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Simultaneous adsorption of acetaminophen, diclofenac and tetracycline by organo-sepiolite: Experiments and statistical physics modelling

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Abstract

Non-selective and simultaneous adsorption of pharmaceutical compounds represents a real approach and a challenging task for researchers. Herein, the single and ternary adsorption of three pharmaceuticals acetaminophen (ACE), diclofenac (DFC) and tetracycline (TTC) on an organo-sepiolite (O-Sep) was studied via statistical physics modeling. A set of physical models was employed to calculate steric and energetic parameters related to the adsorption of ACE, DFC and TTC. An adsorption model based on the formation of a double layer was used to understand the adsorption of tested pharmaceuticals in single solutions, while a multicomponent adsorption model that assumed that these compounds were adsorbed on three different functional groups was applied to analyze the ternary systems. Experimental and theoretical investigations indicated that O-Sep showed the highest adsorption capacities of DFC in single and ternary systems. Adsorption energies were also calculated indicating that endothermic and physical interactions were involved in the removal of these pollutants with the tested adsorbent. Overall, it was obtained that the density of functional groups of DFC and its adsorption energy were higher than those obtained for other pharmaceuticals in single and ternary systems, which agreed with the higher saturation capacities observed for this compound. This paper contributes with new interpretations of the adsorption mechanisms of pharmaceuticals on an organo-sepiolite, which is a promising adsorbent for water treatment.

Keywords: Pharmaceuticals, organo-sepiolite, single and ternary adsorption, statistical physics modeling.

1. Introduction

Pharmaceuticals have been classified as emerging pollutants that are continuously released into the environment. Several studies showed that these compounds can pollute the aquatic systems [1-4] due to their wide utilization and discharges generated in different domains such as hospital wastewater treatment plants and aquaculture facilities [2]. Recently, the consumption of pharmaceuticals by society has grown, including that associated to applications for animal protection, thus leading to an increment of the potential dangers generated by pharmaceuticals in water pollution. The detection of pharmaceuticals in the environment and the analysis of their potential impacts to the human health have become relevant and emerging research subjects in order to find solutions to protect the population health and ecosystems. In particular, tetracycline (TTC), diclofenac (DFC) and acetaminophen (ACE) are pharmaceuticals with potential negative effects on the human health caused by a chronic exposure. For instance, TTC is an antibiotic largely utilized to treat animal infections and diseases caused by bacteria mainly via its application in animal feed [5,6]. Diclofenac is an acidic pharmaceutical that belongs to non-steroidal, anti-inflammatory drugs family. It can be used in human medical care as analgesic, antipyretic, antirheumatic and antiarthritic compound [7,9]. On the other hand, acetaminophen is a common non-steroidal anti-inflammatory drug [10]. These pharmaceuticals are continuously released to the environment, especially to water, due to their worldwide applications and they represent environmental and human health risks. The simultaneous presence of these pharmaceuticals in the environment can potentiate their toxicology profile and can also affect and reduce the efficacy of water treatment technologies applied for their removal [11,12]. In this sense, it is important to analyze and understand not only the single, but also the multicomponent or simultaneous removal of these water pollutants to improve the performance of water purification methods, including the reduction of operating costs. To date, numerous efforts

1 have been performed for the removal of pharmaceuticals from water via physicochemical
2 methods [13-17]. Adsorption is a competitive technology to remove pharmaceuticals from
3 aqueous solutions, where carbon materials [14-20] and clays have been extensively utilized as
4 liquid phase adsorbents [22,23,39]. Clays and derived clay materials are used in adsorption
5 processes due to their unique properties: thermal stability, high availability and low cost [24-
6 26]. Layered clay materials have been used due to their swelling properties and high cation
7 exchange capacities [24-26], although fibrous clay materials have received more attention due
8 to their higher specific surface area, fibrous morphology and functional surface, highlighting
9 the excellent adsorption properties of sepiolite [27-32] and their hybrid derived materials
10 [33,34]. Moreover, modified-sepiolite hybrid materials are characterized by physicochemical
11 adjustable properties leading to an excellent adsorption property [22,35]. In the present paper,
12 an organo-sepiolite (O-Sep) was assessed as adsorbent of pharmaceuticals TTC, DFC and
13 ACE in single and ternary systems at different temperatures to analyze the corresponding
14 adsorption mechanisms. Herein, it is convenient to remark that the theoretical explanation of
15 multicomponent adsorption mechanisms of pharmaceuticals is limited. The reduced
16 multicomponent adsorption data available in literature (mainly for binary systems) has been
17 analyzed via classical adsorption models thus leading to an incomplete comprehension of the
18 steric and energetic parameters that govern the adsorption mechanisms [2,7]. Therefore,
19 single and ternary adsorption models obtained from statistical physics fundamentals were
20 applied to provide insights on the pharmaceutical adsorption mechanisms.

2. Experimental Section

2.1. Materials and chemicals

A commercial organo-sepiolite (O-Sep) supplied by TOLSA (Spain) was used in this work.
O-Sep is a raw sepiolite modified with organic cations, such as Tetranyl® B-2MTH (stearyl

1 dimethyl benzyl ammonium chloride), which was prepared from the commercial tension active
2 cations stearalkonium chloride using 32.4 mmol of organo-cation per 100 g of compound. The
3 complete physicochemical characterization of this material has been reported in a previous
4 study [22]. Briefly, O-Sep is a mesoporous material characterized by a BET surface area ca.
5 to 83 m²/g and a total pore volume of 0.357 cm³/g. The characterization by FTIR
6 demonstrated the presence of alkyl ammonium molecules and different hydroxyl groups at
7 surface [22].
8

9 Acetaminophen (ACE; ≥99%), diclofenac (DCF; analytical standard) and tetracycline (TTC;
10 95%) were purchased from Sigma Aldrich. They were selected as target adsorbates to perform
11 the adsorption studies. Their chemical formulas are provided in Figure 1.
12

