Removal Pharmaceutical Pollutants by Adsorption Competitive using Powdered Activated Carbon CAP (F400)

Abdelkarim Mellah¹,²*, Djamila Harik¹

¹National Polytechnic School, Environmental Sciences and Technology Laboratory, Algiers, Algeria
²Scientific and Technical Research Centre for Arid Areas (CRSTRA), Biskra

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Abstract

The aim of this study is to assess the competitive adsorption of two pharmaceutical products, phenobarbital and ibuprofen using powdered activated carbon (PAC) F400. The adsorption tests were carried out in batch experiments. The kinetic adsorption results showed that the PAC adsorbs good lipophilic ibuprofen with an adsorption capacity reaching 101.46 mg g⁻¹ against 63.46 mg g⁻¹ of phenobarbital. The adsorption capacity was negatively influenced by the presence of both adsorbates compared to their individual adsorption onto PAC. logKow, pKa values, and molecular weights played a crucial role on the adsorption capacities of the target compounds onto PAC. The results obtained show that the adsorption of both pharmaceuticals follows a pseudo-second order model through a complex process including connecting layer and intra-particle diffusion in micropores. According to the results, the isotherm models of Langmuir, Freundlich, and Temkin fit well the experimental data for each selected pharmaceuticals. The br values show that the competitive adsorption process of each pharmaceutical is a physisorption without formation of links.

Keywords: Adsorption; Phenobarbital; Ibuprofen; PAC, Kinetics; Isotherms

1 Introduction

Pharmaceuticals play a dominating role in the improvement of quality and life expectancy of the populations. Every year, thousands of tons of pharmaceutical compounds are utilized in human medicine and veterinary [1]. Many drug molecules were detected in the different effluents of the aquatic environments [2]. Pharmaceuticals have been developed to have effects on the human organism for treating diseases; therefore, their disposal in the environment may cause harm to humans, plants, and animals even at very low concentrations [3-6]. They can be eliminated via the urine without transformation [7]. Thus, they can present a considerable risk because of their direct toxicity and their effects cumulative or synergistic with other micropollutant. Many drugs have biological effects in the organism not targeted such as certain synthetic hormones on the fish [8, 9].

In recent years, their impact on the environment has become a scientific and public health concern, and are the matter of significant attention with respect to their environmental fate, the circumstances of their contact with the organisms and their toxicological risks during the last decade [3, 10-12]. Many specialized research has been reported in that field using several technologies of removal pharmaceuticals such as activated sludge systems [13-16], electro-coagulation coupled electro-flotation process [17], membrane bioreactors [15, 18, 19], photocatalytic oxidation processes [19,20], advanced oxidation processes [21-23], magnetic ion-exchange resins [24], and adsorption [25].

In the present research we studied the efficacy of the competitive adsorption of ibuprofen and phenobarbital as products largely used in the world form water using the powder activated carbon F400, in order to study the effect of the simultaneous presence of two drug molecules.

2 Materials and methods

2.1 Materials

The activated carbon used PAC F400 is presented in the form of a powder with a size granulometry of 50 µm. PAC F400 is prepared by activation of bituminous oil under high temperature in the presence of oxygen. It exhibits a microporous structure with a variable specific surface area of 1050–1200 m² g⁻¹, iodine index of 1050 mg g⁻¹ and acid function of surface 0.23 mEq g⁻¹ [26].
It is recommended to use clarifiers to increase the time of contact between PAC and water [27]. Before each use, PAC undergoes dehydration in the oven at 105 °C during 12 hours. All the chemicals and reagents used in the study are of analytic grade. Phenobarbital [5-(ethy1)-5-phenyl-1,4,6(1H,3H,5H)-pyrimidine trione and ibuprofen [acid (±) 2- (4-isobuty1phenyl) propionique] were supplied by Sigma–Aldrich, Germany. The physico-chemical characteristics and the structural formulas of both pharmaceuticals are shown in Table 1. The pharmaceutical solutions were prepared in ultrapure water (Millipore Milli-Q Direct 8 Water Purification System).

