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Elucidation of the naproxen sodium adsorption onto activated carbon prepared from waste apricot: Kinetic, equilibrium and thermodynamic characterization

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Abstract

In this study, activated carbon (WA11Zn5) was prepared from waste apricot, which is waste in apricot plants in Malatya, by chemical activation with ZnCl₂. BET surface area of activated carbon is determined as $1060 \text{ m}^2/\text{g}$. The ability of WA11Zn5, to remove naproxen sodium from effluent solutions by adsorption has been studied. Equilibrium isotherms for the adsorption of naproxen sodium on activated carbon were measured experimentally. Results were analyzed by the Langmiur, Freundlich equation using linearized correlation coefficient at 298 K. The characteristic parameters for each isotherm have been determined. Langmiur equation is found to best represent the equilibrium data for naproxen sodium–WA11Zn5 systems. The monolayer adsorption capacity of WA11Zn5 for naproxen sodium was found to be 106.38 mg/g at 298 K. The process was favorable and spontaneous. The kinetics of adsorption of naproxen sodium have been discussed using three kinetic models, i.e., the pseudo first-order model, the pseudo second-order kinetic equation could describe the adsorption kinetics for naproxen sodium onto WA11Zn5. The thermodynamic parameters, such as ΔG° , ΔS° and ΔH° , were calculated. The thermodynamics of naproxen sodium–WA11Zn5 system indicates endothermic process.

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1. Introduction

Large amounts of different pharmaceuticals are used worldwide. Pharmaceuticals are class of emerging environmental contaminants that are extensively and increasingly being used in human and veterinary medicine. Medicines have been detected in sewage treatment plant effluents (STP), surface waters, ground water. Non-steroidal anti-inflammatory drugs (e.g. ibuprofen, naproxen or diclofenac) and lipid regulators are extensively used as non-prescription drugs, with an estimated annual consumption in developed countries of several tonnes [1,2].

Naproxen is a member of the arylacetic acid group of nonsteroidal anti-inflammatory drugs. The chemical names for

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naproxen and naproxen sodium are (*S*)-6-methoxy- α -methyl-2-naphthaleneaacetic acid and (*S*)-6-methoxy- α -methyl-2-naphthaleneacetic acid, sodium salt, respectively. Naproxen and other pharmaceuticals are continually introduced into aquatic environs and prevalent at detectable concentrations, which can affect water quality and ecosystem health and potential impact drinking water supplies.

A study of drug adsorption onto activated carbon has a significant place in the literature. Some studies that concerned with drugs adsorption have been reported in the literature. Gereli et al. studied promethazine hydrochloride (cationic drug) sorption onto K10 montmorillonite [3], Melillo et al. ibuprofen adsorption to activated carbons [4], Otero et al. salicylic acid adsorption onto polymeric adsorbents and activated charcoal [5], Bridelli et al. adsorption of some drugs to the surface melanin particles [6]. In addition, various adsorbents are used for water treatment [7]. However, adsorption of naproxen sodium on to activated carbon was not examined in literature.

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The aim of this work is to test adsorption behavior of activated carbon prepared from waste apricot for the removal of naproxen sodium from aqueous solution. Equilibrium, kinetic and thermodynamic parameters are investigated. The present study could be useful for analyzing the adsorption behavior of activated carbon in the removal of naproxen sodium from aqueous solutions.

2. Experimental

2.1. Materials

Anhydrous naproxen sodium (16086488, chemical formula = $C_{14}H_{13}O_3Na$, MW = 252.24 g/mol, 99.8% purity) supplied by Abdi Ibrahim Drug (Istanbul/Turkey), was used in experiments without further purification or processing. One thousand milligrams per liter of stock solution was prepared by dissolving the required amount of naproxen sodium in distillated water. Working solutions of the desired concentrations were obtained by successive dilutions. The concentration of the naproxen sodium solution was determined by UV–vis spectrophotometry at 230 nm in water [8].

