of high performance biosorbents for environmental pollutants. However, it should not be forgotten that *P.oceanica* is a threatened species; therefore, only dead leaves accumulated in recreational area should be collected and evaluated based on the permissions of governmental authorities. The results also exhibited that artificial neural network can also be used in the modelling of the biosorption data in which it helps scientists to estimate biosorption ratio correctly under various conditions.

Keywords: Adsorption, Artificial neural network, Posidonia oceanica (L.), Tetracycline.

Introduction

Posidonia oceanica Linnaeus Delile (order: Posidoniaceae) is an endemic marine plant in the Mediterranean Sea. *P. oceanica* is of paramount importance for the ecosystem of the Mediterranean Sea (Montefalcone, 2009). *P. oceanica* falls off its leaves seasonally like terrestrial plants and the dead leaves of *P. oceanica* are accumulated on the beaches. These marine based wastes cause aesthetic and hygienic problems in the touristic beaches (Cengiz & Cavas, 2010). Thus, these dead leaves are collected and burned to keep beaches clean (Cavas & Mert, 2013). It was reported that *P. oceanica* contains many organic compounds in its dead leaves. These compounds have many important properties such as antifungal, antibacterial, antioxidant, antidiabetic activities (Bernard & Pesando, 1989; Ballesteros, Martin, & Uriz, 1992; Gokce & Haznedaroğlu, 2008; Kartal *et al*., 2009). In the scientific literature, the dead leaves of *P. oceanica* were used as a biosorbent in order to remove the different hazardous material from aqueous solutions (Cengiz & Cavas, 2010; Pinzon *et al*., 2004; Ncibi, Mahjoub, & Seffen, 2006; Chadlia, & Farouk, 2007; Álvarez-Hornos, Gabaldón, & Izquierdo, 2008; Ncibi, Mahjoub, Mansour, Hamissa & Seffen, 2009; Cavas & Gokoglu, 2011; Aydin, Cavas & Merdivan, 2012; Douissa, Dridi-Dhaouadi & Mhenni, 2014). In adsorption literature, generally raw form of these dead leaves (just washed and dried) has been used. But the washed and dried dead leaves contain organic compounds, thus the capacity of adsorption could be limited. Moreover, the organic compounds can be released from these dead leaves to aqueous solutions. Therefore, after extraction of these bioactive molecules, the residue of the pre-treated dead leaves of *P. oceanica* could be used as a high-capacity biosorbent. Antibiotics are generally microbial agents that are used in the treatment of pathogenic microorganisms for health of animals and human. In order to decrease infections in farm animals, antibiotics is used in therapeutic levels (Dasenaki & Thomaidis, 2015). Unfortunately, the therapeutic dosage has been increased because of resistant microorganisms. The increased dosage of antibiotics used in livestock is released to the ecosystem though via urine or faeces of animals (Sarmah, Meyer & Boxall, 2006). The removal of

antibiotics is occurred through biological processes in wastewater treatment plants (Yahiat, Fourcade, Brosillon, & Amrane, 2011). The effluent of wastewater treatment plant is transferred to rivers and streams through discharge. If antibiotics in effluent are not treated, the antibiotics can contaminate the water sources (Halling-Sørensen *et al*., 1998). Especially some types of antibiotics in nature have very long half-life. However, the antibiotics stayed very long-term in nature are caused development of resistant bacterial strains (Heberer, 2002; Hirsch, Ternes, Haberer, & Kratz 1999; Kümmerer, 2003; Turkdogan & Yetilmezsoy, 2009). In the survey of Animal Health Institute (AHI) in the USA in 2007 was reported that approximately 12.6 million kilograms of active antibiotic ingredients has been sold. Moreover, in 2007, AHI members reported that the most consumed antibiotics are tetracyclines at a rate of 39% in veterinary medicine (Mojica & Aga, 2011). Many reports have been published in the literature regarding the detection of antibiotics in seawaters. As examples, Chen *et al* (2015) investigated 38 different antibiotics levels in seawater from Hailing Bay region, South China Sea. They reported the level of oxytetracycline as 15,163 ng/L. Liu *et al* (2016) also studied oxytetracycline in sediments from Bohai Sea in China and surrounding estuaries. The maximum level of oxytetracycline was reported as 4695 µg/kg by Liu *et al* (2016). According to a recent review, the levels of antibiotics in aquatic ecosystem are in a range from ng/L to µg/L (Carvalho & Santos, 2016). Artificial Neural Networks (ANN) is a kind of non-traditional modelling method to classify and recognize the data like human learning system (Hassoun, 1995). In order to solve the non-linear regression data obtained from experiments, ANN is one of the most frequently used methods. The researchers in adsorption field use ANN in the optimization studies. Generally, this method is used to model adsorption capacity as an output parameter. In the present study, we targeted to perform the adsorption of tetracycline from aqueous solutions by using the pre-treated dead leaves of *P. oceanica* as a biosorbent. In this study, we also aimed to model the adsorption data by using ANN.

Materials and Methods

Chemicals and Equipment

Ethanol (Tekkim, 99%), HCl (Merck, 37%), NaCl (Merck, 99.5%), NaOH (Riedel-de Haen, Sigma-Aldrich, 99-100.5%) and Tetracycline hydrochloride (Sigma-Aldrich, T-3383, CAS: 64-75-5) were obtained commercially. Magnetic stirrer, ultrasonic cleaner (Medisson, ultraconic cleaner), vortex (ISOLAB, Labogerate GmbH), temperature controlling shaker (GFL 1086 model), centrifuge (Hettich, D-78532), UV-VIS spectrophotometer (T80+UV/VIS Spectrophotometer, PG Instruments), FT-IR (Perkin-Elmer, Spectrum BX) were used.

Preparation of Adsorbent and Adsorbate

The collection of dead leaves of *P. oceanica* was performed from Dikili coast, İzmir. The official permission was taken from Ministry of Food, Agriculture and Feedstock. Then the dead leaves of *P. oceanica* washed by using pure water. After washing process, the dead leaves of *P. oceanica* were dried at 25 K. The dried leaves were ground with a grinder. The maximum particle size of the dead leaves for adsorption studies was 500 µm. Up to now, untreated *P. oceanica* dead leaves have been used as an adsorbent in the literature (Cengiz & Cavas, 2010, Pinzon *et al*, 2004; Cavas & Gokoglu, 2011; Aydin *et al*, 2012; Dural, Cavas, Papageorgiou, & Katsaros, 2011; Krika, Azzouz, & Ncibi, 2012). However, in the present study, a pre-treatment procedure was carried out. In order to remove the organic compounds in the dead leaves, the ground *P. oceanica* was extracted according to the method of Cuny, Serve, Jupin, & Boudouresque (1995) with some modification. Briefly, the dead leaves of *P. oceanica* were extracted for 3 h in 200 ml of aqueous ethanol (50% (v/v)) at 40°C. Then, the extracted dead leaves of *P. oceanica* washed by using pure water in order to remove the impurities. After extraction, the pre-treated *P. oceanica* (ptPO) residues were dried at room temperature. In all adsorption experiments, the dried dead leaves and pre-treated of *P. oceanica* were used. A 1000 mg/L solution of tetracycline was serially diluted in distilled water.

Determination of Contact Time of ptPO

Adsorption studies for determination of contact time (the time for equal adsorption and desorption amount of adsorbate on adsorbent) of ptPO were performed at 303 K. 30 ml tetracycline solutions (50, 75 and 100 mg/L) and 0.5 g ptPO were mixed in polyethylene vessels. The solutions were agitated at 120 rpm by using shaker with water baths about 3 h. The solutions were centrifuged at 5000 rpm. The tetracycline concentrations in supernatants were determined at 355 nm. All tests were performed triplicate. The following formula was used to estimate the adsorption amount of tetracycline by ptPO at equilibrium time:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

In Equation 1, q is the adsorption at equilibrium (mg/g), C_o is initial concentrations of tetracycline, C_e is concentrations of tetracycline at equilibrium time (mg/L), respectively, V and m are the volume of the tetracycline solution (L) and the adsorbent amount (g), respectively.