### 2.2 Adsorption experiments

For the purpose of our different studies, stock solutions were prepared for the two selected pharmaceutical products: ibuprofen and phenobarbital, at a concentration of 1.0 g L⁻¹ in the methanol. From these solutions, solutions were prepared with the desired concentration. All solutions were prepared with ultrapure water at pH = 6–7. Adsorption experiments were carried out using a batch experimental process. The adsorption kinetic experiments were first performed in order to determine the necessary time to reach the equilibrium (\(t_{eq}\)). Then, equilibrium tests were executed to determine the adsorption isotherms. All experiments were performed in duplicate by incubation under constant shaking 200 rpm, at a constant temperature of 21 ± 2 °C using a magnetic stirrer (Fisher bioblock scientific), with a known mass of the PAC of 40 mg L⁻¹ in ultrapure water. The initial concentration of the pharmaceuticals in ultrapure water is 8 mg L⁻¹.

### 2.3 Sample analysis

To evaluate the residual concentrations of phenobarbital and ibuprofen (Cᵣ), we developed the operating conditions for the proportioning of these two molecules by High-performance liquid chromatography (HPLC). This method was already validated in our laboratory. The protocol followed for this validation was inspired by that used in the Center of Expertise in Environmental Analysis of Quebec [65].

The residual pharmaceutical concentration was determined by HPLC (Waters 600 Controller, iodine bar detector: DAP Waters 2996) using column Nucleosil5 C18, \(L=250\) mm, \(d_i=4.6\) mm (OSI) at a wavelength of 210 nm for phenobarbital and 220 nm for ibuprofen. The developed conditions of analysis allowed the separation of the peaks of two molecules with very reasonable retention times (3.0 and 4.0 minutes respectively for phenobarbital and ibuprofen), which allow the analysis of a great number of samples per day. Chromatograms of a solution containing 8 mg L⁻¹ of each product are presented on Figure 1. Spectra UV relating to each peak is presented on Figure 2.

A volume of 20 µL of the filtrate injected by the injection loop is pulled by the mobile phase made up of a mixture methanol–water (75:25, V : V). The mobile flow phase is fixed at 1 ml min⁻¹. Detection takes place in the field of UV, the quantification and the qualification of the molecules were carried out with the wavelengths corresponding to the maximum of absorption in this field.

The retention times characteristic of the molecules allow their identification. The method of the compared injections (external calibration) and the determination of the chromatographic peak area are used for quantify the residues of the studied molecules.

### 3 Results and discussion

#### 3.1 Kinetics of adsorption

The influence of the agitation time on the mixed adsorption of phenobarbital and ibuprofen at an initial concentration of 8 mg L⁻¹ by PAC F400 at a concentration of 40 mg L⁻¹ is presented in Figure 3. The adsorbed amount can be calculated based on the Eq. (1):

\[
q_e = (C_0 - C_e)V / m
\]  

(1)

where \(q_e\) is the adsorption capacity at the equilibrium, \(C_0\) is the initial concentration of the adsorbate in the solution, \(m\) is the mass of the adsorbent and \(V\) is the volume of the solution.

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**Table 1: Physico-chemical properties of the pharmaceuticals**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular formula</th>
<th>Chemical structure</th>
<th>(w^a)</th>
<th>(M_w^b)</th>
<th>(p_Ka)</th>
<th>(\text{log} k_{ow})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibuprofen</td>
<td>C₁₃H₁₈O₂</td>
<td><img src="image" alt="Ibuprofen Structure" /></td>
<td>206.28</td>
<td>206.28</td>
<td>4.91</td>
<td>3.97</td>
</tr>
<tr>
<td>Phenobarbital</td>
<td>C₅H₁₀N₂O₂</td>
<td><img src="image" alt="Phenobarbital Structure" /></td>
<td>232.23</td>
<td>232.23</td>
<td>3.3118</td>
<td>1.47</td>
</tr>
</tbody>
</table>

\(PSA = \text{Polar Surface Area}
\)

\(^aSw = \text{Water solubility (mg L}^{-1}\) at 25 °C
\)