13 Acetonitrile (HPLC grade) and acetic acid (purity ≥99%) were obtained from Scharlab and
14 Sigma Aldrich, respectively, and they were used as mobile phase for liquid chromatography.
15 Ultrapure water (Type I, 18.2MΩ·cm) and deionized water (Type II) were also used in this
16 study.
17

18 **2.2 Description of pharmaceutical adsorption experiments**

19 Adsorption experiments were performed using an O-Sep load of 250 mg/L and aqueous
20 solutions of ACE, DCF and TTC with different initial concentrations (i.e., 10, 20, 40, 60, 80
21 and 100 mg/L). Adsorption isotherms were quantified using single and ternary solutions with
22 a mass ratio 1:1:1 of tested pharmaceuticals. The suspensions were stirred at 170 rpm for 24 h
23 at different temperatures in a water bath orbital shaker. The adsorption isotherms were
24 determined at 25, 32 and 40 °C and a pH of 6. Samples of 1 mL were collected at the end of all
25 experiments and filtered with PTFE syringe filters (Whatman 0.45 μm). Concentrations of
26 pharmaceuticals in the liquid phase were determined by high performance liquid
27 chromatography (HPLC) using a Shimadzu Prominence-I LC-2030C chromatograph
28 equipped with a diode array detector (SPDM30A) and a C18 column (Eclipse Plus 5 μm,
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Agilent). The mobile phase was a mixture of acetonitrile-acetic acid (0.1 v/v% in type I water) using an isocratic method (50:50%) with a flow rate of 0.9 mL·min⁻¹. The wavelengths were set at 246, 276 and 272 nm for the detection of ACE, DCF and TTC, respectively.

3. Description of isotherms and statistical physics models for pharmaceutical adsorption

Experimental adsorption isotherms of TTC, DFC and ACE for single and ternary aqueous solutions are reported in Figures 2 and 3, respectively. These isotherms showed an increase of the adsorption capacities of the three pharmaceuticals with temperature in both single and ternary systems. Also, it was observed that these adsorption capacities decreased from single to ternary solutions thus indicating the presence of an antagonistic (i.e., competitive) adsorption for tested pharmaceuticals. This multicomponent adsorption trend can be associated to a relative blockage effect on the same functional group due to the presence of several adsorbates (i.e., pharmaceutical molecules).

However, Figure 4 indicated that this competitive effect was limited for ACE and DFC, being their adsorption capacities reduced less than 20% in the presence of the other two pharmaceuticals. On the other hand, TTC adsorption capacities were significantly reduced at low coverage. These findings suggest that the pharmaceuticals were adsorbed on different types of surface functional groups. One hypothesis would be that ACE and DFC, which are much smaller than TTC (see Figure 1), can access to the inner of the O-Sep mesopore network while TTC would be too large to enter the partially occupied pores. Consequently, ACE and DFC can access to either adsorption sites inside and outside the O-Sep, while TTC can access only to those sites located on the external surface of the adsorbent. This would explain that TTC adsorption was more affected in the adsorption of the ternary solutions. To assess this preliminary assumption and provide fundamental insights in the adsorption mechanisms, a set of statistical physics models was used to analyze, from a theoretical point

of view, the adsorption of TTC, DFC and ACE assuming the presence of a monolayer, double-layer or multilayer processes.

3.1 Single solutions

The first model (M1) defines that the adsorption of TTC, DFC and ACE proceeds through monolayer adsorption due to the interactions between the pharmaceuticals with the adsorbent surface of the O-Sep. The expression of this model defining the variation of the adsorption capacity as function of pharmaceutical equilibrium concentration is described as follows [21]:

$$Q_e = \frac{nD_M}{1 + \left(\frac{C_{1/2}}{C_e} \right)^n} \quad (1)$$

where the density of functional groups D_M (mg/g) can be identified when the functional groups of O-Sep are saturated by pharmaceuticals TTC, DFC and ACE, $C_{1/2}$ (mg/L) is the concentration at half-saturation that is in relationship with the adsorption energy and C_e (mg/L) is the equilibrium concentrations of tested pharmaceuticals, respectively.

The second model (M2) suggests that the pharmaceutical adsorption on O-Sep follows a double layer process due to two interaction energies that are associated to the interactions between the pharmaceuticals and the adsorbent surface (first layer), and between the pharmaceuticals (second layer). This double layer model is described as follows [21]:

$$Q_e = nD_M \frac{\left(\frac{C_e}{C_1} \right)^n + 2 \left(\frac{C_e}{C_2} \right)^{2n}}{1 + \left(\frac{C_e}{C_1} \right)^n + \left(\frac{C_e}{C_2} \right)^{2n}} \quad (2)$$

where C_1 and C_2 (mg/L) are the concentrations at half-saturation that were attributed to the first and second layers, respectively, and D_M (mg/g) represents the corresponding density of functional groups.

In the same context, the third model (M3) assumed that the adsorption is a multi-layer process due to two interaction energies that are related to the bindings between the pharmaceuticals and the adsorbent surface (first layer), and between the pharmaceuticals, but considering that the additional layers (N_2) are a variable number depending on temperature and adsorption system. The expression of this third model [21] is given here:

$$Q_e = nD_M \frac{-2\left(\frac{C_e}{C_1}\right)^{2n} + \frac{\left(\frac{C_e}{C_1}\right)^n \left(1 - \left(\frac{C_e}{C_1}\right)^{2n}\right)}{1 - \left(\frac{C_e}{C_1}\right)^n} + \frac{2\left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(1 - \left(\frac{C_e}{C_2}\right)^{nN_2}\right)}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)} + \frac{N_2 \left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(\frac{C_e}{C_2}\right)^{nN_2}}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)} + \frac{\left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^{2n} \left(1 - \left(\frac{C_e}{C_2}\right)^{nN_2}\right)}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)^2}}{\frac{\left(1 - \left(\frac{C_e}{C_1}\right)^{2n}\right)}{\left(1 - \left(\frac{C_e}{C_1}\right)^n\right)} + \frac{\left(\frac{C_e}{C_1}\right)^n \left(\frac{C_e}{C_2}\right)^n \left(1 - \left(\frac{C_e}{C_2}\right)^{nN_2}\right)}{\left(1 - \left(\frac{C_e}{C_2}\right)^n\right)}}$$

(3)

where N_2 is the number of the formed layers with the second energy, while C_1 and C_2 (mg/L) are the concentrations at half-saturation that were related to the first and N_2 layers. For these three models, the parameter n corresponds to the number of bonded pharmaceutical molecules per adsorbent functional group. Note that at high equilibrium concentration of pharmaceuticals, the adsorption capacity at saturation can be estimated using: $Q_{sa} = n \cdot D_m$ (sa: single adsorption), $Q_{sa} = 2 \cdot n \cdot D_m$ and $Q_{sa} = n \cdot D_m (1 + N_2)$ for the first, second and third models, respectively.