Optimization of Tetracycline Adsorption by ptPO

For optimization of adsorption process by ptPO, the effects of the pH (3, 5, 7, 11 and 13), the concentration of tetracycline (100, 150, 200, 250 and 300 mg/L), temperature (293, 303, 313, 323 and 338 K), agitator speed (60, 90, 120, 150 and 180 rpm), the adsorbent amount (0.1, 0.3, 0.5, 0.8 and 1 g), the ionic strength of solvent (0.01, 0.02, 0.03, 0.04 and 0.05 M) and the volume of solvent (25, 30, 35, 40 and 50 mL) on adsorption amount were investigated. All tests were performed triplicate.

ANN Modelling of Tetracycline Adsorption by ptPO

An ANN model was studied on biosorption data by using neural network tool-box of MATLAB (2013b version) and the strategy mentioned in Mert, Topcam and Cavas (2014) was followed. ANN structure in the present paper is consisted of a three-layer feed-forward network by using sigmoid linear transfer (*purelin*) and tangent transfer (*tansig*) functions. The input parameters; the pH (3, 5, 7, 11 and 13), the concentration of tetracycline (100, 150, 200, 250 and 300 mg/L), temperature (293, 303, 313, 323 and 338 K), agitator speed (60, 90, 120, 150 and 180 rpm), the adsorbent amount (0.1, 0.3, 0.5, 0.8 and 1 g), the ionic strength of solvent (0.01, 0.02, 0.03, 0.04 and 0.05 M) and the volume of solvent (25, 30, 35, 40 and 50 mL) were tested. The output parameter was selected as adsorption amount (g) (Figure 1). The size of the experimental data was 87 (72 of them were used to create the network and 15 of them were used to study performance of the created network). In order to fit the training:validation:testing in ANN model, the optimization data was used. Then, by using the best back propagation training algorithm, input parameters were performed to create a network. In this present study, 14 different back propagation algorithms were used.

Kinetic Models of Tetracycline Adsorption by ptPO

Different kinetic models have been applied for adsorption of tetracycline by ptPO and these kinetic models are described below. Lagergren pseudo-first-order the most widely used form of linear equations is given by the equation (Lagergren, 1898):

$$log(q_e - q_t) = log q_e - \frac{k_1}{2{,}303} t \qquad (2)$$

In Equation 2 q_e shows the adsorption amount at equilibrium time (mg/g), q_t is adsorbed tetracycline (mg/g) at a time t (min), k_1 is the rate constant of pseudo first order (1/min).

The pseudo-second order kinetic model is expressed by following equation (Ho & McKay, 1999):

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

In Equation 3, q_t is the adsorbed tetracycline (mg/g) at a time t and k_2 is the rate constant of pseudo second order kinetic (g/mg.min), q_e shows the amount of tetracycline adsorbed at equilibrium (mg/g).

Intraparticle diffusion model is given by

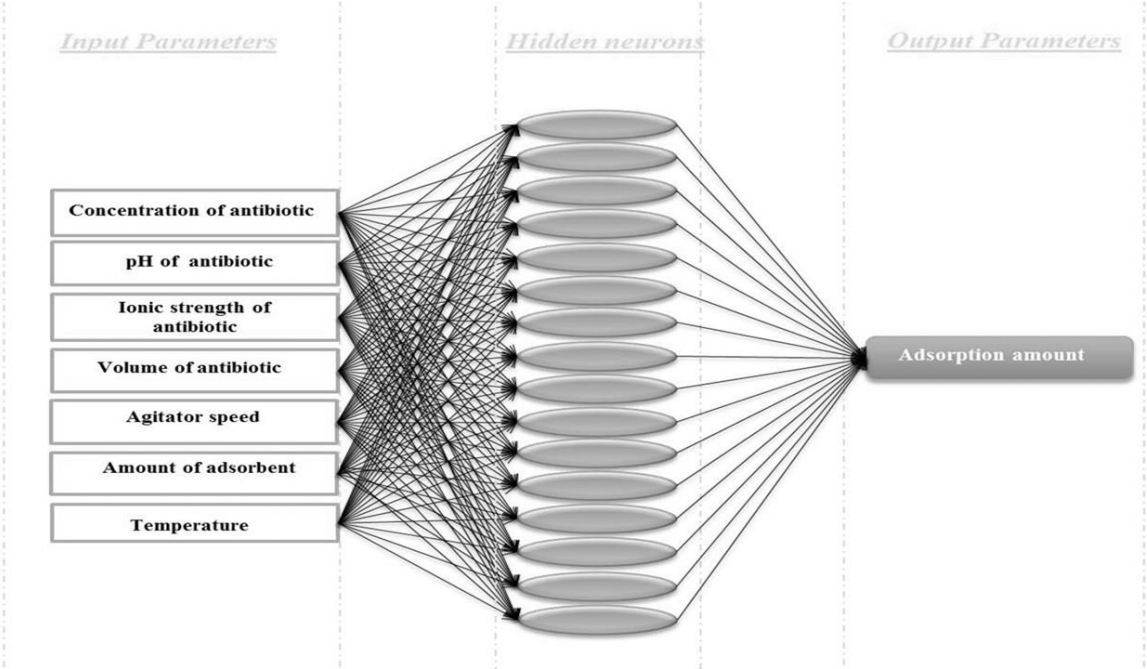

Figure 1. Architecture of artificial neural network structure.

equation (Weber & Morris, 1963):

$$q_t = k_{id}\, t^{1/2} + C \quad (4)$$

In Equation 4, q_t is the adsorbed tetracycline at time t (mg/g) and k_{id} is the rate constant of intraparticle diffusion kinetic ($mg.g^{-1}min^{-1/2}$).

Isotherm Models of Tetracycline Adsorption by ptPO

Adsorption isotherm models are used to calculate isotherm parameters (adsorption capacity, adsorption energy, etc.) and examine the relationship between adsorbent and adsorbate. Langmuir is the first scientist who published the coherent theory of adsorption. This adsorption theory is subjected to kinetic method on flat surface. The Langmuir isotherm model is defined by following equation (Langmuir, 1918):

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

In equation 5, q_e represents the adsorbed tetracycline at equilibrium (mg/g), q_m shows the maximum adsorption capacity (mg/g), b is the constant of Langmuir isotherm (L/mg) and C_e is concentration of tetracycline at the equilibrium time (mg/L).

The Freundlich isotherm is a type of isotherm which is oriented to multi-layered and heterogeneous surface adsorbents (Freundlich, 1906). The Freundlich isotherm is given below:

$$log\, q_e = log K_f + n_f\, log C_e \quad (6)$$

In equation 6, q_e represents the adsorbed of tetracycline at equilibrium (mg/g), K_f is the constant of Freundlich isotherm model, n_f shows heterogeneity factor in heterogeneous factor and C_e is concentration of tetracycline at the equilibrium time (mg/L).

Dubinin-Radushkevich isotherm model is calculated by the following equation (Dubinin & Radushkevich, 1947):

$$ln q_e = ln q_m - \beta\varepsilon^2 \quad (7)$$

In equation 7, q_e represents the adsorbed of tetracycline at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), β shows the energy constant of adsorption process (mol^2/kJ^2) and ε shows the Polanyi potential which is calculated as:

$$\varepsilon = RT ln\left(1 + \frac{1}{C_e}\right) \quad (8)$$

In equation 8, R shows ideal gas constant (kJ/mol.K), T represents temperature (K) and C_e is the concentration of tetracycline at the equilibrium time (mg/L).

Temkin isotherm model was calculated by using the equations given below (Temkin & Pyzhev, 1940):

$$q_e = \frac{RT}{A_T} ln_{K_T} + \frac{RT}{A_T} ln_{C_e} \quad (9)$$

In equation 9, q_e represents the adsorbed of tetracycline at equilibrium (mg/g), R shows ideal gas constant (kJ/mol.K), T represents temperature (K), A_T is a Temkin adsorption energy alteration in between two adjacent regions (J/mol), K_T is Temkin constant and C_e is the concentration of tetracycline at the equilibrium time (mg/L).