\(^bM_w = \text{Molecular weight (g mol}^{-1}\)
In the present study, the adsorbed quantity of individual pharmaceutical was clearly higher than that obtained for mixed substrates solution, which proved visibly a competitive adsorption existing between the target compounds in this research as shown in Figure 2. The adsorption process of phenobarbital in mixture is not fast. Indeed, only 23% equivalent of 45.24 mg g⁻¹ of phenobarbital is adsorbed after 5 min, while the slope becomes very weak with the approach of equilibrium after 180 min indicating a quantity adsorbed of 63.46 mg g⁻¹ equivalent of 32% of the quantity presents initially as shown in Figure 2. The adsorbed quantity of ibuprofen in binary mixture was very quickly reaching a rate of 31% after 5 min, which is equivalent of 62.22 mg g⁻¹ and pseudo-equilibrium is established after 180 min with an adsorption percentage rate of 51% equivalent of 101.46 mg g⁻¹. The mechanism of the binary mixture adsorption is probably influenced by the pKa and log<sub>kow</sub> of the substrates competing for the limited adsorption sites. The dissociation of the electrolyte substrates is governed by the pKa [28]. The pKa of phenobarbital (7.3; 11.8) indicated that it would remain at molecular form over the operation. This property resulted good competitive adsorption with ibuprofen. The log<sub>kow</sub> is considered, as well, as a significant factor for the adsorption capacity evaluation, in which the pharmaceutical pollutants with higher log<sub>kow</sub> values should have a higher adsorption affinity towards PAC [29].

Therefore, the adsorbed quantity of ibuprofen was higher than that obtained with phenobarbital. Phenobarbital presents the lowest log<sub>kow</sub> value, which indicates that is the most hydrophilic compound among the tow selected pharmaceuticals. However, log<sub>kow</sub> played out a crucial role in controlling the adsorbed quantity in the competitive adsorption of pharmaceuticals. At neutral pH, ibuprofen exists in non-polar state, whereas the phenobarbital is dissociated into anions. The PAC surface is principally non-polar, which facilitates to adsorb non-polar molecules [30]. Some reported works confirm the low adsorption capacity of PAC towards phenobarbital, such as the works mentioned above, of Cooney using the activated carbons Instachar and Liquichar to adsorb phenobarbital [31], and the reported work of Papciak and co-workers about adsorption of ibuprofen onto Norit SA super and Carbopol MB5 [32].

The Lagergren model governing the pseudo-first order adsorption kinetics is the most widely used in its linearized form as shown the Eq. (2) [66]:
\[ \ln(q_e - q_t) = \ln(q_e) - K_1 t / 2.303 \]  (2)

where \( q_e \) and \( q_t \) are the amounts of solute adsorbed in mg g\(^{-1}\) at equilibrium and at time \( t \), respectively, and \( K_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)). The graphs given by plotting \( \ln(q_e - q_t) \) as a function of time are presented in Figure 3 for the adsorption of ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) on PAC at a concentration of 40 mg L\(^{-1}\). The pseudo first-order kinetic parameters are presented in Table 2. A wide variance can be observed between experience and theory using the Lagergren model and the correlation coefficient \( R^2 \) values for the pseudo-first-order kinetic model were 0.872 and 0.860 for phenobarbital and ibuprofen, respectively, indicating that the Eq. (2) does not adequately describe the adsorption processes of ibuprofen and phenobarbital onto PAC.

\[ t / q_t = 1 / K_2 q_e^2 + t / q_e \]  (3)

where \( q_e \) and \( q_t \) are the quantities of aqueous solution adsorbed out in mg g\(^{-1}\) at equilibrium and at moment \( t \), \( K_2 \) is the speed constant of the pseudo-second order (g mg\(^{-1}\) min\(^{-1}\)). The initial velocity of the adsorption \( h \) is given in this case by the Eq. (4):

\[ h = K_2 q_e^2 \]  (4)

The graphs given by plotting \( t / q_e \) as a function of time for the adsorption of ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at a concentration of 40 mg L\(^{-1}\) are presented in Figure 4. The linear adjustment of the experimental values obtained during the kinetic adsorption tests for the pseudo-second order model were given coefficients of correlation \( R^2 \) very close to the unit showing that this model is in perfect agreement with the obtained experimental values. Some works were reported that pseudo-second order is adequate to describe the adsorption of ibuprofen and phenobarbital onto activated carbons [35, 39-42]. The calculated \( q_e \) values of 125 mg g\(^{-1}\) and 76.92 mg g\(^{-1}\) of ibuprofen and phenobarbital, respectively, according to the pseudo-second order kinetic model of the adsorption by PAC (F400) agreed well with the experimental data as shown in Table 3. According to these results, the ibuprofen presents an initial velocity \( h \) of 12.5 mg g\(^{-1}\) min\(^{-1}\) higher than 6.21 mg g\(^{-1}\) min\(^{-1}\) of phenobarbital.

