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Biosorption of Oxytetracycline with Waste Pine Tree Needles

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Abstract: In this study, it was aimed to remove Oxytetracycline (Oxy), one of the pharmaceutical wastes, with the powder of pine tree (*Pinus nigra* Arn.) needle waste (*Pn*-nw). Experimental data obtained from batch adsorption studies carried out at pH 5.0 ±0.5 and temperature of 23±2 ^{0}C were tested with Pseudo first order, Pseudo second order and Intraparticle diffusion kinetic models and Freundlich, Langmuir and Temkin isotherm models and also error functions (Error Sum of Squares (SSE), Sum of Absolute Errors (SAE) and Average relative errors (ARE)). Furthermore, to support the adsorption of Oxy onto *Pn*-nw's, the characterization of both raw and Oxy charged particles was done by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) analyses. The most appropriate kinetic model in the study was determined to be the Pseudo second order with an R^2 value of 0.999 and the Freundlich isotherm model with an R^2 value of 0.991. Additionally, the amount of Oxy removed per unit *Pn*-nw (q_{max}) was calculated as 30.35 mgOxy/g*Pn*-nw. The results show that *Pn*-nw is a very promising and environmentally friendly adsorbent for Oxy removal.

Key words: Oxytetracycline, *Pinus nigra* Arn., needle wastes, adsorption, kinetics, isotherm.

Atık Çam Ağacı İğneleri ile Oksitetrasiklin'in Biyosorpsiyonu

Öz: Bu çalışmada, farmasötik atıklardan biri olan Oksitetrasiklin'in (Oks), çam ağacı (*Pinus nigra* Arn.) iğne atığı (*Pn*-ia) tozları ile giderimi amaçlanmıştır. pH 5,0±0,5 ve 23±2 ^{0}C sıcaklıkta gerçekleştirilen kesikli adsorpsiyon çalışmalarından elde edilen deneysel veriler, Pseudo first order, Pseudo second order ve Intra-particle diffusion kinetik modelleri ve Freundlich, Langmuir ve Temkin izoterm modelleri ile test edilmiş ve sonuçlar hata fonksiyonları (Hata Kareler Toplamı (HKT), Mutlak Hatalar Toplamı (MHT) ve Ortalama Bağıl Hatalar (OBH)) ile incelenmiştir. Ayrıca, *Pn*-ia'lar üzerine Oks'nin adsorpsiyonunu desteklemek amacıyla hem ham hem de Oks yüklü parçacıkların karakterizasyonu Fourier transform infrared spectroscopy (FTIR) ve scanning electron microscope (SEM) analizleri ile yapılmıştır. Çalışmada en uygun kinetik modelin 0,999 R^2 değeri ile Pseudo second order ve 0,991 R^2 değeri ile Freundlich izoterm modeli olduğu belirlenmiştir. Ayrıca birim *Pn*-ia başına giderilen Oks miktarı (q_{max}) 30,35 mgOks/g*Pn*-ia olarak hesaplanmıştır. Sonuçlar *Pn*-ia'ların Oks gideriminde oldukça umut verici ve çevre dostu bir adsorban olduğunu göstermektedir.

Anahtar kelimeler: Oksitetrasiklin, *Pinus nigra* Arn., iğne atıkları, adsorbsiyon, kinetik, izoterm.

1. Introduction

Various types and quantities of wastewater are formed as a result of human consumption water and industrial processes. Rapid population growth, industrialization and changing living conditions cause the production and consumption of new products in many sectors. In this context, the composition of the wastewater formed is also changing. While in the past, the focus was on the removal of basic pollutants in wastewater, today there are many pollutants called emerging contaminants that have many toxic effects on the receiving environment [1]. These can be listed as pharmaceuticals, pesticides and personal care products formed as a result of human and animal consumption. Among these, antibiotics from pharmaceutical waste are frequently consumed by both humans and animals [1,2].

Antibiotics are needed to continue vital activity in our country and around the world. It is known that antibiotics, discovered in 1910 and used since then, extend the lifespan of living things. With the discovery of penicillin, its use gained momentum and is widely used today [3]. It is estimated that approximately 100 thousand to 200 thousand tons of antibiotics are used in the world. Tetracyclines were discovered in 1948 and Oxy has an important place in this group. Oxy is a highly preferred antibiotic in both land farming and aquaculture [4]. After these antibiotics enter the body, 5-90% of them are excreted directly from the body with feces or urine without being used, and reach the receiving environment through various means [5,6].

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Antibiotics entering the aquatic environment can be degraded by various mechanisms. They are first broken down into macromolecules and then into small molecules. Antibiotics in this state create pollutant potential in the aquatic ecosystem and cause toxic effects on living creatures in the environment. There are various methods for the treatment of pharmaceutical wastes in the aquatic environment. These are biological, electrochemical oxidation, photocatalysis, UV degradation and adsorption processes that remove organic and inorganic contaminants [7–10]. Although each of the listed treatment technologies has advantages and disadvantages over each other, the most important thing is that there is a tendency towards technologies that are cheap, fast and have high removal efficiency [1]. One of the most frequently used treatment methods in this context is adsorption. Although there are various studies with on activated carbon [11,12], or nanoparticles [13,14] produced using various methods, there are also studies on the removal of agricultural or some industrial wastes with cheap and easily available biosorbents [15–18] .