Thermodynamics of Tetracycline Adsorption by ptPO

Thermodynamics parameters were also studied in this paper. The following equations were used to calculate these parameters (Brown, LeMay, Bursten, Murphy, & Woodward, 2014):

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

$$\Delta G = -RT ln K_d \quad (11)$$

$$ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

$$K_d = \left(\frac{q_e}{C_e}\rho\right) \quad (13)$$

In these Equations (10-13), ΔG is change in the Gibbs free energy (kJ/mol), ΔH is changes in the Enthalpy, ΔS is the change in the entropy (J/molK), R is ideal gas constant (8.314 J/mol K), T is the temperature in Kelvin unit (K), K_d represents equilibrium constant, q_e is the adsorption amount at equilibrium time (mg/g) and C_e is the concentration of tetracycline at equilibrium time (mg/L) and ρ is the density of water (1000 g/L).

FT-IR Analysis of Adsorbent

In order to determine possible functional groups in the ptPO, a Fourier transform infrared (FT-IR) spectrum analysis was performed before and after adsorption process (4000-400 cm^{-1}). The pellets for FT-IR analysis were prepared by using the 100 mg dried KBr powder and 1 mg ptPO powder.

Results and Discussion

Adsorption Studies of Tetracycline by ptPO

The adsorption experiments were studied up to 180 minutes at 303 K in different tetracycline concentrations. In this study, the adsorption of all of tetracycline concentrations reached the equilibrium within 60 min (Figure 2). This shows that the

adsorption sites on adsorbent's surfaces are saturated by tetracycline molecules within 60 minutes. In different studies, the similar contact time was found by using different adsorbent (Gao *et al*., 2012; Liu *et al*., 2013; Oladoja, Adelagun, Ahmad, Unuabonah, & Bello, 2014; Zhang, Lan, Liu, & Qu, 2015).

Optimization of Adsorption Process by ptPO

The effects of the concentration of tetracycline, temperature, agitator speed, the adsorbent amount, pH, the ionic strength of solvent and the volume of solvent were also studied on tetracycline adsorption by ptPO. According to the literature, the pH is the most important parameter since it affects dissolution within aqueous solution. Tetracycline is an amphoteric molecule and it can be cationic (H_3TC^+, pH 3.30), zwitterionic (H_2TC, pH 3.30-7.68) and anionic form (HTC^- and TC_2^-, pH 7.68) (Figueroa, Leonard, & MacKay, 2004; Liu, Zheng, Zhong, & Cheng, 2015). When the effect of pH on tetracycline adsorption by ptPO was examined, it is said that the adsorption amount was increased when pH value of the tetracycline solution was increased from 3 to 5 (Figure 3.a). The maximum adsorption amount was observed at pH 5 and it was 8.50 mg/g. After this point the adsorption amount was slightly decreased. According to these results, the optimum pH value for tetracycline adsorption by ptPO was 5. In this pH, tetracycline is zwitterionic form and it could be said that hydrophobic interactions (via side chains of hydrophobic amino acids or aliphatic chains of fatty acids within the membrane etc.) might have been effective in the adsorption. According to the recent studies about removal of tetracycline, the highest adsorption amounts were observed when the acidic pH values were applied (Kang, Liu, Zheng, Qu, & Chen, 2011; Zhu *et al*., 2014; Liu *et al*., 2015). The temperature is also one of the most effective parameters in adsorption experiments. The maximum adsorption was observed at 323 K in the temperature based experiments (Figure 3.b). In higher temperature, slightly lower adsorption values were observed. The decrease in adsorption amount could be explained with the degradation of tetracycline or active groups on the ptPO surfaces. In the optimization studies, the effect of initial concentration of tetracycline on the biosorption of tetracycline by ptPO was also studied. When the initial concentration of the tetracycline increased, the adsorption amount also increased at 303 K. The adsorption amounts at this temperature were 5.57 mg/g for 100 mg/L and 16.65 mg/g for 300 mg/L (Fig. 3.c). The adsorption amount increased dependent on the increasing initial concentration of tetracycline. In the next optimization step, the speed of agitation was studied. The adsorption amount did not change until 120 rpm. However, it increased significantly after 120 rpm (Fig. 3.d). Increased agitation might have caused increased the collision among adsorbate and adsorbent surface. The effect of adsorbent amount on the tetracycline biosorption by ptPO was also investigated in this study. The removal percentage of tetracycline increased with increasing ptPO (Fig 3.e). Erşan, Bağda and Bağda (2013) obtained similar results in the adsorption process of tetracycline onto cryogels. It is discussed in some reports that the increased adsorbent amount can prevent over adsorption of adsorbates by adsorbents that is known as "*screening effect*" (Yahaya, Don, & Bhatia 2009; Erşan *et al*, 2013). The effect of ionic strength by varying the concentration of NaCl in tetracycline

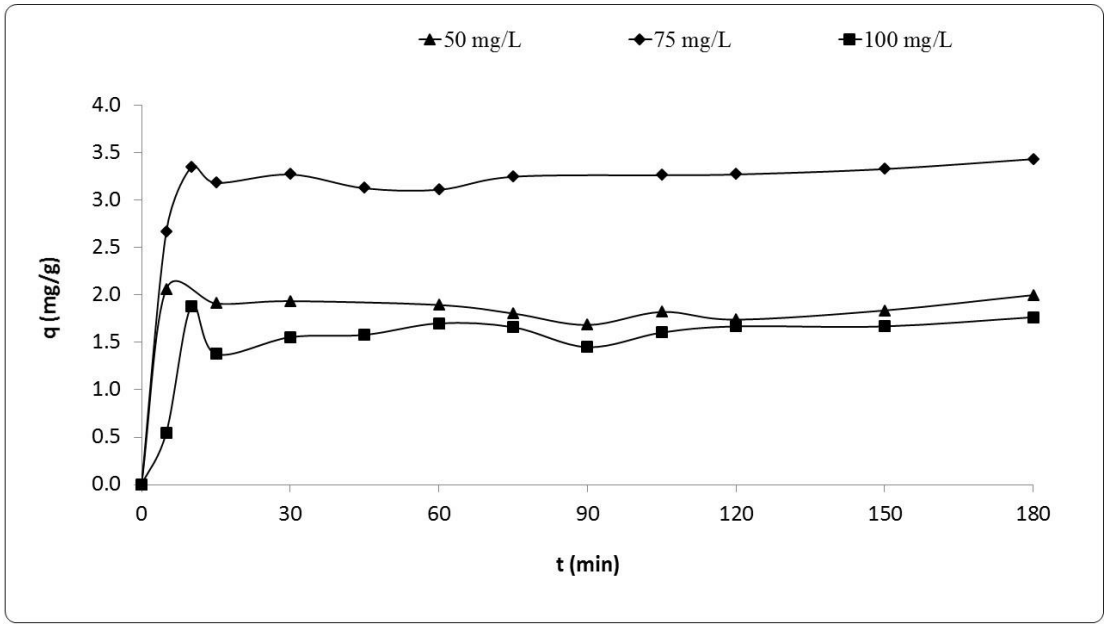

Figure 2. Time and concentration dependent adsorption of tetracycline by pre-treated *P. oceanica* (Adsorbent amount: 0.5 g; agitator speed: 120 rpm; pH: 5; ionic strength: 0.01 M; temperature: 323 K; the volume of solvent: 30 mL).

solution was also investigated. According to the results, maximum adsorption was observed when there was no NaCl in the medium. Based on the increasing concentration of NaCl, the adsorption was slightly decreased (Fig. 3.f). It could be said that negatively charged areas of ptPO residues could be suppressed by Na^+ cations. Moreover, existed cations in the same mediums exhibit different effects on adsorbents (Yang, Chen, Zhu, & Xing, 2016). Since slight effect of ionic strength was observed, hydrophobic–hydrophobic interaction and hydrogen bonding might have been effective in the adsorption of tetracycline by ptPO. These interactions were also observed by other researchers (Maurya, Mittal, Cornel, & Rother, 2006; Hu *et al*., 2013; Dahri, Kooh, & Lim, 2015). Finally, the effect of solvent volume on adsorption of tetracycline by ptPO was examined (Figure 3.g). The optimum solvent volume was found as 40 ml.

