ISSN-1996-918X

Cross Mark

Pak. J. Anal. Environ. Chem. Vol. 24, No. 1 (2023) 13 – 30

http://doi.org/10.21743/pjaec/2023.06.02

Removal of 17β-estradiol (E_2) from Aqueous Solutions by Adsorption Using Oak Jaft and Tea Waste, Isotherm Investigation, and Adsorption Kinetics

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Received 15 September 2022, Revised 06 May 2023, Accepted 10 May 2023

Abstract

The present study aims to investigate wastewater treatment of hormones by oak jaft and tea waste adsorbents. Various factors were used to evaluate the adsorption process, such as the initial pollutant concentration, adsorbent concentration, contact time, and pH. The results showed that both adsorbents, jaft, and tea waste, can adsorb 17β-estradiol. Maximum adsorption was 82.4% for jaft adsorbent and 81.5% for tea waste at 85 min, 7 g/L of adsorbent dose, and pH = 4.5, respectively. The adsorption equilibrium was performed using Langmuir, Freundlich, and Liu models, based on the results, Freundlich model with R^2 values >0.97 demonstrated better agreement with the adsorption experimental data. To obtain information on adsorption velocity, three models of pseudo-first-order, pseudo-second-order, and Elovich were used. The findings revealed that the pseudo-second-order model with $R^2 > 0.98$ is a better fit for the experimental data. Therefore, the jaft adsorbent and tea waste can be used as effective and economical adsorbents for the removal of organic pollutants in wastewater treatment plants.

Keywords: 17β-estradiol, Hormone, Adsorption, Natural Adsorbent, Optimization, Kinetic.

Introduction

A major environmental problem threatening human health and aquatic ecosystems is the severe environmental pollution by industrial/natural pharmaceutical or chemical compounds and the thousands of chemicals used by humans that enter aquatic ecosystems. The Toxic Substances Control Act (TSCA) has introduced > 85,000 chemicals, ~1% of which are endocrine disruptive compounds (EDCs) [1]. These compounds have also been found in aquatic environments, particularly in rivers that receive effluent from wastewater treatment plants, as well as in drinking water. That has caused great concerns in recent years [2]. Permanent or prolonged exposure to these pollutants will have negative effects on human and organisms health [2]. The main groups of these compounds include phytoestrogens, steroid hormones (natural and synthetic), surfactants, pesticides, chlorinated biphenyls, phthalates, dioxins, and plastics [1]. Among these, natural and synthetic steroid hormones have received more attention from researchers [2]. The majority of hormones entering the environment are 17β-estradiol (E_2), Strone (E_1), and hormones excreted by humans and animals, and this type of pollution is observed all over the world. Another hormone that is important in the environment is progesterone, which is naturally excreted in large quantities by pregnant women, is taken orally, or is ingested via medicine and healthcare, birth control pills, hormone replacement medications, and cancer treatment, and can increase the protection of these environmental pollutants [3]. Hormones are either naturally or synthetically present in the environment. Natural hormones are produced in the human or animal body, while their synthetic form is found in contraceptives. Among the natural estrogens, the largest and most resistant form is 17β-estradiol, which can be described as the most worrying EDC [4]. 17β-estradiol and progesterone are endocrine disrupters (EDCs) and of great concern, as they pose potential hazards to humans and the environment. These pollutants are either natural (produced by humans or animals) or synthetic (medicinal). If used as a drug, ~50 to 90% of them is excreted in the body without decomposition. Many studies show that small amounts of hormones are found in wastewater treatment plants because steroid hormones are not eliminated in wastewater treatment plants [5]. The amount of hormones in wastewater is too high (12.5-23.7 ng/L) in many countries and these hormones are highly resistant to natural elimination [6]. The ways through which hormones enter the environment include the use of chemicals such as estrogenic cosmetics, lotions, detergents, and shampoos [7]. They can daily enter the sewage through urine and thus into the environment. These hormones also enter the environment through the use of drugs, especially contraceptives. When a drug is taken, ~50 to 90% of it is excreted without any changes in the body, and the rest is excreted in the form of chemical metabolites such as by-products from the body's interactions [8]. These hormones are released to the environment through the wastewater from hospital, animal, and municipal wastewater, or sewage sludge due to the addition of fertilizers to agricultural lands for soil fertility. However, the main route of environmental pollution is usually through wastewater; after incomplete removal from the wastewater treatment plant, these compounds enter the free water at the municipal landfill and are then released into the aquatic environment [2]. After entering the aquatic ecosystems, hormones can pose serious risks to human society and the environment. Their negative effects can be divided into two main categories. The first group includes impact on human health, e.g. increased breast cancer, testicular and prostate cancer, and endometriosis, while the second group comprises impacts on wildlife and fisheries, e.g. impairing the reproductive system of fish, reptiles, birds, and mammals; altering the marine mammalian immune system; decreasing the hatching of birds, fish, and turtles, and the male fish becoming female [9, 10]. Although the concentration of hormones in the environment is low, they exert their effects at very low doses (ng/L) due to their high hormonal activity [10]. By eliminating the hormone contaminants from the sewage, their negative and dangerous effects, as well as waterborne diseases, can be prevented [11]. To resolve the many problems caused by EDCs and to prevent any negative effects on the environment it is essential to remove steroid hormones before effluent discharge by alternative, sustainable, and economical treatment processes [9, 10]. One of the methods proposed for this purpose is the adsorption process, which is a superior and widespread method due to its high removal efficiency, easy accessibility, low environmental risk, reusability, and stabilization of organic matter from wastewater [12]. In general, adsorption is a process whereby materials accumulate in the joint phase between two phases. Activated carbon as the most common adsorbent in the adsorption process is a very effective technology for removing EDC from wastewater. However, because of its heavy costs and the disappearance of part of the adsorbent during the process, researchers have been looking for newer and cheaper adsorbents. Recently, biosorbents such as green almond shells, date fiber, sawdust, barley straw, wheat, tea waste, rice bran, and oak shell (jaft) have been utilized to remove organic and inorganic pollutants. This study used oak shell (jaft) and tea waste to remove 17β-estradiol from synthetic wastewater and compared it with adsorption on activated carbon. Tea waste and oak jaft were used as adsorbents for acetaminophen and ibuprofen, Cesium, Nitrophenol, and lead removal from wastewater in similar studies [13-17].

Materials and methods

Materials

Jaft was obtained from local trees in Yasuj, Iran, and tea waste was collected from human communities. Hormones and other chemicals were purchased from Merck, Germany. Sodium hydroxide and 0.01 N hydrochloric acid were used to adjust the pH. The Metrohm 511 model was used to measure pH. The KNUER HPLC device was employed to determine the initial and final concentrations of progesterone and 17β-estradiol (E_2) at 254 and 205 nm, respectively, for progesterone and E_2. Laboratory glass containers were also utilized for preparing mother solutions and samples that were prepared in 100 mL volumes.

Preparation and Modification of Adsorbents

To prepare oak and tea waste adsorbents, oak fruits were first collected from forests around Yasuj, and the middle layer of the fruit (the layer between the edible part and the hard shell called jaft) was dried. Dry tea was also purchased. Each adsorbent was then boiled individually several times until it was completely brown. Subsequently, they were immersed in 0.05 N sulfuric acid for 8 h and washed several times with distilled water to remove the acid. After being exposed to sulfuric acid for 24 h at 48°C, they were placed in the oven; after cooling for a period, they were separated by a standard ASTM sieve and stored in a polyethylene container [18, 19].

Performing the Adsorption Process

To prepare 10000 µg/L (0.01 g/L) of the hormone solution, 0.01 g of E_2 was dissolved in double-distilled water and the volume was added to a volume of 1000 mL. Subsequent standard solutions (0.5- 8.5 µg/L) were prepared by diluting a certain volume of this mother solution.