2.2. Preparation of activated carbon (WA11Zn5)

Waste apricot supplied by Malatya (Turkey) apricot plant. This was dried under laboratory conditions and then dried again at 100 °C (Model FN 400, Nüve).

In the first step of activation, the starting material was mixed with $ZnCl_2$ at the $ZnCl_2$ /starting material weight ratio of 1:1 and the mixture was kneaded with adding distillated water. The mixture was then dried at 110 °C to prepare the impregnated sample.

In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (i.d. = 60 mm). The impregnated sample was heated up to activation temperature (500 °C) under N₂ flow (100 mL min⁻¹) at the rate of 10 °C min⁻¹ and hold at the activation temperature for 1 h. After activation, the sample was cooled down under N₂ flow and 0.5N HCl was added on to activated sample. Activated sample was washed sequentially several times with hot distillated water to remove residual chemical until it did not give chloride reaction with AgNO₃. The washed sample was dried at 110 °C to prepare activated carbon and then sieved to -200 mesh fraction (average particle size 0.075 mm) [9,10].

2.3. Instrumentation

A Tri Star 3000 (Micromeritics, USA) surface analyzer was used to measure nitrogen adsorption isotherm at 77 K in the range of relative pressure 10^{-6} to 1. Before measurement, the sample was degassed at 300 °C for 2 h. The surface areas were calculated by the BET (Brunauer–Emmett–Teller) method assuming that the surface area occupied by per physisorbed nitrogen molecule was 0.162 nm². The total pore volumes were estimated to be the liquid volume of N₂ at relative pressure (*P*/*P*_o) of 0.9814. The *t*-plot method was applied to calculate the micropore volume and mesopore surface area, and mesopore volume was determined by subtracting the micropore volume from total pore volume. The average pore radius were estimated from BET surface area and total pore volume assuming an open-ended cylindrical pore model without pore networks and from BJH (Barret–Joymer–Halenda) method [11].

The spectrophotometric determination of naproxen sodium was done on a Shimadzu UV/vis spectrophotometer (model UV-2100S, Japan).

2.4. Adsorption experiments

Naproxen sodium solutions were prepared in distilled water at desired concentrations. Adsorption experiments were carried out by agitating 0.1 g of WA11Zn5 with 50 mL solutions of desired concentration, pH and temperature (25, 37 and 50 °C) in a thermostatic bath operating at 400 rpm. The amount of naproxen sodium adsorbed onto WA11Zn5, q_t (mg/g), was calculated by mass-balance relationship Eq. (1):

$$q_t = (C_0 - C_t) \frac{V}{W} \tag{1}$$

where C_0 and C_t are the initial and time *t* liquid-phase concentration of the naproxen sodium (mg/L), respectively, *V* the volume of the solution (L) and *W* is the weight of the dry WA11Zn5 used (g).

3. Results and discussion

3.1. Pore structure characterization of the prepared adsorbent (WA11Zn5)

Nitrogen adsorption is the standard procedure for the characterization of porosity texture of carbonaceous adsorbents. The adsorption isotherm is the information source about the porous structure of the adsorbent, heat of adsorption, characteristic of physic and chemistry and so on. Adsorption isotherm may be grouped six types. As illustrated in Fig. 1, Nitrogen adsorption at 77 K is standard method used in characteriza-



Fig. 1. Adsorption isotherm of nitrogen at 77 K for activated carbon (WA11Zn5) [9,10].

Table 1	
Porous structure	parameters of the activated carbon (WA11Zn5) [9,10]

S_{BET} (m ² /g)	S _{ext} ^a		S _{mic}		$V_t (\mathrm{cm}^3/\mathrm{g})$	V _{mic}	V _{mic}		V _{meso}	
	m ² /g	%	m ² /g	%		cm ³ /g	%	cm ³ /g	%	
1060	778	74	282	36	0.79	0.15	19	0.64	81	2.98

^a $S_{\text{ext}} = S_{\text{meso}}$.

