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# Removal of acetaminophen from the contaminated water using adsorption onto carbon activated with $NH_4Cl$

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ABSTRACT

The efficacy of $NH_4Cl$-induced activated carbon (NAC) in removing acetaminophen (ACT) as a model of non-steroidal anti-inflammatory pharmaceutical compounds in aqueous solution is investigated in this study. The experiments were performed in different conditions of solution pH, contact time, initial concentration, adsorbent concentration, and solution temperature to the adsorption of ACT on NAC. The results showed that ACT adsorption onto adsorbent was not pH-dependent in the range of 2–9; but, at higher pH values, the removal efficiency was significantly decreased. Adsorption of ACT by NAC followed pseudo-second order kinetics, and the equilibrium adsorption data best fitted the Langmuir isotherm. The maximum capacity was 233 mg/g. Overall, NAC efficiently adsorbed ACT; thus, it can be considered as an affordable and cost-effective system for the removal of pharmaceutical compounds from aqueous solutions.

*Keywords:* Pharmaceutical compounds; Adsorption; Activated carbon; Acetaminophen

## 1. Introduction

In recent decades, the production and use of pharmaceutical compounds for curing human and veterinary diseases have increased rapidly [1]. A significant portion of these compounds is excreted from the body via feces or urine. So, pharmaceutical compounds will find their way to the sewage collection systems which are finally discharged into wastewater treatment plants [2,3]. The conventional wastewater treatment plants are usually designed for the removal of suspended solids, biochemical oxygen demand (BOD), and pathogeneses; thus, they cannot efficiently remove pharmaceutical compounds. Therefore, these compounds are finally released to the environment through the effluent of wastewater treatment plants. Moreover, pharmaceutical compounds enter the environment from pharmaceutical industries. Due to the toxic effects of pharmaceutical compounds for human and environmental health, direct (e.g., pharmaceutical industry wastewater) and indirect (e.g., municipal and hospital effluents) discharges of pharmaceutical compounds into the environment and water resources have become one of the increasingly recognized emerging concerns in recent years [4]. Effluent comprising pharmaceutical compounds should be treated by a proper process in order to avoid adverse effects on human and environment from contaminated waters.

There are several chemical, biological, and physical techniques for removing pharmaceutical compounds from contaminated water, which include advanced

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Table 1
Summary of recently published literature on ACT adsorption by several activated carbon

| Adsorbent | Condition of experiment | Optimum pH | Adsorption rate order (degree) | Fitted isotherm model | Adsorption capacity (mg/g) | Reference |
|---|---|---|---|---|---|---|
| Present study animal hair-based activated carbon | pH 2–11 | Independent | Pseudo-second | Langmuir | 233 | – |
| | pH 2–11 | Independent in 2–9 | Pseudo-second | Freundlich | 61.8 | [9] |
| | $C$ = 0.04–0.4 mmol/mol Activated by phosphoric acid | | | | | |
| Activated carbon derived from lignocellulose | pH 2–11 | Independent in 2–9 | Pseudo-second | Freundlich | 59.9 | [9] |
| | $C$ = 0.04–0.4 mmol/mol Activated by phosphoric acid | | | | | |
| Carbon-based pine gasification residues | ACT concentration = 120–480 mg/L, Different weight ratios of adsorbent and $K_2CO_3$ | Natural pH (around 5) | Pseudo-second | Langmuir | 188.7–270.3 | [10] |
| Peach stone-based PAC derived by chemical activation with $K_2CO_3$ | adsorbent dose (5–10 mg) | Without pH adjustment (5.8) | Pseudo-second | Langmuir | 204 | [11] |
| | $C_o$ (20–180 mg $dm^{-3}$) solution volumes (15, 30 $cm^3$), $pH_{zpc}$ = 9 | | | | | |
| Cork waste-based PAC obtained by chemical activation with $K_2CO_3$ | adsorbent dose (5–10 mg) | Without pH adjustment (5.8) | Pseudo-second | Langmuir | 200 | [11] |
| | $C_o$ (20–180 mg $dm^{-3}$) solution volumes (15, 30 $cm^3$), $pH_{zpc}$ = 7.5 | | | | | |
| PET waste-based PAC obtained by physical activation at 925°C under $CO_2$ atmosphere | adsorbent dose (5–10 mg) $C_o$ (20–180 mg $dm^{-3}$) | Without pH adjustment (5.8) | Pseudo-second | Langmuir | 113 | [11] |
| | solution volumes (15, 30 $cm^3$), $pH_{zpc}$ = 10.7 | | | | | |
| Commercial coal-based PAC obtained from physical activation | adsorbent dose (5–10 mg) | Without pH adjustment (5.8) | Pseudo-second | Langmuir | 255 | [11] |
| | $C_o$ (20–180 mg $dm^{-3}$) solution volumes (15, 30 $cm^3$), $pH_{zpc}$ = 9.2 | | | | | |
| Commercial wood-based PAC obtained from physical activation | adsorbent dose (5–10 mg) | Without pH adjustment (5.8) | Pseudo-second | Langmuir | 267 | [11] |
| | $C_o$ (20–180 mg $dm^{-3}$) solution volumes (15, 30 $cm^3$), $pH_{zpc}$ = 9 | | | | | |
| Graphene nanoplatelets carbon | pH 2–12 temp = 296–323, initial concentration of 20 mg/L, 200 mg of adsorbent and 200 ml of solution volume | Almost independent in 2–8 | Pseudo-second | – | 18.06 (equilibrium capacity) | [12] |

(*Continued*)