The natural adsorbents of oak shell (jaft), tea waste, and activated carbon in synthetic samples were used to adsorb 17β-estradiol. Sampling was performed based on experiments designed by the Design-Expert 7 software. Oak and tea waste biosorbents were used to remove estrogenic hormones from the solution under different conditions. The effect of different parameters such as contact time, hormone concentration, the amount and type of the adsorbent, and pH was investigated for the maximum adsorption of the hormone. Precisely, the solutions (stock solutions and dilutions) were prepared according to the experimental design table, the samples were made for each type of hormone and adsorbed separately for both adsorbents (oak and tea waste). Solutions of different concentrations of hormones (0.5 to 8.5 µg/L) were poured into a 100 cc beaker and after adjusting the pH (2-12), a certain amount of the adsorbent (1 to 9 g) was added to the hormone solution. Samples were then placed on the shaker during the contact time (10 to 110 min) for better adsorption of the hormone. After a predetermined contact time, the samples were filtered using Whatman filter paper. The filtrate of samples were then analysed using HPLC to estimate the residual hormone concentration. Finally, the amount of hormone adsorbed was calculated based on the difference in the concentrations of initial (before adsorption) and final (after adsorption) solutions. Using optimal conditions determined during the experiments, the kinetic constants, and the type of adsorption isotherm on these adsorbents were investigated and compared. To validate the results, the experiments were conducted under optimum conditions in three replicates for each of the adsorbents (jaft, tea waste, and activated nanocarbon), which demonstrated the adsorption efficiency under optimum conditions. Also, biosorbents and activated nanocarbon were compared in these conditions. The following formulas were used to calculate the amount of 17β-estradiol removal and the equilibrium capacity of the adsorbent with respect to the amount of adsorbent dose and the concentration of 17β-estradiol.

$$R\% = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

Where, R% denotes the percentage of removal efficiency, C_0 the initial solution concentration, and C_e the equilibrium concentration [20]:

$$qe \frac{(C_o - C)}{M} . V \qquad (2)$$

C_o and C_e denote the initial and equilibrium concentrations in the liquid phase (mg/L), V represents the volume of solution (L), q_e the amount of component adsorbed (mg/g) and M is the adsorbent amount (g) [21].

Adsorption Isotherm Studies

The adsorption temperature curve displays the changes in the amount of adsorption (q_e) with the residual pollutant concentration (C_e) in the solution at a constant temperature. The three parameters of time (120 min), the amount of adsorbent (jaft and tea waste: 7 g/L), pH (4.5 for jaft and 5.5 for tea waste), and E_2 hormone at 10 different concentrations (1-50 μg/L) were considered. Then, Langmuir, Freundlich, and Liu equilibrium adsorption models were investigated. Table 1 presents the equations corresponding to the isotherm models.

The Langmuir isotherm is the simplest and most widely used theory for monolayer adsorption [22, 23]. One of the features of this model is the dimensionless parameter separation coefficient R_L. Equation (3) represents this parameter. If $R_L>1$, the type of adsorbent is undesirable; $0>R_L>1$ represents the desired adsorbent; and $R_L=0$ denotes an irreversible adsorbent [21].

$$RL = \frac{1}{(1 + kCO)} \qquad (3)$$

The parameters q_m, adsorption capacity at the equilibrium time, and b, Langmuir constant, are obtained by using the slope and width of the origin of the graph of C_e/q_e versus C_e. In the Freundlich model, it is assumed reversible adsorption takes place, and this model is suitable for multilayer adsorption [22]. 1/n in the Freundlich equation also indicates the adsorption intensity of the isotherm type, which is irreversible if 1/n is zero, is optimal if it is 0-1, and is undesirable if greater than 1. n_f and K_f are the Freundlich adsorption constants related to the adsorption capacity and intensity, respectively. By plotting the log q_e versus log C_e, a line with a width of K_f and a slope of 1/n is yielded, which can be obtained by this coefficient. The Liu model predicted that the active sites do not have the same energy adsorber [24].

Adsorption Kinetics Studies

The adsorption kinetics was evaluated by mixing the adsorbent amounts of 0.85 g, 4.2 (for oak jaft), and 5.6 (for tea waste) at time points of 1 to 120. The pseudo-first-order and pseudo-second-order kinetics, intra-particle diffusion, and Elovich models were employed. Table 1 illustrates the kinetic models [21, 22, 24-27].

***Table 1.* Adsorption Isotherm and Kinetic Equations.**

	Equations	**Isotherm and Kinetic models**
$q_e = K_f C_e^{\frac{1}{n}}$	(4)	Freundlich [25]
$C_e/q_e = \left(1/K_a Q_m\right) + C_e/Q_m$	(5)	Langmuir [22]
$q_e = \frac{Q_{max}(K_g \cdot C_e)}{1+(K_g \cdot C_e)}.$ V	(6)	Liu [24]
$\log(q_e - q_t) = \log q_e - K_1 t/2.303$	(7)	Pseudo- first order [26]
$\frac{t}{q_t} = 1/K_2 q_e^2 + t/q_e$	(8)	Pseudo -second order [21]
$h_0 = K_2 \cdot q_e^2$	(9)	
$1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$	(10)	Elovich [27]

K_1 represents the initial adsorption value of the contaminant obtained by plotting Log (q_e –q_t) against t. In the second-degree equation, K_2 is the constant value obtained from the slope of the curve t/q_t versus t. According to the Elovich equation, α and β are calculated from the plot of the curve q_t versus ln (t). K_g, n_L and Q_{max} represent Liu equilibrium constant (L/mg), parameters without the Liu equation and Maximum adsorption capacity (mg/g), consecutively.

Modeling by CCD Method

The Design-Expert 7 software was used to design the experiments and perform the statistical analyses. Also, for optimization, pH (2-12), initial pollutant concentration (0.5 - 8.5 µg/L), adsorbent dose (1-9 g), and contact time (10-110 min) were taken into account. To extract the model and to find a maximum effect, central composite (CCD) and surface-response (RSM) methods were used. Thus, the range of each variable was coded in the range of -2 to +2 for optimal regression analysis. The variables were coded using the following equation:

$$X = \frac{x - \frac{[x_{max} + x_{min}]}{2}}{\frac{[x_{max} - x_{min}]}{2}} \qquad (11)$$

where X is the factor code, x is the actual value of the factor, and X_{min} and X_{max} are the minimum and maximum factor values. The axial values are the maximum factor. The intermediate level is defined as the (-1) level between the minimum level (-α) and central level (0) and the positive level of a (+1) value between the central level (0) and maximum values (+α). Table 2 shows the coded and actual values of the variables affecting 17β-estradiol removal. The number of experiments were also determined by Equation (12). In total, 30 experiments were performed by oak jaft, 30 by tea waste, and 20 under optimal conditions for isotherm and kinetic studies.

$$n = 2k + 2^k + cp \qquad (12)$$

n denotes the total number of trials, k is the number of variables, and cp is the number of central points. The model used in the level-response method is generally the quadratic model equation or its reduced form. The quadratic model can be expressed as follows:

$$Y = b_0 + \Sigma b_i x_i + \Sigma b_{ii} x_i^2 + \Sigma\Sigma b_{ij} x_i x_j + e \qquad (13)$$

Here, β_0, β, β_{ii}, and β_{ij} are the coefficients of constant, linear, quadratic, and regression interactions, respectively, and X_i and X_j are the encoded independent variables [28, 29].

Table 2. **Coded and actual values of the variables affecting the adsorption of 17β-estradiol by jaft and tea waste sorbents.**

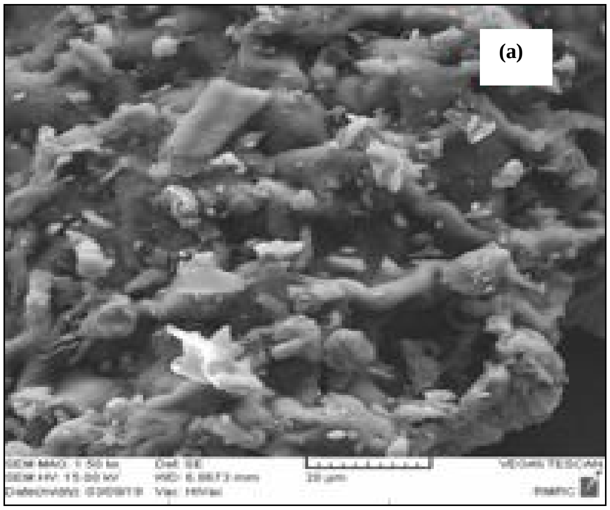
Variables	Symbol	Coded values				
		+α	*+1*	*0*	*-1*	*-α*
		actual values				
pH	X1	12	9.5	7	4.5	2
Adsorbent dose (g/L)	X2	0.9	0.7	0.5	0.3	0.1
Contact time (min)	X3	110	85	60	35	10
Hormone concentration (μg/L)	X4	8.5	6.5	4.5	2.5	0.5

An analysis of variance (ANOVA) was performed to test the validity of the quadratic polynomial model, as well as the relationship between the four independent variables and the response variable. The general predictive capability of the model was expressed by the coefficient of explanation (R^2) and coefficient of variation, and its statistical significance was determined by Fisher's exact test (F-value). From a statistical point of view, it is appropriate to have a correlation between predicted R^2, adjusted R^2, and experimental R^2 (>0.95). The significance of each coefficient related to the quadratic equation variables was evaluated by p-value and F-value, and the factors in the model were evaluated using the p-value set at a 95% confidence interval.