^b 4V/A by BET.

tion of the adsorbents. WA11Zn5 exhibited adsorption isotherm of type IV according to IUPAC [12]. The Type IV isotherm represents the micro-meso porous structure of the adsorbents. The initial part of the isotherm follows the same path as the corresponding type II isotherm and therefore the result of monolayer-multilayer adsorption on the mesopore walls [13]. Characterization of activated carbon used in this study is investigated by Akmil Başar and Önal [9,10]. The BET surface area (S_{BET}) , external surface area (including only mesopores S_{ext}), micropores surface area (S_{mic}) , total pore volume (V_t) and average pore diameter (D_p) results obtained by applying the BET (Brunauer-Emmett-Teller) equation to N₂ adsorption at 77 K and BJH (Barret-Joymer-Halenda) equation to N₂ adsorption at 77 K are listed in Table 1.

Fig. 2 shows the pore size distribution was calculated by using DFT plus software (with BJH method) [11]. It appears that activated carbon include micropores and mesopores. Percentages of micropores and mesopores area are 36% and 74%, respectively.

3.2. Effect of the initial concentration naproxen sodium on the adsorption

Effect of initial naproxen sodium concentration on adsorption was investigated at concentration ranging from 100 to 500 mg/L at $25 \degree$ C. Fig. 3 illustrates the effect of initial naproxen sodium concentration on the adsorption. The uptake is almost 100% at 100 mg/L naproxen sodium concentration and 42–90% at the other concentration. The percentage of naproxen



Fig. 2. Pore size distribution of the WA11Zn5 [9,10].



Fig. 3. Effect of initial naproxen sodium concentration (0.1 g activated carbon (WA11Zn5)/50 mL naproxen sodium solution, pH 5.82 natural pH, contact time = 1 h, 400 rpm, at 25 $^{\circ}$ C).

sodium removal decreased while naproxen sodium concentration increases. Naproxen sodium concentrations 100 mg/L were selected in this study to investigate the effect of temperature.

3.3. Effect of the temperature and contact time on the naproxen sodium adsorption

Effect of temperature on removal of naproxen sodium by activated carbon (*WA11Zn5*) is presented in Fig. 4. The percentage of naproxen sodium removal increased from 99.38 to 99.52 as the adsorption temperature was increased from 25 to $50 \,^{\circ}$ C for 100 mg/L naproxen sodium concentration. The fact that the



Fig. 4. Effect of temperature on the naproxen sodium adsorption (naproxen sodium concentration: 100 mg/L, 0.1 g activated carbon (WA11Zn5)/50 mL naproxen sodium solution, pH 5.82 natural pH, contact time = 1 h, 400 rpm, at 25, 37 and 50 °C adsorption temperature).

adsorption increases with an increase in temperatures indicates the increase in the mobility of naproxen sodium molecules with increasing temperatures and the ongoing adsorption process is endothermic [14,15].

3.4. Adsorption isotherm

Several models have been used in the adsorption studies to describe the experimental data adsorption isotherms. Langmuir and Freundlich isotherms are the most frequently used models. Both models were investigated in this work.

The naproxen sodium adsorption followed the linearized Langmuir model as shown in Fig. 5. Langmuir [16] proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many real sorption processes. The linearized Langmuir isotherm is represented by following equation:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{Q_0 b} + \frac{C_{\rm e}}{Q_0} \tag{2}$$

where C_e is the naproxen sodium concentration at equilibrium (mg/L), q_e the adsorption capacity in equilibrium (mg/g), *b* the Langmuir adsorption constant (L/mg) and Q_0 signifies adsorption capacity (mg/g). It can be seen from Fig. 5 that the isotherm data fit the Langmuir equation well ($R^2 = 0.9998$). The values of Q_0 and *b* were determined from figure and found to be 106.38 mg/g and 0.514 L/mg, respectively. To determine if adsorption process is favorable or unfavorable, for the Langmuir type adsorption process, isotherm can be classified by a term ' R_L ', a dimensionless constant separation factor, which is defined as below [17].

$$R_{\rm L} = \frac{1}{1 + bC_0} \tag{3}$$

The R_L values are found as 0.019, 0.0095, 0.0064, 0.0048 and 0.0034 at 100, 200, 300, 400 and 500 mg/L initial Naproxen concentration, respectively, showing favorable adsorption.