In this study, *Pn*-nw, which is frequently found in the natural environment and does not have any economic value and is evaluated as waste, was tried to be evaluated as a biosorbent. The adsorption of Oxy, one of the pharmaceutical wastes that has a toxic effect in the aquatic environment, was carried out with the obtained biosorbent. Three different kinetic and isotherm models were tried and various error functions were used to find the most suitable one. Additionally, FTIR and SEM images of raw and Oxy-loaded *Pn*-nw charged particles were examined.

2. Materials and Methods

2.1. Chemicals

Pan Trivalent injection solution (containing 30 mg Oxytetracycline hydrochloride in 1 mL volume, Zoetis, Turkey) was used as the oxytetracycline source. For pH adjustment, 0.1 M sodium hydroxide (NaOH, 40.00 g/mol, ≥99.0%, Sigma-Aldrich) in pellet form and 0.1 M sulfuric acid ($H_2(SO_4)_3$, 1.81 g/cm^3, ≥ 90-91 %, Merck) in liquid form were used. Distilled water was used in dilution processes.

2.2. Preparation and characterization of *Pn*-nw

Pn-nw used in the study was obtained from Diyarbakır region (Türkiye). Pine needles collected as litter from under the tree were first washed with tap water, then passed through pure water and dried in sunlight. After the dry wastes were ground in the laboratory mill, they were passed through 75-micron sieves and made ready for use in experiments.

SEM images (Gemini 500, Zeiss) were taken to see the changes before and after the adsorption of Oxy molecules onto the surface of *Pn*-nw. In addition, FTIR (Spotlight 400, Perkin Elmer) analysis was performed to determine the surface functional groups before and after the reaction.

2.3. Adsorption studies

Batch adsorption experiments were carried out at room temperature (23±2 ^{0}C). On the other hand, the highest water solubility of Oxy was found in the pH range of 4-7, especially pH 5.0 ±0.5 [19]. On the other hand, Oxy stock solution with a concentration of 500 mg/L was prepared. Certain dilutions were made from this stock solution and a calibration curve was produced on a UV-Vis spectrophotometer (DR6000, Hach) at a wavelength of 354 nm [15,20,21]. Also, wavelength scanning was performed on the UV-Vis spectrophotometer (DR6000, Hach) to see the peak of the Oxy solution at the maximum point (Figure 1). In addition, a polystyrene spectrophotometer cuvette with dimensions of 12.5x12.5x45 mm was used. The equation $y = 0.0279x + 0.0243$ ($R^2 = 0.9987$) was obtained. In experimental studies, the concentration calculation was calculated with the help of this equation.

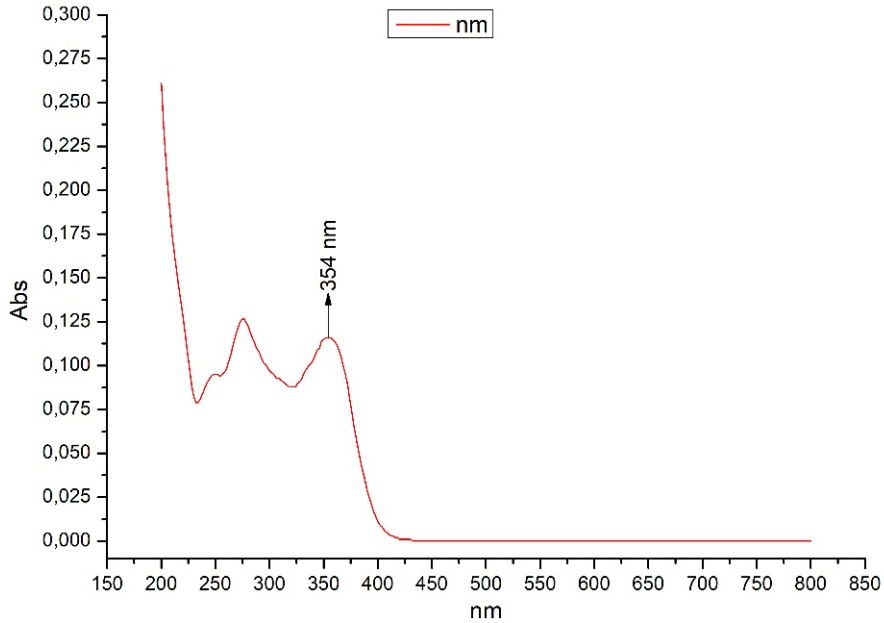

Figure 1. Wavelength scanning of Oxy solution in UV-VIS Spectrophotometer (*C*: 3.28 mg/L, *T*: 23±2 ^{0}C).

Batch adsorption tests were performed in an orbital mixer (Heidolp, Unimax1010, Germany) at 200 rpm. As a result of the experiments, equations 1 and 2 were used to calculate the removal efficiency (*R*) as a percentage and the amount of pollutant removed per unit adsorbent (q_e).

$$R(\%) = \frac{C_0 - C_e}{C_0}.100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e).V}{m} \quad (2)$$

The terms C_0 and C_e used in both equations express the Oxy concentration (mg/L) at the beginning and end of the experiment. The term q_e expresses the amount of Oxy removed per unit *Pn*-nw at equilibrium (mg/g). In addition, the term *V* represents the solution volume (L) and the term *m* represents the amount of *Pn*-nw (g).