Results and Discussion

Characterization of Oak Jaft and Tea Waste Adsorbent

Fig. 1 displays the morphological characteristics of the jaft of oak and tea waste obtained by SEM. The reason is the cellular structure of the jaft. However, lignin-containing adsorbents have large pores. The porous structure of the adsorbent surface increases the specific surface area and leads to the adsorption of more amounts of hormones. SEM images demonstrated that the surface of the tea waste particles had a stem and porous structure due to their main constituents, such as cellulose and hemicellulose. Its roughness or heterogeneity can be due to activation with sulfuric acid [19, 30]. Fig. 2 illustrates the FTIR spectrum before and after E_2 adsorption on oak and tea waste sorbents. By comparing the FTIR adsorbents before and after adsorption, it was observed that factor peaks in tea waste had declined dramatically after adsorbent use. This reflects the reaction between the functional groups and the hormone present in the solution and demonstrates the role of chemical reactions in the adsorption process. The FTIR spectra offer valuable information about the chemical composition of the material.



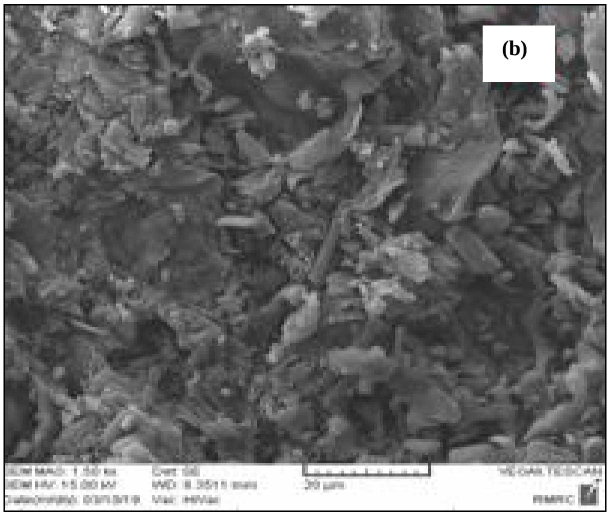


Figure 1. **SEM images of tea waste (a) and oak jaft (b)**

The functional groups present on the tea waste surface include -OH, aliphatic -CH, aromatic C=C and C=O, secondary amine groups: NH, $-CH_3$, CO, $-SO_3$, P=O, CO, C=O. These functional groups are sites at the adsorbent surface that increase its ability to adsorb. When 17β-estradiol was adsorbed into the tea waste or oak jaft, the peaks of the functional groups present on the oak jaft and tea waste were changed. Thus, groups of adsorbents may interact with 17β-estradiol (e.g. hydrogen bonding and electrostatic adsorption) [30, 31].

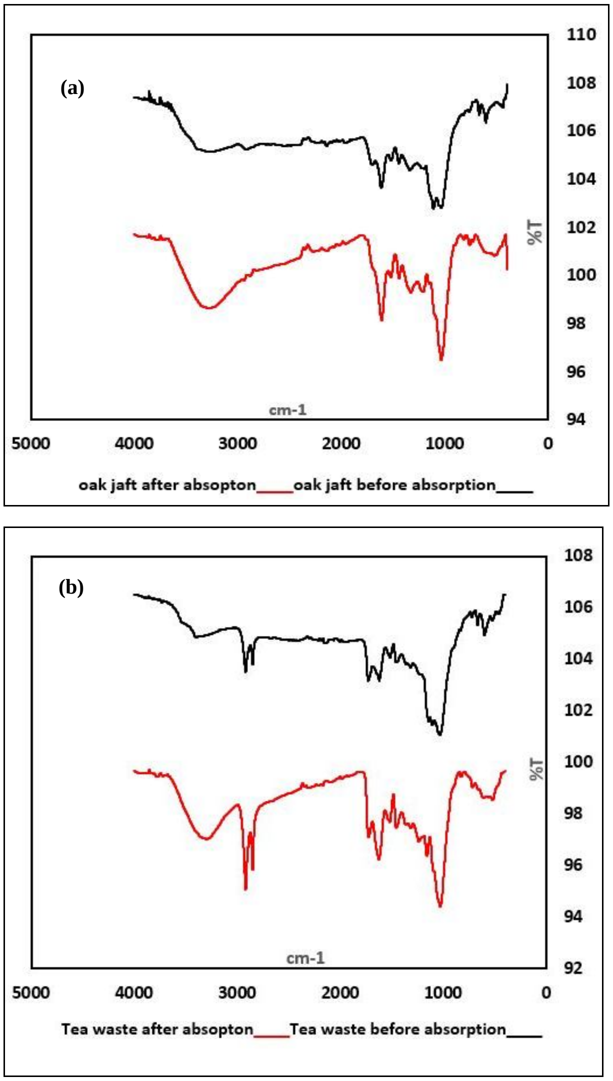


Figure 2. **FTIR spectra: (a) oak jaft adsorbent, and (b) tea waste before and after adsorption**

The XRD patterns displayed in Fig. 3 show that there are two broad peaks in both the oak jaft and the tea waste adsorbent, which could be due to a random graphite structure, indicating the amorphous structure of the adsorbents. In one part of the curve, some peaks are much less intense than the others, and this may be due to the removal of device noise. XRD results also show that both adsorbents had gypsum in the structure.

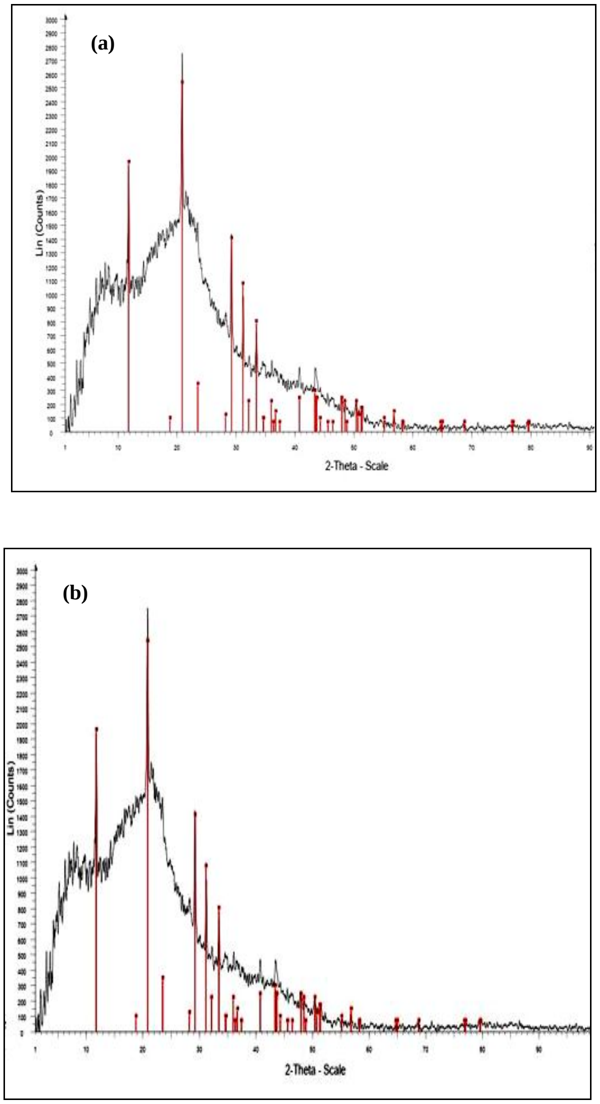


Figure 3. **Distribution of x-rays: (a) tea waste, and (b) oak jaft**

Experimental Design and Statistical Analysis

The order of the experiments performed by the RSM method by Design-Expert is presented in Table 3.