The naproxen sodium adsorption isotherm followed the linearized Freundlich model as shown in Fig. 6. The Freundlich



Fig. 5. Langmuir isotherm model (0.1 g activated carbon (WA11Zn5)/50 mL naproxen sodium solution, contact time = 1 h, 400 rpm, at 25 $^{\circ}$ C).



Fig. 6. Freundlich isotherm model (0.1 g activated carbon (WA11Zn5)/50 mL naproxen sodium solution, contact time = 1 h, 400 rpm).

adsorption isotherm can be expressed [18] as

$$\log q_{\rm e} = \log k_{\rm f} + \frac{1}{n} \log C_{\rm e} \tag{4}$$

where the intercept log k_f is a measure of adsorbent capacity and the slope 1/n is the adsorption intensity. The values of the constants k_f and 1/n were calculated to be 55.58 L/g and 0.128. Since the value of 1/n is less than 1, it indicates a favorable adsorption [19,20]. According to the R^2 values, it is found the Langmiur equation is more suitable for the description of the adsorption isotherm of naproxen sodium onto activated carbon prepared waste apricot.

3.5. Adsorption kinetics

The relationship between contact time and naproxen sodium removal by activated carbon obtained by $ZnCl_2$ activation of waste apricot for three different temperatures is presented in Fig. 4 for adsorbent dosage of 0.1 g/50 mL and natural pH of the solution.

Several kinetics models have been proposed to elucidate the mechanism by which pollutants may be adsorbed [14,21–24]. In order to investigate the mechanism of naproxen sodium adsorption, three kinetic models are selected in this work.

The pseudo first-order equation is expressed [11] as:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_1(q_{\mathrm{e}} - q_{\mathrm{t}}) \tag{5}$$

The integrated form of Eq. (5) becomes:

$$\log(q_{\rm e} - q_{\rm t}) = \log q_{\rm e} - \frac{k_1}{2.303}t$$
(6)

where q_e and q_t are amounts of naproxen sodium adsorbed (mg/g) at equilibrium and time *t* (min), respectively, and k_1 is the rate constant of pseudo first-order (min⁻¹).

The pseudo second-order kinetic model of Ho and McKay [25,26] is

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_2 (q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{7}$$



Fig. 7. The pseudo first-order adsorption kinetics of naproxen sodium at different temperatures.

The integrated form of Eq. (7) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\rm e}^2} + \frac{1}{q_{\rm e}} t \tag{8}$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg min) and $h = k_2 q_e^2$ where h is the initial adsorption rate (mg/g min).

The activation energy was calculated from linearized Arrhenius equation (9):

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{9}$$

where k_2 is the rate constant of adsorption (g/mol s), k_0 the temperature independent factor (g/mol s), E_a the activation energy (kJ/mol), *R* the gas constant (J/mol K) and *T* is the adsorption temperature (K).

The rate parameter for intraparticle diffusion is determined using the following equation [27].

$$q_t = k_{\rm int} t^{1/2} + C \tag{10}$$

where *C* is the intercept and k_{int} is the intraparticle diffusion rate constant (mg/g min^{1/2}). The plot may present multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes the gradual adsorption stage, where intraparticle diffusion is rate limiting. The third portion is attributed to the final equilibrium stage [27]. The values of $\log(q_e - q_t)$ were calculated from the kinetic data of Fig. 4. The plots of $\log(q_e - q_t)$ versus *t* for the pseudo first-order model given in Eq. (6) were given at temperatures of 298, 310 and 323 K in Fig. 7. The k_1 and q_e values were calculated from slope and intercept of this plot. The k_1 values, q_e calculated and correlation coefficient is given in Table 2. The correlation coefficient (R^2) is low, ranging from 0.959 to 0.839. Moreover, the experimental $q_{e,exp}$ values do not agree with the calculated ones. This shows that the adsorption of naproxen sodium onto WA11Zn5 is not the first-order reaction.

