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

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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. logk_{ow}, 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 b_T 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 m^2 g^{-1}, iodine index of 1050 mg g^{-1} and acid function of surface 0.23 mEq g^{-1} [26].

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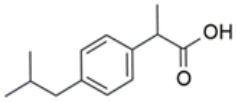
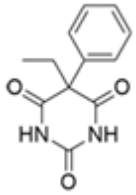
Table 1: Physico-chemical properties of the pharmaceuticals

Compounds	Molecular formula	Chemical structure	w[a]	Mw[b]	pKa	logk_{ow}
Ibuprofen	$C_{13}H_{18}O_2$		206.28	206.28	4.91	3.97
Phenobarbital	$C_8H_9NO_2$		232.23	232.23	.3;11.8	1.47

PSA = Polar Surface Area
[a] Sw = Water solubility (mg L^{-1}) at 25 °C
[b] Mw = Molecular weight (g mol^{-1})

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 all of analytic grade. Phenobarbital [5 -éthyl- 5phényl - 1,4,6(1H, 3H, 5H) - pyrimidine trione and ibuprofen [acide (±) 2 - (4 - isobutyphényl) 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 tow 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 (*C*r), 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 mn 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):

$$q_e = (C_0 - C_e)V / m \quad (1)$$

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.

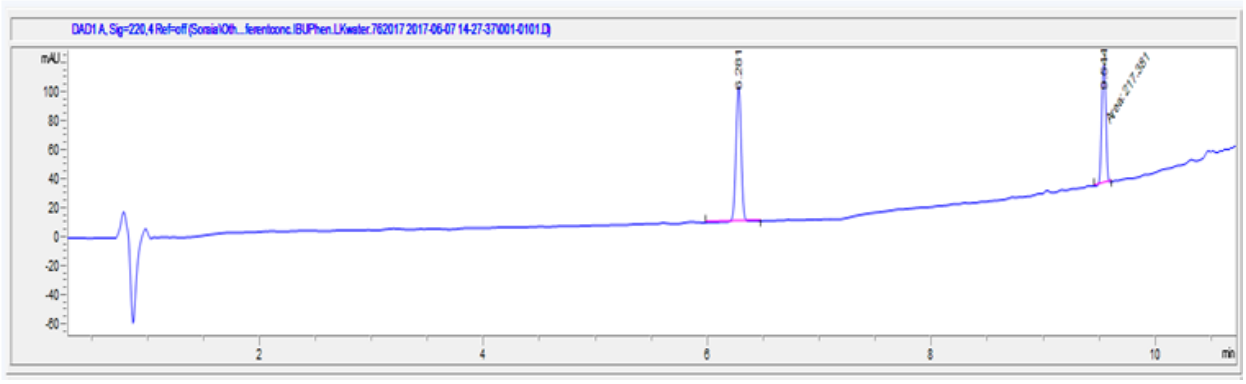


Figure 1: Chromatograms of a solution made up of the mixture of phenobarbital and ibuprofen at concentration of 8 mg L^{-1} to λ = 210 nm

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 logk_{ow} of the substrates competing for the limited adsorption sites. The dissociation of the electrolyte substrates is governed by the pKa [28]. The pKa of phenopbarbital (7.3; 11.8) indicated that it would remain at molecular form over the operation. This property resulted good competitive adsorption with ibuprofen. The logk_{ow} is considered, as well, as a significant factor for the adsorption capacity evaluation, in which the pharmaceutical pollutants with higher logk_{ow} 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 logk_{ow} value, which indicates that is the most hydrophilic compound among the tow selected pharmaceuticals. However, logk_{ow} 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].

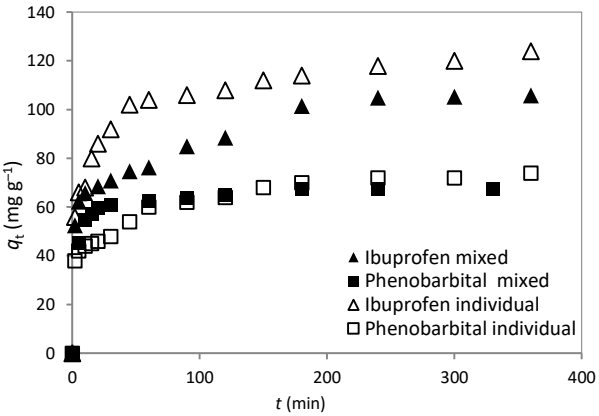


Figure 2: Adsorption Kinetics of ibuprofen with phenobarbital mixed and individual expressed as quantity adsorbed (mg g^{-1}) by PAC F400 at 20 ± 2 °C in ultrapure water at pH = 6.6 ± 0.2 (C_0(pharmaceutical) = 8 mg L^{-1}; C(PAC) = 40 mg L^{-1}

