RESEARCH ARTICLE

STUDY OF THE ADSORPTION INTERACTION POTENTIAL IN A MICROPOROUS SOLID.

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Abstract

In this paper, we proposed an approach to understand the mechanism of gas adsorption in a microporous solid. This approach is deduced from the concept of flow; the flow of the quantity of material which crosses a closed surface is proportional to the potential adsorbate-adsorbent interaction. For this first study, we used two couples; activated carbon AC35 with ethanol and acetone at the same temperature 30 ° C, in order to over complicate the issue for this first approach. Our study of the adsorption potential as a function of the pore radius allowed us to show that there are two types of interaction forces. The first type active, as in the case of adsorption in micropores and mesopores, and the second is active, as for the macropores and side surfaces of the grains. These findings justify the existence of two models: the Dubinin-Astakov (filling volume), and the Brunauer, Emmet and Teller (adsorption layer). Adsorption follows three steps, the micropore filling will occur the first followed by the filling of mesopores and the macropores and finally the surface adsorption corresponds to the side surface of the microporous solid grains. The order in which the filling pore has allowed us to establish the link between the time parameter and the pore radius

Introduction:-

The importance of microporous solids in industry stems from their use as catalysts, as ion exchange and their gas separation power. These applications exploit the chemical, physical and structural properties (cage structures and canal structure).

Surface area and porosity are two important physical properties that impact the quality and utility of solid phase chemicals including agrochemicals, additives and pharmaceutical active ingredients. Differences in the surface area and porosity of particles within the material, which otherwise may have the same physical dimensions; can greatly influence its performance characteristics. Surface area and porosity play major roles in the purification, processing, blending of chemical products as well as product function, efficacy and stability (Bandosz et al., 2009).

The microporous structure of these adsorbent materials is a key element for the implementation of all these industrial applications. The quantitative description of the pore structure in terms of size distribution micropores (Pore Size Distribution) plays an important role in the prediction of adsorption by activated carbon. Typically, the size distribution of the micropores of a microporous solid is evaluated from the analysis of the adsorption isotherms.

Activated carbons contain highly developed networks of micropores, which are the source of their power very important adsorbing power (Bandosz et al., 2009).

The pores of solids are of different kinds. The individual pores may vary in size and shape. With respect shape, in activated carbons, the predominant type is the slit-shape pore. But the width of the pores is also of special interest for many purposes. A classification of pores according to their average width, which was adopted by the IUPAC (Carlos et al., 2012).

In recent years, the microspore range has been subdivided into very narrow pores (until 0.8 nm) or ultramicropores, where the enhancement of interaction potential is caused by the similarity in size between the pore and molecules, and supermicropores having a width (0.8 to 2.0 nm) between ultramicropores and mésopores (Carlos et al.,2012). Carbon-based materials usually have a bimodal pore size distribution, with one dominant peak being less than approximately 2 nm and the other major peak usually greater than 50 nm (Do et al., 2008). Increasing the potential interaction is due to the similarity between the pore size and those molecules in the case of ultramicropores (Do et al., 2008).

The volume of macropores is usually on the order of 0.2-0.5 cm^3 g^{-1}, but the associated area is very small, on the order of 0.5 m^2 g^{-1}, which is negligible in an activated carbon (Do et al., 1998). It is necessary to distinguish that during adsorption by a microporous solid, there are two types of adsorption; adsorption in volume and surface adsorption. So, there are two different models. The first model used mainly in the case of filling the micropores called the model Dubinin -Astakov. The origin of this theory is based on the correlation between the amount adsorbed and the thermodynamic potential while the other, focusing on the multilayer adsorption, is named the BET model (Hugi et al., 2000).

Macropores are not important for the adsorption capacity, but their importance lies in the fact that they act as transport pores to the meso- and micropores. Mesopores have a volume in the range of 0.1 to 0.4 cm^3 g^{-1}, and the surface area is in the range of 10-100 m^2 g^{-1}. Their contribution to adsorption is significant, and they act as a transport to micropores. Micropores have a similar volume, but the surface area is the most important, sometimes close to 1000 m^2g^{-1} (Carlos et al., 2012).