Table 2

Kinetic parameters for the effects of solution temperature and concentration

Temperature (K)	298	310	323
$q_{\rm e,exp} \ ({\rm mg/g})$	49.69	49.75	49.78
Pseudo first-order equation			
$q_{\rm e} ({\rm mg/g})$	14.26	14.65	13.64
$k_1 \times 10^2 ({\rm min}^{-1})$	11.49	22.17	28.02
R^2	0.958	0.936	0.839
Pseudo second-order equati	ion		
$q_{\rm e} ({\rm mg/g})$	50.76	50.25	50
$k_2 \times 10^3$ (g/mg min)	18.6	45.5	59.7
$h (mg/g \min)$	49.92	114.89	149.25
R^2	0.999	0.999	1
E _a (kJ/mol)		37.33	
Intraparticle diffusion equa	tion		
$k_{\text{int}} (\text{mg/g min}^{1/2})$	11.324	13.517	13.523
С	14.09	16.589	18.289
R^2	0.999	0.998	0.997



Fig. 8. The pseudo second-order adsorption kinetics of naproxen sodium at different temperatures.

On the other hand, the plots of (t/q_t) versus *t* for the pseudo second-order model given in Eq. (8) were drawn at different temperature in Fig. 8. q_e and k_2 values were calculated from slope and intercept of this plots, respectively. As can be seen from Table 2, the correlation coefficient (R^2), for the second-order kinetic model are between 1 and 0.999 and the experimental $q_{e,exp}$ values agree with the calculated ones. These results imply that the adsorption system studied follows to the pseudo second-order kinetic model.

The plots of $\ln k_2$ versus the absolute temperature 1/T, give straight line for all concentration as shown in Fig. 9. The activation energy value is given in Table 2. The activation energy value falls less than 42 kJ/mol the adsorption process. The type of

adsorption of naproxen sodium on the WAZn115 was defined as physical adsorption and the process is confirmed to be diffusion controlled [28,29].

The intra particle diffusion rate, obtained from the plots q_t versus $t^{1/2}$. The plots are shown in Fig. 10. As can be seen from Fig. 10 for the system investigated, the relationships are not linear. All plots have an initial curved portion, followed by intermediate linear portion and a plateau. The intermediate linear part is due to intraparticle diffusion. At a certain time limit (between 3 and 7 min at 298 K and between 1 and 5 min at 310 and 323 K, respectively) the curves revealed linear characteristic as shown in Fig. 11. However the linear plots at each temperature did not



Fig. 9. Arrhenius plot for adsorption of naproxen sodium on WA11Zn5.



Fig. 10. Plots of the intraparticle diffusion kinetics equation for adsorption of naproxen sodium onto WA11Zn5 at different temperatures.

Table 3



Fig. 11. Plots the intermediate linear portion of the intraparticle diffusion kinetics equation at different temperatures.

pass through the origin and this result indicates that the intraparticle diffusion was not only rate controlling step [30,31]. k_{int} values are determined from the slope of linear portion of this plot. The values of intercept, *C* give an idea about the boundary layer thickness, i.e. the larger the intercept, the greater is the boundary layer effect. k_{int} values and the values of *C* is summarized in Table 2. The values of intraparticle rate constant, k_{int} (mg/g min^{1/2}), obtained for adsorption of naproxen sodium onto WaZn115 are determined as 11.324, 13.517 and 13.523 at 298, 310 and 323 K, respectively. The results show that intraparticle rate constant, k_{int} , increases with increase the temperature. This effect could be attributed to aggregation effect. Aggregation decreases as the temperature is raised and the diffusion of the naproxen sodium is then enhanced [32,33].