Table 3. **The number of tests of the 17β-estradiol adsorption process using oak jaft and tea waste in Design-Expert.**

Run	A: pH	B: Adsorption Dose (g/L)	C: Hormone concentration (mg/L)	D: contact time (min)	Response Removal % (by oak jaft)	Response Removal % (by tea waste)
1	2	5	4.5	60	61.9	33.49
2	7	5	0.5	60	73	71.94
3	7	5	8.5	60	47.7	48.06
4	4.5	3	6.5	85	48.6	38.91
5	4.5	7	2.5	35	63.2	39.17
6	9.5	3	2.5	35	33.04	32.74
7	9.5	3	6.5	35	20.8	23.48
8	12	5	4.5	60	29.1	15.63
9	9.5	7	6.5	85	49.6	49
10	9.5	3	6.5	85	37.65	24.53
11	9.5	7	2.5	85	59.27	61
12	7	5	4.5	60	53.5	70.56
13	7	5	4.5	60	55.9	68.24
14	7	5	4.5	60	53.7	70.75
15	9.5	3	2.5	85	48.7	44.85
16	7	5	4.5	60	55.2	69.26
17	9.5	7	6.5	35	30.7	30.55
18	4.5	7	6.5	35	51.6	34.11
19	7	1	4.5	60	26.75	34.67
20	4.5	3	2.5	85	60.9	53.28
21	4.5	7	6.5	85	71.3	69.86
22	7	9	4.5	60	61.42	63.49
23	7	5	4.5	60	52.3	67.95
24	4.5	7	2.5	85	82.41	81.05
25	9.5	7	2.5	35	38.57	36.21
26	4.5	3	6.5	60	29.04	23.45
27	7	5	4.5	60	54	70.39
28	7	5	4.5	110	66.93	69.84
29	4.5	3	2.5	35	43.2	34.08
30	7	5	4.5	10	28.57	21.84

According to Table 3, the maximum adsorption was 82.4% for the jaft adsorbent and 81.5% for tea waste at the time of 85 min, the adsorbent dose of 7 g/L, and pH = 4.5.

Figure 4 depicts the difference between the actual response and the predicted response to help identify values or groups of values not predicted by the model. According to the normal probability plots, the removal of E_2 by both adsorbents was linear to some extent, so the data distribution was assumed normal. In other words, there is no significant difference between the actual data and the data predicted by the model; therefore, the data are well-predicted by the model.

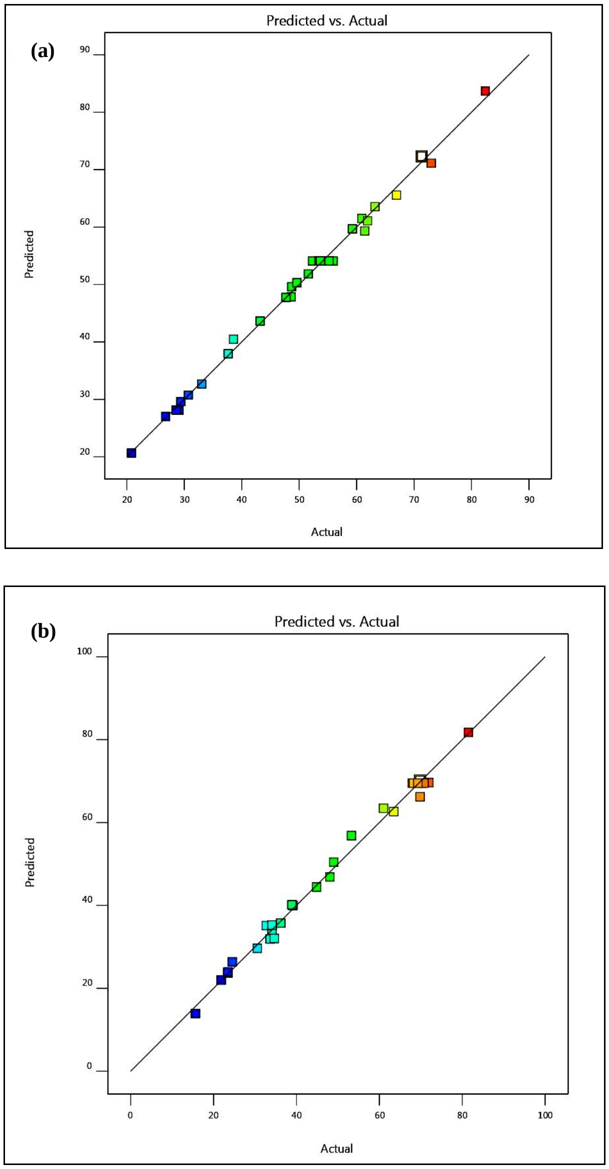


Figure 4. **Actual values versus predicted values: (a) removal of E_2 by oak jaft, and (b) tea waste**

ANOVA and Model Analysis

Table 4 presents the results of ANOVA and regression analysis on the 17β-estradiol adsorption regression equation by oak jaft and tea waste. According to the results, the model was found to be significant. The significance of each coefficient related to the quadratic equation variables was evaluated by p-value and F-value. Evidently, for the process variables (oak adsorbent concentration, initial E_2 concentration, contact time, and pH), a large F-value and a small P-value are obtained. Hence, the effect of all four parameters was significant. Low values of the coefficient of variation and standard deviation indicated the high accuracy of the quadratic model. Also, the analysis showed that the hormone is adsorbed by both oak jaft and tea waste adsorbents, and the increasing in pH, adsorbent dose, and contact time and decreasing the initial pollutant concentrations, increase the adsorption of E_2.

Table 4: Results of regression analysis and ANOVA for E2 adsorption by the tea waste and oak jaft.

Source	**Adsorbent**	**Sum of Squares**	**Df**	**Mean Square**	**F-Value**	**p-value Prob>F**	
Model	Oak Jaft	6761.06	14	482.93	245.85	<0.0001	Significant
	Tea Waste	10897.84	14	778.42	152.65	<0.0001	Significant
A: pH	Oak Jaft	1631.52	1	1631.52	830.58	<0.0001	
	Tea Waste	486.18	1	486.18	95.34	<0.0001	
B: Adsorbent Dose	Oak Jaft	1563.32	1	1563.32	795.68	<0.0001	
	Tea Waste	1406.38	1	1406.38	275.80	<0.0001	
C: Hormone Concentration	Oak Jaft	819.47	1	819.47	417.18	<0.0001	
	Tea Waste	778.62	1	778.62	152.69	<0.0001	
D: Contact Time	Oak Jaft	2102.63	1	2102.63	2101.63	<0.0001	
	Tea Waste	2929.13	1	2929.13	574.43	<0.0001	
AB	Oak Jaft	146.77	1	146.77	74.72	<0.0001	
	Tea Waste	35.28	1	35.28	6.92	0.0189	
AC	Oak Jaft	3.98	1	3.98	2.03	0.1751	
	Tea Waste	1.92	1	1.92	0.38	0.5488	
AD	Oak Jaft	0.86	1	0.86	0.44	0.5193	
	Tea Waste	198.39	1	198.39	38.91	<0.0001	
BC	Oak Jaft	5.22	1	5.22	2.66	0.1238	
	Tea Waste	25.55	1	25.55	5.01	0.0408	
BD	Oak Jaft	5.18	1	5.18	2.63	0.1254	
	Tea Waste	377.64	1	377.64	66.21	<0.0001	
CD	Oak Jaft	0.12	1	0.12	0.061	0.8089	
	Tea Waste	48.02	1	48.02	9.42	0.0078	
Residual	Oak Jaft	29.46	15	1.96			
	Tea Waste	76.49	15	5.1			
Lack of fit	Oak Jaft	21.24	10	2.12	1.29	0.4101	not Significant
	Tea Waste	68.97	10	6.9	4.58	0.0553	not Significant

Results of regression analysis for E2 adsorption

R^2	Oak Jaft	0.9957	CV	Oak Jaft	2.82
	Tea Waste	0.9930		Tea Waste	4.66
Predicted R^2	Oak Jaft	0.9802	Standard Deviation	Oak Jaft	1.40
	Tea Waste	0.9628		Tea Waste	2.26
Adjusted R^2	Oak Jaft	0.9916	Enough Accuracy	Oak Jaft	63.6
	Tea Waste	0.9865		Tea Waste	42.5

Effect of Operational Factors and Process Optimization

According to the validation tests, it was found that in the removal of E_2, the maximum removal by activated carbon, tea waste, and oak jaft equaled 87%, 81%, and 74%, respectively. By comparing these three adsorbents in the adsorption of E_2, it can be stated that tea waste and oak jaft can compete with activated carbon in the removal of steroid hormones.