Table 1 (*Continued*)

| Adsorbent | Condition of experiment | Optimum pH | Adsorption rate order (degree) | Fitted isotherm model | Adsorption capacity (mg/g) | Reference |
|---|---|---|---|---|---|---|
| Sisal waste | Activation with $K_2CO_3$ | Natural pH (around 6) | Pseudo-second | – | – | [13] |
| Alumina | Initial concentration of 10 mg/L, and pH in Neutral range | 7.4 | – | Freundlich | – | [14] |
| Silica | Initial concentration of 10 mg/L, and pH in Neutral range | 6.8 | – | Freundlich | – | [14] |
| Porapak P | Initial concentration of 10 mg/L, and pH in Neutral range | 7.2 | – | Freundlich | – | [14] |

oxidation processes (AOPs) [5], biodegradation, membrane filtration, coagulation, and adsorption [4,6,7]. Although chemical oxidation processes such as AOPs can effectively remove pharmaceutical compounds, they are complex and costly, and may generate toxic by-products and secondary pollutants. Although biological processes are the method of choice for treating biodegradable contaminants, they are inefficient in the complete degradation of such recalcitrant compound as pharmaceutical compounds [8]. Adsorption is one of the promising techniques for the elimination of pharmaceutical compounds, which is related to its high adsorption capacity, low energy cost, and being environmental friendly. Activated carbon is the most widely used adsorbent. High performance and no generation of toxic by-products are the significant advantages of activated carbon in terms of removing pharmaceutical compounds from drinking water. Table 1 summarizes some published literature on ACT removal by adsorption onto different activated carbon. Although several studies have been performed to examine removal of pharmaceutical compounds by different activated carbon, no one has utilized $NH_4Cl$-induced activated carbon (NAC) for ACT adsorption [9–14].

ACT (paracetamol and para-acetylaminophenol) is a non-steroidal anti-inflammatory drug that is widely used for pain relief and fever reduction all over the world today [15,16]. This antipyretic drug is easily available in most countries even without medical prescription. In the United States, ACT was one of the top 200 prescriptions in 2003. The usage of ACT in Japan was about $10^9$ g in 2003 [17]. In the UK, the consumption of ACT with and without prescription was about 3.5 billion of 500 mg tablets in 2000. According to previous studies [18], about 58–68% of ACT is excreted from the body when ingested in therapeutic dosage. So, the concentration of ACT can be significant in wastewater and water resources similar to other pharmaceutical compounds. For example, Rivera-Utrilla et al. [19] detected the concentration of ACT in the inlet and outlet of WWTP as about 10,194 and 2,102 ng/L, respectively. Detected values of ACT in Europe varied from 59 to 220 ng/L for the effluent of WWTP and 12–777 ng/L for freshwater [20]. At therapeutic doses, ACT is relatively safe; but, at overdoses, concentration has some dangers such as liver failure, gastrointestinal disease, and centrilobular necrosis in the liver, and eventually hepatotoxic potential. Studies have shown that ACT could prevent testosterone production by about 100 times less than the therapeutic plasma concentration [21].

The aim of this study was to explain the potential of NAC by a waste biomass for the pharmaceutical compounds adsorption, which is one of the important water contaminants. ACT was selected as a model of non-steroidal anti-inflammatory pharmaceutical compounds for extensive usage and possibility of polluting water resources. This study was conducted on the variables including adsorbent dosage, contact time, solution pH, solution temperature, and pollutant concentration. Isotherm, thermodynamic of ACT adsorption on NAC, and kinetic were also evaluated.

## 2. Material and methods

### 2.1. Preparation and characterization of activated carbon

Properties of NAC are similar to the adsorbent of Moussavi et al. [22] study. Dried pomegranate wood obtained from discarded agricultural waste was used as the base material for the preparation of activated carbon. After soaking carbonized waste granules in $NH_4Cl$, the activation step was performed at 500–800 ˚C

under $N_2$ oven conditions. The prepared activated carbon was then powdered and used. Hydroxyl, aliphatic, carboxylic, and carbonyl were the important functional groups on the surface of the NAC. The BET surface area and total pore volume (at $P/P_0 = 0.99$) of NAC were 1,029 $m^2/g$ and 0.633 $cm^3/g$, respectively. The monolayer volume ($V_m$) of NAC was 236.4 $cm^3/g$. Also, mean diameter of pores was 2.46 nm that was calculated based on the following equation:

$$D_p = \left(\frac{4V}{S}\right) \times 10^3 \quad (1)$$

where $D_p$ is the mean pore diameter (nm), $V$ is the total pore volume ($cm^3/g$), and $S$ is the BET area ($m^2/g$).

### 2.2. Material

Commercial ACT was prepared from Aria Company in Iran. Physicochemical properties of ACT are listed in Table 2 [23,24]. The purity of each ACT tablet was 325 mg. The ACT solution of 325 mg/L was prepared by dissolving one tablet in 1 L of distilled water on any working day. This stoke solution was kept in the refrigerator at 4°C and other require solution concentration provided from it.