3.2 Ternary solutions

The first ternary adsorption model suggested that three different functional groups were responsible for pharmaceutical adsorption where each functional group can accept n_1 , n_2 and n_3 molecules of TTC, DFC and ACE, respectively. At saturation, three different densities of functional groups can be identified. The ternary adsorption on three types of functional groups implied three adsorption energies that typify the interactions between the TTC, DFC and ACE pharmaceuticals and their corresponding functional groups. Based on these assumptions, the expressions of this model for the equilibrium adsorption on the three different adsorption sites are [37]:

$$Q_{e1} = \frac{n_1 D_{M1}}{1 + \left(\frac{C_1}{C_e} \right)^{n_1}} \quad (4)$$

$$Q_{e2} = \frac{n_2 D_{M2}}{1 + \left(\frac{C_2}{C_e} \right)^{n_2}} \quad (5)$$

$$Q_{e3} = \frac{n_3 D_{M3}}{1 + \left(\frac{C_3}{C_e} \right)^{n_3}} \quad (6)$$

where n_1 , n_2 and n_3 are the numbers of TTC, DFC and ACE molecules bonded per adsorbent functional group, respectively; D_{M1} , D_{M2} and D_{M3} (mg/g) are the densities of these functional groups and C_1 , C_2 and C_3 (mg/L) are the concentrations at half-saturation of the first, second and third type of functional groups. At saturation, the ternary adsorption capacities can be calculated via:

$$Q_{ta1} \text{ (TTC)} = n_1 \cdot D_{M1} \text{ (ta: ternary adsorption)} \quad (7)$$

$$Q_{st2} (DFC) = n_2 \cdot D_M \quad (8)$$

$$Q_{st3} (ACE) = n_3 \cdot D_M \quad (9)$$

Contrary to the last model, the second multicomponent adsorption model considered that the TTC, DFC and ACE pharmaceuticals can interact with the same type of adsorbent functional group (i.e., one functional group can adsorb any of the three pharmaceuticals). It was also assumed that this functional group can accept n_1 , n_2 and n_3 amounts of TTC, DFC and ACE, respectively. Using this hypothesis, one density of functional group D_M was considered and the mathematical expression of this model [37] is described as follows:

$$Q_{e1} = n_1 D_M \frac{\left(\frac{C_{e1}}{C_1}\right)^{n_1}}{1 + \left(\frac{C_{e1}}{C_1}\right)^{n_1} + \left(\frac{C_{e2}}{C_2}\right)^{n_2} + \left(\frac{C_{e3}}{C_3}\right)^{n_3}} \quad (10)$$

$$Q_{e2} = n_2 D_M \frac{\left(\frac{C_{e2}}{C_2}\right)^{n_2}}{1 + \left(\frac{C_{e1}}{C_1}\right)^{n_1} + \left(\frac{C_{e2}}{C_2}\right)^{n_2} + \left(\frac{C_{e3}}{C_3}\right)^{n_3}} \quad (11)$$

$$Q_{e3} = n_3 D_M \frac{\left(\frac{C_{e3}}{C_3}\right)^{n_3}}{1 + \left(\frac{C_{e1}}{C_1}\right)^{n_1} + \left(\frac{C_{e2}}{C_2}\right)^{n_2} + \left(\frac{C_{e3}}{C_3}\right)^{n_3}} \quad (12)$$

where C_1 , C_2 and C_3 (mg/L) are the half-saturation concentrations of TTC, DFC and ACE pharmaceuticals, respectively; D_M (mg/g) is the density of functional group, n_1 , n_2 and n_3 are the numbers of bonded adsorbates per adsorption functional group. The saturation adsorption capacities for TTC, DFC and ACE can be calculated with:

$$Q_{tal} (TTC) = n_1 \cdot D_M \quad (13)$$

$$Q_{ta2} (DFC) = n_2 \cdot D_M \quad (14)$$

$$Q_{ta3} (ACE) = n_3 \cdot D_M \quad (15)$$

3.3 Adsorption data fitting and discussion of model selection

All statistical physics models were applied to correlate the single and ternary adsorption data of tested pharmaceuticals. The fitting results indicated that satisfactory correlations between these models and experimental data were obtained at tested temperatures, but some of the adjusted parameters were not physically acceptable, mainly for Models 1 and 3 in single adsorption systems. For the ternary mixtures, the parameters of model that assumed that the pharmaceutical adsorption via three types of functional groups (Eqs 4-6) were easily interpreted. On the other hand, the competitive model showed a numerical convergence problem since the number of adjustable parameters was equal to the experimental points. Another possibility to fit the ternary adsorption data via the competitive model relied in the assumption that $n_1 = n_2 = n_3 = 1$ (Langmuir case) thus demonstrating that the adjustable parameters were not plausible for interpretation. This result means that the adsorbent functional groups had not accepted one pharmaceutical at each temperature as considered in Langmuir model. In other words, the functional groups can interact with a portion of one pharmaceutical molecule or simultaneously with several adsorbate molecules. In conclusion, the double layer model and the multicomponent equation, assuming that three pharmaceuticals were adsorbed via three different functional groups, were selected to interpret the corresponding adsorption mechanisms. Tables 1 and 2 summarize the parameters of single and ternary models and examples of fitting results of single and ternary data are provided in Figures S1 and S2 of the Supplementary Material.