Influence of Operation Parameters on Process Efficiency

Figure (5a) shows the interaction of 17β-estradiol concentration and the adsorption dose of tea waste. The removal percentage increased from 1 to 7 mg/L by increasing the concentration of tea waste and reached its maximum value; then, by increasing the amount of tea waste in the solution, the efficiency of removal was reduced. This increase can be explained as follows: First, as the amount of adsorbent increases, the available sites for hormone adsorption and the probability of the adsorbent colliding with the hormone molecules increase, leading to better adsorption. Later, as the amount of adsorbent rises, the removal efficiency is reduced [14]. Here, simultaneously with the increased amount of waste, the solution pH may have increased; because some of the basic agents' bonding is weakened when the tea waste is activated, the bonds are broken when being mixed with the 17β-estradiol solution. In this way, alkaline agents overcome the acidic agents, and the pH of the alkaline solution is reduced by the removal of 17β-estradiol. It is observed that, in these conditions, the highest removal amount of 17β-estradiol was ~72%. Also, as to the effect of tea waste concentration on 17β-estradiol removal, the adsorption efficiency by oak jaft and tea waste decreased with increasing the initial 17β-estradiol concentration. This may be explained by the fact that the active sites of the adsorbent level are limited, and with an increase in the contaminant, a deficiency in the surface and the active sites occur, so the adsorption decreases [16].

Figure (5b) displays the concomitant effect of the concentration of oak jaft and pH on 17β-estradiol removal efficacy. The highest efficiency of 17β-estradiol removal (79%) occurred at a concentration of 9 mg/L and pH=2. Both the concentration of oak jaft and the level of pH were effective on 17β-estradiol removal. By increasing the adsorption dose of the oak jaft, the driving force (including van der Waals forces) may be increased, and the transfer of hormone particles on the active sites of the adsorbent surface may occur more rapidly [32]. Also, the reason for the high efficiency in acidic pHs can be as follows: The active sites at the level of the oak jaft adsorbent (carboxylic, phenolic, hydroxyl) are protonated, and the positive charge on the adsorbent level of the jaft increases. This increases the electrostatic force between the hormone molecules and the surface of the jaft particles, resulting in better adsorption [33]. Fig. (5c) shows the simultaneous effect of pH and adsorption concentration of tea waste. At near-neutral pH (slightly acidic pH), both at high and low levels of tea waste, the adsorption efficiency is at its highest, but the removal intensity is more pronounced at high concentrations. In alkaline and very acidic pHs, the removal amount is reduced. The highest removal degree of 17β-estradiol was 70.75%. In alkaline pHs, the repulsive force between the adsorbent and the hormone may be increased, in this area, the jaft particles and the 17β-estradiol are both negative, which is consistent with the results of previous studies[14, 34]. The reason for the lower adsorption percentage at very acidic pHs is probably the competition of H^+ ions with the causative agents of 17β-estradiol cation levels [19].

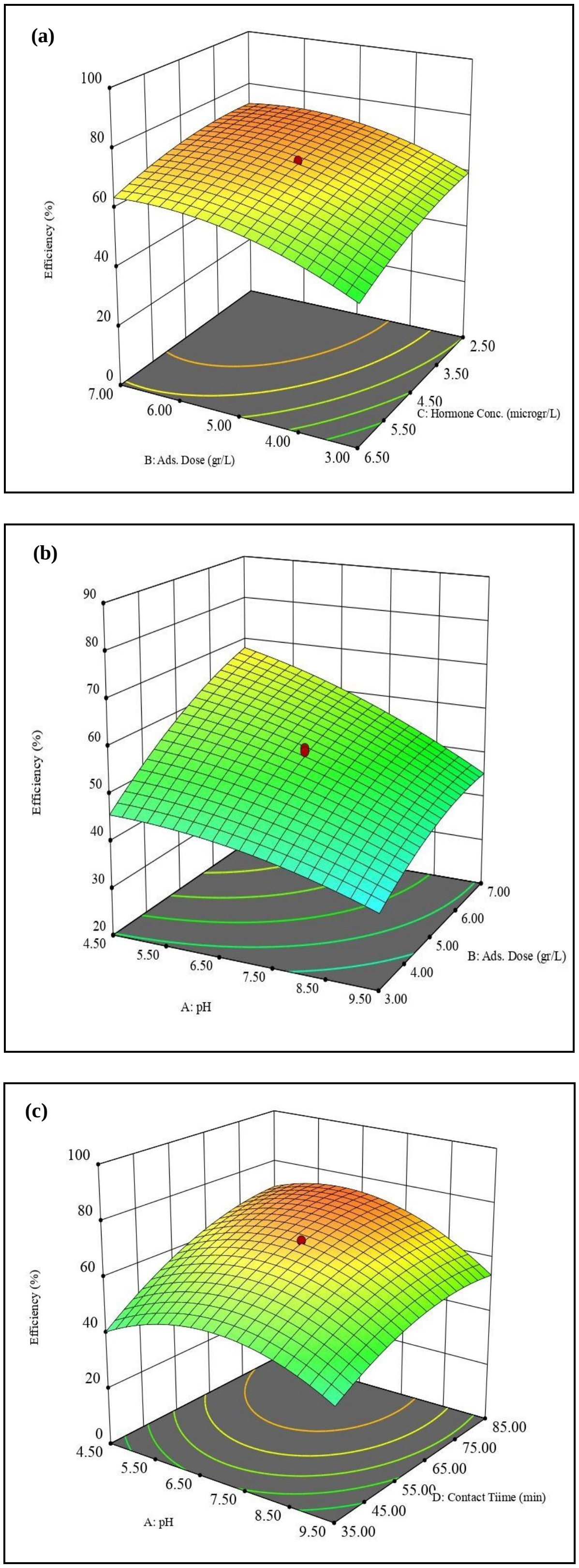


Figure 5. **3D plots of the effect of variables on the E_2 elimination efficiency: (a) E_2 concentration and tea waste, (b) pH and oak jaft, (c) pH and the dose of tea waste**

Figures (6a) and (6b) depict the interaction of contact time and pollutant concentration. Figure (6a), which is related to the adsorption of the oak jaft, shows that at each concentration of the hormone, the adsorption amount increased with increasing the contact time. If the concentration of 17β-estradiol in the solution is lower and the contact time is increased, the contamination is better adsorbed. The highest 17β-estradiol removal amount was 82%. Also, in Fig. (6b), which is related to the adsorption of tea waste, it is observed that both at low concentrations of the hormone and high concentrations, with increasing the time, elimination increased to some extent (60 min) and then decreased. The highest removal of 17β-estradiol in this case (78%) occurred with 17β-estradiol 0.5 µg/L and the contact time of 60 minutes.

As the contact time increased from 10 to 110 minutes, the efficiency of 17β-estradiol removal by both adsorbents increased. As contact time increases, there is a greater opportunity for hormone particles to bind to functional groups at the adsorbent level, resulting in a better adsorption process. The maximum removal time was up to 85 min, and after this time, efficiency did not change much; thus, 85 min can be the equilibrium time of adsorption. In terms of thermodynamic equilibrium at this point, the degree of adsorption equals the degree of desorption. This is because, during the process of 17β-estradiol uptake, 17β-estradiol molecules were initially degraded rapidly by mass transfer power to reach the boundary layer adsorbent. Then, slowly they enter from the boundary layer to the surface of the adsorbent. Since, most active sites of the adsorbent surface are occupied, the adsorbent particles release hormones into the holes [35].

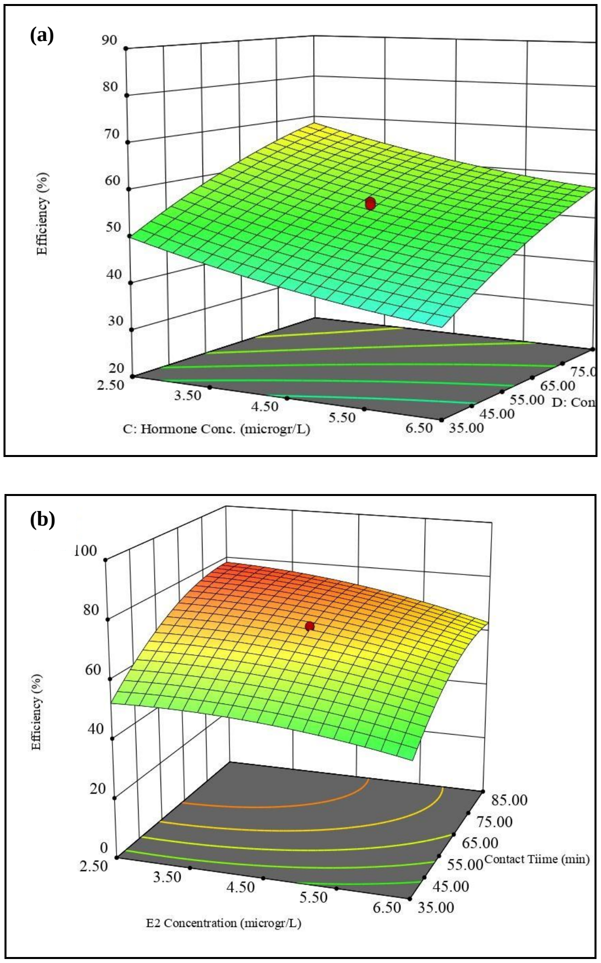


Figure 6. **3D plots of the effect of variables on the E_2 elimination efficiency: (a) time and concentration of hormone (oak jaft), (b) time and concentration of hormone (tea waste)**