ANN Modeling of Adsorption by ptPO

An ANN model was developed based on the adsorption data in the present study. In the first step of development of ANN model, hidden neuron numbers were optimized by using default settings. Optimum neuron number was found as 16 with lowest MSE and highest R^2 values (Table 1). After that data percentages were studied and it was found that defaults settings revealed optimum percentages (70% (51 samples), 10% (7 samples) and 20% (14 samples)) (Table 2). In the last step, fourteen back-propagation algorithms were studied under previously optimized conditions and Bayesian-Regulation back-propagation algorithm was found as the best algorithm among tested (Table 3). In order to study the performance of the developed ANN, 15 input data (a different data set) was used and the related output was estimated by developed ANN model. The experimental adsorption amount values were plotted versus the predicted adsorption amount values. High coefficients of determination were observed between the experimental and predicted adsorption amount values (data not shown). In the literature, ANN was used to model adsorption data. Asl, Ahmadi, Ghiasvand, Tardast, & Katal (2013) carried out the adsorption of Cr (VI) by zeolite prepared from raw fly ash. According to their results of ANN modelling process, the numbers of hidden neuron were calculated as 6. The percentages for training, validation and testing were calculated as 70, 15 and 15%, respectively. In their ANN model, the values of R^2 and MSE were found to be 0.98 and 0.00027, respectively. Çelekli, Birecikligil, Geyik and Bozkurt, (2012) was carried out prediction process of the adsorption of LRG onto walnut husk by using ANN. They mentioned that ANN is suitable method to describe the adsorption process. In the scientific

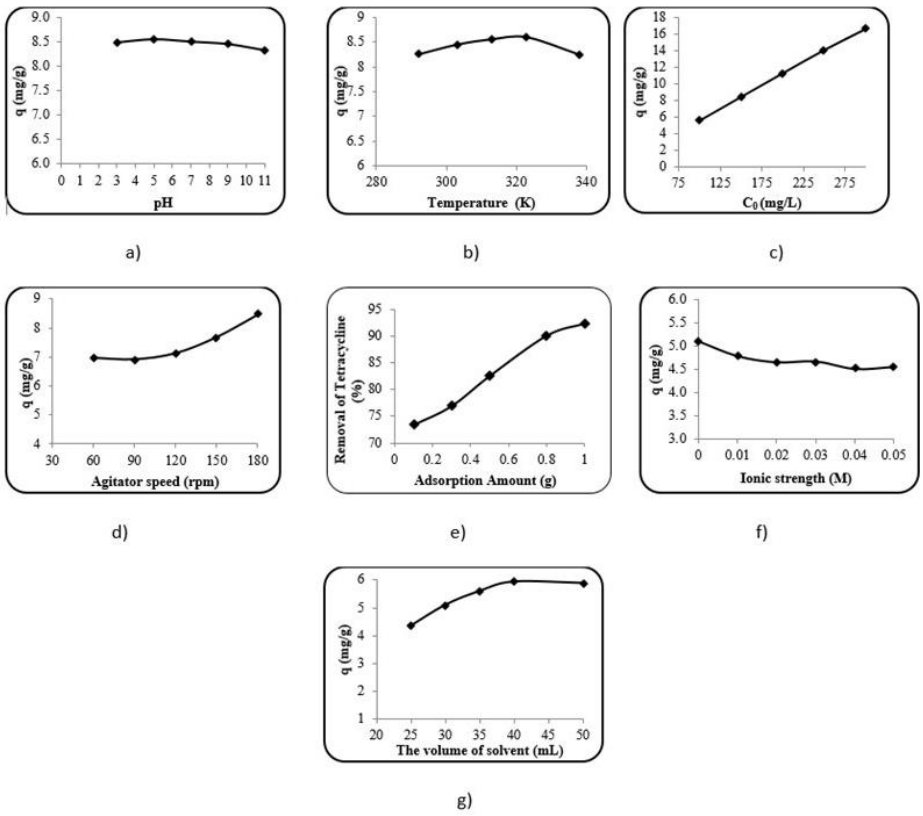

Figure 3. Effect of pH (a), the concentration of tetracycline (b), temperature (c), agitator speed (d), the adsorbent amount (e), the ionic strength of solvent (f) and the volume of solvent (g) on tetracycline adsorption by pre-treated P. oceanica.

Table 1. The optimization of number of hidden neuron in ANN modeling (Back propagation algorithm: Levenberg–Marquardt back propagation; percentage of training-validation-testing: 70-15-15)

Number of Hidden Neuron	Epoch Number	MSE			R^2		
		Training	Validation	Testing	Training	Validation	Testing
1	15	7.19298	23.73705	0.23971	0.82246	0.88745	0.98470
2	41	0.05240	23.31501	25.19145	0.99655	0.84217	0.90003
3	9	6.38311	0.28034	25.21615	0.92258	0.97864	0.94626
4	18	0.07209	0.92302	0.73567	0.99844	0.91450	0.99462
5	29	0.00522	0.11099	0.02544	0.99992	0.99576	0.99932
6	15	0.01607	0.00979	0.00757	0.99997	0.99976	0.99977
7	10	0.08270	0.80786	0.98105	0.99886	0.97990	0.93430
8	20	0.00099	2.79996	1.38981	0.99977	0.98250	0.96536
9	27	0.01064	0.00067	0.18738	0.99977	0.99995	0.98929
10	12	0.00990	0.00148	0.01479	0.99978	0.99996	0.99924
11	15	0.00193	0.00361	0.08614	0.99997	0.99992	0.99668
12	13	0.01563	0.30851	0.16620	0.99983	0.98231	0.99053
13	10	0.04697	0.89758	0.02559	0.99961	0.96752	0.99167
14	15	0.01940	0.04856	0.02684	0.99973	0.99715	0.99883
15	12	0.10801	0.88738	1.22605	0.99899	0.93128	0.93095
16	**10**	**0.01006**	**0.00290**	**0.01057**	**0.99984**	**0.99985**	**0.99965**
17	7	0.00196	0.08159	0.00187	0.99997	0.99084	0.99972
18	10	0.23526	0.26305	1.05147	0.99508	0.99246	0.99158
19	7	0.01074	0.02116	0.04847	0.99978	0.99983	0.99142
20	9	0.01054	0.26420	0.13903	0.99976	0.99825	0.99519
21	12	0.89228	0.97505	0.57980	0.98794	0.99653	0.94323
22	6	0.01030	0.00561	0.00234	0.99985	0.99990	0.99925
23	11	9.23318	0.22390	7.07794	0.86985	0.99643	0.90700
24	9	0.24218	0.08531	0.08686	0.97760	0.98860	0.97875
25	9	0.02317	0.01429	0.01058	0.99959	0.99795	0.99993
26	6	0.01728	14.73978	14.52013	0.99951	0.98636	0.95056
27	9	0.00164	0.85285	4.47286	0.99998	0.97412	0.68292
28	6	0.01165	0.07247	0.07269	0.99984	0.99353	0.99258
29	6	0.01084	0.00163	0.05107	0.99975	1.00000	0.99832
30	7	0.02049	0.13986	0.07149	0.99987	0.99070	0.99693

Table 2. The optimization of percentage of training-validation-testing in ANN modeling (Back propagation algorithm: Levenberg–Marquardt back propagation; number of hidden neuron: 16)