The adsorption kinetics study is gaining more and more interest as it is invading many domains such as: sorption chemistry, bio-sorption, agro-chemistry, pharmaco-chemistry, the environment applications, security and the molecule separation. Certain studies assume that the adsorption is a diffusion phenomenon which happens in an isotropic and homogenous media and therefore they use Fick's law (Mhiri et al., 2011; Mhiri et al., 2010). Others underscore the effect of interaction forces such as forces of Van Der Walls such as the London dispersion force, the electrostatic interaction forces between the field cations and dipoles and intermolecular forces interaction adsorbate-adsorbate, on the adsorption speed (Mhiri et al., 2010; Mhiri et al., 2009). Mhiri et al (2010, 2009) have shown that the interaction molar energy increases with the adsorbate mass contained in this media, which induces heterogeneity of the interaction energy in this media (Mhiri et al., 2014).

Generally, the adsorption speed is controlled by the adsorbed mass and the resistance to the heat transfer instead of the adsorption intrinsic kinetics, for example, the mass and heat transfer of the adsorbate to and from the exterior surface of the adsorbent (known as interparticle transport); Maxwellian diffusion (bulk molecular diffusion) in moderately large pores (macropores) or Knudsen diffusion in pores (micropores) (Mhiri et al., 2011).

The gas transportation in microporous solids is controlled by an active diffusion and a molecular sieve mechanism. It is essentially influenced by the adsorption features, the geometry of the adsorbed molecule and the microspore structure (Xiaojun et al., 2004; Joaquin et al., 2003).

The adsorption of a gas in a microporous solid is the result of the existence of interaction forces and therefore of potential energy of interaction. These adsorbate-adsorbent interaction forces are most often too complex to be described.

The role and importance of the confinement effects in microporous solids have been quantified by us (Eric et al., 2007). As a result of the confinement effects, heats of adsorption can be amplified by a factor of up to about 5 and the effective van der Waals diameter of the adsorbed molecules reduced substantially to about 85% of its value in

the gas phase, when they are adsorbed in micropores whose dimensions closely match their sizes and shapes (Eric et al., 2007) relative to a reference material for which the confinement effects are negligible. It was shown recently by Trens et al. that the confinement effects may also occur in mesoporous solids although some results cannot be explained by geometric effects only (Trens et al., 2004) and that the modification of intermolecular interactions resulting from confinement should also be taken into account when considering the adsorption and behavior of molecules for materials with pores larger than those of microporous solids.

Derijcke et al. (1991) and Cook et al. (1999) proposed two different explanations for such observations. The contribution by Derijcke, et al. (1991) is a comprehensive theoretical description of the physical interaction between a substrate and its microporous environment, demonstrating that the situation of the lowest potential energy for a molecule adsorbed in a spherical cavity corresponds to its trapping in a cage whose diameter is only about 85–90% of the molecule van der Waals diameter in the gas phase, and that this interaction energy remains negative for pore diameters equal to only 75% of the same (Derijcke et al., 1991)

The conclusions of Derijcke et al. (2007, 1991) are based on the analysis of the interaction potential dependence on the confinement parameter s, with s = d/L, where in their model d is the average equilibrium distance of the molecule to the pore wall and L the average pore diameter. Values of the s parameter smaller than the unity corresponding to the most stable situation (maximum interaction), This shows that whatever the value of the radius of the molecules (classical cross section of van der Waals in the ' free gas phase'), they can penetrate the pores with smaller sizes because their effective cross section van der Waals is reduced in a microporous environment following the confinement effect.

However, Trens et al. (2004) have shown that the adsorbate-adsorbent interactions are enhanced in the micropores of the activated carbon and adsorbate-adsorbate intermolecular interactions are not negligible and that they play an important role in the micropores.

Materials and Methods:-
Experimental conditions:-
The measurements of the adsorbed mass are realised in a fluidised bed in isotherm conditions. The used adsorbate is the active carbon PICANC60, the grain radius is between 0.3 and 0.6 mm; the bed mass is 0.3 kg; the bed height is 0.12 m and the reactor diameter is 100 mm. All the trials are realized with a solvent concentration at the input of 30 gm^{-3} (Fig.1).