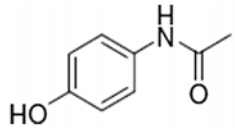
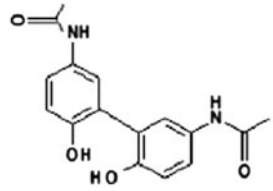
### 2.3. Adsorption experiments

Table 3 presents the experimental runs and conditions. All the adsorption tests were conducted in batch reactor conditions by an Erlenmeyer flask. In each test, 50 mL of the solution containing the given concentration of ACT was transferred to the flask and pH level of the solution was adjusted (with 0.1 N NaOH and HCl) to the required value. The given amount of NAC was added to the reactor, and the suspension was placed on the magnetic instrument and stirred at 150 rpm for the preset time. While reaching the predetermined mixing time, the suspension was filtered through a cellulose acetate filter with 0.2 μm of pore size and then the filtrate solution was analyzed for the residual ACT. The determined variables and their ranges were as follows: pH of the solution (2–12), NAC concentration (0.1–2 g/L), initial ACT concentration (50–500 mg/L), solution temperature (10–40°C), and reaction time (0.5–60 min in kinetic experiment and 2 h in equilibrium tests). An equilibrium study was performed in the concentration range of 100–500 mg/L ACT by adding the given mass of 0.05 g NAC at 50 mL of solution to the Erlenmeyer flasks at the pH of 7.1.

### 2.4. Analysis

Concentration of ACT in the solution was determined using a spectrophotometer (Unico-UV 2,100) at 242 nm. The pH was measured by a Sense Ion 378, Hack pH meter. Solution temperatures were determined by a thermometer. The amount of ACT

Table 2
Physicochemical properties of Acetaminophen [23,24]

| | |
|---|---|
| Structure (monomer form) |  |
| Structure (dimmer form) |  |
| Formula | $C_8H_9NO_2$ |
| MW | 151.2 |
| $pK_a$ | 9.38 |
| Log $k_{ow}$ | 0.46 |
| $K_H$ (atm $m^3/mol$) | $6.4 \times 10^{-13}$ |
| MDL (μg/L) | 0.5 |
| CAS no. | 103-90-2 |
| Rec. ± RSD (%) | 112 ± 6 |
| Water solubility (mg/L) | 12,900 |
| Application | Non-steroidal anti-inflammatory drug |

Note: Rec: recovery in DI water; RSD: relative standard deviation.

Table 3
Experimental runs and conditions

| Experiment | Condition | | | | |
|---|---|---|---|---|---|
| | Solution pH | NAC dose (g/L) | ACT concentration (mg/L) | Temperature (°C) | Contact time (min) |
| Effect of pH | 2–12 | 0.8 | 100 | 25 | 20 |
| Effect of NAC dose and initial ACT concentration | 7.1 | 0.1–2 | 50, 100, and 200 | 25 | 20 |
| Effect of contact time | 7.1 | 1 | 50, 100, and 200 | 25 | 0.5–60 |
| Equilibrium of adsorption | 7.1 | 1 | 100–500 | 10–40 | 120 |
| Effect of temperature | 7.1 | 1 | 50 | 10–40 | 120 |

adsorption onto NAC was calculated based on removal percentage (Eq. (2)) and adsorption capacity (Eq. (3)).

$$\text{Acetaminophen removal } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

$$\text{Adsorption capacity } (\text{mg/g}) = \frac{V(C_0 - C_e)}{m} \quad (3)$$

where $C_0$ and $C_t$ indicate the ACT concentration at initial time and time $t$ of the contact time, respectively. $V$ is the volume of the ACT solution and $m$ is the mass of added adsorbent.

All the tests were performed in duplicate to ensure the reproducibility of the results; the mean of these two measurements was taken to represent each evaluation. Isotherm, kinetic, and thermodynamic analyses were performed using the related models and equations. Pseudo-first order (PFO) and pseudo-second order (PSO) models were utilized for adsorption kinetic analyses. Langmuir and Freundlich models were done for the isotherm analysis.

### 2.5. Adsorption thermodynamics and modeling

The thermodynamics of ACT adsorption onto NAC was evaluated by the adsorption experiments performed in an Erlenmeyer flask, containing 50 mL of solution, in the conditions presented in Table 3. The solution was shaken in a temperature-controlled shaker incubator. This experiment was conducted at various temperatures of 10, 20, 30, and 40°C. At the end of each test, the suspension was analyzed as described in Section 2.4. The thermodynamics of ACT adsorption onto NAC was analyzed using an estimated change in adsorption free energy ($\Delta G^\circ$), adsorption enthalpy ($\Delta H^\circ$), and adsorption entropy ($\Delta S^\circ$) as described in the following equations [25]:

$$\Delta G^\circ = -RT \ln K \quad (4)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (6)$$

where $R$ (8.314 J/mol K) is the gas constant, $T$ (K) is the absolute temperature, and $K_c$ (L/g) is the standard thermodynamic equilibrium constant defined by $q_e/C_e$. By plotting a graph of ln $K_c$ vs. $1/T$, the values $\Delta S^\circ$ and $\Delta H^\circ$ can be estimated from the slopes and intercepts [26].

## 3. Results and discussion

### 3.1. Influence of solution pH

Effect of the solution pH was examined for ACT removal by NAC in the range of 2–12 under the conditions given in Table 3. The results are shown in Fig. 1. The influence of ACT hydrolysis was also evaluated and demonstrated no significant decomposition at various pH levels. As shown in Fig. 1, the percentage of adsorption did not significantly change by alternating the pH value. The adsorption percentage of ACT decreased very slowly from 90 to 83% with the pH increase from 2 to 10. But, with further increases of pH up to 12, the adsorption capacity declined considerably from 83 to 70%. These phenomena can be justified by considering the $pH_{zpc}$ of NAC and $pK_a$ of ACT. At the solution pH level of lower than 7.8 ($pH_{zpc}$), the surface of NAC charged to positively. On the other hand, because ACT is a weak acid [9], the form of neutral species mostly exists at the pH below its $pK_a$ (9.38). So, the adsorption mechanism is not based on the electrostatic attraction in the noted pH ranges. For the protonated neutral species of ACT solution with positive charged of adsorbent, removal