Number of hidden neuron	Training	Validation	Testing	Epoch number	MSE			R^2		
					Training	Validation	Testing	Training	Validation	Testing
16	90(64)	5(4)	5(4)	10	0.01097	0.00217	0.00647	0.99982	0.99973	0.99994
16	85(61)	5(4)	10(7)	8	0.00174	0.22286	0.00210	0.99997	0.99516	0.99994
16	80(57)	5(4)	15(11)	11	0.00933	0.00904	0.00408	0.99977	0.99625	0.99997
16	75(54)	5(4)	20(14)	9	2.21809	0.12920	4.36355	0.96733	0.99057	0.97749
16	70(50)	5(4)	25(18)	13	0.00096	0.01007	0.25253	0.99999	0.99985	0.98908
16	65(46)	5(4)	30(22)	14	0.01122	0.00338	0.04713	0.99976	0.99714	0.99939
16	60(43)	5(4)	35(25)	12	0.01133	0.04042	0.02535	0.99977	0.94781	0.99962
16	85(61)	10(7)	5(4)	15	0.40264	0.06964	0.26453	0.99818	0.99114	0.99939
16	80(58)	10(7)	10(7)	16	0.00947	0.10213	0.01904	0.99985	0.99949	0.99954
16	75(54)	10(7)	15(11)	14	0.01499	0.00788	0.01770	0.99980	0.99950	0.99977
16	**70(51)**	**10(7)**	**20(14)**	**9**	**0.01011**	**0.00662**	**0.00274**	**0.99984**	**0.99988**	**0.99986**
16	65(47)	10(7)	25(18)	10	0.77908	0.07122	0.40012	0.99059	0.98665	0.97709
16	60(43)	10(7)	30(22)	10	0.13964	3.36151	0.21548	0.99739	0.98655	0.92467
16	55(40)	10(7)	35(25)	9	0.46617	8.64586	3.71212	0.99965	0.92958	0.95082
16	80(57)	15(11)	5(4)	7	0.06077	0.23580	0.34061	0.99964	0.98033	0.99999
16	75(54)	15(11)	10(7)	8	0.00217	0.07915	0.00285	0.99997	0.99627	0.99987
16	70(50)	15(11)	15(11)	12	0.01070	0.00698	0.02032	0.99975	0.99996	0.99923
16	65(47)	15(11)	20(14)	6	0.01077	2.12404	3.25608	0.99985	0.93667	0.93615
16	60(43)	15(11)	25(18)	7	0.00162	0.06490	2.85263	0.99998	0.99650	0.54370
16	55(39)	15(11)	30(22)	13	0.65958	0.08159	1.22093	0.99499	0.99805	0.92938
16	50(36)	15(11)	35(25)	10	0.01241	0.25219	0.20499	0.99978	0.99185	0.99653
16	75(54)	20(14)	5(4)	9	0.04093	0.07939	0.22685	0.99964	0.99366	0.98978
16	70(51)	20(14)	10(7)	6	0.16089	11.95939	26.01381	0.99652	0.92529	0.93288
16	65(47)	20(14)	15(11)	9	0.00228	0.16314	0.51078	0.99995	0.99835	0.99627
16	60(44)	20(14)	20(14)	9	0.07262	2.28684	0.29756	0.99855	0.93696	0.99720
16	55(39)	20(14)	25(18)	6	0.00168	0.06474	22.08624	0.99992	0.99628	0.93716
16	50(36)	20(14)	30(22)	8	4.35438	3.99552	3.58858	0.97083	0.73139	0.81546
16	45(33)	20(14)	35(25)	9	0.00240	2.47141	2.64920	0.99997	0.89625	0.93478
16	70(50)	25(18)	5(4)	9	0.00240	0.09839	0.32717	0.99995	0.99880	0.98977
16	65(47)	25(18)	10(7)	8	0.01385	0.31758	0.00511	0.99981	0.96350	0.99943
16	60(43)	25(18)	15(11)	10	0.04871	2.04119	3.17135	0.99962	0.92507	0.80151
16	55(40)	25(18)	20(14)	12	0.01170	0.29443	0.19364	0.99985	0.97804	0.99425
16	50(36)	25(18)	25(18)	13	0.05021	0.21263	5.88327	0.99937	0.99777	0.45924
16	45(32)	25(18)	30(22)	7	2.28319	4.61932	2.39620	0.98462	0.80058	0.95284
16	40(29)	25(18)	35(25)	8	7.08658	2.45919	3.80087	0.98683	0.78665	0.83101

Table 2. Continued.

Number of hidden neuron	Training	Validation	Testing	Epoch number	MSE			R^2		
					Training	Validation	Testing	Training	Validation	Testing
16	65(46)	30(22)	5(4)	11	0.00230	0.42470	0.00053	0.99997	9.94935	1.00000
16	60(43)	30(22)	10(7)	6	0.01072	0.16302	0.17977	0.99984	0.99824	0.99981
16	55(39)	30(22)	15(11)	8	0.00110	0.01046	12.88486	0.99999	0.99964	0.53581
16	50(36)	30(22)	20(14)	11	0.00253	0.06224	0.02570	0.99997	0.99711	0.99891
16	45(32)	30(22)	25(18)	6	0.00061	0.78354	1.20969	0.99999	0.96089	0.98834
16	40(28)	30(22)	30(22)	7	2.12525	8.08889	8.88271	0.98121	0.91030	0.91621
16	35(25)	30(22)	35(25)	5	4.33702	30.27100	18.37156	0.96604	0.57132	0.81950
16	60(43)	35(25)	5(4)	9	0.19170	0.62333	0.27879	0.99745	0.99152	0.92152
16	55(40)	35(25)	10(7)	9	0.18679	20.58319	5.24768	0.99463	0.88147	0.98926
16	50(36)	35(25)	15(11)	7	0.04894	9.55971	21.18632	0.99914	0.91243	0.95367
16	45(33)	35(25)	20(14)	7	0.02438	1.03906	1.29465	0.99978	0.98735	0.94398
16	40(29)	35(25)	25(18)	8	0.56847	5.26400	6.96075	0.99225	0.93193	0.06758
16	35(25)	35(25)	30(22)	11	2.51246	1.92279	1.31736	0.99137	0.88236	0.92986
16	30(22)	35(25)	35(25)	8	1.59847	10.88751	14.17122	0.99273	0.84530	0.75654

Table 3. The performance results of different back propagation algorithms (Percentage of training-validation-testing: 70-10-20; number of hidden neuron: 16)

Back propagation algorithms	Functions	Iteration number	MSE	R^2
BFGS quasi-Newton back propagation	*trainbfg*	7	0.00050	0.99898
Bayesian Regulation	*trainbr*	124	0.0314	0.99933
Powell–Beale conjugate gradient back propagation	*traincgb*	6	0.15162	0.99753
Fletcher–Reeves conjugate gradient back propagation	*traincgf*	11	0.89733	0.99353
Polak–Ribiére conjugate gradient back propagation	*traincgp*	6	0.27023	0.99573
Batch gradient descent	*traingd*	6	583.09880	0.19619
Batch gradient descent with momentum	*traingdm*	6	3475.61320	0.45623
Gradient descent with Adaptive Learning Rate	*traingda*	18	17.64060	0.64439
Variable learning rate back propagation	*traingdx*	14	3.90070	0.99933
Levenberg–Marquardt back propagation	*trainlm*	8	0.67093	0.98685
One step secant back propagation	*trainoss*	23	0.08916	0.99807
Random Weight/Bias Rule	*trainr*	1000	0.05349	0.99889
Resillient back propagation (Rprop)	*trainrp*	6	1.43070	0.98313
Scaled conjugate gradient back propagation	*trainscg*	7	0.26845	0.99616

literature, there are a lot of papers regarding to ANN modeling on optimization of adsorption process (Myhara, Sablani, Al-Alawi, & Taylor, 1998; Aber, Daneshvar, Soroureddin, Chabok, & Asadpour-Zeynali, 2007; Yetilmezsoy & Demirel, 2008; Kumar & Porkodi, 2009; Çelekli & Geyik, 2011).