2.4. Kinetic and isotherm models and error functions

In order to make a kinetic evaluation as a result of adsorption experiments, adsorbent was added to a 50 mL volume solution with 50 mg/L Oxy concentration, with a concentration of 1 g/L, and samples were taken at certain time intervals and the Oxy concentration was read on the spectrophotometer in the upper phase water. On the other hand, in order to evaluate isotherm models, *Pn*-nw was added to 7 different samples with initial Oxy concentration ranging from 17.24 to 128.40 mg/L and each with a volume of 10 mL, with an initial adsorbent amount of 1.5 g/L. At the end of the study, Oxy concentration was determined in the upper phase water. The equations of the kinetic and isotherm models used are presented in Table 1.

The terms C_0 and C_e specified in the table indicate the Oxy concentrations (mg/L) in the solution at the beginning and end of the experiment, respectively, and q_t and q_e indicate the amount of Oxy removed per unit *Pn*-nw (mg/g) at a time *t* and in equilibrium, respectively. On the other hand, k_1 term is Pseudo-first-order, k_2 term is Pseudo-second-order and K_{id} is Intra-particle diffusion model constant. In addition, the terms K_f and *n* represent the constant in the Freundlich model, and the terms K_L and a_L represent the constant in the Langmuir model, while R_L represents the dispersion constant. In addition, while *B* in the Temkin model represents the model constant, the term b_T represents the isotherm constant based on heat (kj/mol), the term *R* represents the universal gas constant (8.314 J/mol.K) and *T* represents the temperature (K).

Table 1. Kinetic and isotherm models and error functions used in the study.

	Model	Equation	References
Kinetic models	Pseudo-first-order	$q_t = q_e(1 - e^{-k_1 t})$	[22]
	Pseudo-second-order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	[23]
	Intra-particle diffusion	$q_t = K_{id} t^{1/2} + C$	[24]
Isotherm models	Freundlich	$q_e = K_F C_e^{1/n}$	[25,26]
	Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ $R_L = \frac{1}{1 + a_L C_e}$	[27,28]
	Temkin	$q_e = B ln(A_T C_e)$ $B = \frac{RT}{b_T}$	[28,29]
Error functions	Error Sum of Squares (SSE)	$SSE = \sum (q_{e,cal} - q_{e,exp})^2$	[30]
	Sum of Absolute Errors (SAE)	$SAE = \sum_{i=1}^{n} \lvert q_{e,exp} - q_{e,cal} \rvert$	
	Average relative errors (ARE)	$RAE = \frac{1}{n} \sum_{i=1}^{n} \left\lvert \frac{q_{e,cal} - q_{e,exp}}{q_{e,exp}} \right\rvert$	

3. Results and Discussion

3.1. Fourier transform infrared (FTIR) spectroscopy

In order to determine the surface characteristics in the adsorption of Oxy onto *Pn*-nw, FTIR spectroscopic analysis of both raw and Oxy-charged particles was performed. In this way, information about the functional groups and chemical composition of the material was provided. The obtained results are presented in Figure 2. Accordingly, functional groups are observed on both raw and Oxy charged particles. The strong peaks seen in the 1000 bands in the figure are considered to be –C–C– and –C–N– bonds [31]. Again, the peaks in the range of 1500-1600 represent the carbonyl group and NH group [32]. The peaks around 1750 cm^{-1} can be identified as the vibration of C=O and C=C [33]. The peak in the 2900 bands represents the -CH_2 group [34].

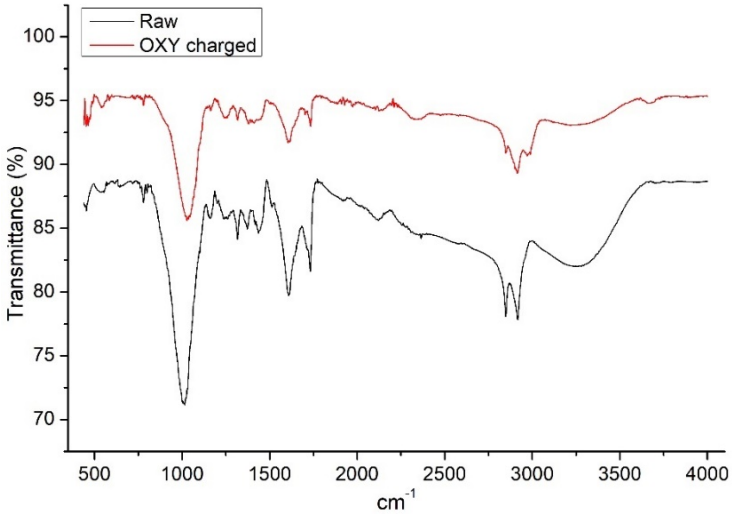

Figure 2. FTIR diagram of *Pn*-nw before and after the reaction.

3.2. Scanning electron microscopy (SEM)

The morphological structure of *Pn*-nw before and after adsorption was visualized and presented in Figure 3. When looking at the raw image of *Pn*-nw in Figure 3 (a), irregularity is seen, but there are some indentations/protrusions. It can be said that after adsorption, the indentation/protrusion on the surface increases and blurriness occurs in the image.