The difference in the adsorption capacity for both pharmaceuticals at equilibrium could be related to competitive adsorption on the sites of PAC. Similar results were reported by Weber and co-workers [33], were studied the influence of solute size and molecular configuration in which they found a relation between the speed of adsorption and the molar mass. Hydrophobic phenobarbital exhibits a higher molar mass and bit large molecular structure compared to lipophilic ibuprofen, its adsorption get equilibrium a bit slightly with less adsorption capacity than ibuprofen. In addition, the least soluble compounds are adsorbed more easily and the structure of the carbonaceous chain plays a significant role in the case of competitive adsorption. The molecules containing of the unsaturated connections are more easily adsorbed than the molecules with saturated connections (electronic exchanges) [34]. Carvalho and co-workers were reported similar times of equilibrium in their study adsorption of ibuprofen onto powdered activated carbons prepared from cork waste [35].

3.1.1. Kinetics the pseudo-first order

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]:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \ /2.303 \quad (2)$$

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.

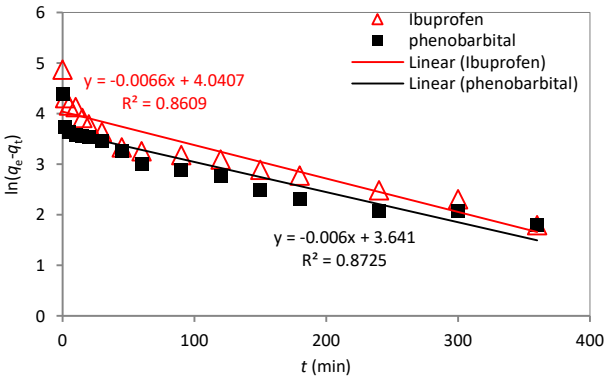


Figure 3: Pseudo-first order kinetics results on the removal of ibuprofen (λ = 220 nm) mixed with phenobarbital (λ = 210 nm), by PAC (F400) at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1}; C(PAC) = 40 mg L^{-1})

3.1.2 Kinetics the pseudo-second order

The pseudo-second order model is suggested by certain authors as being adapted to describe certain kinetics of adsorption [36-38], it is especially used in the following linearized form as it shown by the Eq. (3):

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (3)$$

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):

$$h = K_2 q_e^2 \quad (4)$$

The graphs given by plotting t/q_t as a function of time for the adsorption of ibuprofen and phenobarbital at an intial 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.

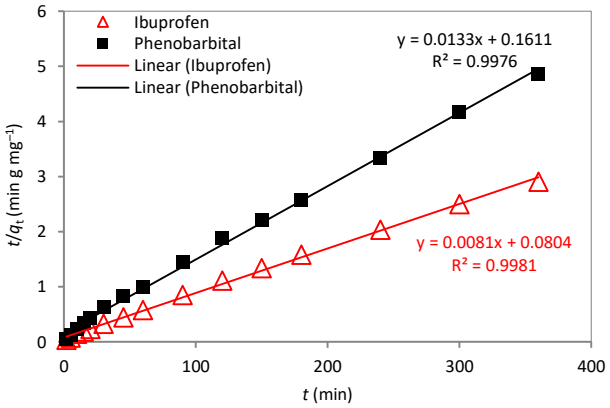


Figure 4: Pseudo-second order kinetics results on the removal of ibuprofen (λ = 220 nm) mixed with phenobarbital (λ = 210 nm), by PAC (F400) at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1}; C(PAC) = 40 mg L^{-1}).

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

	k_1(min^{-1})	R^2	$q_{e,exp}$ (mg g^{-1})	$q_{e,calc}$ (mg g^{-1})
Phenobarbital	0.013	0.872	74.45	38.13
Ibuprofen	0.014	0.860	124.31	56.82

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

	K_2 (g mg^{-1} h^{-1})	h (mg g^{-1} min^{-1})	R^2	$q_{e\ exp}$ (mg g^{-1})	$q_{e\ calc}$ (mg g^{-1})
Phenobarbital	0.0010	6.21	0.997	74	76.92
Ibuprofen	0.0008	12.5	0.998	124	125

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):

$$q_t = K_p\, t^{1/2} \quad (5)$$

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 multilinear plots, where two steps could be influencing the process. The plots for the adsorption of ibuprofen and phenobarbital at an intial 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]. The plotted curves of the mixed pharmaceuticals were presented the existence of two stages. In the first stage, both ibuprofen and phenobarbital diffuse through the solution to the external surface of the adsorbent. The second stage relates to the equilibrium stage, in which the intra-particle diffusion starts to slow down and level out [45, 46]. Thus, in order to calculate the speed constants of diffusion of each stage, the linear regression is applied to each section. The coefficient of diffusion was also calculated for each element using the Eq. (5). The multilinearity of the curves of the intra-particle diffusion is described in the literature for many couples adsorbate-adsorbent such us cations natural metal-materials [47], diuron and metribuzine-activated carbon [48]. Only one part is regarded as limiting factor speed in a particular field of time [49].