Adsorption Kinetics

The adsorption studies of tetracycline by ptPO was carried out by using different concentrations of tetracycline solutions (50, 75 and 100 mg/L) at temperature varying from 293 to 323 K over predetermined time interval (0-180 min). For the determination of adsorption mechanism, pseudo first order, pseudo second order and intra-particle diffusion kinetic models were studied (Figures 4, 5 and 6). According to obtained results from kinetic studies, the highest determination coefficient was calculated as 0.991 by using pseudo second order kinetic model in which tetracycline concentration and temperature were 100 mg/L and 328 K, respectively. The adsorption kinetics of tetracycline was studied by using different adsorbents in the literature. The adsorption data was well in line with pseudo second order model (Ho & McKay, 1999; Cavas & Gokoglu, 2011; Fernández-Calviño *et al.*, 2015). The rate constants of tetracycline adsorption were shown in Table 4, 5 and 6. In these tables, all raw data was presented although we obtained very low R^2 values so that the readers can see the raw data. For missing data in Table 4, 5 and 6, the relevant data was not fitted with the equations.

Adsorption Isotherms

In this study, the various isotherm equations such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were applied to the experimental data obtained during the isothermal adsorption studies of tetracycline onto ptPO (Figure 7). Freundlich and Temkin isotherm models were not fit well with the experimental results. Dubinin-Radushkevich isotherm model was well in line with the experimental results at high temperatures (323 and 338 K). However, Langmuir isotherm model was better fitted to the experimental results compared to other isotherm models. The maximum adsorption capacity of ptPO in tetracycline adsorption process was calculated as 90.1 mg/g at 303 K by using Langmuir isotherm model. However, the relevant R^2 was 0.8830. All results of adsorption isotherm parameters were presented in Table 7. We also wanted to give all raw data in these tables and figures

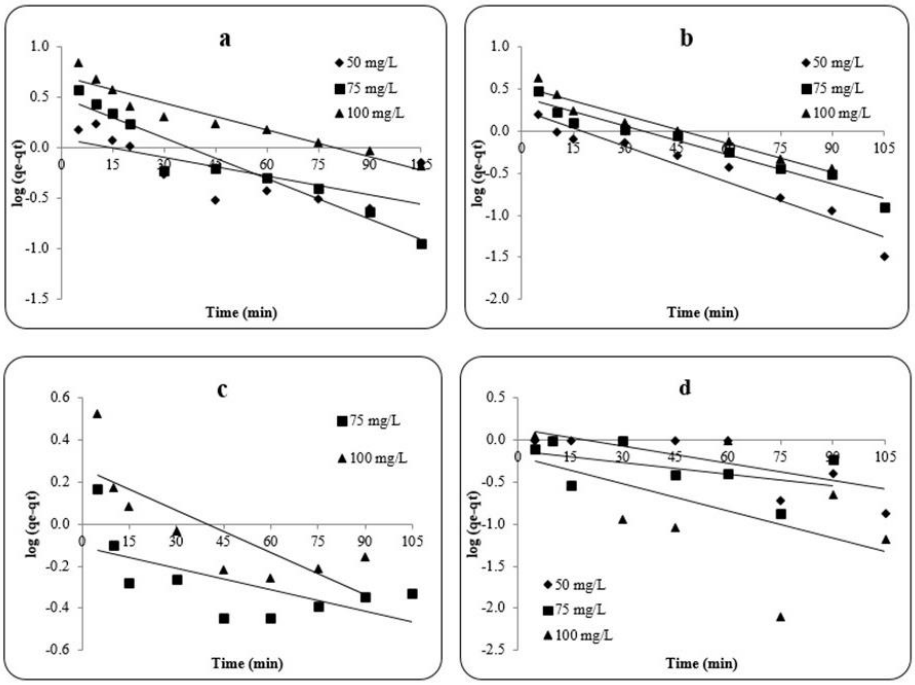

Figure 4. Pseudo first order kinetics of adsorption of tetracycline by pre-treated *P. oceanica* at 293 K (a), 303 K (b), 313 K (c) and 323 K (d) (pH: 5; agitator speed: 120 rpm; adsorbent amount: 0.5g; ionic strength: 0.01 M; the volume of solvent: 30 mL).

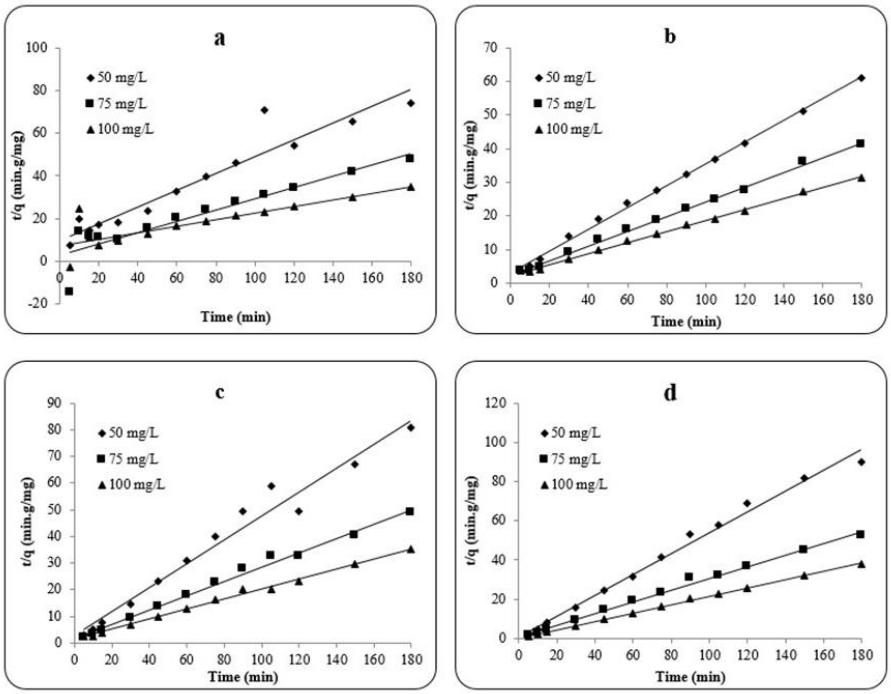

Figure 5. Pseudo second order kinetics of adsorption of tetracycline by pre-treated *P. oceanica* at 293 K (a), 303 K (b), 313 K (c) and 323 K (d) (pH: 5; agitator speed: 120 rpm; adsorbent amount: 0.5g; ionic strength: 0.01 M; the volume of solvent: 30 mL).

so that the readers can see them. The calculated adsorption capacity in this study was slightly higher than those of other studies by using different adsorbents (Sithole & Guy, 1987; Kang, Liu, Zheng, Qu, & Chen, 2010; Liao *et al*., 2013; Zhang *et al*., 2014; Ersan, Guler, Acikel, & Sarioglu, 2015). The

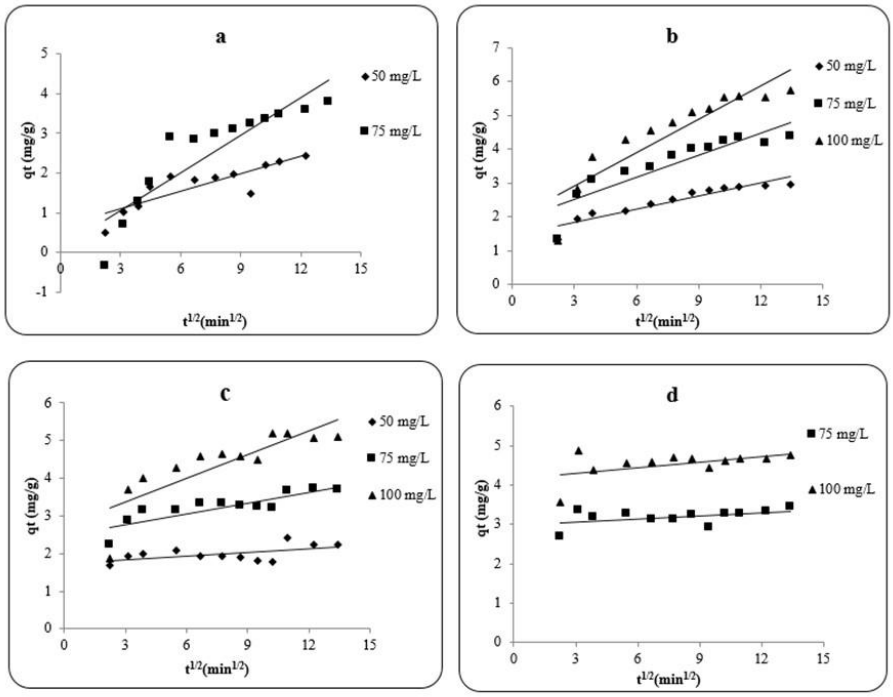

Figure 6. Intra particle diffusion of adsorption of tetracycline by pre-treated *P. oceanica* at 293 K (a), 303 K (b), 313 K (c) and 323 K (d) (pH: 5; agitator speed: 120 rpm; adsorbent amount: 0.5g; ionic strength: 0.01 M; the volume of solvent: 30 mL).