By considering the variation of the partial molar flow of the adsorbate between the column input and output equivalent to the adsorbed adsorbate quantity per unit of time, we can write the following relation:
Input – output = accumulation
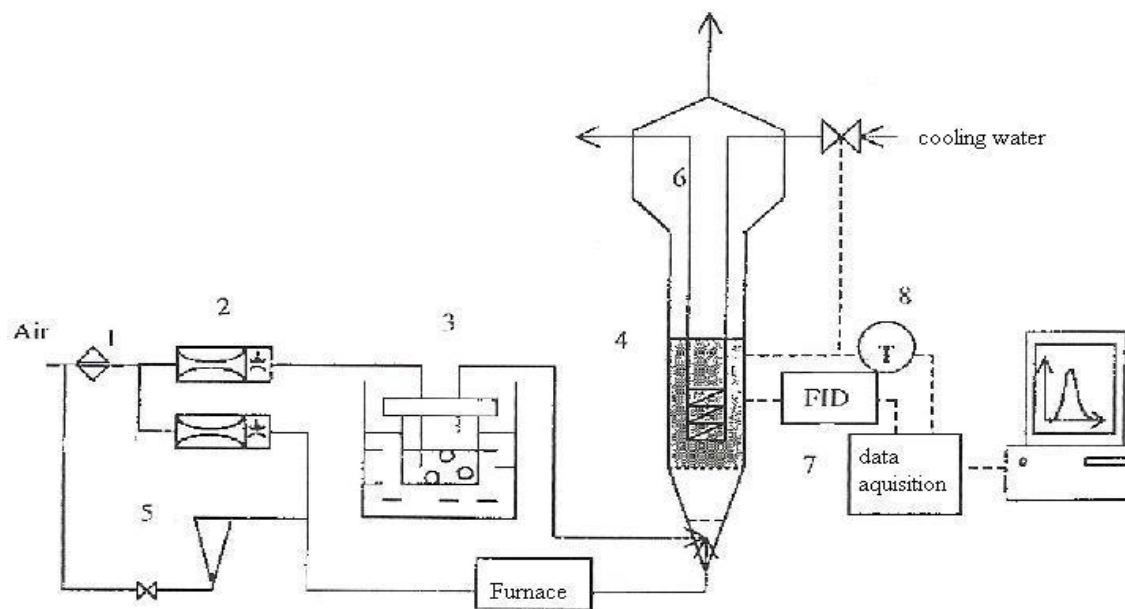
$$G_0 \ (X_0 - X) = M_{bed} \ \frac{dn}{dt}$$

$$\text{With} \ \ X = \frac{x}{1-x} \ \ \text{and} \ \ x = \frac{C_0}{M} \frac{RT}{p}$$

We deduce n

$$n = \frac{X_0 \ G_0}{M_{lit}} \int_{t=0}^{t=t_f} (1 - \frac{X}{X_0}) \, dt$$

By integrating the previous equation, we obtain the value of n.
Where X represents the molar fraction and M_{lit} is the mass of activated carbon bed.

Figure1: Representative diagram of the installation utilized for the experimental tracing of isotherms.1: filter. 2: Mass volumetric governor. 3: Wash-bottle. 4: fluidized bed reactor. 5: Conical float rotameter; 6: Exchanger with cool water. 7: Detector with ionization of flame; 8: Thermocouple K.

Experimental adsorption isotherm:-
We performed the kinetic adsorption measurements of two adsorbates (ethanol and acetone) on a microporous solid (Activated carbon AC35) and we plotted the isotherm of the variation of the adsorbed amount versus time.
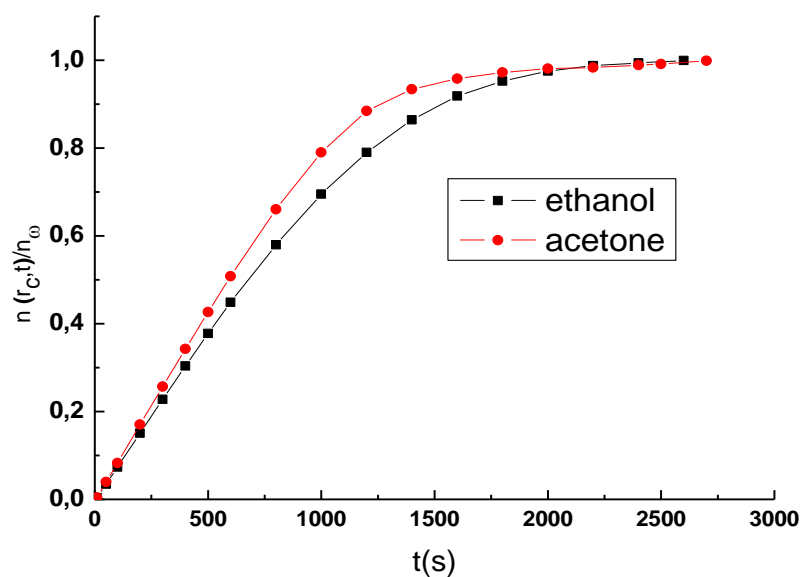
Figure 2: adsorption isotherm of ethanol and acetone on activated carbon at 30 °C.