![Figure 3: Pseudo-first order kinetics results on the removal of ibuprofen (λ = 220 nm) mixed with phenobarbital (λ = 210 nm), by PAC (F400) at 21 °C in ultrapure water at pH 6–7, \( C_0 \) (pharmaceutical) = 8 mg L\(^{-1}\), C(PAC) = 40 mg L\(^{-1}\).](image1)

![Figure 4: Pseudo-second order kinetics results on the removal of ibuprofen (λ = 220 nm) mixed with phenobarbital (λ = 210 nm), by PAC (F400) at 21 °C in ultrapure water at pH 6–7, \( C_0 \) (pharmaceutical) = 8 mg L\(^{-1}\), C(PAC) = 40 mg L\(^{-1}\).](image2)

Table 2: Pseudo-first order kinetic parameters for mixed ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at a concentration of 40 mg L\(^{-1}\) at 21 °C and pH=6–7

<table>
<thead>
<tr>
<th></th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( R^2 )</th>
<th>( q_e)exp (mg g(^{-1}))</th>
<th>( q_e)calc (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenobarbital</td>
<td>0.013</td>
<td>0.872</td>
<td>74.45</td>
<td>38.13</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.014</td>
<td>0.860</td>
<td>124.31</td>
<td>56.82</td>
</tr>
</tbody>
</table>

Table 3: Pseudo-second order kinetic parameters for ibuprofen mixed with phenobarbital at \( C_0 \) = 8 mg L\(^{-1}\) by PAC (F400) at concentration of 40 mg L\(^{-1}\) at 21 °C and pH=6–7

<table>
<thead>
<tr>
<th></th>
<th>( K_2 ) (g mg(^{-1}) h(^{-1}))</th>
<th>( h ) (mg g(^{-1}) min(^{-1}))</th>
<th>( R^2 )</th>
<th>( q_e)exp (mg g(^{-1}))</th>
<th>( q_e)calc (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenobarbital</td>
<td>0.0010</td>
<td>6.21</td>
<td>0.997</td>
<td>74</td>
<td>76.92</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.0008</td>
<td>12.5</td>
<td>0.998</td>
<td>124</td>
<td>125</td>
</tr>
</tbody>
</table>
The low speed of phenobarbital in mixture may be due to the influence of the competition phenomenon, which negatively affect its adsorption [34], and the lipophilic ibuprofen would be adsorbed more quickly thus occupying the sites and reducing the adsorption of phenobarbital indicating a good affinity to PAC than phenobarbital.

3.1.3 Intra-particle diffusion

The intra-particle diffusion of the adsorbates into adsorbents during the process of adsorption is explored to understanding the stage which controls the speed of adsorption [43], using the Eq. (5):

\[ q_t = K_p t^{1/2} \]  

(5)

where \( q_t \) is the adsorbed quantity per unit mass of adsorbent at time \( t \) (mg g\(^{-1}\)) and \( K_p \) is the intra-particle velocity constant (mg g\(^{-1}\) min\(^{1/2}\)). According to the plotted data of the intra-particle diffusion model (Figure 5) \( q_t \) versus \( t^{1/2} \) exhibits multilineal plots, where two steps could be influencing the process. The plots for the adsorption of ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at a concentration of 40 mg L\(^{-1}\) do not result in a linear relationship passing via the origin, but multimodal graphs with two distinct regions, indicating that intra-particle diffusion is affected by more than one process [44].

Figure 5: Intra-particle diffusion model for the adsorption kinetics of the mixed ibuprofen (\( \lambda = 220 \text{ nm} \)) and phenobarbital (\( \lambda = 210 \text{ nm} \)) by PAC (F400) at 21 °C in ultrapure water at pH 6–7.  

\( (C_e/\text{pharmaceutical}) = 8 \text{ mg L}^{-1}; C(\text{PAC(F400)}) = 40 \text{ mg L}^{-1} \)

3.2 Modeling of the isotherms

Equilibrium adsorption isotherms are the most commonly data used to understand the adsorption mechanisms, in which many isotherm models are available. In this study, the three most used models in literature were tested: the isotherms of Langmuir [54], Freundlich [55], and Temkin [56].