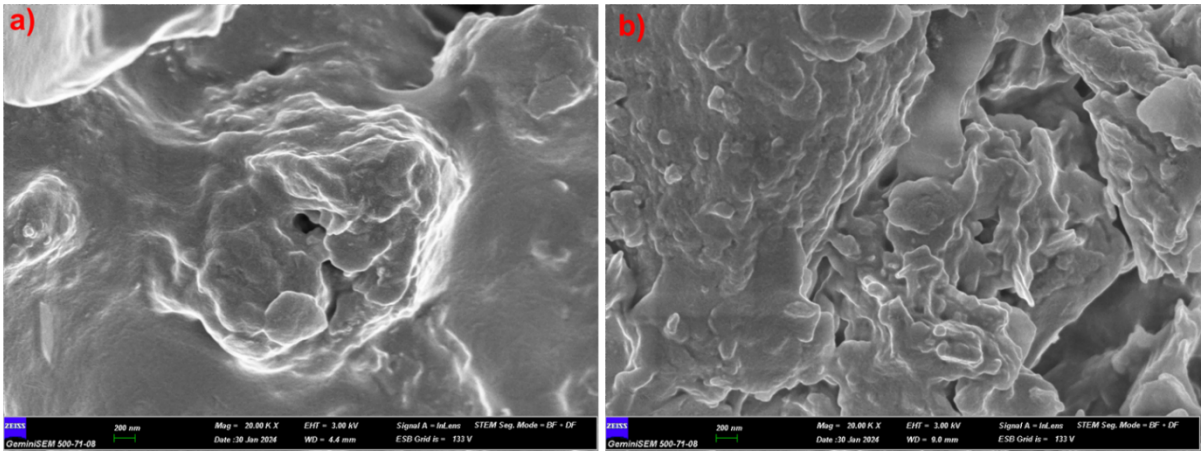

Figure 3. SEM images of *Pn*-nw before (a) and after (b) reaction.

3.3 Adsorption kinetics

The numerical values obtained in the laboratory for the adsorption of Oxy molecules by *Pn*-nw particles were tested in Pseudo first order, Pseudo second order and Intra-particle diffusion models, and a summary of the results is presented in Table 2. On the other hand, the regression curves obtained from the linear forms of the models are shown in Figure 4 (a), (b) and (c), and the comparison of the results obtained in experimental studies with each model is shown in Figure 4 (d).

When Table 2 is examined, the R^2 values of the Intra-particle diffusion and Pseudo first order models are calculated as 0.815 and 0.972, respectively, while the R^2 value of the Pseudo second order model is calculated as 0.999. In choosing the most appropriate model, evaluation of error functions is very important for the accuracy of the result. In this context, when we look at the SSE value, which is the sum of the squares of the difference between the amount of pollutants removed per unit adsorbent ($q_{e,cal}$) obtained from each model and the results obtained from experimental studies ($q_{e\,exp}$), it is seen that the lowest value is 6.24 in the Pseudo second order kinetic model.

Table 2. Summary of kinetic models calculated for the adsorption of Oxy molecules onto *Pn*-nw.

Kinetic models	Parameters	R^2	SSE	SAE	ARE
Pseudo first order	$k_1 = 0.052$	0.972	93.53	23.81	35.73
Pseudo second order	$k_2 = 0.003$ $q_e = 29.55$	0.999	6.24	6.646	9.85
Intra-particle diffusion	$k_i = 1.898$ $a = 5.312$	0.815	190.22	40.79	45.06

In addition, the Pseudo second order kinetic model has the lowest SAE value, which is the sum of the absolute value of the difference between the experimental results and the model results, with a value of 6.65. Finally, when we look at the ARE, which is obtained from the absolute value of dividing the difference between the model and the experimental results by the experimental results, it is seen that the Pseudo second order kinetic model is the lowest.