best isotherm model in removal studies of tetracycline was generally reported as Langmuir isotherm. The reported adsorbents are montmorillonite (Figueroa *et al*., 2004), bio-char (Liu *et al*., 2012), graphene oxide (Lin, Xu, & Li, 2013), tannin based cryogels and hydroxyapatite/clay (Erşan *et al*., 2013; Ersan *et al*., 2015). A comparison of adsorption capacities of other adsorbents developed for tetracycline in the literature was given in Table 8.

Thermodynamic Parameters of Adsorption Process

The thermodynamic studies of tetracycline adsorption were carried out in the range of 293-338 K by using different initial concentration of tetracycline (37.5, 50, 75 and 100 mg/L). The calculated thermodynamic parameters of adsorption process of tetracycline, ΔH, ΔS and ΔG were shown in Table 9. According to the results, ΔH and ΔS was calculated as 18.323 kJ/mol and 0.107 kJ/mol, respectively. The adsorption process of tetracycline was endothermic process due to the value of ΔH was positive. The positive values of ΔS showed that the adsorption process of tetracycline by ptPO was irreversible. In addition, the value of ΔG was calculated at the range of -12.920 and -17.719 kJ/mol. The negative values of ΔG confirm that the adsorption process of tetracycline by ptPO was occurred in spontaneous nature. Besides, the values of ΔG decreased with increasing the temperature and tetracycline concentrations. Cavas and Gokoglu (2011) founded the similar results in biosorption process of tetracycline by *C. scalpelliformis*. In the adsorption of tetracycline by using $MnFe_2O_4$/activated carbon, the values of ΔG was founded at the range of -25,285 and -29,704 kJ/mol (Shao, Ren, Zhang, & Chen, 2012).

FT-IR Analysis of Adsorbent

In this study, the functional groups in the ptPO were analysed by FT-IR. The FT-IR spectrum was recorded in both raw ptPO and antibiotic loaded ptPO. The magnitude of band shifting indicates the degree of interaction between tetracycline and functional groups of ptPO. The functional groups were identified as hydroxyl group (O-H), carboxyl (COOH), carbonyl stretching group (C=O), and sulfonyl (S=O) groups at 3410-3404, 2913-2919, 1613−1612 and 1061-1054 cm^{-1}, for raw and antibiotic loaded ptPO respectively.

Conclusion

In this study, a beach waste in Turkish coastline, *P. oceanica* residues, was used to remove the tetracycline from aqueous solutions. It was reported that *P. oceanica* dead leaves have the capacity to adsorb various hazardous materials. We for the first time studied the adsorption of tetracycline by using pre-treated dead leaves of *P. oceanica*. The data obtained from adsorption studies was evaluated with both classical (kinetic and isotherm models) and a

Table 4. The pseudo first order kinetic parameters of adsorption of tetracycline by pre-treated *P. oceanica*

Temperature (K)	293				303				313				323			
C_0 (mg/L)	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2
50	2.212	1.223	0.014	0.5004	2.893	1.760	0.003	0.9367	-	-	-	-	1.839	1.321	0.016	0.6494
75	3.485	3.188	0.031	0.9264	4.352	2.523	0.026	0.9494	3.679	0.784	0.008	0.4063	3.266	0.732	0.195	0.2253
100	5.163	5.169	0.020	0.9603	5.544	2.472	0.021	0.9900	5.196	1.837	0.015	0.6324	4.669	0.641	0.025	0.3127

Table 5. The pseudo second order kinetic parameters of adsorption of tetracycline by pre-treated *P. oceanica*

Temperature (K)	293				303				313				323			
C_0 (mg/L)	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2
50	2.212	2.560	0.015	0.9166	2.893	3.093	0.034	0.9979	2.423	2.232	0.073	0.9710	1.839	1.881	0.391	0.9907
75	3.485	3.381	0.023	0.8474	4.352	4.585	0.021	0.9974	3.679	3.729	0.044	0.9916	3.266	3.378	0.099	0.9947
100	5.163	6.614	0.003	0.6931	5.544	6.173	0.011	0.9975	5.196	5.316	0.025	0.9953	4.669	4.730	0.145	0.9991

Table 6. The intra particle diffusion kinetic parameters of adsorption of tetracycline by pre-treated *P. oceanica*

Temperature (K)	293			303			313			323		
C_0 (mg/L)	k_{id}	C	R^2	k_{id}	C	R^2	k_{id}	C	R^2	k_{id}	C	R^2
50	0.1511	0.4733	0.8026	0.1307	1.4349	0.8833	0.0319	1.7458	0.3024	-	-	-
75	0.3150	0.125	0.8036	0.2181	1.8559	0.8007	0.0948	2.4916	0.7161	0.0282	2.9616	0.2412
100	-	-	-	0.3296	1.9268	0.8183	0.2119	2.7255	0.6900	0.0471	4.1681	0.2561

Table 7. The constants of Langmuir, Freundlich, Dubinin-Radushkevich, Temkin models of adsorption of tetracycline by pre-treated *P. oceanica*

Temperature (K)	Langmuir isotherm constants			Freundlich isotherm constants				Dubinin-Radushkevich isotherm constants				Temkin isotherm constants		
	q_m (mg/g)	b (L/mg)	R^2	K_f	n	n_f	R^2	q_m (mg/g)	$Bx10^{-6}$ (mol^2L^{-2})	E (kJ/mol)	R^2	A_T (kJ/mol)	K_T	R^2
293	30.8	0.0065	0.9994	0.338	1.210	0.826	0.6312	12.9	132	0.087	0.7760	0.414	0.0042	0.5508
303	90.9	0.0025	0.8830	0.309	1.166	0.858	0.6281	11.9	97	0.102	0.5752	0.380	0.0032	0.6120
313	64.1	0.0038	0.9455	0.130	0.816	1.226	0.9432	14.1	65	0.124	0.8398	0.460	0.0128	0.6606
323	58.5	0.0061	0.9996	0.643	1.229	0.814	0.6492	19.3	8	0.354	0.9664	0.305	0.0072	0.6139
338	63.3	0.0066	1.0000	0.707	1.215	0.823	0.7042	20.7	9	0.333	0.9682	0.290	0.0077	0.6880