3.2.1 Langmuir isotherm

The Langmuir isotherm model [54] for the adsorption of mixed ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at varying concentrations was tested using the Eq. (6) in its linear form:

\[ C_e / q_e = C_e / q_m + 1 / q_m b \]

(6)

where \( q_e \) is the adsorbed amount of solute per unit weight of adsorbent at equilibrium (mg g\(^{-1}\)), \( C_e \) is the concentration of the solute at the equilibrium in the bulk solution (mg L\(^{-1}\)), \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), and \( b \) is the constant related to the free energy of adsorption (L mg\(^{-1}\)). The graphs fitting \( C_e q_e \) as a function of \( C_e \) is presented in Figure 6. The Langmuir isotherm constants \( b, 1/b, q_m \) and the correlation coefficients \( R^2 \) are presented in Table 5.

The Langmuir isotherm model for the adsorption of mixed ibuprofen and phenobarbital onto PAC (F400) fits well the experimental data (Figure 6) based on the relatively high values of correlation coefficient \( R^2 \) 0.983 and 0.960 for phenobarbital and ibuprofen, respectively (Table 5).
Table 4: Intra-particle diffusion parameters for the mixed ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at a concentration of 40 mg L\(^{-1}\) at 21 °C and pH=6–7

<table>
<thead>
<tr>
<th></th>
<th>(k_d) (mg g(^{-1}) min(^{-1/2}))</th>
<th>(R^2)</th>
<th>(k_d) (mg g(^{-1}) min(^{-1/2}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenobarbital</td>
<td>3.116</td>
<td>0.948</td>
<td>1.228</td>
<td>0.902</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>7.899</td>
<td>0.969</td>
<td>0.065</td>
<td>0.973</td>
</tr>
</tbody>
</table>

Figure 6: Langmuir isotherm of adsorption of ibuprofen (\(\lambda = 220\) nm) mixed with phenobarbital (\(\lambda = 210\) nm) by PAC (F400) at different concentrations \(C(PAC) = 20–280\) mg L\(^{-1}\), at 21 °C in ultrapure water at pH 6–7, \(C_{(\text{pharmaceutical})} = 8\) mg L\(^{-1}\)

These results were confirmed by Morley and co-workers, who indicated that Langmuir fits well their result of adsorption of ibuprofen onto activated carbon F400 [57]. Carvalho and co-workers have as well reported that Langmuir model fits best their results of adsorption onto activated carbons CAC and CPAC compared to Freundlich model [35]. Papciak and co-workers were furthermore reported that Langmuir fits well the results of adsorption of ibuprofen onto Norit and Carbopol [32].

Some works were indicated that Langmuir isotherm fits very well the results of phenobarbital adsorption onto activated carbons such as the adsorption onto activated charcoal reported by El-Mabrouk and co-workers [58], and onto activated carbons like SuperChar, Darco KB-B, Norit B Supra, Norit USP XX by Wurster and co-workers [59]. Langmuir fits best the results of adsorption of phenobarbital onto activated carbon Norit USP XX, Ch3J, and MI in which presented a high \(R^2\) of 0.99, followed by Temkin and then Freundlich models according to Gallardo and co-workers [41].

The calculated values of maximum adsorption capacities (\(q_{\text{max}}\)) show that the PAC (F400) exhibits better adsorption capacities towards ibuprofen arriving to 1000 mg g\(^{-1}\) than phenobarbital with 333.3 mg g\(^{-1}\) highlighting well the competitive adsorption between both selected pharmaceuticals. The \(b\) factor relates to the dissociation constant of the adsorbate determined for the ibuprofen is 0.25 L mg\(^{-1}\) \((b<1)\) showing the good affinity of PAC (F400) towards ibuprofen compared to phenobarbital [60].

3.2.2 Freundlich isotherm

Freundlich isotherm [55] presents an empirical model for multilayer and heterogeneous adsorption sites. Its linear form is commonly given by the Eq. (7):

\[
\ln(q_e) = \ln(K_f) + 1/n \ln(C_e)
\]

where \(q_e\) is the adsorbed amount of solute per unit weight of adsorbent (mg g\(^{-1}\)), \(C_e\) is the concentration of solute at equilibrium in the bulk solution (mg L\(^{-1}\)), \(K_f\) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg g\(^{-1}\)), and \(1/n\) is the heterogeneity factor.