4. Statistical physics-based analysis of the pharmaceutical adsorption mechanism

4.1 Number of bonded pharmaceutical molecules per adsorption functional group, n

To initiate the understanding of single and ternary adsorption mechanisms of ACE, DFC and TTC on O-Sep, it is important to interpret the three parameters describing the bonded number of pharmaceuticals by their corresponding functional groups in tested adsorption systems. Overall, Table 1 shows that the values of parameter n in single systems have a different order of magnitude at the tested adsorption temperatures. For instance, the values of this parameter were 4.62, 1.13 and 2.05 for the adsorption of TTC, DFC and ACE at 25 °C, respectively. This difference could be probably associated to the chemical structures of these pharmaceuticals. They can be attracted by the main functional groups of the adsorbent surface via the interactions with different atoms, which can differ depending on the chemical structure of pharmaceutical molecules. For ternary systems, the difference in the bonded number values could be also associated to the different interactions of three pharmaceuticals with the main functional groups. Both statistical physics models were used to estimate the orientation sketching of DFC, ACE and TTC on the adsorbent surface at each adsorption temperature. Table 3 provides the possible adsorption orientations of the pharmaceuticals on O-Sep surface based on the calculated values of n .

Table 3 indicates that three scenarios can occur in terms of the adsorption orientations of pharmaceutical molecules bonded on the O-Sep surface. Specifically, the first case describes a total horizontal orientation of the pharmaceutical loaded on O-Sep surface. For this case, the pharmaceutical molecules can be adsorbed via an interaction with at least two functional groups from adsorbent surface. Contrary to this case, the second scenario is associated to a mixed adsorption orientation of pharmaceutical molecules (i.e., horizontal and non-horizontal orientations). Finally, the last case implies that all pharmaceuticals can be adsorbed via an interaction with one adsorbent functional group providing a total non-horizontal orientation. The values of parameter n for single systems were greater than 1 for most of the operating conditions analyzed, thus indicating that, in general, these pharmaceuticals were adsorbed via

a total non-horizontal orientation (i.e., a multi-molecular pharmaceutical adsorption process). Clearly, this result suggested that the pharmaceutical molecules could interact with one functional group during the adsorption process where the main adsorption functional group can be characterized by a high affinity. For the ternary systems, several values of n_1 , n_2 and n_3 were obtained between 0.5-1.0 and greater than the unity indicating that horizontal, non-horizontal, and total non-horizontal orientations occurred during the ternary adsorption mechanism. These results can be explained by a dominance and free existence of the adsorbates on their corresponding functional groups with a lower degree of steric hindrance. The effect of temperature on the parameters n are described in Figure 5. In single systems, it is clear that the adsorption temperature increased the parameter n for the removal of DFC. The increase of temperature caused the improvement of the bonded number of pharmaceutical molecules per adsorption functional group where it changed from 1.13 to 2.06. It can be concluded that the temperature promoted the binding between the DFC molecules leading to the formation of a dimer ($n=2.06$) at 40 °C. Contrary to this case, the temperature caused a decrement of the parameter n for ACE adsorption, see Figure 5. It could be expected that the increment of temperature broken the bindings between the ACE molecules leading to a reduction of aggregation degree. Finally, the parameter n for TTC adsorption had a dual behavior with both increment and decrement caused by adsorption temperature. This behavior could be explained assuming that TTC molecule interchanged its adsorption functional group as function of temperature. For ternary systems, the increment of temperature caused a decrement of ACE adsorption, which was due to the thermal agitation effect. But, nonlinear trends for parameter n were observed in the adsorption of TTC and DFC. These adsorbates also showed a partially interchange of their adsorption functional groups.

4.2 Density of adsorption functional groups, D_m

Figure 6 displays the effect of temperature on the density of functional groups available for adsorption on the adsorbent surface for the single compound and multicomponent adsorption of tested pharmaceuticals. Adsorption temperature showed a contrary effect to the number of bonded pharmaceutical molecules per adsorbent functional group. For all single systems, the density of functional group decreased when the parameter n increased and vice versa. This behavior was consistent because an increment of the bonded number of pharmaceuticals per functional group caused a reduction in the available adsorption space on O-Sep surface. Contrary to this scenario, a decrease of the bonded number of pharmaceutical molecules per adsorbent functional group generated an increment of the anchorage number, then an increase of the functional group density. The same behavior was observed for ternary systems except for TTC adsorption. In particular, it was identified that the functional group density for ternary adsorption of ACE always increased as function of temperature. This total increment with respect to temperature could be related to the activation of additional functional groups that participated in the adsorption of this pharmaceutical.

4.3 Adsorption capacity at saturation, Q_{sa}

Pharmaceutical adsorption capacities for single and ternary systems are reported in Tables 1 and 2. First, it is important to remark that: $Q_{sa} (DFC) > Q_{sa} (TTC)$ and $Q_{sa} (ACE)$ and $Q_{ta} (DFC) > Q_{ta} (TTC)$ and $Q_{ta} (ACE)$ in single and ternary systems, respectively. Considering that it was assumed that three pharmaceuticals were adsorbed on three different types of functional groups in the ternary system, it could be feasible that the adsorbate DFC interacted with the functional group of the investigated adsorbent (receptor site) that was characterized by a high affinity for the pharmaceutical molecule thus leading to a fast attraction and, consequently, the highest adsorption capacity. A second possible explanation implies that the three adsorbates interacted with three different atoms leading to dissimilar adsorption bonds

thus causing different adsorption capacities. In another words, it is possible that each adsorbate can interact through one its atoms with the adsorbent surface. The pharmaceutical adsorption capacities in single and ternary systems were determined with the next expressions: $Q_{sa} = 2 \cdot n \cdot D_m$ for single adsorption and $Q_{tai} = n_i \cdot D_{Mi}$ ($i=1,2$ and 3) for ternary adsorption. Modeling results indicated that: D_M (DFC) $>$ D_M (ACE and TTC) and D_{M2} (DFC) $>$ $D_{M1,3}$ (TTC and ACE) in single and ternary adsorption systems, respectively. It is clear that the density of functional groups (D_M and D_{Mi}) showed the same behavior in single and ternary systems as the adsorption capacity. The highest adsorption capacity of DFC in single and ternary systems was due to its highest density of functional group. Adsorbent O-Sep was more effective to remove DFC molecules from aqueous solution. On the other hand, the effect of temperature on the adsorption capacities in single and ternary systems is given in Figure 7. An endothermic adsorption was identified for all systems where the adsorption capacities increased with the temperature. This thermal effect can be explained by the increment of mobility of pharmaceutical molecules from free solution phase to the adsorbent phase [36].