The intra-particle parameters are presented in Table 4. The values of the correlation coefficients R^2 for the intra-particle diffusion model of Weber–Morris obtained for the mixed pharmaceuticals are all above 0.901 indicating that the intra-particle model fits well the obtained experimental values. The slope of the linear part indicates the speed of adsorption; and the weakest slope corresponds to the slowest process of adsorption noting that the least soluble compounds are adsorbed more easily.

The values of the intra-particle velocity constants k_{p1} and k_{p2} showed that the first stage due to the external mass transfer is the fastest followed by the slowest intra-particule diffusion stage confirmed by $k_{p1} > k_{p2}$. Lipophilic ibuprofen characterized by its high logk_{ow} of 3.97 than 1.47 of phenobarbital was presented a highest initial velocity, that can be explained by the good affinity of organic adsorbents towards lipophilic adsorbates [29, 50, 51]. The adsorption of both mixed pharmaceutical products supposed competing on the sites of PAC [52]. Therefore according to our study, ibuprofen diffuses more easily onto the PAC. The results suggested that organic PAC adsorbent could serve as a good adsorbent for lipophilic organic pharmaceutical pollutants [53].

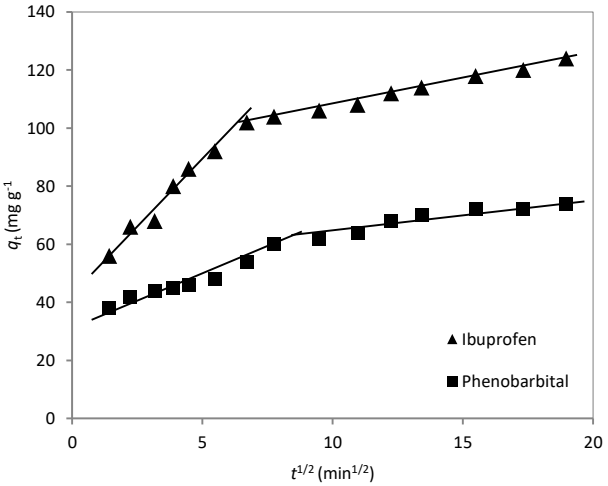


Figure 5: Intra-particle diffusion model for the adsorption kinetics of the mixed ibuprofen (λ= 220 nm) and phenobarbital (λ= 210 nm) by PAC (F400) at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1}; C(PAC(F400)) = 40 mg L^{-1})

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:

$$Ce/q_e = Ce/q_m + 1/q_m b \quad (6)$$

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_{max} 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

	k_{p1} (mg g^{-1} $min^{-1/2}$)	R^2	k_{p2} (mg g^{-1} $min^{-1/2}$)	R^2
Phenobarbital	3.116	0.948	1.228	0.902
Ibuprofen	7.899	0.969	0.065	0.973

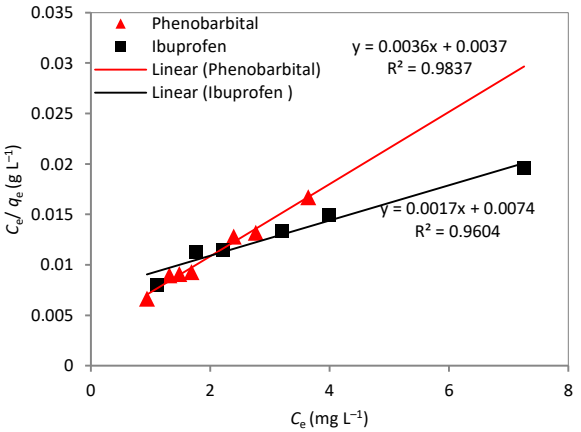


Figure 6: Langmuir isotherm of adsorption of ibuprofen (λ= 220 nm) mixed with phenobarbital (λ= 210 nm) by PAC (F400) at different concentrations C(PAC) = 20–280 mg L^{-1}, at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1})

These results were confirmed by Morley and co-werkers, who indicated that Langmuir fits well their result of adsorption of ibuprofen onto activated carbon F400 [57]. Carvalho and co-werkers have as well reported that Langmuir model fits best their results of adsorption onto activated carbons CAC and CPAC compared to Freundlish 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 us 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-woerkers [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_{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):

$$\ln(q_e) = \ln k_f + 1/n \ln(C_e) \quad (7)$$

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 lnK_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

	R^2	q_m (mg g^{-1})	b (L mg^{-1})	1/b (mg L^{-1})
Phenobarbital	0.983	333.33	1	1
Ibuprofen	0.960	1000	0.14	7