Theoretical study:-
Flow of matter:-
Scientific logic used in this work is deduced from the Concept of flow. This concept studies the flow of a physical quantity through a closed surface.

In the case where there is a field relating to remote interaction forces, this concept leads to the study of the field from the flow. According to classical physics, any field relating to remote interactions pores derives from a potential. This allows us to affirm that the flow is proportional to the interaction potential.

A solid microporous grain of a radius r_c was used. This grain is placed inside an enclosure externally communicating by means of a pipe. The concentration is maintained in the enclosure constant (C_0) by a continuous injection of the adsorbate. Considering a spherical surface of radius r_c^+, slightly higher than r_c and at the same center as the grain.
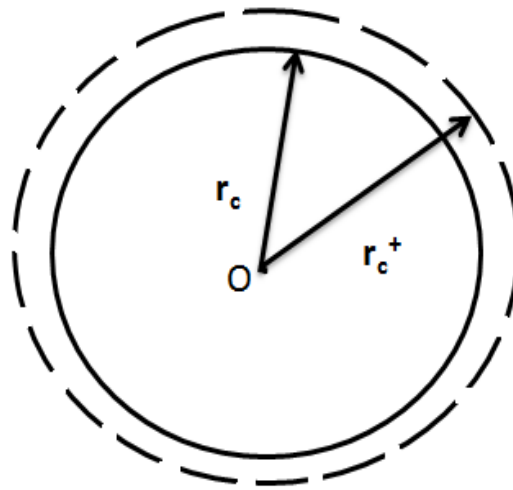
Figure 3: choice of the closed surface for the application of the Gauss theorem.

The appearance of the adsorption phenomenon implies the existence of an adsorption potential which is due to interactions between adsorbate and adsorbent (Terzyk et al., 1999).
The flow of matter through a spherical surface of radius r_c^+ per unit time is proportional to the gradiant adsorbate-adsorbent interaction potential. Whether ϕ_m the average flow of matter per unit of time and U the adsorption potential due to the adsorbate-adsorbent interaction forces, we can write:

$$\phi_m = \beta.\frac{dU}{dL} \qquad \text{(Annexes I)}$$

Where β is the proportionality constant.

The experimental study of the average flow of matter per unit time through a spherical surface of radius r_c^+ is equal to the amount of material adsorbed by the grain of radius r_c during the same time interval since r_c^+ is slightly greater than r_c.

Experimentally, we have studied the adsorbed amount versus time (g/kg), then, we have determined the ratio n (r_c, t) /n_∞ where n_∞ is the maximum adsorbed amount by the adsorbent at 30°C per kilogram for given pair. The adsorbed mass ratio at time t (m (t)) by the adsorbed mass at infinity time and at 30°C (m_∞) is equal to the ratio of the adsorbed moles at time t within the grain of radius r_c onto the number of adsorbed moles by the same grain at saturation and at a temperature of 30°C [Mhiri et al.; 2011; Mhiri et al., 2014].

$$\frac{m(t)}{m_\infty} = \frac{n(r_c, t)}{n_\infty}$$

This ratio has the advantage of being independent of the mass and volume of the adsorbent. It is very practical for the development of a theory.

The average flow of matter per unit time through the spherical surface of radius r_c^+ is given by:

$$\phi_m = \frac{\Delta n}{\Delta t}$$

With $\Delta n = \dfrac{n_{i+1}(r_c, t_{i+1}) - n_i(r_c, t_i)}{5}$

And

$$\Delta t = \frac{t_{i+1} + t_i}{2} = 5\,s$$

It is known that the adsorption of a gas in a microporous solid follows the following process:
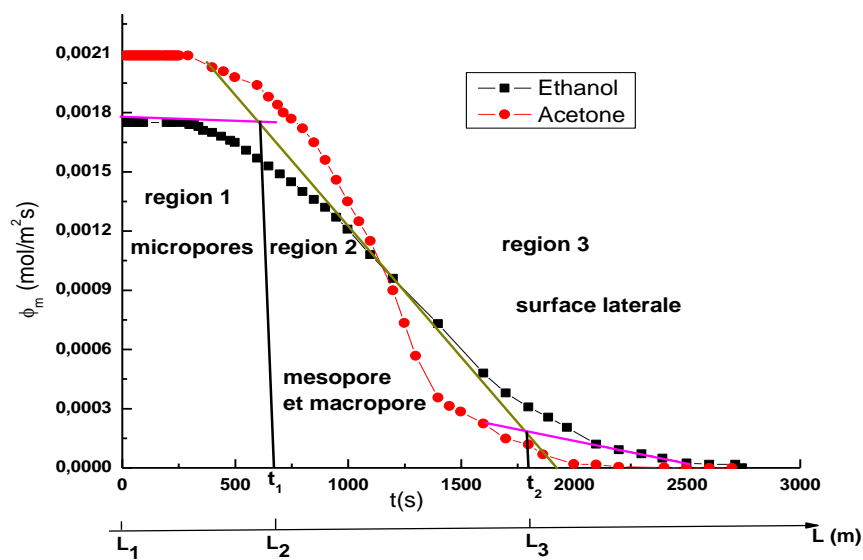- Micropores filling
- Mesopores and macropores Filling
- Side surface Filling

The kinetic study of the adsorption of a gas by a microporous solid has provided information on the volume available to the gas consequently on the porous structure of the solid.

The structure of the porous medium, and in particular, the pore structure plays an important role in the adsorption of the particles according to the size and the pore geometry.

Results and Discussion:-

The variation of the material flow per unit time (Figure 4) shows that there are three regions: In the case of ethanol, the maximum amount adsorbed of ethanol by activated carbon AC35 at 30 ° C is 468 g / kg or 10.158 mol /kg . For the first regime, $0 < t < 700$ s or $L_1 < L < L_2$ which corresponds to a number of moles adsorbed per unit mass of adsorbent in the range [0; 3.5 mol /kg]. In this regime, we see that the flow of the amount of matter per unit time is constant and this flow is the highest. According to the hypothesis made previously: the flow of the amount of matter per unit time is proportional to the potential adsorbate-adsorbent interaction, we can affirm that this regime corresponds to an adsorption in micropores and that this adsorption occurs with a high and constant gradient potential.

Figure 4: variation of flow of adsorbed amount of ethanol and acetone at 30°C.

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Some authors (Terzyk et al., 1999) have shown that the micropores filling takes place at a very low time interval and the gas-solid interactions are the highest, while Terzyk et al (1999) have shown that the large pores filling occurs in the highest time interval and they involves the filling of the large pores as a result of the co-operative effects between the adsorbate-adsorbent interactions and the adsorbed molecules.

As the pore diameter increases, the variation of flow per unit time decreases linearly (regime 2), $t_1 < t < t_2$ or $L_2 < L < L_3$. This decrease is due to a decrease in the interaction potential. This regime concerns adsorption in mesopores and macropores. This adsorption ends at time t_2 that is about 1800s, which corresponds to an amount adsorbed by the macropores and mesopores in the range [3.5 mol/kg; 9.8 mol /kg] where the amount adsorbed by the pores is $n_2 - n_1 = 6.3$ mol /kg. In this interval, it is found that the tangent intersects the curve of the flow variation of the amount of matter per unit time (or pore radius) (Figure 4).

Mathematically, this implies that the curve of figure 4, can be described by two equations, one relating to the part corresponding to adsorption in the micropores and the mesopores ($10 < t < t_2$ or $L_1 < L < L_3$) and the other relating to adsorption by the macropores and side surface of the grains of the microporous solid. The existence of two mathematical equations for the interaction potential physically implies the existence of two types of infraction forces. An active type of forces in the case of adsorption in the micropores and mesopores and the other is active during adsorption in the macropores and by the side surface what justifies the existence of two models in the literature of the adsorption phenomena: that Dubinin-Astakov and BET.

In the latter regime, the flow of adsorbed matter is lower, which means that the interaction potential is low for the lateral surface interactions of the adsorbent and that the saturation is almost reached. The amount adsorbed by the side surface is $n_\infty - n_2 = 0.3$ mol/ kg

According to figure 5, we note that the pore distribution of the activated carbon presents three peaks. The majority peak is that corresponding to the size of the smaller pores that means the micropores whereas the others are relative to those higher, which corresponds to the mesopores and macropores (Claire et al., 2010). This curve justifies the adsorption process: adsorption by the micropores followed there by adsorption by the mesopores then that by the macropores and finally by a surface adsorption. Moreover, the existence of the peaks in this curve justifies the existence of the three regime experimentally found on the curve of the flow of the amount of matter as a function of time (or the pore radius corresponds) (Figure 4).