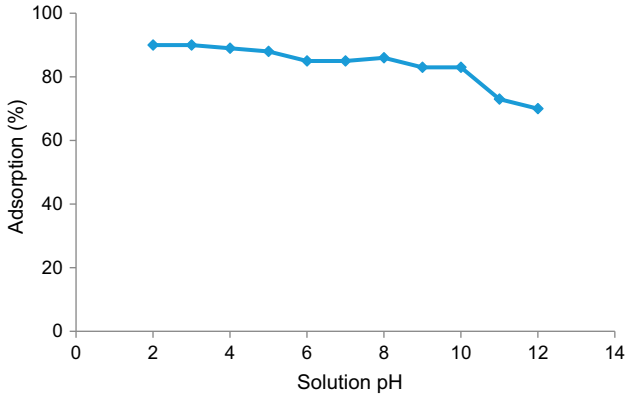



Fig. 1. Influence of solution pH on ACT adsorption onto NAC (ACT concentration: 100 mg/L; solution pH: 2–12; NAC concentration: 0.8 g/L; contact time: 20 min).

was nearly constant (90–83%) and pH was independent in the pH range of 2–10; but, when the pH was enhanced over the $pK_a$, the sorption decreased by 70%. The reasons may be related to the anionic species of ACT and NAC surfaces and finally electrostatic repulsion between them. According to another investigation mentioned in Table 1, almost all the researchers have similarly reported the nearly constant adsorption of ACT by different adsorbents in the pH range of 2–10. In these studies, adsorption has been either pH-independent or performed at the natural pH of solution with proper removal percentage. For example, the adsorption of pharmaceutical pollutants onto graphene nanoplatelets [12] showed that the adsorption of ACT did not change at the pH of 2–8 (about 80%); but, at further pH values (up to 11), efficiency decreased by 73%. In another research performed by Liu et al. [9] on the sorption of norfloxacin and acetaminophen by animal hair-based activated carbon, the ACT adsorption had a constant rate from 88 to 92% at the pH of 2–9; but, in a higher pH range, the removal efficiency was significantly decreased by 70%.

The independent performance of ACT adsorption to pH on NAC can be considered an advantage, because the treatment process can perform at any pH or natural pH of the solution and for full-scale application; changing water pH level to optimum point is eliminated. So, this process will be more cost-effective than other pharmaceutical compounds adsorption mechanisms which may need acidic or basic agents for attaining proper pH level.

### *3.2 Influence of initial ACT concentration and adsorbent dosage*

Since in adsorption process, economic considerations of adsorbent preparation are important, determination of optimum dosage and amount of available surface for sorption should be calculated. On the other hand, pharmaceutical effluent and water-polluted resources may have variant pharmaceutical compounds concentrations; so, answering the following question is challenging: How could different ACT concentrations influence the performance of NAC for removing ACT? Considering the aforementioned magnitude, the adsorption of 50, 100, and 200 mg/L of ACT concentrations was investigated as a function of various NAC concentrations under the conditions given in Table 3. The result is presented in Fig. 2.

According to Fig. 2, two important achievements are considerable. First, with increasing NAC concentration, the removal percentage of ACT will be enhanced to the maximum value for all three initial ACT concentrations. Enhanced adsorption efficiency with increasing NAC dose for each specific concentration of ACT can be attributed to the increase in free available adsorption sites and adsorbent to adsorbate ratio. The present results were in accordance with those reported previously for the adsorption of ACT onto animal hair-based activated carbon [9], in which an increase in adsorbent concentration can led to increased removal percentage; however, removal percentage of the present findings was contrary, which may be due to different experimental conditions and adsorbent properties.

The second point that can be extracted from Fig. 2 is the dosage of NAC at different ACT concentrations; with increasing initial concentration, the optimum dosage of NAC needs to be increased as well. For example, at the removal efficiency of 92% for 50, 100, and 200 mg/L of ACT concentration, the optimum adsorbent dosage was 0.6, 0.8, and 1.8 g/L, respectively. This result shows that the determination of optimum NAC

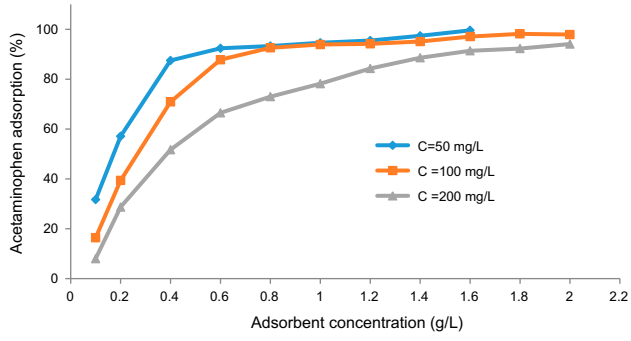



Fig. 2. Influence of initial concentration on adsorption of ACT onto NAC as a function of NAC concentration (contact time: 20 min; solution pH: 7.1; NAC concentration: 0.1–2 g/L; initial concentration: 50–200 mg/L.; solution temperature: 25°C).

dosage depends straightly on the concentration of ACT in solution; higher ACT concentration (up to 0.8 g/L of NAC) requires greater dose of NAC. Liu et al. [9] reported 89–92% removal of 15.2 mg/L ACT for 0.6 g/L of cattail fibers-activated carbon (CFAC) and high-pressure animal hair activated carbon (H-AHAC), respectively, after 3 d of contact time. Compared to this study at the specific removal efficiency of 92% for ACT adsorption, NAC had significantly higher experimental adsorption capacity than CFAC and H-AHAC (0.08 vs. 0.025 mg/g). Considering the above-mentioned findings, NAC can be one of the promising adsorbents that are provided from agricultural wastes, as low-cost raw material to prepare, to removal of ACT in aqueous solution. Unlike other adsorbents such as animal hair and fruit waste which are very hard to gather and consumer-dependent, NAC is easily available with high adsorption capacity.