4.4 Adsorption energy

The adsorption energies for single and ternary systems were calculated to characterize the thermodynamic nature of the main interactions between pharmaceutical molecules and adsorbent surface. The double layer model provided two adsorption energies that corresponded to the interactions of both formed layers (adsorbate-adsorbent and adsorbate-adsorbate), while the ternary model allowed to calculate the adsorption interactions between the pharmaceuticals and the adsorbent surface. These adsorption energies are defined by the next expressions [37-39]:

$$E_1 = R \cdot T \cdot \ln(C_s/C_1) \quad (16)$$

$$E_2 = R \cdot T \cdot \ln(C_s/C_1) \quad (17)$$

$$E_i = R \cdot T \cdot \ln(C_s/C_i) \quad (i=1,2 \text{ and } 3) \quad (18)$$

where C_s is the solubility of tested pharmaceuticals in water (mg/L) and R is the ideal gas constant. Statistical physics calculations estimated low adsorption energies for all systems (Table 1 and 2). This theoretical finding indicated that physisorption was involved in the removal of tested pharmaceuticals with O-Sep. Note that all adsorption energies corresponded to an endothermic process and these calculations were consistent with the experimental data. For single systems, it was noted that $E_1 > E_2$ at all operating temperatures. Note that the first adsorption energy was related to the interactions of pharmaceuticals and adsorbent surface, while the second adsorption energy described the interactions between the adsorbate molecules. Calculated adsorption energies of DFC followed the trend observed for the adsorption capacity at saturation in single and ternary systems where $E(\text{DFC}) > E(\text{TTC}, \text{ACE})$ and $E_2(\text{DFC}) > E_{1,3}(\text{TTC}, \text{ACE})$. These calculations indicated that the adsorption energy played an important role to explain the variation of the adsorption capacity especially for DFC. In conclusion, the density of functional groups and the adsorption energy were key parameters to explain the trends observed for the adsorption capacity of DFC and other pharmaceuticals.

5. Performance of organo-sepiolite

When comparing with the literature (see Table 4), it is clear that the O-Sep adsorbent had an excellent performance in the adsorption of the three pharmaceuticals, making it potentially a relevant choice for wastewater treatment. For instance, the single maximum adsorption capacity of ACE on O-Sep is 67.7 mg/g, being higher than those reported for other adsorbents as indicated in the Table 4 [40,41]. In the same context, the maximum adsorption capacity of DFC on O-Sep is found to be 242.9 mg/g. This amount of adsorbed DFC is largely beyond the amounts found in the literature for various adsorbents (between 22 and 64 mg/g, see Table 4) [40-45]. Finally, the TTC adsorption capacity on adsorbent O-Sep is 85.5 mg/g, more than

two times higher than MnFe₂O₄/reduced graphene oxide nanocomposite (41 mg/g) [42-47] or biochar derived from rice straw iron hydroxides (11-14 mg/g) [48,49]. In conclusion, the O-Sep adsorbent can be considered as an excellent option to remove the pharmaceutical compounds from the water.

Conclusions

Mono- and multi-component statistical physics models were applied to characterize and understand the adsorption mechanism of pharmaceuticals on an organo-sepiolite. Modeling results suggested that the adsorption of pharmaceutical DFC was the highest due to its interactions with adsorbent surface and density of functional groups. Horizontal and non-horizontal orientations were estimated for pharmaceutical adsorption at most of tested operating temperatures. This adsorbent showed the best performance for the pharmaceutical removal at high temperatures. It was concluded that the single and ternary adsorption of these pharmaceuticals on the organo-sepiolite was an endothermic physisorption. These modeling results as well as the specific distribution of adsorption sites inside and on the external surface area explained the high ability of organo-sepiolite to capture simultaneously organic molecules with very different sizes, making this adsorbent very promising for the treatment of wastewater containing pharmaceutical residues. Moreover, these findings contribute to the understanding of adsorption processes of emerging water pollutants using novel materials.

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	T (°C)	n	D _M (mg/g)	Q _{st} (mg/g)	E ₁ (kJ/mol)	E ₂ (kJ/mol)
TTC	25	4.62	3.4	31.2	5.1	3.1
	32	0.61	52.1	63.2	3.2	1.0
	40	1.06	40.3	85.5	4.0	1.3
DFC	25	1.13	70.1	158.4	11.5	9.3
	32	1.75	59.7	209.1	11.3	9.5
	40	2.06	59.0	242.9	11.4	9.4
ACE	25	2.05	13.2	54.2	6.5	6.1
	32	1.44	20.5	59.1	5.6	4.8
	40	1.16	29.2	67.7	5.8	5.6

Table 1: Parameters of the double layer model for the single adsorption of pharmaceuticals on O-Sep.

	T (°C)	n_i	D_{Mi} (mg/g)	Q_{st} (mg/g)	E_i (kJ/mol)
TTC	25	2.59	10.1	28.0	3.3
	32	0.62	88.2	54.7	3.1
	40	0.80	100.2	80.1	2.4
DFC	25	3.11	32.5	101.1	10.7
	32	0.46	301.5	138.7	10.3
	40	0.55	248.0	136.1	11.1
ACE	25	3.08	11.9	36.5	8.6
	32	0.92	47.1	43.3	7.9
	40	0.86	57.8	49.9	7.7

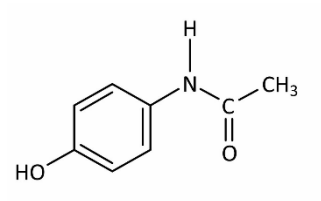
Table 2: Parameters of the multicomponent model for the ternary adsorption of pharmaceuticals on an organo-sepiolite.