According to reference (Terzyk et al., 1999) the authors have shown that the adsorption energies can be compared with the enthalpies of adsorption of the molecules and the enhancement of the adsorption potential in micropores (U) can be calculated. If we assume that the adsorption enthalpy at zero coverage is equivalent to the energy of the adsorbate-adsorbent interaction, the value of this enhancement is strictly related to the pore diameter (L) and

$$U = c.d / L$$

Where c is a constant and d is the diameter of the adsorbate molecule.

However, specific adsorbate-adsorbent interactions in the micropores of carbon enlarge the adsorption potential at a low coverage of molecules.
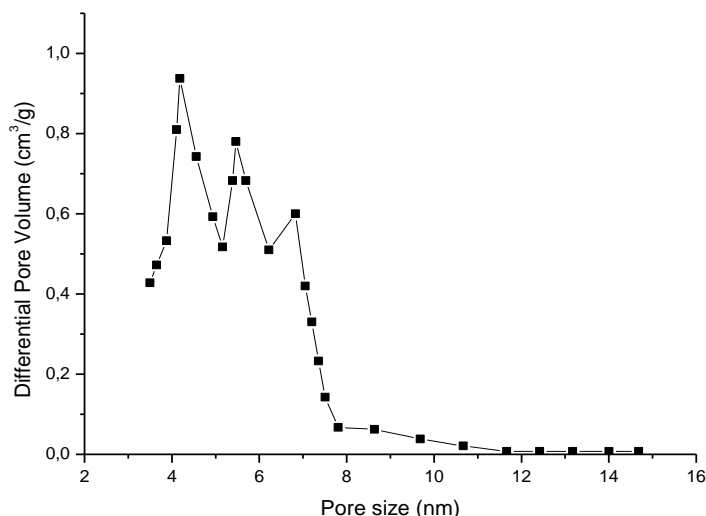
Figure 5: Pore size distribution of activated carbon.

Annexes:-

$$\phi = \iint \rho \, \vec{u} \, \vec{ds}$$

And

$$m \frac{d\vec{u}}{dt} = -\vec{\nabla} U - \lambda \vec{u}$$

Where U is the interaction potential

If $\quad \dfrac{d\vec{u}}{dt} = \vec{0}$

So the previous equation gives us:

$$\vec{u} = \frac{-1}{\lambda} \vec{\nabla} U$$

Conclusion:-

In this work, we made a first approach to the study of the adsorption potential of a gas in a microporous solid. This approach is purely experimental; it allowed us to show that there are two types of forces. The first type is active in the case of adsorption by micropores and mesopores, the second type is active during the adsorption by macropores and lateral surface of the microporous solid. Experience shows that the adsorption potential is constant and higher in the micropores and it linearly decreases in the case of mesopores and macropores. The tangent intersects the curve in the part related to the adsorption of mesopores and macropores, which implies a change in the type of adsorbate-adsorbent interaction forces. These observations are in perfect agreement with the pore size distribution curve for activated carbon AC35. Our study shows that there is no contradiction between the Dubinin-Astakov model and that of BET. The Model Dubinin-Astakov applies for filling micropores and mesopores and that of BET to the adsorption in the macropores and in the side surface, surface adsorption.

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Nomenclature:-

P: pressure (Pa), assumed to be constant
G_0 : model flow of inert gas (mol s^{-1})
M: mass of adsorbed particles (kg mol^{-1});
M_{bed} : mass of active carbon bed (kg);
X_0: partial molar fraction of initial solvent in the air;
X: partial molar fraction of solvent at time instant t in the air
C_0 : mass concentration of the solvent at the column input (g m^{-3})
$n(r_c, t)$: Number of adsorbed molecules in (mol kg^{-1}) by spherical volume of r_c radius at time t;
$n_\infty= \lim n_{t\to\infty} (r_c ,t)$ at 30°C (mol kg-1)
r_c : radius of spherical grain of adsorbent (m);
r_c+: radius of spherical surface (m)
L_1: minimum diameter in order to the molecule can penetrate (m);
L_2: diameter of molecule in order to can penetrate into the microspores (m);
L_3: diameter of molecule in order to can penetrate into the macropores (m);
t: time (s);
T: temperature (°K);

R: constant of ideal gas (J mol^{-1} K^{-1})
ϕ_m : flow of matter (mol/m^2 s)
β: proportionality constant
U: adsorption potential (J)
c: constant
 d: diameter of the adsorbate molecule (m)
 L: pore diameter (m)
s: confinement parameter