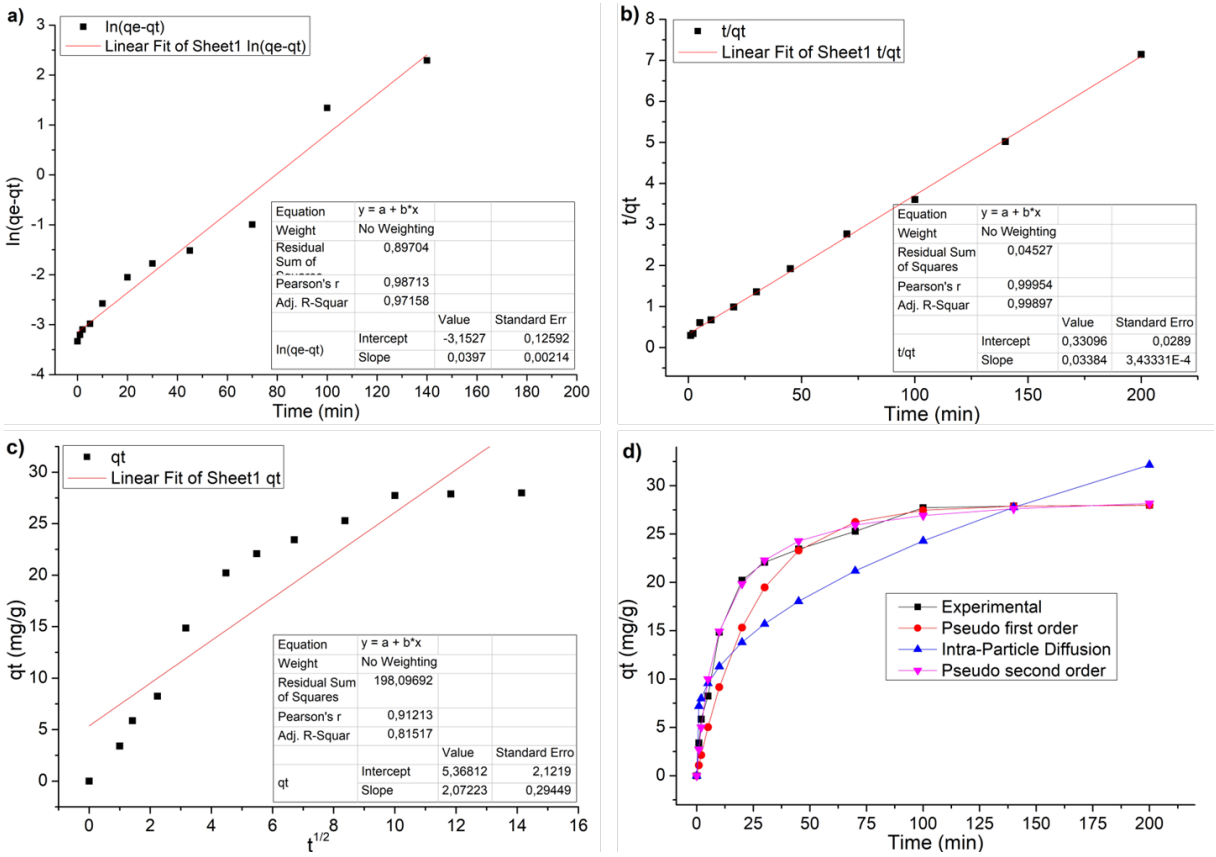

Figure 4. Regression curves of kinetic models a) Pseudo first order, b) Pseudo second order, c) Intra-particle diffusion, d) Comparison graph of q_t values against time.

On the other hand, the standard deviations between the points obtained in each model and the linear fit line were examined and presented in the tables in Figure 4 a, b and c. When the standard errors in terms of intercept are examined, it is seen that the standard deviations of the Pseudo first order and Intra-particle diffusion models are 0.126 and 2.122. However, it is seen that this value is 0.0289 in the Pseudo second order. Again, when the standard deviation of the slope value is examined, it is seen as 0.002, 0.295 and 0.0003 in the Pseudo first order, Intra-particle Pseudo second order models, respectively. As can be seen from the R^2 and error functions, the adsorption of Oxy molecules onto *Pn*-nw fits the Pseudo second order kinetic model. The findings were compared with the literature and presented in Table 3. Willow waste was used as a biosorbent and in a study where Oxy removal was performed, it was reported that the removal mechanism was Pseudo first order with an R^2 value of 0.956 at the end of the 90-minute reaction [35].

Also, it was reported that in a study in which spiky green horse chestnut bark was used as a biosorbent and acetaminophen removal was carried out, the removal mechanism complied with the Pseudo second order kinetic model with an R^2:0.999 value [36]. On the other hand, in a study where *Posidonia oceanica* was used as a biosorbent and oxy removal was carried out, it was reported that the most suitable model was Pseudo second order [15]. In a different study where eggshells were used as biosorbents and various pharmaceuticals were removed, it was reported that the removal mechanism was applied to the Pseudo second order model [37]. In another study, in which 5 different pharmaceutical wastes were eliminated with tomato wastes, it was reported that the R^2 value was >0.995, again complying with the Pseudo second order model [38]. When we look at the mechanism in the pseudo second order kinetic model, it can be said that the removal occurs in 4 steps. The first of these is the mass transfer of the pollutant to the boundary film on the adsorbent, the second step is diffusion through the film surrounding the surface of the adsorbent, and the third step is diffusion in the pores of the adsorbent (here ions are both absorbed into the active sites and ion exchange occurs). The last one can be expressed as adsorption occurring in free regions on the adsorbent [39].

Table 3. Comparison of results with literature.

Parameters	This study	[35]	[16]	[40]	[15]
Origin of biosorbent	*Pn*-nw	Willow	Rice husk ash	*Phaeodactylum tricornutum*	*Posidonia oceanica*
Pollutant type	Oxy	Oxy	Oxy	Oxy	Oxy
q_{max} (mg/g)	30.35	5.94-21.93	>3.34	29.18	11.8
Optimum pH	5.0	7.0	4-6	8.2	6.0
Working time (min)	200	90	540	11 h	60
Initial pollutant conc. (mg/L)	17.24-128.40	5-30	50-200	2.5-15	20-175 µmol/L
Best fit kinetic model	Pseudo second order	Pseudo first order	Bangham	Pseudo first order	Pseudo second order
Kinetic model R^2	0.999	>0.956	>957	>0.971	-
Best fit isotherm model	Freundlich	Langmuir	Sips	Langmuir	Langmuir
Isotherm model R^2	0.991	>0.962	>981	0.998	-

3.4. Adsorption isotherms

Freundlich, Langmuir and Temkin isotherm models were used to interpret the numerical expressions obtained from the experiments carried out on the adsorption of Oxy molecules on *Pn*-nw particles. The results obtained from the models are presented in Table 3. In addition, the graphics obtained from the linear forms of each model are presented in Figure 5 (a), (b) and (c). In addition, the amount of Oxy removed per unit adsorbent obtained from each model, compared to the Oxy concentrations remaining in solution in the experimental unit, is displayed in Figure 5 (d).

