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# Application of statistical physics formalism to the modeling of adsorption isotherms of ibuprofen on activated carbon

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ABSTRACT

The adsorption isotherms network at three temperatures of ibuprofen on a raw activated carbon and two chemically modified samples of the same carbon were simulated using models established through statistical physics formalism. Among the different tested models, a multilayer model with saturation was found to be the best to reproduce the experimental data. In this model, five parameters affecting the adsorption process were adjusted, namely the number of molecules per site, the density of receptor sites, the two energetic parameters and the number of layers. These parameters deduced from the fitting of the experimental adsorption isotherms by numerical simulation were discussed and interpreted for their temperature dependence.



## 1. Introduction

In the past few decades, the scientific community has become increasingly concerned about the potential public health impact of the new environmental contaminants such as pharmaceutical molecules, solvents, pesticides, etc. originating from human activities. Among them, pharmaceuticals are emerging environmental contaminants which are frequently found in water, at concentrations below μg/L, even after treatment at the exhaust of wastewater treatment plants [1]. One of the possibilities for removing these molecules which are highly toxic when accumulated in environment is the adsorption on activated carbons. Due to its widespread applications as an anti-inflammatory and antipyretic drug, ibuprofen is frequently detected in the wastewater treatment plants among several other pharmaceutical molecules [2]. Recently, several works have studied the removal of ibuprofen by using activated carbons [3,4].

Several authors have proposed conventional models (Langmuir, Freundlich, or Langmuir–Freundlich, etc.) for the phenomenological description of adsorption isotherms of ibuprofen on activated carbon. However, most of these models do not provide any indications about the adsorption mechanism, and the isotherm equations of Freundlich or Langmuir–Freundlich have no physical significance or relationship with the physico-chemical parameters involved in the adsorption process.

To better understand and analyze the adsorption process of ibuprofen, a saturation multilayer model has been developed in this work and applied to the case of ibuprofen adsorption on some chemically modified surfaces-bearing activated carbons. The theoretical expression of the adsorption isotherms was established by statistical physics. The present paper aims to propose a physical interpretation at a microscopic level of the ibuprofen adsorption onto three activated carbons (at temperature ranging from 298 to 323 K) previously and experimentally studied at equilibrium in reference [5].

## 2. Materials and methods

### 2.1. Materials

The three studied activated carbons were a raw granular activated carbon (Sigma–Aldrich, ref. 292591, 4–14 mesh) referred to AC, an AC sample oxidized by ultrasonic irradiation in 35% $H_2O_2$ named AC($H_2O_2$)US and an AC sample heat-treated at 973 K under a nitrogen flow (for 1 h) named AC(700$N_2$). The preparation of the

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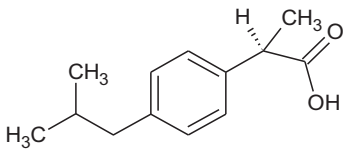


**Fig. 1.** Molecular structure of ibuprofen.

AC($H_2O_2$)US and AC(700$N_2$) and the characterization of the surface chemistries and porosities of the three activated carbons were described in details in Ref. [5].

### 2.2. Adsorption isotherms experiments

The ibuprofen (99%, Sigma) solutions were prepared from UHQ water (Ultra High Quality, 18.2 MΩ purity) containing 10 vol% of methanol (99.9%, Sigma–Aldrich) in order to increase the solubility. The chemical structure of ibuprofen is depicted in Fig. 1. The ibuprofen adsorption isotherms on the various activated carbons were determined at three constant temperatures: 298, 313 and 323 K at pH 3 following the experimental conditions described in [5]. Activated carbons (10 mg) were introduced in ibuprofen solutions (30 mL) of varying concentrations (5–100 mg $L^{-1}$) and stirred for 5 days. The ibuprofen concentrations were determined by UV–vis spectrometry (Varian, Cary50) at the maximum absorbance observed at 220 nm.