Possible cases	Type of orientation
Case 1: n, n_1, n_2 and $n_3 < 0.5$	Total horizontal
Case 2: $0.5 < n, n_1, n_2$ and $n_3 < 1$	Horizontal and non-horizontal with two different percentages
Case 3: n, n_1, n_2 and $n_3 > 1$	Total non-horizontal

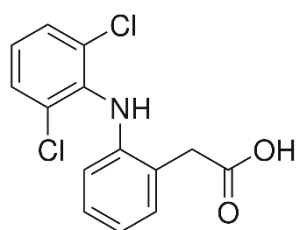
Table 3: Interpretation of the possible scenarios for the adsorption orientation of the pharmaceuticals on adsorbent surface based on the statistical physics parameter n .

Adsorbents	Q _{max} (mg/g)	References
ACE		
O-Sep	67.7	This work
Oak fruits	45.4	40
Pyrolyzed pulp mill sludge	19.7	41
DFC		
O-Sep	242.9	This work
Acid-washed CAC	64	[42]
GAC	62.2	[43]
Pine bark	54.7	[44]
GAC	36.3	[45]
Orange peel	22.3	[46]
Cyclamen persicum tuber	22.2	[47]
TTC		
	85.5	This work
Biochar samples derived from rice straw iron hydroxides	11.8–14.16	[48]
MnFe ₂ O ₄ / reduced graphene oxide nano-composite	41	[49]

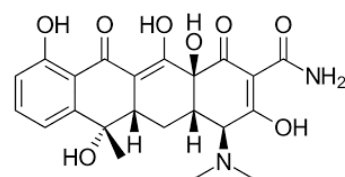
Table 4: Comparison of the pharmaceuticals adsorption capacities of O-Sep adsorbent with several adsorbents reported in the literature.



(a)



(b)



(c)

Figure 1.Chemical formulas of: (a) acetaminophen, (b) diclofenac and (c) tetracycline.

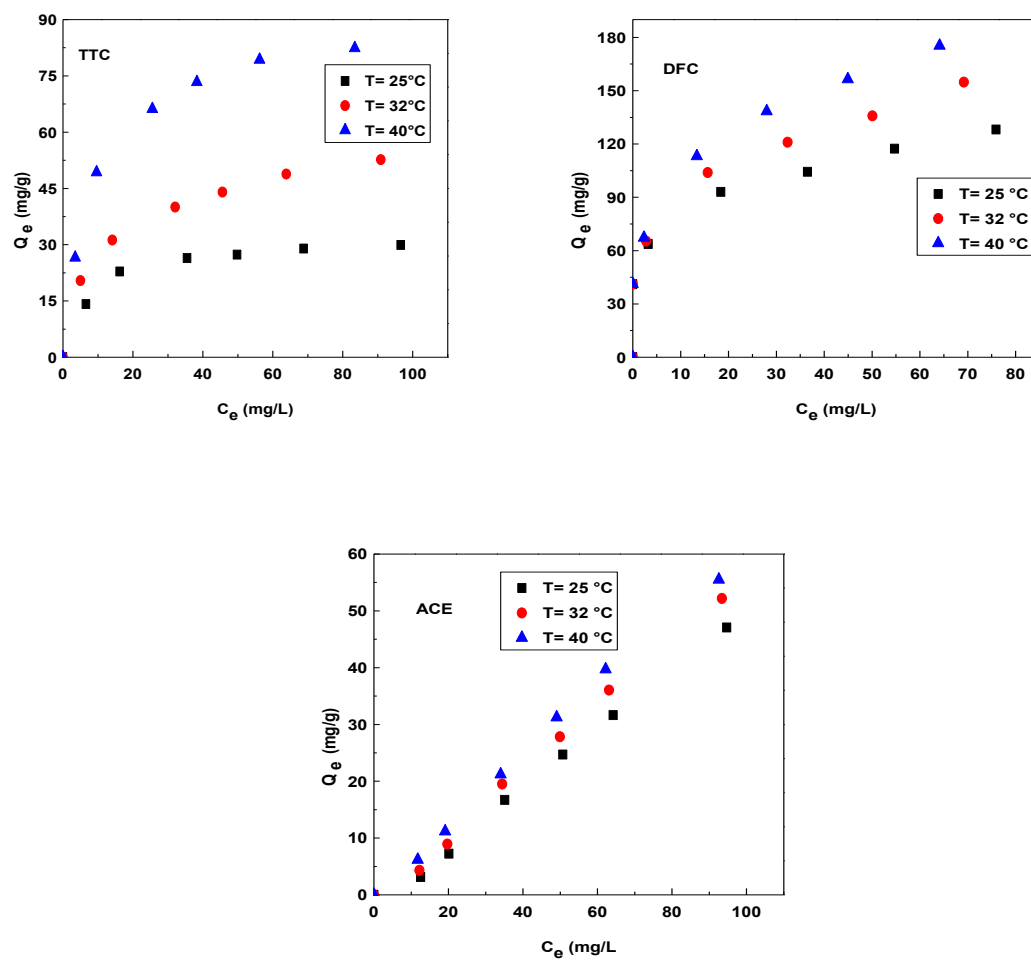


Figure 2. Experimental isotherms of the single adsorption of TTC, DFC and ACE on O-Sep at 25, 32 and 40°C and pH 6.