Table 3. Summary of isotherm models calculated for the adsorption of Oxy molecules onto *Pn*-nw.

	Parameters	R^2	SSE	SAE	ARE
Freundlich	k_F = 0.029 1/n = 1.573	0.991	25.64	9.55	12.3
Langmuir	k_L = 0.006 R_L = 0.855 q_{max} = 30.35	0.826	1949.2	77.22	66.7
Temkin	B_T = 0.113 k_T = 0.053	0.852	218.45	34.70	118.1

When Table 3 is examined, the R^2 values of the Langmuir and Temkin models were calculated as 0.826 and 0.852, respectively, while the R^2 value of the Freundlich model was found to be 0.991. Considering the SSE, SAE and ARE values, they are calculated as 25.64, 9.55 and 12.3, respectively. Again, as in the kinetic model, the standard deviations between the points obtained in each model and the linear fit line are examined and presented in the tables in Figure 4 a, b and c. When the standard errors in terms of intercept are examined, it is seen that the standard deviations of the Langmuir and Temkin models are 0.024 and 13.688. However, it is seen that this value is 0.101 in the Freundlich model. Again, when the standard deviation of the slope value is examined, it is seen that it is 0.001, 3.602 and 0.061 in the Langmuir, Temkin and Freundlich models, respectively.

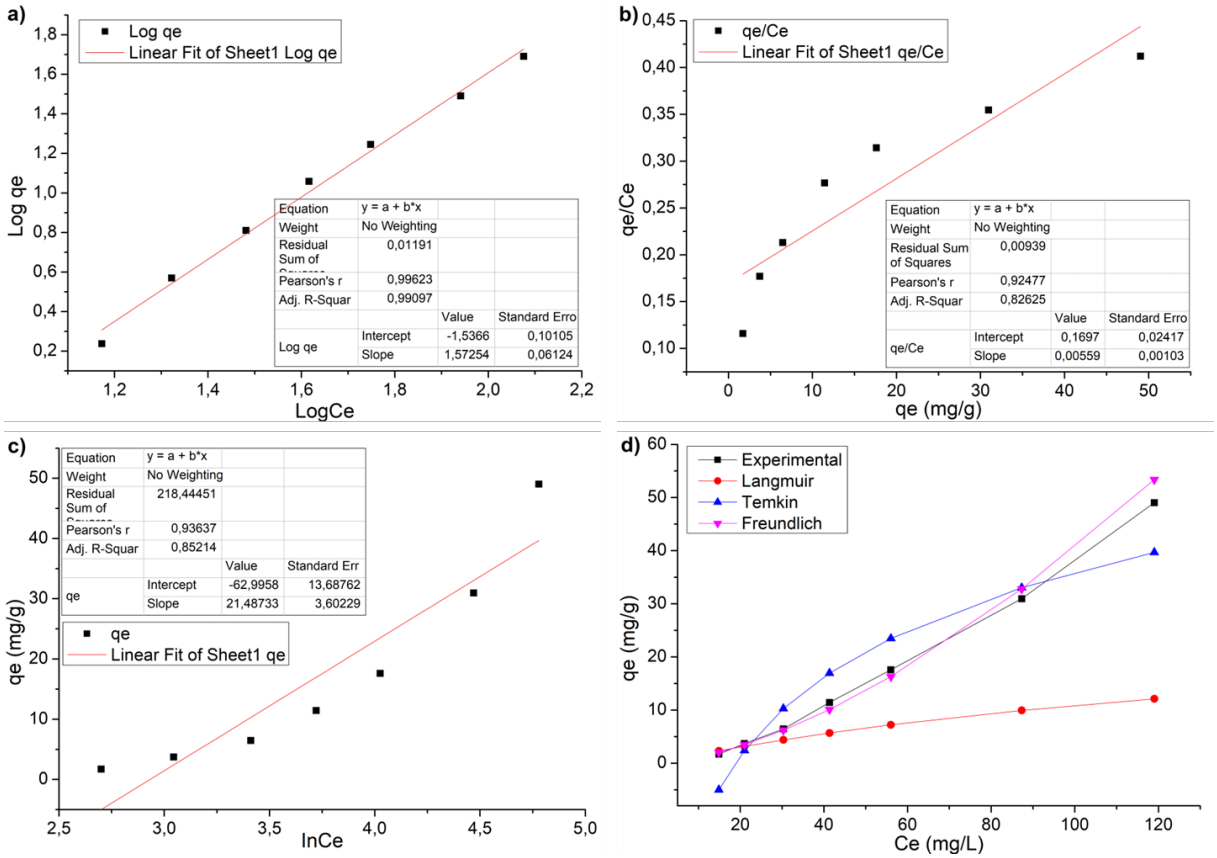

Figure 5. Regression curves of isotherm models (a) Freundlich, b) Langmuir, c) Temkin, d) Comparison plot of q_t values against C_e values.