3.6. Adsorption thermodynamics

Effect of temperature on the naproxen sodium adsorption is shown in Fig. 4. While temperature increases, the percentage of naproxen sodium removal increases. The change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated from the following equation.

$$\Delta G^{0} = -RT \ln K_{c} \tag{11}$$

where *R* is gas constant, K_c the equilibrium constant and *T* is temperature in K. The K_c value is calculated from Eq. (12).

$$K_{\rm c} = \frac{C_{\rm Ae}}{C_{\rm Se}} \tag{12}$$

where C_{Ae} and C_{Se} is the equilibrium concentration of naproxen sodium ions on adsorbent (mg/L) and in the solution (mg/L), respectively.

Standard enthalpy (ΔH°) and entropy (ΔS°) , of adsorption can be estimated from van't Hoff equation given in

$$\ln K_{\rm c} = \frac{-\Delta H_{\rm ads}^{\rm o}}{RT} + \frac{\Delta S^{\rm o}}{R}$$
(13)

The slope and intercept of the van't Hoff plot is equal to $-\Delta H_{ads}^{\circ}/R$ and $\Delta S^{\circ}/R$, respectively. The van't Hoff plot for



Fig. 12. van't Hoff plots of naproxen sodium adsorption onto WAZn115 for 100 mg/L initial naproxen sodium concentration.

Thermodynamic parameters for the adsorption of naproxen sodium onto WAZn115

Concentration (mg/L)	Temperature (K)	K _c	$-\Delta G^{\circ}$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	
	298	161.127	12.59			
100	310	190.490	13.53	8.824	71.285	
	323	210.950	14.37			

the adsorption of naproxen sodium onto WAZn115 is given in Fig. 12. Thermodynamic parameters obtained are summarized in Table 3.

 $K_{\rm c}$ values are calculated from Eq. (12). The standard Gibbs free energy for the adsorption process was obtained as -12.59, -13.53 and -14.37 kJ/mol at 298, 310 and 323 K, respectively. The negative ΔG° values at different temperatures is due to the fact that adsorption process is spontaneous and negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of the adsorption of naproxen sodium are inversely proportional to the temperature. Generally, the absolute magnitude of the change in free energy for adsorption is between 0 and -20 kJ/mol. Adsorption type can be explain as physisorption [3]. Positive values of ΔH° indicate the endothermic nature of the process. Moreover, the standard enthalpy change is lower than the value of 40 kJ/mol. It indicates that the adsorption is physical nature [34]. The positive values of ΔS° reflects the affinity of adsorbent material towards naproxen sodium.

4. Conclusion

The results of this work can be summarized as follows:

- (1) The N₂ adsorption isotherm of WA11Zn5 is of type IV. The values of S_{BET} , V_t and S_{mic} and V_{mic} are 1060 m²/g, 0.79 cm³/g and 282 m²/g and 0.15 cm³/g, respectively. Results show that activated carbon activated carbon includes micropores and mesopores.
- (2) The amount of naproxen sodium adsorbed onto WA11Zn5 for 100 mg/L initial naproxen sodium concentration are

49.69, 49.75, 49.76 mg/g at 25, 37, $50 \,^{\circ}$ C, respectively. Adsorption of naproxen sodium onto WA11Zn5 increased slightly with an increase in temperature, indicating that the process is endothermic.

- (3) Langmiur equation is more suitable for the description of the adsorption isotherm of naproxen sodium onto activated carbon prepared waste apricot.
- (4) The kinetics of adsorption of naproxen sodium on WA11Zn5 was studied by using three kinetic models. The adsorption of naproxen sodium from aqueous solution onto WA11Zn5 proceeds according to the pseudo second-order model which provides the best correlation of the data in all cases and the experimental $q_{e,exp}$ values agree with the calculated ones.
- (5) The intraparticle diffusion was not only rate controlling step.
- (6) The positive values of enthalpy change conform to the endothermic nature of the adsorption process. The parameters, ΔH , ΔS and ΔG , for the naproxen sodium-activated carbon prepared from waste apricot interactions changed in away that made the adsorption thermodynamically feasible with high degree of affinity of the naproxen sodium molecules for the WA11Zn5 surface.

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