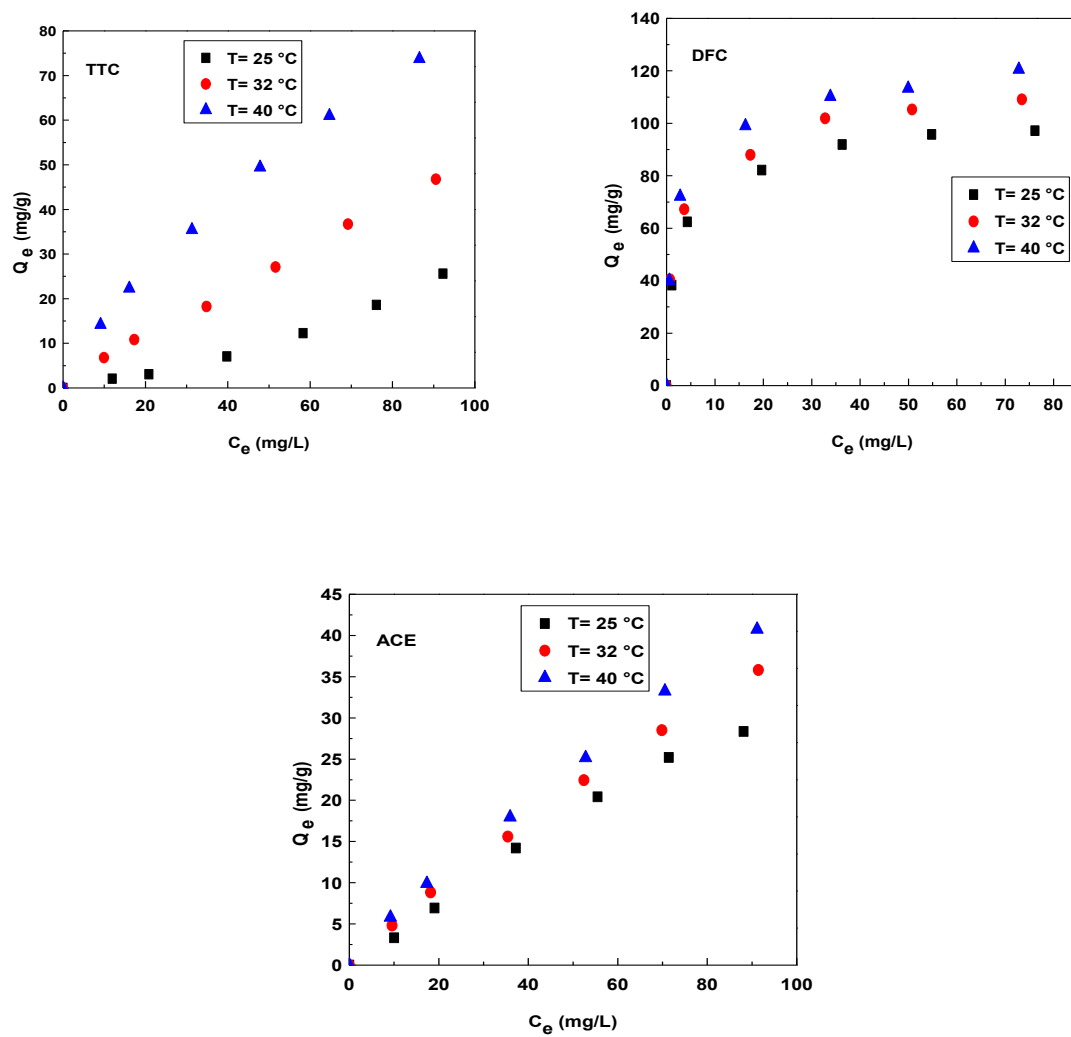


Figure 3. Experimental isotherms of the multicomponent adsorption of TTC, DFC and ACE on O-Sep using ternary solutions at 25, 32 and 40°C and pH 6.