### 3.3. Influence of contact time

Adsorption of varying initial ACT concentrations onto NAC was evaluated at different contact time under the conditions provided in Table 3. Fig. 3 represents the average results of duplicated experiment. As can be seen in Fig. 3, adsorption percentage of ACT was increased by increasing the contact time at each concentration. About 95 and 90% of ultimate ACT adsorption occurred just at 10 min at the concentrations of 50 and 100 mg/L, respectively. The equilibrium adsorption times of ACT at the concentrations of 50, 100, and 200 mg/L under optimum conditions were 45, 30, and 30 min, respectively, with the corresponding percentage removals of approximately 99, 94, and 77%. A similar trend was reported for ACT equilibrium adsorption time of about 9 h at the initial concentration of 15.2 mg/L [9], compared to the present work, it was very high at long contact time, which may be related to high affinity of ACT to NAC and structure properties of NAC.

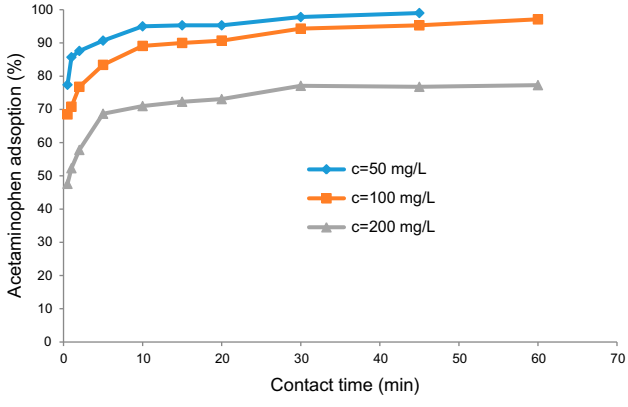



Fig. 3. ACT adsorption as a function of contact time (initial concentration: 50–200 mg/L; solution pH: 7.1; NAC concentration: 1 g/L; solution temperature: 25°C).

As illustrated in Fig. 3, before stabilizing equilibrium at each concentration, the adsorption efficiency at each contact time was decreased by an increase at the initial concentration of ACT with constant concentration of the adsorbent. According to the specific amount of adsorbent applied in this section of the experiment, a decrease in the efficiency of ACT removal with an increase in the initial concentration can be due to restricted adsorption sites and a decrease in intra-particle diffusion. So, the adsorption of ACT onto NAC depends on the initial ACT concentration and contact time.

The experimental adsorption capacity of ACT onto the adsorbent was increased by an increase in the initial concentration and contact time. For any equilibrium time of ACT concentration, adsorption capacities reached 49.5, 94.3, and 154.2 mg/g, respectively. An increase in adsorption capacity (mg/g) with the increased initial concentration of ACT may be due to enhanced osculation between ACT ions and NAC particles; increased concentration gradient and rate of mass transfer had the same explanations [12]. In general, these forces led to the enhancement of ACT uptake by NAC particles.

### 3.4. Kinetic modeling

Kinetic information is needed for designing and modeling adsorption processes as well as determining optimum operating conditions, adsorbate uptake rate, and finally time for equilibrium specification [27]. To attain these aims, the experimental data were fitted with two of the most widely used kinetic models of PFO and PSO at the adsorbent concentrations of 0.4 and 1 g/L. The kinetic information is acquired from the models presented in Table 4. The fitted linear regression plots demonstrated that the experiment data had better coordination with the PSO model for all the three investigated concentration and two adsorbents with higher determination coefficient ($R^2 > 0.99$) than those of the PFO model. Moreover, the validity of the PFO and PSO order models was assessed by calculating standard deviation ($\Delta q$) between experimental and model-predicted adsorption capacities according to the following equation:

$$\Delta q = \sqrt{\frac{\sum [(q_{exp} - q_{cal})/q_{exp}]^2}{n-1}} \quad (7)$$

Table 4
Kinetic details of ACT adsorption onto NAC

| | Adsorbent concentration = 0.4 g/L | | Adsorbent concentration = 1 g/L | |
|---|---|---|---|---|
| Kinetic model | Pseudo-first order | Pseudo-second order | Pseudo-first order | Pseudo-second order |
| Equation | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | $t/q_t = (1/k_2 q_e^2) + t/q_e$ | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | $t/q_t = (1/k_2 q_e^2) + t/q_e$ |
| Plot | $\ln(q_e - q_t)$ vs. $t$ | $t/q_t$ vs.$t$ | $\ln(q_e - q_t)$ vs. $t$ | $t/q_t$ vs.$t$ |
| Concentration (50 mg/L) | | | | |
| Fitted model | $\ln(q_e - q_t) = 3.5993 - 0.0466\ t$ | $t/q_t = 0.0126 + 0.0086\ t$ | $\ln(q_e - q_t) = 1.9717 - 0.062\ t$ | $t/q_t = 0.0054 + 0.0204\ t$ |
| $R^2$ | 0.9304 | 0.9981 | 0.933 | 0.9997 |
| Constant | $k_1 = -0.0466$ L/min | $k_2 = 0.006$ mg/g min | $k_1 = -0.062$ L/min | $k_2 = 0.77$ mg/g min |
| Calculated $q_e$ ($q_e$, cal) | 36.5 | 116.3 | 7.17 | 49.1 |
| Experimental $q_e$ ($q_e$, exp) | 118 | 118 | 49.7 | 49.7 |
| Concentration (100 mg/L) | | | | |
| Fitted model | $\ln(q_e - q_t) = 3.6516 - 0.0617\ t$ | $t/q_t = 0.0091 + 0.0063\ t$ | $\ln(q_e - q_t) = 3.1777 - 0.0301t$ | $t/q_t = 0.0079 + 0.0103\ t$ |
| $R^2$ | 0.8886 | 0.9999 | 0.8663 | 0.9995 |
| Constant | $k_1 = -0.0617$ L/min | $k_2 = 0.004$ mg/g min | $k_1 = -0.0301$ L/min | $k_2 = 0.013$ mg/g min |
| Calculated $q_e$ ($q_e$, cal) | 38.5 | 158.7 | 23.8 | 97.1 |
| Experimental $q_e$ ($q_e$, exp) | 156 | 156 | 98.5 | 98.5 |
| Concentration (200 mg/L) | | | | |
| Fitted model | $\ln(q_e - q_t) = 3.0696 - 0.0548\ t$ | $t/q_t = 0.0033 + 0.0055\ t$ | $\ln(q_e - q_t) = 3.6372 - 0.0824\ t$ | $t/q_t = 0.0048 + 0.0064\ t$ |
| $R^2$ | 0.9308 | 1.0 | 0.8975 | 0.9997 |
| Constant | $k_1 = -0.0548$ L/min | $k_2 = 0.009$ mg/g min | $k_1 = -0.0824$ L/min | $k_2 = 0.009$ mg/g min |
| Calculated $q_e$ ($q_e$, cal) | 21.5 | 181.8 | 37.9 | 156.3 |
| Experimental $q_e$ ($q_e$, exp) | 181 | 181 | 157.3 | 157.3 |
| $\Delta q$ | 1.34 | 0.022 | 1.372 | 0.019 |

As shown in Table 4, the values of $\Delta q$ for all the concentrations and adsorbents were very low for PSO than PFS, which confirmed the last result. Therefore, ACT adsorption onto NAC is favored by PSO model. The number of studies related to ACT adsorption, especially information correlating adsorption kinetic, is very restricted. Nevertheless, nearly all of the available works have reported PSO as the best fitted model with the experimental data (Table 1), which is in agreement with the finding of the present work. Fitness of the experimental data to the PSO implies that adsorption is likely to be controlled by chemisorption [28]. The fitted linear regression plots of PSO are shown in Fig. 4. The value of PSO adsorption constant ($k_2$) for the adsorbent concentration of 1 g/L (optimum amount) at the ACT concentrations of 50, 100, and 200 mg/L was 0.77, 0.013, and 0.009 mg/(g min), respectively. Considerable decrease of $k_2$ with the increased ACT concentration represented the result that the mass transfer may be the limiting step of adsorption and that the rate of ACT mass transfer to NAC could be improved with enhanced initial concentration gradient [27]. This result was not observed at adsorbent concentration of 0.4 g/L. On the other hand, as shown in Table 4, an increase in PSO kinetic constant ($k_2$) with increased NAC concentration confirmed the conclusion that the mass transfer is the controlling step in adsorption [29]. In fact, by increasing the NAC concentration as an adsorbent, the adsorption sites for the specific numbers of ACT molecules concentration increased and also the resistance of ACT mass transfer from solution bulk onto NAC decreased [30]. Also, Cabrita et al. [11] showed very higher PSO kinetic constant ($k_2$) than the present work, which indicated that the mass transfer of ACT in their work was not a limited step.

### 3.5. Equilibrium adsorption and isotherm modeling of ACT onto NAC

The equilibrium adsorption of ACT was evaluated under the conditions given in Table 3. The results are shown in Fig. 5 as removal efficiency and adsorption

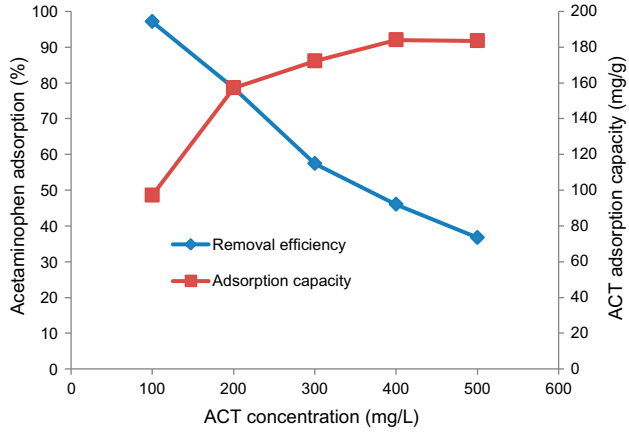



Fig. 5. The removal efficiency and capacity of ACT adsorption onto NAC under equilibrium condition prepared in Table 3.