As can be seen from the table, it is seen that the adsorption of Oxy molecules on *Pn*-nw particles complies with the Freundlich isotherm model. When the literature was examined, in a different study where *Phaeodactylum tricornutum* culture was used as a biosorbent, a study was conducted at Oxy concentrations in the range of 2.5-15 mg/L and the most suitable model was reported to be Langmuir with an R^2 value of 0.998. It was also reported that the q_{max} value was determined as 29.18 mg/g [40]. Also, it was reported that *Prunus domestica* L. biomass was modified and used as a biosorbent and 6 different pharmaceutical wastes were eliminated, and that it complied with the Freundlich isotherm model with an R^2>0.942 value. Additionally, the maximum pollutant removed per unit adsorbent was calculated as 17.503-22.104 mg/g [41]. In another study, Oxy removal was done with willow waste and the most suitable isotherm model was reported to be Langmuir and the q_{max} value was 21.93 [35]. In a different study, the removal of 5 different drugs was achieved with the biosorbent obtained by modification of the green alga *Scenedesmus obliquus* and it was reported that the most suitable model was Freundlich. In addition, the maximum removal capacity of the adsorbent was reported to be 39-68 mg/g in the study [42].

4. Results

In this study, Oxy, one of the pharmaceutical wastes frequently used in veterinary services, was attempted to be removed by *Pn*-nw, a waste product. Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion kinetic models and Freundlich, Langmuir and Temkin isotherm models were tried and also error functions (SSE, SAE and ARE) were used for comparison of results. Additionally, FTIR and SEM images of raw and loaded *Pn*-nw were examined to support the adsorption mechanism. According to the results obtained, the most suitable kinetic and isotherm models were found to be Pseudo second order (R^2: 0.999) and Freundlich (R^2: 0.991), respectively. On the other hand, q_{max} was calculated as 30.35 mgOxy/g*Pn*-nw. This study determined that it is possible to use *Pn*-nw in the removal of Oxy, one of the emerging contaminants.

References

[1] Cüce H, Cagcag Yolcu O, Aydın Temel F. Combination of ANNs and heuristic algorithms in modelling and optimizing of Fenton processes for industrial wastewater treatment. International Journal of Environmental Science and Technology 2023; 20:6065-78.

[2] Taheran M, Naghdi M, Brar SK, Verma M, Surampalli RY. Emerging contaminants: Here today, there tomorrow! Environ Nanotechnol Monit Manag 2018; 10: 122-6.

[3] Hutchings MI, Truman AW, Wilkinson B. Antibiotics: past, present and future. Curr Opin Microbiol 2019; 51: 72-80.

[4] LI Z jun, QI W ning, FENG Y, LIU Y wang, Ebrahim S, LONG J. Degradation mechanisms of oxytetracycline in the environment. J Integr Agric 2019; 18: 1953-60.

[5] Pelosato R, Bolognino I, Fontana F, Sora IN. Applications of Heterogeneous Photocatalysis to the Degradation of Oxytetracycline in Water: A Review. Molecules 2022; 27: 2743.

[6] Li D, Shao H, Huo Z, Xie N, Gu J, Xu G. Typical antibiotics in the receiving rivers of direct-discharge sources of sewage across Shanghai: occurrence and source analysis. RSC Adv 2021; 11: 21579-87.

[7] Rivera-Utrilla J, Ocampo-Perez R, Sanchez-Polo M, Lopez-Penalver JJ, Gomez-Pacheco CV. Removal of Tetracyclines from Water by Adsorption/Bioadsorption and Advanced Oxidation Processes. A Short Review. Curr Org Chem 2018; 22: 1005-21.

[8] Huang A, Yan M, Lin J, Xu L, Gong H, Gong H. A Review of Processes for Removing Antibiotics from Breeding Wastewater. Int J Environ Res Public Health 2021; 18: 4909.

[9] Li D, Yang M, Hu J, Ren L, Zhang Y, Li K. Determination and fate of oxytetracycline and related compounds in oxytetracycline production wastewater and the receiving river. Environ Toxicol Chem 2008; 27: 80-6.

[10] Cüce H, Aydın Temel F. Efficient Removal Performance of COD in Real Laundry Wastewater via Conventional and Photo-Fenton Degradation Systems: A Comparative Study on Oxidants and Operating Time by H2O2/Fe2+. Arab J Sci Eng 2023; 48: 15823-35.

[11] Solmaz A, Karta M, Depci T, Turna T, Sari ZA. Preparation and characterization of activated carbons from Lemon Pulp for oxytetracycline removal. Environ Monit Assess 2023; 195: 797.

[12] Kazak Ö. Single-step pyrolysis for producing activated carbon from sucrose and its properties for methylene blue removal in aqueous solution. Environmental Research and Technology 2021; 4: 165-75.

[13] Fan Y, Su J, Xu L, Liu S, Hou C, Liu Y, vd. Removal of oxytetracycline from wastewater by biochar modified with biosynthesized iron oxide nanoparticles and carbon nanotubes: Modification performance and adsorption mechanism. Environ Res 2023; 231: 116307.

[14] Lin X, Xu Q, Gan L, Owens G, Chen Z. Cyclodextrin modified green synthesized graphene oxide@iron nanoparticle composites for enhanced removal of oxytetracycline. J Colloid Interface Sci 2022; 608: 3159-67.

[15] Ferchichi K, Amdouni N, Chevalier Y, Hbaieb S. Low-cost Posidonia oceanica bio-adsorbent for efficient removal of antibiotic oxytetracycline from water. Environmental Science and Pollution Research 2022; 29: 83112-25.