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

	K_F	$1/n$	n	R^2
Phenobarbital	137.14 $mg^{0.575}$ g^{-1} $L^{0.425}$	0.425	2.35	0.908
Ibuprofen	123.10 $mg^{0.417}$ g^{-1} $L^{0.583}$	0.583	1.72	0.954

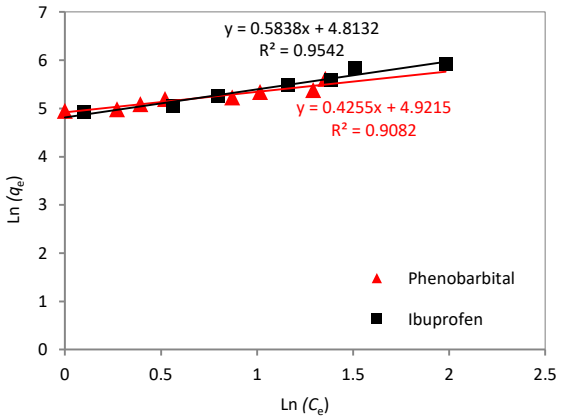


Figure 7: Freundlich isotherm of adsorption of mixed ibuprofen (λ= 220 nm) and phenobarbital (λ= 210 nm) by PAC (F400) at different concentrations C(PAC) = 20–280 mg L^{-1}, at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1})

The calculated values of Freundlich constant ($1/n$) 0.425, and 0.583 for phenobarbital and ibuprofen, respectively, are less than 1, indicating that the adsorption of the selected drugs is favorable. A high adsorbent capacities were indicated by the K_F values 137.14 $mg^{0.507}$ g^{-1} $L^{0.493}$, 123.10 $mg^{0.743}$ g^{-1} $L^{0.257}$ for phenobarbital and ibuprofen, respectively.

3.2.3 Temkin isotherm

The derivation of the Temkin isotherm model presumes that the diminution of the adsorption heat is linear rather than logarithmic, as applied in the Eq. (7) of Freundlich model. The Temkin isotherm is mostly presented in its form given by the Eq. (8) [56]:

$$q_e = (RT/b_T)\log A + (RT/b_T)\log C_e \quad (8)$$

where: T is the temperature (°K); R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$); b_T is the constant relative to the heat of adsorption (J mol^{-1}), and A is the Temkin isothermal constant (L g^{-1}).

The application of the Eq. (8) of Temkin isotherm model is presented in Figure 8 by fitting q_e as a function of ln(C_e) for the adsorption of ibuprofen and phenobarbital at an intial concentration of 8 mg L^{-1} by PAC (F400) at different concentration. The adsorption isotherms derived from the experimental data for each of the tested adsorbate and adsorbent are presented in Table 7. According to the correlation coefficient values R^2 of 0.861 and 0.924 for ibuprofen and phenobarbital, respectively, the Temkin isotherm model for the adsorption of selected pharmaceuticals by PAC (F400) do not fit well the experimental data (Figure 8). The adsorption of ibuprofen 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].

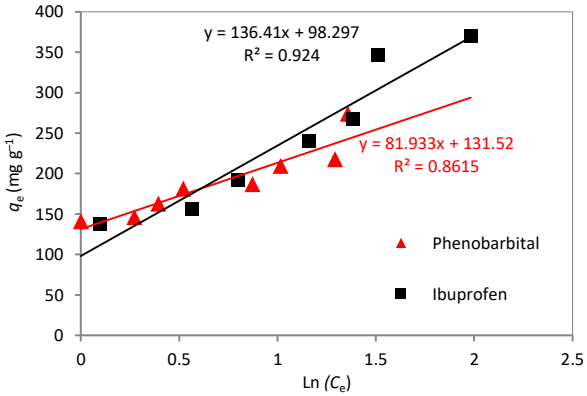


Figure 8: Temkin isotherm of adsorption of mixed ibuprofen (λ= 220 nm) and phenobarbital (λ= 210 nm), by PAC (F400) at different concentrations C(PAC) = 20–280 mg L^{-1} at 21 °C in ultrapure water at pH 6–7, (C_0(pharmaceutical) = 8 mg L^{-1})

4 Conclusion

The adsorption processes of tow pharmaceuticals, ibuprofen and phenobarbital onto PAC were evaluated in ultrapure water. The PAC F400 can effectively eliminate the pharmaceutical pollutants from the water. logk_{ow}, pKa values, and molecular weights were affected the adsorption capacities of the trajet compounds onto PAC. Non-polar ibuprofen had have 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.

	b_T (kJ mol^{-1})	A (L g^{-1})	R^2
Phenobarbital	29.85	4.98	0.924
Ibuprofen	17.92	2.06	0.861

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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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