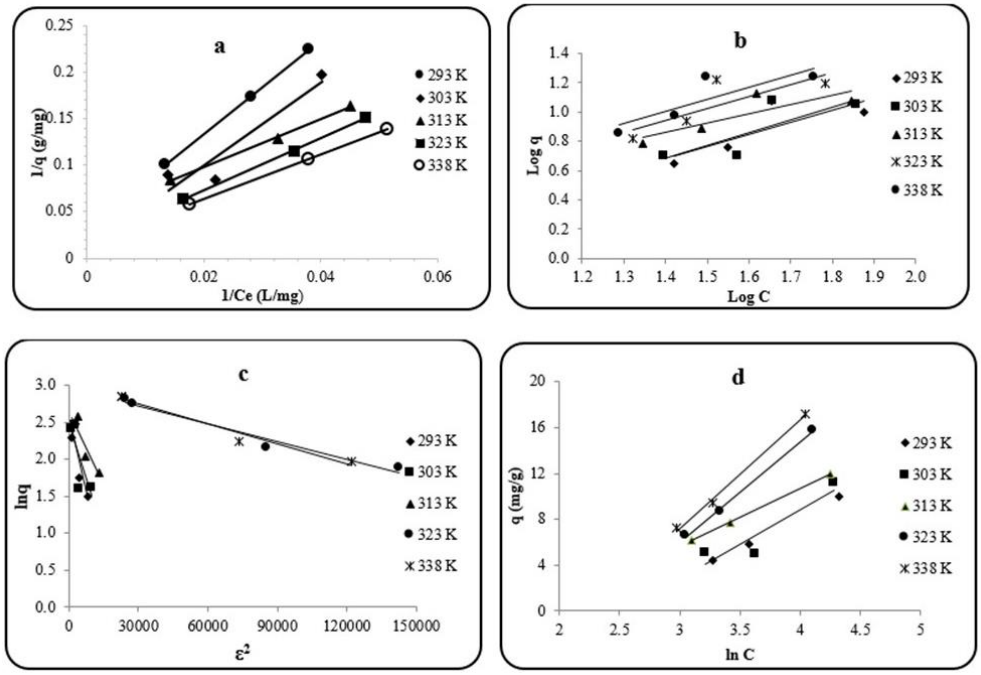

Figure 7. Langmuir (a), Freundlich (b), Dubinin-Radushkevich (c) and Temkin (d) isotherm models of adsorption of tetracycline by pre-treated *P. oceanica* (pH: 5; agitator speed: 150 rpm; adsorbent amount: 0.1g; ionic strength: 0.01 M; the volume of solvent: 40 mL).

Table 8. Comparison of adsorption of tetracycline by various adsorbent

		Adsorption conditions			
Adsorbent type	Maximum adsorption parameters	Equilibrium time	pH	Temp.	Reference
Hyroxyapatite/clay (HA-C)	qmax: 76.02 mg/g, b: 0.0369 L/mg (Langmuir) K_F: 4.30 (Freundlich) $q_{D–R}$: 8×10^{-4} mol/g (Dubinin–Radushkevich)	120 min	8	20 ºC	Ersan *et al*., 2015
Soil 1	q_{max}: 29.6 mmol/kg k_a: 0.0043 min^{-1} [fitting equation: $dq_a/dt = k_a(-q_{amax}–q_a)$]	-	4.6 ± 0.1	25±0.1 °C	Fernández-Calviño *et al*., 2015
Fe-N,N-SBA15	q_{max}: 96.91 mmol/kg, b: 0.067 L/mg (Langmuir) K_F: 271.77 (Freundlich)	6 h	5.0 ± 0.1	298 K	Zhang *et al*., 2015
Chitosan (MRC)	q_{max}: = 20.704 mg/g, b: 0.0133 L/mg (Langmuir) K_F: 1.111 (Freundlich)	120 min	3-4	-	Oladoja *et al*., 2014
Activated Carbon	q_{max}: 1.98mg/g, b: 1.87 L/mg (Langmuir) K_F: 0.54 (Freundlich)	8 h	2	25 ± 2 ºC	Pouretedal and Sadegh, 2014
Tannin based cryogels (TAB CRGs – CRGs)	TAB CRGs q_{max}: 67.11 mg/g, Ka: 0.040 L/mg (Langmuir - Type 1) K_F: 6.11 (Freundlich) CRG q_{max}: 108.70 mg/g, Ka: 0.21 L/mg (Langmuir - Type 2) K_F: 3.86 (Freundlich)	150 min	9	-	Erşan *et al*., 2013
Tire powder char (C800)	K_F: 20984 (1221) ($mg^{1-n} L^n/kg$) (Freundlich)	3 days	7.1	25 ± 1 ºC	Lian, Song, Liu, Zhu, and Xing, 2013
Bamboo charcoal	q_{max}: 22.7 mg/g, b: 0.02 (Langmuir) K_F: 0.76 (Freundlich) $q_{D–R}$: 3.1×10^{-5} mol/g (Dubinin–Radushkevich)	24 h	7	303 ± 1 K	Liao *et al*., 2013
GO-MPs (Graphene oxide)	q_{max}: 39.1 mg/g, K_L: 0.452 L/mg (Langmuir) K_F: 4.34 mg/g (Freundlich)	10 min	3-10	Room temp.	Lin *et al*., 2013
BiOI microspheres	q_{max}: 28.35 mg/g, b: 0.417 L/mg (Langmuir) K_F: 10.142 ($mg^{1-1/n} L^{1/n} g^{-1}$) (Freundlich)	6 h	-	298 K	Hao, Xiao, Zuo, Nan and Zhang, 2012
C. scalpelliformis	K_F: 0.667 (Freundlich) $q_{D–R}$: 3.171 mg/g (Dubinin–Radushkevich)	90 min	6.8	323 - 308 K	Cavas and Gokoglu, 2011
Granular sludge	q_{max}: 15.22 mg/g, b: 0.0312 1/mg (Langmuir) K_F: 0.6645 mg/g (Freundlich)	36 h	7.5-8	308 K	Shi *et al*., 2011
Chitosan	q_{max}: 53.82 mmol/kg, b: 1.22 L/mmol (Langmuir)	24 h	7	25 ± 1 ºC	Kang *et al*, 2010
Montmorillonite	q_{max}: 111 mmol/kg, b: 11 (L/mmol) (Langmuir)	24 h	5.5	-	Figueroa *et al*., 2004
Activated sludge	q_{max}: 72 mg/g, b: 0.061 L/mg (Langmuir) K_F: 4.13 L/g (Freundlich)	24 h	4	298	Prado, Ochoa, and Amrane, 2009
ptPO (this study)	q_m: 90.90 mg/g, b: 0.0025 L/mg (Langmuir) q_m: 20.7 mg/g (Dubinin-Radushkevich)	60 min	5	303	This study

Table 9. Thermodynamic parameters of the adsorption process of tetracycline by pre-treatment *P. oceanica*

C_0 (mg/L)	R^2	ΔH (kJ/mol)	ΔS (kJ/molK)	ΔG (kJ/mol)				
				293 K	303 K	313 K	323 K	338 K
37.5	0.9691	14.881	0.094	-12.551[1]	-13.487[1]	-14.423[1]	-15.359[1]	-16.764[1]
				-12.497[2]	-13.385[2]	-14.631[2]	-15.457[2]	-16.613[2]
50	0.9825	14.614	0.093	-12.481[1]	-13.406[1]	-14.331[1]	-15.256[1]	-16.642[1]
				-12.413[2]	-12.317[2]	-14.397[2]	-15.388[2]	-16.512[2]
75	0.9986	18.323	0.107	-12.920[1]	-13.986[1]	-15.053[1]	-16.119[1]	-17.719[1]
				-13.588[2]	-14.014[2]	-15.010[2]	-16.689[2]	-17.732[2]
100	0.9793	16.066	0.095	-11.870[1]	-12.824[1]	-13.777[1]	-14.730[1]	-16.161[1]
				-11.912[2]	-12.693[2]	-13.374[2]	-14.927[2]	-16.054[2]

[1,2]ΔH values were determined by $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RTlnK_d$, respectively.

modern method (ANN). ANN method is used for analysing and modelling adsorption data. *P. oceanica* can be evaluated as a low-cost biosorbent for tetracycline because of low equilibrium time and high biosorption capacity. Besides, dead leaves of *P. oceanica* should be used as an economic and renewable source for industrial application. The adsorbents obtained from *P. oceanica* can be used for the removal of other types of antibiotics from aqueous solutions. Therefore, further studies are recommended. However, *P. oceanica* is an endemic macrophyte and it is an important seagrass for the Mediterranean Sea ecosystem. Therefore, the authors of this study never recommend to collect alive leaves of *P. oceanica* from underwater. Only accumulated dead leaves around recreational areas should be evaluated with permission from local authorities as we mentioned in our previous studies on *P.oceanica*.

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