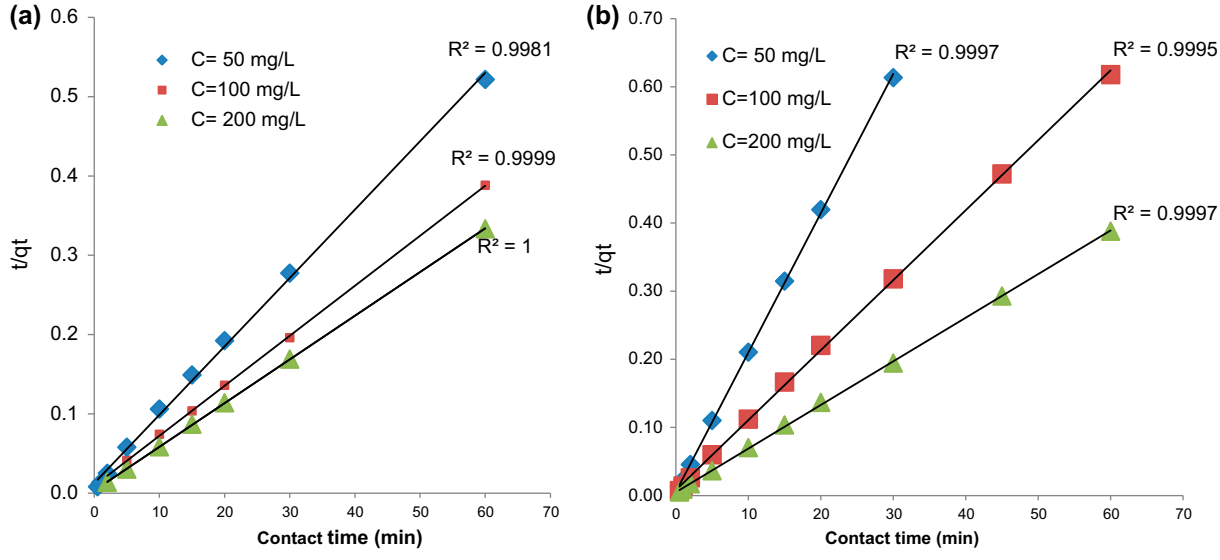



Fig. 4. Pseudo-second-order plots of adsorption of different concentrations (50–200) of ACT onto NAC in adsorbent concentration of 0.4 (a) and 1 g/L (b).

Table 5
Isotherm modeling of ACT onto NAC

| Isotherm model | Information/unit | Equilibrium temperature (℃) | | | | |
|---|---|---|---|---|---|---|
| Langmuir | $C_e/q_e = 1/k_L q_{max} + C_e/q_{max}$ | 10 | 20 | 25 | 30 | 40 |
| Plot | $(C_e/q_e)$ vs. $C_e$ | | | | | |
| Fitted model | | $C_e/q_e = 0.0187 + 0.0043 C_e$ | $C_e/q_e = 0.0411 + 0.0044 C_e$ | $C_e/q_e = 0.0335 + 0.0053 C_e$ | $C_e/q_e = 0.0474 + 0.005 C_e$ | $C_e/q_e = 0.061 + 0.0052 C_e$ |
| $q_{max}$ | mg/g | 233 | 228 | 193 | 196 | 193 |
| $K_L$ | L/mg | 0.23 | 0.107 | 0.155 | 0.107 | 0.085 |
| $R^2$ | | 0.999 | 0.996 | 0.999 | 0.997 | 0.993 |
| $R_L$ | $1/1 + k_L C_i$ | 0.008–0.08 | 0.018–0.15 | 0.012–0.11 | 0.018–0.15 | 0.022–0.19 |
| Freundlich | $\ln q_e = \ln K_F + 1/n \ln C_e$ | | | | | |
| Plot | $\ln q_e$ vs. $\ln C_e$ | | | | | |
| Fitted model | | $\ln q_e = 4.315 + 0.2253 \ln C_e$ | $\ln q_e = 4.017 + 0.2697 \ln C_e$ | $\ln q_e = 4.4599 + 0.1398 \ln C_e$ | $\ln q_e = 3.9 + 0.2632 \ln C_e$ | $\ln q_e = 3.7926 + 0.2734 \ln C_e$ |
| $K_F$ | | 74.8 | 55.5 | 85.6 | 49.4 | 44.2 |
| $n$ | $(mg/g(L/mg)^{1/n})$ | 4.43 | 3.7 | 7.1 | 3.8 | 3.65 |
| $R^2$ | | 0.912 | 0.914 | 0.9679 | 0.835 | 0.849 |

capacity. As depicted in Fig. 5, ACT removal efficiency in equilibrium conditions was decreased from 97.1 to 36.7% at the initial ACT concentration of 100–500 mg/L, respectively. But, ACT adsorption capacity in equilibrium conditions was increased from 2.9 mg/g at the initial ACT concentration of 100 mg/L–316.5 mg/g when the ACT concentration was increased to 500 mg/L. Considering the constant concentration of NAC as the adsorbent in the solution, the decreased percentage of the removal as a function of ACT concentration can be related to the decrease of adsorbated ACT molecules vs. the remainder ACT concentration. In other words, by increasing the ACT concentration, the availability adsorption sites became limited [31]. As shown in Fig. 5, the enhanced adsorption capacity with increased ACT concentration under the conditions of these experiments can be attributed to the increased mass transfer of ACT molecules to the given mass of adsorbent, thus increasing the adsorption capacity [32].

The equilibrium adsorption data were also applied for the analyses of isotherm obtained from the experiments at different temperatures. Isotherm studies are beneficial tools for describing the behavior of adsorption reaction, designing and optimizing process, and determining the maximum capacity of NAC for adsorbing ACT. Therefore, the conformity of the experimental data was evaluated using two of the most widely used isotherm models: Langmuir and Freundlich. The linear forms of these models and also the information obtained from fitting the experimental equilibrium adsorption data are summarized in Table 5. Based on the determination coefficient ($R^2$), the best fitted model was selected.