## 3. Theoretical formalism of the adsorption at equilibrium

In a first approximation, the interaction between the adsorbed molecules was neglected as assumed by some authors [6,7], because the studied concentrations are lower than the saturated ibuprofen concentration (solubility) which is higher than the ibuprofen adsorption saturation. The model suppose that a variable number of molecules is adsorbed (exchange of molecules between the free and adsorbed phase) onto $N_M$ receptor sites per unit surface of the adsorbent according to the adsorption reaction [6] of ($A$) dissolved liquid molecules onto ($S$) receptor sites including a $n$ stoichiometric coefficient.

$$nA + S \rightleftarrows A_nS \tag{1}$$

The $n$ parameter, as a stoichiometric coefficient, represents the number of adsorbate molecules per site. The $n$ parameter is for the whole system, an average number (integer number in case of one site), which can be greater or smaller than the unity. An $n$ value greater than 1, represents the number of anchored molecules per site, according to a multimolecular adsorption mechanism [6,7]. An $n$ value smaller than 1, represents the fraction of molecule per site if a multianchorage adsorption mechanism may be assumed [8,9]. According to this hypothesis, $1/n$ would represent the anchorage number of one molecule on several different receptor sites [6,8].

The grand canonical partition function of one receptor site when the system is placed at $T$ and $\mu$ values according to the microscopic states of the system [8,9] is given by Eq. (2):

$$z_{gc} = \sum_{N_i=0,1\ldots} \exp -\beta(-\varepsilon_i - \mu)N_i \tag{2}$$

where $\varepsilon_i$ is the receptor site adsorption energy, $\mu$ is the chemical potential of the adsorbed molecule, $N_i$ is the receptor site occupation state, and $\beta$ is defined as $1/k_BT$ (where $k_B$ is the Boltzmann constant and $T$ the absolute temperature). The total grand canonical partition function related to $N_M$ receptor sites per surface unit, which we assume identical and independent, is written:

$$Z_{gc} = (z_{gc})^{N_M} \tag{3}$$

The average site occupation number $N_o$ can be written as previously reported [9,10]:

$$N_o = k_BT\frac{\partial \ln Z_{gc}}{\partial \mu} \tag{4}$$

When the thermodynamic equilibrium is reached, the equality between the chemical potentials can be written as $\mu_m = \mu/n$: where $\mu$ is the chemical potential of the adsorbed molecule, $n$ the number or fraction of molecules per site, and $\mu_m$ is the chemical potential of dissolved molecule as written in Ref. [11]:

$$\mu_m = k_BTln\left(\frac{N}{z_{tr}}\right) \tag{5}$$

where $z_{tr}$ is the translation partition function, according to Ref. [8]:

$$z_{tr} = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} \tag{6}$$

where $m$ is the adsorbed molecule mass, $h$ the Planck's constant and $V$ the volume of studied system. The total number of the adsorbed molecules is then:

$$Q = nN_o \tag{7}$$

The adsorbed quantity ($Q$) is given per unit surface, because the density of receptor sites ($N_M$) is written per unit surface. This formalism can be applied to any adsorption isotherms of liquids or gases.

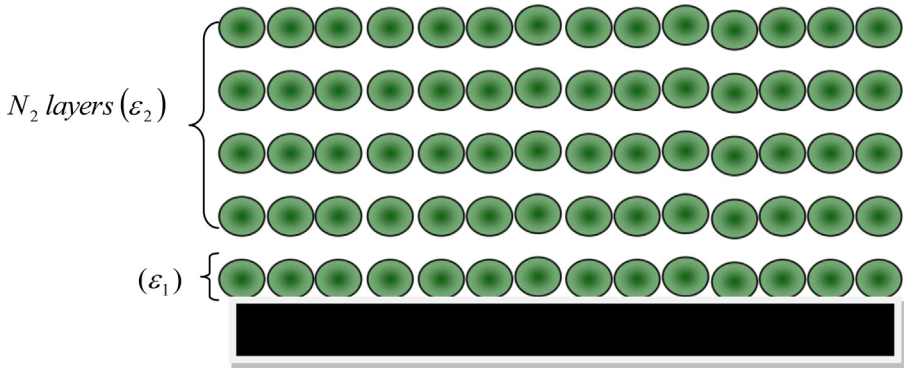


**Fig. 2.** Distribution of the molecules adsorbed on a solid material according to a multilayer model with saturation.