The Freundlich isotherms are presented in Figure 7 by fitting \(\ln(q_e)\) as a function of \(\ln(C_e)\) for the adsorption of ibuprofen and phenobarbital at an initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at different concentrations. Straight lines are obtained with origin \(\ln(K_f)\) and slope \(1/n\). The Freundlich isotherm parameters \(K_f\), \(1/n\), \(n\) and the correlation coefficients \(R^2\) are presented in Table 6. The values of the coefficients of correlation \((R^2)\), 0.908 and 0.954 for the adsorption of the mixed phenobarbital and ibuprofen, respectively indicate that Freundlich isotherm model seems good to adjust the obtained experimental results. Morley and co-workers had reported that Freundlich model fits well their results about adsorption of ibuprofen onto activated carbon F400 [57]. Papciak and co-workers were furthermore reported that Freundlich isotherm fits well the results of adsorption of ibuprofen onto Norit and Carbopol [32]. The application of the Freundlich isotherm model for the adsorption of ibuprofen onto activated carbons F300 by Ociepa-Kubicka and co-workers showed a best fitting of this model [61].

Table 5: Langmuir isotherm parameters for adsorption of mixed ibuprofen and phenobarbital at initial concentration of 8 mg L\(^{-1}\) by PAC (F400) at different concentrations at 21 °C and pH=6–7

<table>
<thead>
<tr>
<th></th>
<th>(q_{\text{max}}) (mg g(^{-1}))</th>
<th>(b) (L mg(^{-1}))</th>
<th>(1/b) (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenobarbital</td>
<td>333.33</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>1000</td>
<td>0.14</td>
<td>7</td>
</tr>
</tbody>
</table>

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and phenobarbital have been presenting a values of adsorption energy variation $b_T$ of 17.92 and 29.85 kJ mol$^{-1}$, respectively, indicating a physical adsorption [46,62,63]. The positive values of the adsorption energy variation $b_T$ (Table 7) indicate an endothermic adsorption process [64].

![Figure 7: Freundlich isotherm of adsorption of mixed ibuprofen ($\lambda=220$ nm) and phenobarbital ($\lambda=210$ nm) by PAC (F400) at different concentrations ($C_{PAC}=20-280$ mg L$^{-1}$) at $21^\circ C$ in ultrapure water at pH 6–7, ($C_{0}$ (pharmaceutical) = 8 mg L$^{-1}$).](image)

![Figure 8: Temkin isotherm of adsorption of mixed ibuprofen ($\lambda=220$ nm) and phenobarbital ($\lambda=210$ nm), by PAC (F400) at different concentrations $C_{PAC}=20-280$ mg L$^{-1}$ at $21^\circ C$ in ultrapure water at pH 6–7, ($C_{0}$ (pharmaceutical) = 8 mg L$^{-1}$).](image)

### 4 Conclusion

The adsorption processes of two pharmaceuticals, ibuprofen and phenobarbital onto PAC were evaluated in ultrapure water. The PAC F400 can effectively eliminate the pharmaceutical pollutants from the water. $\log k_w$, $pK_a$ values, and molecular weights were affected the adsorption capacities of the target compounds onto PAC. Non-polar ibuprofen had a good adsorption capacity compared to phenobarbital. Activated carbon had had a less affinity to soluble organic compounds. Competitive adsorption influenced negatively on the kinetics of the pharmaceuticals. The kinetic of pseudo-second order appears more suitable model to describe the competitive adsorption process. The investigation results are best described by the Langmuir model for both ibuprofen and phenobarbital, followed, in decreasing order, by the Freundlich and Temkin models. This study carried out on a synthetic water and for two molecules, gave very promising results as for the possibility of eliminating the residues of pharmaceutical products from water. It would be interesting to continue this research by studying the behavior of other pharmaceutical molecules and especially to apply it in real waters (rejections of manufacturing plant of drugs, drinking water...) to seek and eliminate the residues of pharmaceutical products which can harm human health.
Table 7: Temkin isotherm parameters for adsorption of mixed ibuprofen and phenobarbital at an initial concentration of 8 mg L⁻¹ by PAC (F400)
at different concentrations at 21 °C and pH=6–7.

<table>
<thead>
<tr>
<th></th>
<th>$b_T$ (kJ mol⁻¹)</th>
<th>$A$ (L g⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenobarbital</td>
<td>29.85</td>
<td>4.98</td>
<td>0.924</td>
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<tr>
<td>Ibuprofen</td>
<td>17.92</td>
<td>2.06</td>
<td>0.861</td>
</tr>
</tbody>
</table>

Acknowledgements

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors’ contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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