In the general examination of pH, it was found that pH plays a key role in the adsorption process. According to Table 3, the maximum 17β-estradiol uptake on the oak jaft and tea waste was 82.4 and 81.5, respectively, at pH = 4.5. The adsorption amount was high in acidic pHs and in alkaline pHs. The high degree of adsorption in acidic pHs can be justified by the use of the adsorbent isoelectric point (PH_{ZPC}); given PH_{ZPC}, the point where the positive and negative charges are equal to the level of adsorption, the jaft and the tea waste were 5 and 5.5, respectively. At higher pHs than this point, the potential charge surface area is negative and, at lower pHs, the adsorption surface charge potential is positive. As a result, in solutions with pH above the isoelectric point, due to the negative surface charge of the adsorbent, a repulsion is created between the hormone anions and the adsorbent, and the elimination is reduced. In contrast, at pHs lower than PH_{ZPC}, due to the positive charge of the adsorbent surface, the hormone surface anions are adsorbed by the electrostatic force of the adsorption of the positively charged surface, and the adsorption is enhanced [23, 31, 33].

Optimum Condition and Adsorption Model

Optimal conditions were obtained using Design-Expert, as described in Table 5.

Table 5. **Optimal values of independent variables studied in E2 removal.**

Processes Variable	**E_2-tea waste**	**E_2-oak jaft**
pH	5.4	4.2
Adsorbent concentration	6.6	8.5
Hormone concentration	1.74	5.4
Contact time	85	105

To validate the experiments for the natural adsorbents of oak jaft and tea waste as well as activated carbon adsorbents, experiments were carried out under optimal conditions with three replications for each adsorbent with a specific concentration of E_2 hormone. The results showed that in the removal of E_2, the maximum removal by activated carbon adsorbents, tea waste, and oak jaft was 87%, 81%, and 74% (from three replicates of each adsorbent, respectively). A comparison of these three adsorbents in the removal of E_2 revealed that the adsorption of 17β-estradiol by activated carbon and tea waste was not significantly different. It can be stated that tea waste and oak jaft adsorbents produced in this study can compete with commercial activated carbon for the removal of steroid hormones. The proposed model between 17β-estradiol adsorption and selected variables was designed by using a quadratic multivariate equation modeled as Equation

(14) by the design expert software. Equation (14) is the final equation in terms of coded factors:

$$Efficiency = 5410-8.25A+228.07B-5.84C+9.36D-3.03AB+0.5AC-0.23AD+0.57BC+0.57BD-2.38A^2-2.73B^2+1.34C^2-1.81D^2 \quad (14)$$

Here, A is the variable pH, B the amount of adsorbent, C the initial concentration of 17β-estradiol, and D the duration of contact. Accordingly, the quadratic equation analysis as proposed by the software was performed to find the relationship between the main variables and E_2 hormone removal.

Adsorption Isotherms

Adsorption isotherm is a major and effective parameter of adsorption studies due to the relationship between the adsorbent and adsorption, as well as its determining role in adsorbent surface properties, optimization, and adsorption capacity [13, 34]. Fig. 7 shows the Langmuir, Freundlich, and Liu isotherm models. The results indicated that all three models were highly correlated, but the Freundlich model with R^2 values > 0.97 demonstrated better agreement with the adsorption experimental data. According to the data from adsorption studies, Freundlich showed the best interpretation of E_2 adsorbed by the jaft and tea waste adsorbents. Therefore, these results suggested that the reversible adsorption and desorption layer is not limited. In a study by Shafiee et al. it was found that the adsorption of toxic metals from aqueous solutions on an oak adsorbent follows the Freundlich model [36].

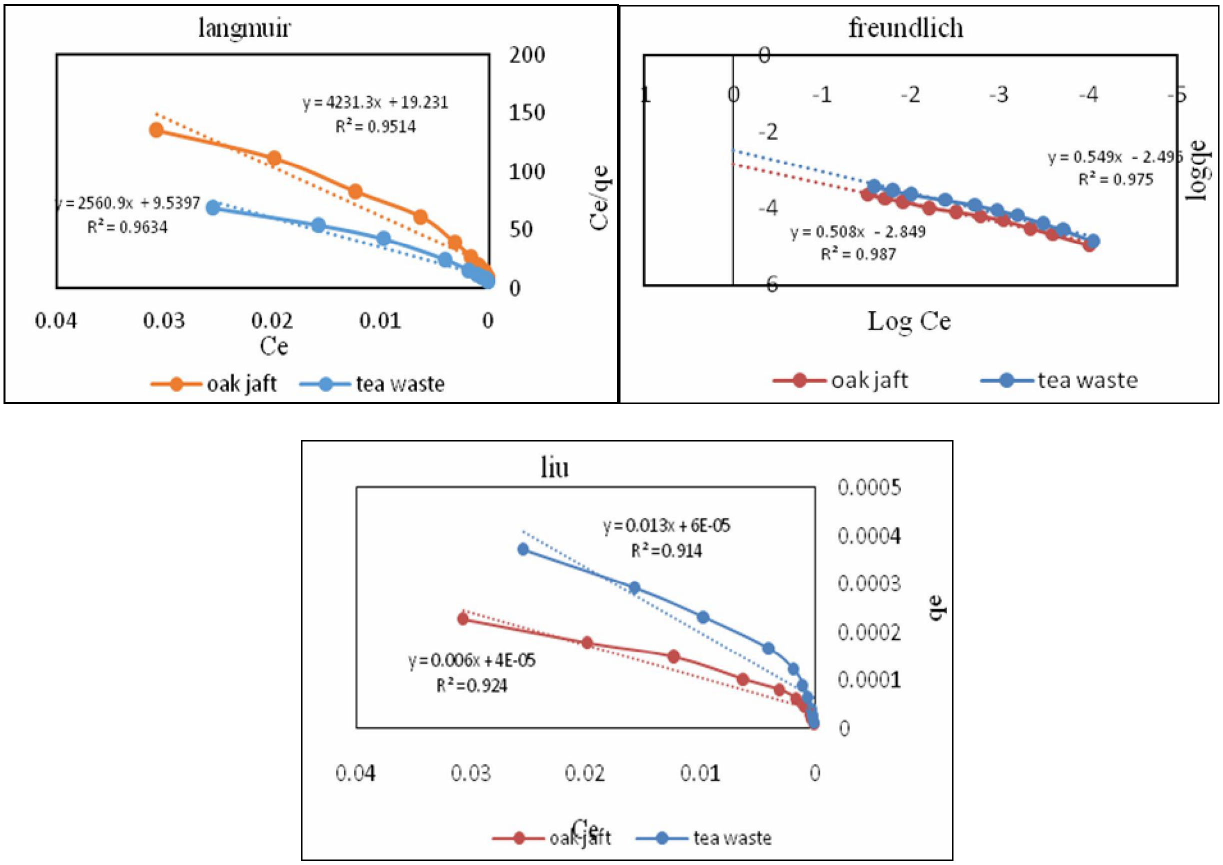


Figure 7. **The Liu isotherm diagram of E_2 adsorption by jaft and tea waste sorbents**

Table 6. **Parameters calculated for adsorption isotherm models.**

Adsorbent	Langmuir				Freundlich				Liu			
	Q_m(mg/g)	b(mg/l)	R_L	R^2	1/n	N	K_F (L/mg)	R^2	Q_m (mg/g)	n_L	K_g (Lmg^{-1})	R^2
Oak jaft	0.00023	226.08	0.387	0.95	0.2532	3.94	0.0014	0.98	149.25	0.273	0.0041	0.92
Tea waste	0.00039	269.05	0.347	0.96	0.5492	1.82	0.0032	0.97	74.07	0.321	0.0025	0.91

The results of examining the adsorption of 17β-estradiol with activated carbon were described by Freundlich and Langmuir models as suitable isotherm models[34]. According to Table 6, the maximum adsorption capacity (Q_m) of 17β-estradiol by oak jaft and tea waste is 0.00023 and 0.00039 mg/g, respectively. From the consistency between the parameter (Q_m) in this study and that of other similar studies, it can be deduced that due to the different conditions of the experiments, the parameters cannot be directly compared across studies. Therefore, R_L and 1/n parameters can be used to express the suitability of oak jaft and tea waste adsorbents for 17β-estradiol adsorption. The R_L parameter, or separation coefficient, in the present study had values of 0-1 for both jaft and tea waste. Also, the value of 1/n (sorption intensity) according to Table 6 was between 0 and 1; a value of 1/n in this range indicates more efficient adsorption and formation of relatively strong bonds between oak jaft and tea waste with the 17β-estradiol molecule. These data are similar to the results of Malhotra on the use of tea waste sorbents in the adsorption process [35]. Therefore, considering the desirability of R_L and 1/n, it can be stated that the adsorbents used here were desirable for the removal of E_2. The parameters of the Liu model can also be adapted to determine the adsorption mechanism. The parameters of this model are in line with the parameters of the other two models and their coefficient of determination is high.