As seen in Table 5, it is evident that the $R^2$ of Langmuir isotherm model was higher than another fitted model for all the tested temperature. This finding suggests that the adsorption of ACT onto NAC particle sites is distributed as homogeneous monolayer and has a free-energy change for all adsorption sites [9,33]. Furthermore, the favorability of ACT adsorption onto NAC was assessed by equilibrium dimensionless parameter ($R_L$) acquired from Langmuir equation, where $C_i$ is the initial concentration of ACT in each temperature. Based on $R_L$ factor, the adsorption process can be considered as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [31,34]. The analyzed values of $R_L$ of this work fell between 0 and 1 at the temperature ranging from 10 to 40˚C (Table 5), suggesting that the adsorption process of ACT onto NAC was favorable. At higher ACT concentration at each temperature, $R_L$ values were lower and tended to zero, which demonstrated that the adsorption process was therefore more favorable. On the other hand, the value of constant $n$ in the Freundlich model was also greater than unity (Table 5), which verified that NAC is an appropriate and beneficial adsorbent for ACT removal [29,35]. The maximum calculated adsorption capacity ($q_{max}$) from Langmuir model in this work was 233 mg/g at 10˚C. The $q_{max}$ of NAC at different temperatures did not have significant variations. Based on a few available reports on the isotherm of ACT adsorption onto different adsorbents (Table 1), no higher maximum adsorption capacity has been found, which is in contrast to NAC, except commercial activated carbon that has very similar capacity to NAC.

### 3.6. Thermodynamics of adsorption and its modeling

Thermodynamic analysis prepares valuable information on the mechanism of adsorption. To investigate the thermodynamics of ACT adsorption onto NAC, the adsorption experiments were investigated at various solution temperatures from 10 to 40˚C. The results in terms of ACT removal percentage as a function of solution temperature are shown in Fig. 6. As can be seen in Fig. 6, the ACT adsorption percentages onto NAC were slightly decreased from 99.4 to 93.8% with the increased temperature from 10 to 40˚C. The decrease of ACT adsorption with increased temperature suggested that the ACT adsorption was an exothermic process at the elevated temperature [36].

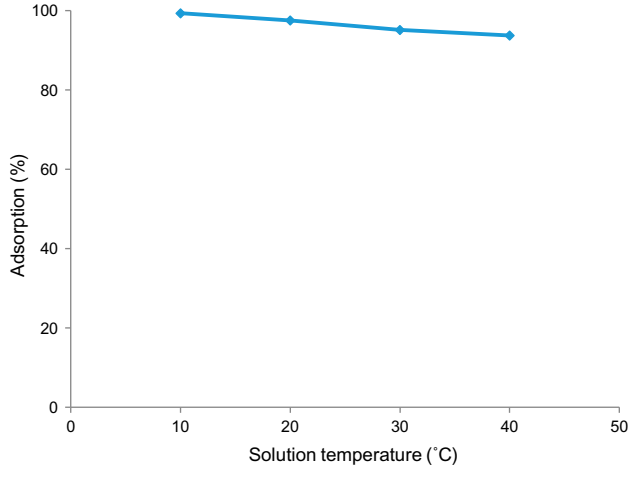



Fig. 6. The effect of solution temperature (10–40˚C) on adsorption of ACT onto NAC (contact time: 120 min; solution pH: 7.1; NAC concentration: 1 g/L; initial concentration: 50 mg/L).

Table 6
Thermodynamic parameters of ACT adsorption onto NAC

| Parameter | Temperature (K) | | | | |
|---|---|---|---|---|---|
| | 283.15 | 293.15 | | 303.15 | 313.15 |
| $\Delta G^\circ$ (kJ/mol) | −105 | −106.6 | | −108.29 | −109.94 |
| $\Delta S^\circ$ (kJ/mol) | | | −0.165 | | |
| $\Delta H^\circ$ (kJ/mol) | | | −58.28 | | |

In order to explain and confirm the mechanism of ACT adsorption onto NAC, the thermodynamics of adsorption was evaluated using $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ given by Eqs. (4)–(6). The obtained thermodynamic information is given in Table 6. Accordingly, the value of $\Delta H^\circ$ was negative, confirming that ACT adsorption onto NAC is an exothermic process; hence, the amount adsorbed at equilibrium must decrease with increasing temperature [25]. Also, negative enthalpies indicated that the adsorption process was energetically favorable [37]. The negative value of $\Delta S^\circ$ reflected that randomness was decreased at the solid/liquid interface during the adsorption of ACT onto NAC particles. The low value of $\Delta S^\circ$ indicated no significant changes on entropy [38].

## 4. Conclusion

The adsorption of ACT, as a model of non-steroidal anti-inflammatory pharmaceutical compounds, on an activated carbon, which was prepared from agricultural waste using innovated $NH_4Cl$-induced activation method, was examined under different operational variables. The experiments indicated that the adsorption rate of ACT onto NAC was independent from the solution pH. Also, it was found that NAC was able to remove high concentration of ACT at relatively short contact time (less than 5 min) with the low concentration of adsorbent. PSO and Langmuir models were fitted to kinetic and equilibrium experimental data, respectively. The maximum adsorption capacity was achieved ranging from 233 to 193 mg/g for the temperature between 10 and 40˚C. The preparation of NAC from agricultural waste and its independence from the solution pH made it an available and cost-effective adsorbent for the ACT removal from aqueous solution.

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