[16] Andrade CA, Zambrano-Intriago LA, Oliveira NS, Vieira JS, Quiroz-Fernández LS, Rodríguez-Díaz JM. Adsorption Behavior and Mechanism of Oxytetracycline on Rice Husk Ash: Kinetics, Equilibrium, and Thermodynamics of the Process. Water Air Soil Pollut 2020; 231: 103.

[17] Şentürk İ, Alzein M. Adsorption of Acid Violet 17 onto Acid-Activated Pistachio Shell: Isotherm, Kinetic and Thermodynamic Studies. Acta Chim Slov 2020; 67: 55-69.

[18] Cüce H, Temel FA. Reuse of agro-wastes to treat wastewater containing dyestuff: sorption process with potato and pumpkin seed wastes. International Journal of Global Warming 2021; 24: 14.

[19] Sun Y, Yue Q, Gao B, Li Q, Huang L, Yao F, vd. Preparation of activated carbon derived from cotton linter fibers by fused NaOH activation and its application for oxytetracycline (OTC) adsorption. J Colloid Interface Sci 2012; 368: 521-7.

[20] Yildiz S, Canbaz GT, Mihçiokur H. Photocatalytic degradation of oxytetracycline using <scp>ZnO</scp> catalyst. Environ Prog Sustain Energy 2024; 43.

[21] Berger M, Ford J, Goldfarb JL. Modeling aqueous contaminant removal due to combined hydrolysis and adsorption: oxytetracycline in the presence of biomass-based activated carbons. Sep Sci Technol 2019; 54: 705-21.

[22] Lagergren SK. About the theory of so-called adsorption of soluble substances. Sven. Vetenskapsakad. Handingarl 1898; 24: 1-39.

[23] Ho YS, Wase' D, Forster CF. Removal of lead ions from aqueous solution using sphagnum moss peat as adsorbent. Water SA 1996; 22: 214-9.

[24] Boyd GE, Adamson AW, Myers LS. The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics. J Am Chem Soc [Internet] 1947 [a.yer 2023 Oca 6]; 69: 2836-48.

[25] Freundlich HMF. Over the adsorption in solution . J Phys Chem 1906; 57: 1100-7.

[26] Wang J, Guo X. Adsorption isotherm models: Classification, physical meaning, application and solving method. Chemosphere 2020; 258: 127279.

[27] Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. Solids. J Am Chem Soc [Internet] 1916 [a.yer 2022 Ağu 17]; 38: 2221-95.

[28] Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 2010; 156: 2-10.

[29] Temkin MI. Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physiochim 1940; 12: 327-56.

[30] Ncibi MC. Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis. J Hazard Mater 2008; 153: 207-12.
[31] Kumar NS, Asif M, Al-Hazzaa MI. Adsorptive removal of phenolic compounds from aqueous solutions using pine cone biomass: kinetics and equilibrium studies. Environmental Science and Pollution Research 2018; 25: 21949-60.
[32] Mahmoodi NM, Hayati B, Arami M, Lan C. Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies. Desalination 2011; 268: 117-25.
[33] Sen TK. Adsorptive Removal of Dye (Methylene Blue) Organic Pollutant from Water by Pine Tree Leaf Biomass Adsorbent. Processes 2023; 11: 1877.
[34] Assefi M, Davar F, Hadadzadeh H. Green synthesis of nanosilica by thermal decomposition of pine cones and pine needles. Advanced Powder Technology 2015; 26: 1583-9.
[35] Wang D, Xu H, Yang S, Wang W, Wang Y. Adsorption Property and Mechanism of Oxytetracycline onto Willow Residues. Int J Environ Res Public Health 2017; 15: 8.
[36] Parus A, Gaj M, Karbowska B, Zembrzuska J. Investigation of acetaminophen adsorption with a biosorbent as a purification method of aqueous solution. Chemistry and Ecology 2020; 36: 705-25.
[37] Mutavdžić Pavlović D, Ćurković L, Macan J, Žižek K. Eggshell as a New Biosorbent for the Removal of Pharmaceuticals From Aqueous Solutions. Clean (Weinh) 2017; 45.
[38] Santaeufemia S, Torres E, Mera R, Abalde J. Bioremediation of oxytetracycline in seawater by living and dead biomass of the microalga Phaeodactylum tricornutum. J Hazard Mater 2016; 320: 315-25.
[39] Mutavdžić Pavlović D, Ćurković L, Mandić V, Macan J, Šimić I, Blažek D. Removal of Pharmaceuticals from Water by Tomato Waste as Novel Promising Biosorbent: Equilibrium, Kinetics, and Thermodynamics. Sustainability 2021; 13: 11560.
[40] Żółtowska-Aksamitowska S, Bartczak P, Zembrzuska J, Jesionowski T. Removal of hazardous non-steroidal anti-inflammatory drugs from aqueous solutions by biosorbent based on chitin and lignin. Science of The Total Environment 2018; 612: 1223-33.
[41] Turk Sekulic M, Boskovic N, Slavkovic A, Garunovic J, Kolakovic S, Pap S. Surface functionalised adsorbent for emerging pharmaceutical removal: Adsorption performance and mechanisms. Process Safety and Environmental Protection 2019; 125: 50-63.
[42] Ali MEM, Abd El-Aty AM, Badawy MI, Ali RK. Removal of pharmaceutical pollutants from synthetic wastewater using chemically modified biomass of green alga Scenedesmus obliquus. Ecotoxicol Environ Saf 2018; 151: 144-52.