Adsorption Kinetics

Kinetic parameters provide valuable information for determining the velocity and adsorption mechanism; therefore, their use in adsorption studies is useful and necessary. There are several models for this purpose, the most common of which is the pseudo-first-order and the pseudo-second-order equation. Herein, the pseudo-first-order, pseudo-second-order, and Elovich models were used. The graphs of these equations are presented in Figure 8, and the correlation coefficients and kinetic parameters of the models are given in Table 7. The results of kinetic adsorption experiments showed that the pseudo-second-order model with $R^2 > 0.98$ describes the kinetic data better than the pseudo-first-order and all-in-one models. Therefore, it can be stated that chemical adsorption is a limiter step in the process of E_2 uptake by jaft and tea waste adsorbents. In general, E_2 adsorption on oak and tea waste follow two mechanisms; in the first stage, a rapid bond is formed between E_2 molecules and the adsorbent surface (jaft or tea waste), and in the next step, intrusion occurs within the particle. By determining the constant process and the slope of the q_t curve relative to the root, the adsorption resistance against intrusion into the particle is measurable. According to Figure 8, t/Q_t increased with increasing time. This could be because, initially, E_2 molecules are rapidly transported to the oak jaft or tea waste adsorbent boundary layer by a high-velocity mass, and then penetrate the adsorbent surface at a slower rate. The reason for the slowdown is the occupation of active sites. Eventually, the hormone particles are released into the adsorbent cavities [37]. It is also observed that the adsorption capacity increases with increasing the initial concentration of the hormone. This indicates that as the initial concentration of the hormone increases, the force of mass transfer increases, and eventually, the reaction between the hormone and the adsorbent increases; consequently, the adsorption capacity increases [38]. The results of a large number of adsorption studies have shown a better description of kinetic data by the pseudo-second-order model [19, 30, 36].

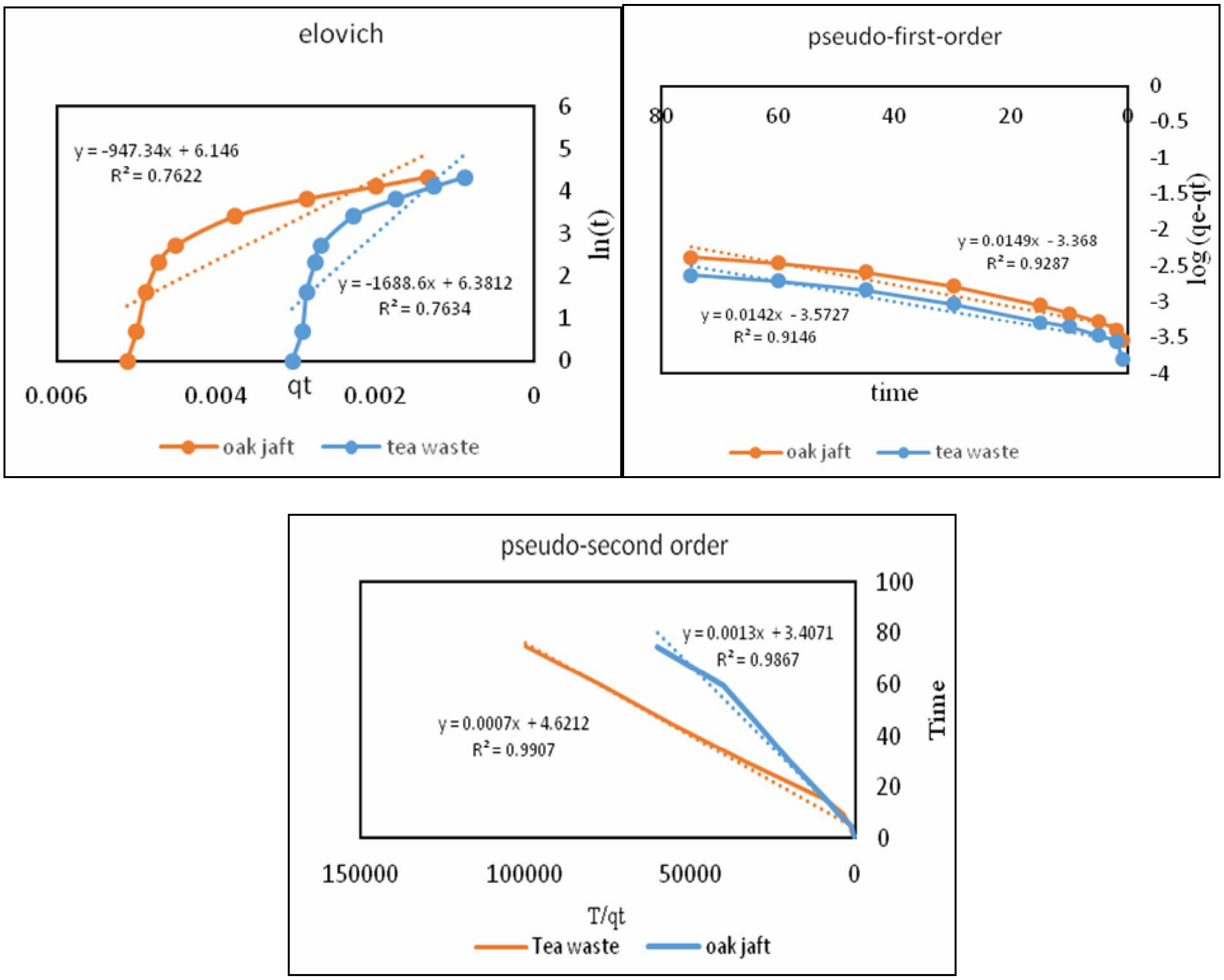


Figure 8. **Plots of the kinetics of E_2 adsorption by oak jaft and tea waste**

Table 7. Parameters calculated for the adsorption kinetics models.

	Pseudo-first order			Pseudo-second order				Elovich	
Adsorbent	K_1	q_e(mg/g)	R^2	$K_2 \times 10^{-3}$	q_e (mg/g)	H (mg/g min)	R^2	β (mg/g)	R^2
Oak	0.32	3738.52	0.92	0.00049	769.23	0.000053	0.98	0.00059	0.76
Tea waste	0.34	2333.45	0.91	0.00105	1428.57	0.000043	0.99	0.00105	0.76

Conclusion

The percentage of E_2 removal is largely dependent on the pH of the solution; the maximum removal of 17β-estradiol on the oak jaft and tea waste occurs in an acidic pH. An evaluation of the effect of the adsorbent dose revealed that the adsorption amount of E_2 was somewhat similar in both adsorbents, but the effect of tea waste was slightly different from that of the oak jaft. In other words, the removal efficiency was enhanced by increasing the amount of jaft in the hormone solution. However, in the case of tea waste, with increasing the dose of tea waste, the percentage of removal of the hormone increased, and then the amount of E_2 decreased with increasing this value. In the process of 17β-estradiol adsorption, the Freundlich model was selected as the model of choice due to its better fit to the experimental data. This model showed the reversible adsorption of E_2 onto the adsorbents. Moreover, based on the suitability of R_L and 1/n parameters, the adsorption of E_2 was favorable on both oak jaft and tea waste.

Acknowledgments

This study is based on a master's thesis entitled "Investigation of Steroid Hormones' Removal from Aquatic Environments Using Natural Absorbents," Approved by Yasuj University of Medical Sciences with approval Code IR.YUMS. REC.1397.098. The authors extend their gratitude to Yasuj University of Medical Sciences for helping facilitate this research.

Conflict of Interest

The authors have declared no conflict of interest.