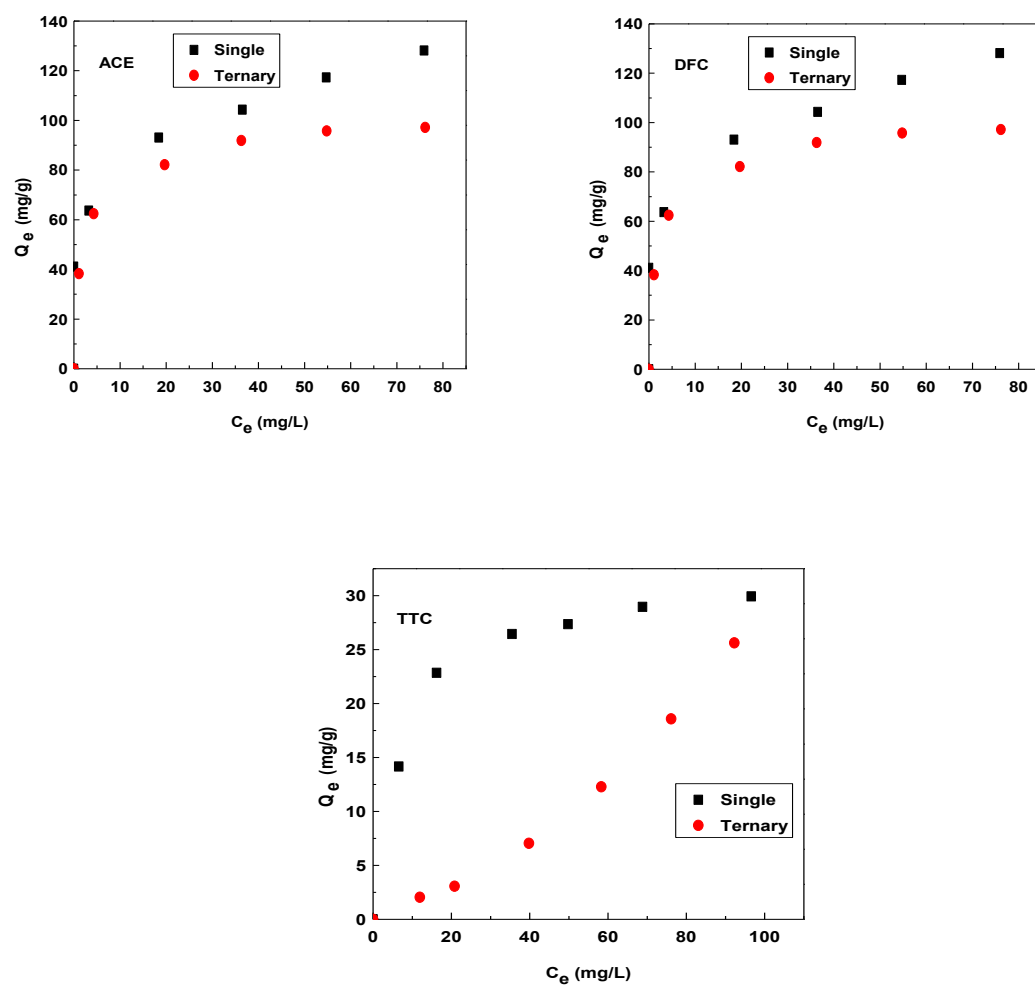


Figure 4. Pharmaceutical adsorption isotherms in single and ternary systems. Comparison with single-component adsorption data at 25°C.

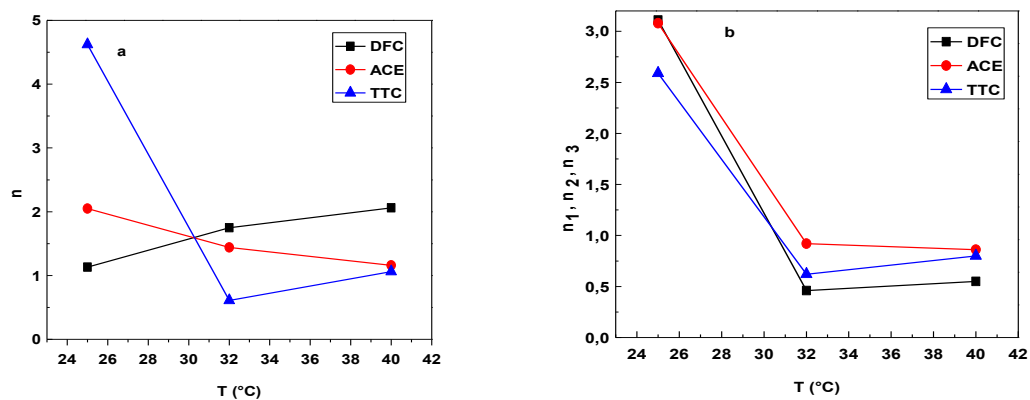


Figure 5. Impact of temperature on the parameter n for the pharmaceuticals adsorption on O-Sep in a) single and b) ternary systems.

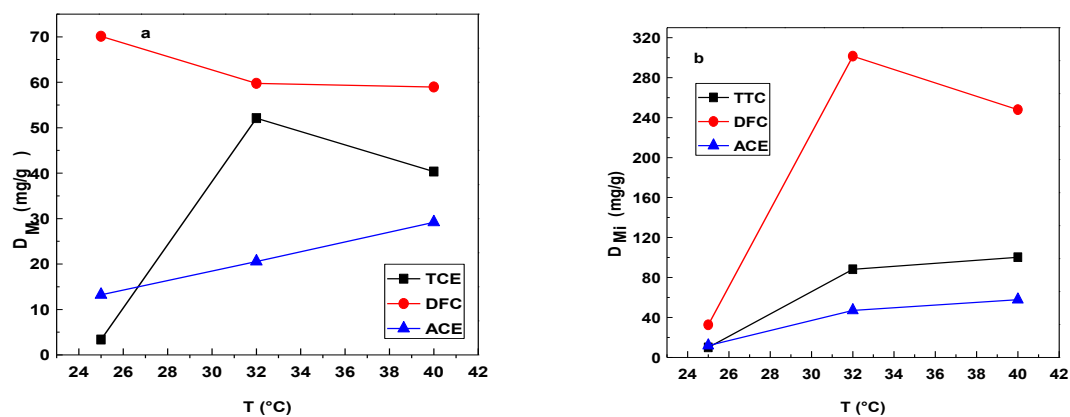


Figure 6: Impact of the temperature on the density of functional groups D_M for the pharmaceutical adsorption on O-Sepin a) single and b) ternary systems.

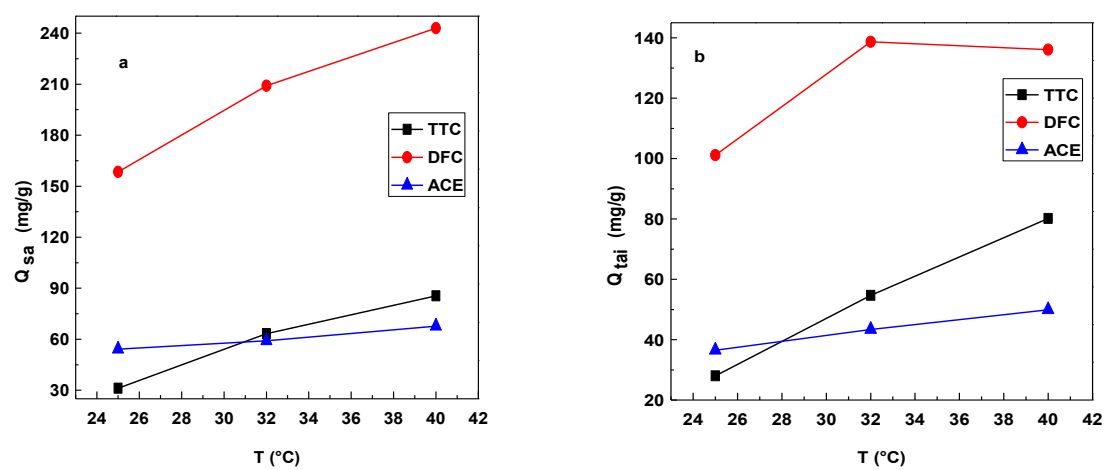


Figure 7. Impact of temperature on the adsorption capacity at saturation for the removal of pharmaceuticals using O-Sep in a) single and b) ternary systems.



Declaration on interest statement

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