References

1. K. Czarny, D. Szczukocki, B. Krawczyk, S. Skrzypek, E. Miękoś and R. Gadzała-Kopciuch, *J. Appl. Phycol.*, 31 (2019) 389. https://doi.org/10.1007/s10811-018-1589-9.
2. A. C. Naldi, P. B. Fayad, M. Prévost and S. Sauvé, *Chem. Cent. J.*, 10 (2016) 30. https://doi.org/10.1186/s13065-016-0174-z.
3. J. O. Ojoghoro, A. J. Chaudhary, P. Campo, J. P. Sumpter and M.D. Scrimshaw, *Sci Total Environ.*, 579 (2017) 1876. https://doi.org/10.1016/j.scitotenv.2016.11.176.
4. C. Qin, D. Troya, C. Shang, S. Hildreth, R. Helm and K. Xia, *Environ. Sci Technol.*, 49 (2015) 956. https://doi.org/10.1021/es504815t.
5. G. Hassani, A. Babaei, A. Takdastan, M. Shirmardi and F. Yousefian, *Glob. Nest J.*, 18 (2016) 855. https://doi.org/10.30955/gnj.002053.
6. M. Clara, B. Strenn, E. Saracevic and N. Kreuzinger, *Chemosphere*, 56 (2004) 843. https://doi.org/10.1016/j.chemosphere.2004.04.048.
7. Y. Zhang, J. Zhou and B. Ning, *Water Res.*, 41 (2007) 19. https://doi.org/10.1016/j.watres.2006.09.020.
8. A.R. Yazdanbakhsh, A.S. Mohammadi, A.A. Alinejad, G. Hassani, S. Golmohammadi, S.M. Mohseni, M. Sardar and V. Sarsangi, *Water Environ. Res.*, 88 (2016) 2121. https://doi.org/10.2175/106143016X14733681695447.
9. R.F. Brocenschi, R.C. Rocha-Filho, N. Bocchi and S.R. Biaggio, *Electrochim. Acta*, 197 (2016) 186.

https://doi.org/10.1016/j.electacta.2015.09.170.

10. A. Hom-Diaz, M. Llorca, S. Rodríguez-Mozaz, T. Vicent, D. Barceló and P. Blánquez, *J. Environ. Manage.*, 155 (2015) 106. https://doi.org/10.1016/j.jenvman.2015.03.003.
11. C. Joel, E. Kiprop and L. Mwamburi, *Appl. Environ. Microbiol.*, 5 (2017) 1. https://doi.org/10.12691/jaem-5-1-1.
12. G. Hassani, A. Alinejad, S. Rezaei, A. Jamshidi, S. Fazeli Farsani and M.R. Zare, *Fresenius Environ. Bull.*, 25 (2016) 2919.
13. S. Patel, J. Han, and W. Gao, *J. Environ. Chem. Eng.*, 3 (2015) 1562. https://doi.org/10.1016/j.jece.2015.04.027.
14. H. Nourmoradi, K.F. Moghadam, A. Jafari, and B. Kamarehie, *J. Environ. Chem. Eng.*, 6 (2018) 6807. https://doi.org/10.1016/j.jece.2018.10.047.
15. S. Yamauchi, T. Yamagishi, K. Kirikoshi, and M. Yatagai, *J. Wood Sci.*, 60 (2014) 473. https://doi.org/10.1007/s10086-014-1431-1.
16. M.K. Mondal, *Korean J. Chem. Eng.*, 27 (2010) 144. https://doi.org/10.1007/s11814-009-0304-6.
17. M. Ahmaruzzaman and S.L. Gayatri, *J. Chem. Eng. Data*, 55 (2010) 4614. https://doi.org/10.1021/je100117s.
18. F. Bolat, S. Govori, A. Haziri, S. Spahiu and F. Faiku, *J. Int. Environ. Appl. Sci.*, 5 (2010) 63.
19. M.A. Ahsan, S.K. Katla, M.T. Islam, J.A. Hernandez-Viezcas, L.M. Martinez, C.A. Díaz-Moreno, J. Lopez, S.R. Singamaneni, J. Banuelos, J. Gardea-Torresdey and J.C. Noveron, *Environ. Technol. Innov.*, 11 (2018) 23. https://doi.org/10.1016/j.eti.2018.04.003.
20. N.K. Niazi, I. Bibi, M. Shahid, Y.S. Ok, S.M. Shaheen, J. Rinklebe, H. Wang, B. Murtaza, E. Islam, M. Farrakh Nawaz and A. Lüttge, *Sci Total Environ.*, 621 (2018) 1642. https://doi.org/10.1016/j.scitotenv.2017.10.063.
21. S. Kuppusamy, P. Thavamani, M. Megharaj, K. Venkateswarlu, Y.B. Lee and R. Naidu, *Water, Air, Soil Pollut.*, 227 (2016) 62. https://doi.org/10.1007/s11270-016-2760-z.
22. H. Hamad, Z. Ezzeddine, S. Kanaan, F. Lakis, A. Hijazi and M.-A. Moussawi, *Adv. Powder Technol.*, 27 (2016) 631. https://doi.org/10.1016/j.apt.2016.02.019.
23. H. Godini, F. Hashemi, L. Mansuri, M. Sardar, G. Hassani, S. Mohseni, A. Alinejad, S. Golmohammadi and A. Sheikhmohammadi, *J. Water Reuse Desal.*, 6 (2016) 544. https://doi.org/10.2166/wrd.2016.068.
24. F.M. Machado, C.P. Bergmann, E.C. Lima, M.A. Adebayo and S.B. Fagan, *Mater. Res.*, 17 (2014) 153. https://doi.org/10.1590/S1516-14392013005000204.
25. A. Gupta and C. Balomajumder, *J. Environ. Chem. Eng.*, 3 (2015) 785. https://doi.org/10.1016/j.jece.2015.03.003.
26. T. Madrakian, A. Afkhami, and M. Ahmadi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 99 (2012) 102. https://doi.org/10.1016/j.saa.2012.09.025.
27. M. Vithanage, S.S. Mayakaduwa, I. Herath, Y.S. Ok and D. Mohan, *Chemosphere*, 150 (2016) 781. https://doi.org/10.1016/j.chemosphere.2015.11.002.
28. G. Hassani, A. Takdastan, M. Ghaedi, G. Goudarzi, A. Neisi and A.A. Babaei, *Int. J. Electrochem. Sci.*, 11 (2016) 8471. https://doi.org/10.20964/2016.10.36.
29. A. Jamshidi, S. Rezaei, G. Hassani, Z. Firoozi, H.R. Ghaffari and H. Sadeghi, *J. Environ. Health Sci. Eng.*, 18 (2020) 163.

https://doi.org/10.1007/s40201-020-00449-0.

30. L. Liu, S. Fan and Y. Li, *Int. J. Env. Res. Public Health*, 15 (2018) 1321. https://doi.org/10.3390/ijerph15071321.
31. L. Niazi, A. Lashanizadegan and H. Sharififard, *J. Clean. Prod.*, 185 (2018) 554. https://doi.org/10.1016/j.jclepro.2018.03.026
32. H. Nourmoradi, M. Avazpour, N. Ghasemian, M. Heidari, K. Moradnejadi, F. Khodarahmi, M. Javaheri and F.M. Moghadam, *J. Taiwan Inst. Chem. Eng.*, 59 (2016) 244. https://doi.org/10.1016/j.jtice.2015.07.030.
33. Z. Aksu and Ö. Tunç, *Process Biochem.*, 40 (2005) 831. https://doi.org/10.1016/j.procbio.2004.02.014.
34. I. Turku, T. Sainio and E. Paatero, *Chem. Eng. Trans.*, 17 (2009) 1555. https://doi.org/10.3303/CET0917260.
35. M. Malhotra, S. Suresh and A. Garg, *Environ. Sci. Pollut. Res.*, 25 (2018) 32210. https://doi.org/10.1007/s11356-018-3148-y.
36. M. Shafiee, R. Foroutan, K. Fouladi, M. Ahmadlouydarab, B. Ramavandi and S. Sahebi, *Adv. Powder Technol.*, 30 (2019) 544. https://doi.org/10.1016/j.apt.2018.12.006.
37. S. Senthilkumaar, P.R. Varadarajan, K. Porkodi and C.V. Subbhuraam, *J. Colloid Interface Sci.*, 284 (2005) 78. https://doi.org/10.1016/j.jcis.2004.09.027.
38. I.A.W. Tan, A.L. Ahmad and B.H. Hameed, *J. Hazard. Mater.*, 154 (2008) 337. https://doi.org/10.1016/j.jhazmat.2007.10.031.