

PERCOLATION PARAMETERS OF BIOMOLECULES ADSORPTION ON TWO-DIMENSIONAL NETWORK SURFACES

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Abstract. *The influence of molecular types in the understanding of the phenomena of adsorption in surfaces is fundamental in the development of materials of high performance, which are used in a number of processes of great industrial relevance. The modeling of surfaces by means of network models has great potential because it may allow the analysis of the main phenomena of interest at the microscopic level, incorporating a series of statistical parameters important in understanding the surface interaction mechanisms. In this work two-dimensional square networks were used with the purpose to study the isotherms of adsorption at batch processes. In the mass transfer simulations were considered different types of molecules, being observed the behavior of the Freundlich adsorption isotherm in accordance with the type of molecule adsorbed. With this approach the isotherms parameters are obtained, being observed a strong dependence with the size of the molecule, since the selectivity for the adsorption increased with the molecular size.*

Keywords: *Mass transfer mechanisms, Network Models, Chromatography, Stochastic Modeling, Adsorption, Diffusion.*

1. INTRODUCTION

The interest of the pharmaceutical industry and chemistry fine in the development of technologies of chromatographic separation, as the technique in simulated moving bed (*SMB*) its has been growing during the last decade (Juza et al., 2000, Nicoud, 1998, e Francotte et. al., 1988). Recently, new chromatographic processes, with separation multicomponents and gradient applications, they have been appearing. The application of techniques of chromatographic separation has been making possible the development of continuous processes that take to high productivities with low solvent consumption if compared to the conventional agitated batch processes. These techniques are of great interest in the division of molecular systems with enantioselectivity, that are of difficult separation.

The chromatographic, for being a separation method, usually, its considers mixtures of diluted compositions (Guiochon et al., 1994). In many cases, the own movable phase is not formed by a single pure solvent, but a mixture of compositions that if absolve differently with the stationary phase. The equilibrium concentration of a certain substance in the middle, besides depending on its concentration in the movable phase, it also depends on the concentration of the other present substances. In high concentrations, the molecules of several components of the movable phase and of the feeding they compete for the adsorption in the stationary phase, presenting a capacity limits. In the chromatographic solid-liquid, the competition is originating from the finite capacity of adsorption of the surface of the adsorventes.

Several approaches in the modeling of chromatographic systems can be considered starting from experimental data of equilibrium. The simplest case is related to the condition of constant selectivity's, in that classic thermodynamic models are used, as the very known equation multicomponents of Lagmuir. Being like this, in many works in that the capacities of saturation of the compositions are not identical, it is observed correlations no satisfactory with isotherms of adsorption that don't consider that condition type.

The use of tools of modeling computational in the description of biotechnological processes, as the chromatographic, it is a concrete step in the development of more efficient separation systems than they can take to more favorable economical conditions. Application of methods of microscopic modeling, as the methods Monte-Carlos, it is a promising possibility in the understanding of the separation mechanisms at molecular level. With that, new concepts regarding the separation mechanisms can be established, what would be a contribution for the implementation and better acting of the separation systems.

The modeled problem consists of a tank containing a liquid phase, a fluid and a surface adsorvente in its bottom. That tank is agitated and left sufficiently in rest a time big, in other words, the process of adsorption reaches a balance, and molecules adsorbed for the solid phase percolation are been able to in the bottom of the tank.

The modelling of the percolation threshold was accomplished applying a model of net two-dimensional square (100 X 100), representing the surface adsorvent in the solid phase with molecules adsorbed. Each molecule adsorbed corresponds to a busy ranch that can percolation the whole system, leaving an end to another of the lattice forming the cluster.

2. STRUCTURAL MODELING AND PHENOMENOLOGICAL

Through an stochastic approach, the phenomena of adsorption were simulated with the help of a generating routine of uniform random numbers. Like this to each stage of time – discrete variable, a random number (R) is generated and compared with a probability of adsorption (P_{ads}). Such probability is determined by the Eq. (1) shown below.

$$P_{ads} = \frac{C_{it}}{C_{i0}} \quad (1)$$

where C_{it} and C_{i0} they represent the concentration of molecules in the liquid phase in the instant t and $t=0$, respectively. It is known that in $t=0$, $C_{it} = C_{i0}$. The adsorbed molecules are reduced of the liquid phase, doing with that the concentration is increased in the adsorbent phase (q). Therefore, at each time, P_{ads} it is updated, so that each molecule that if adsorbed contributes to the decrease of this probability of adsorption.

With that so that a molecule of the liquid phase if adsorbed in the surface, it is necessary that on that moment, a certain site is empty and that (R) be smaller than P_{ads} . In the beginning of the simulation, the surface has all their available sites for adsorption, so that in agreement with the Eq. (1), $P_{ads}=1$. What determines the adsorption of a molecule on that moment. The site in that the molecule will leave adsorbed or not, it is random chosen, with the help once again of the routine of random numbers. The Fig. (1) it shows the dynamics of adsorption between the molecules of the liquid phase and the surface of the bottom of the tank.

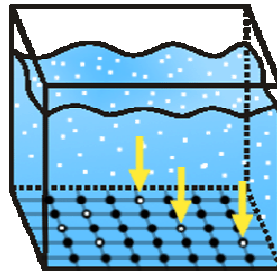


Figure 1 – Representation of the agitated tank in that the surface of adsorption it is represented by a square two-dimensional network.

Interaction between the adsorbed molecules and processes of superficial diffusion is inconsiderate of this model.

As it is a stochastic simulation needs to accomplish several simulations and to calculate the arithmetic average of the concentrations in the adsorbents phase (q_m). In the measure in that the number of simulations tends to the infinite, the results tend to a smaller dispersion in relation to the Real.

3. SYSTEMIZATION OF THE SIMULATIONS

The modeled problem consists of a rigid tank containing a liquid phase – a fluid – and a adsorbent surface in its bottom. That tank is agitated and left sufficiently in rest a time big, or be, the process of adsorption reaches a equilibrium, and adsorbed molecules of the solid phase can happen the percolation in the bottom of the tank.

The modeling of the percolation threshold was accomplished applying a model of square two-dimensional network (100 X 100), representing the adsorbent surface in the solid phase with adsorbed molecules. Each adsorbed molecule corresponds to a busy site that can happen the percolation the whole system, leaving an end to another of the lattice forming the cluster Fig. (2).

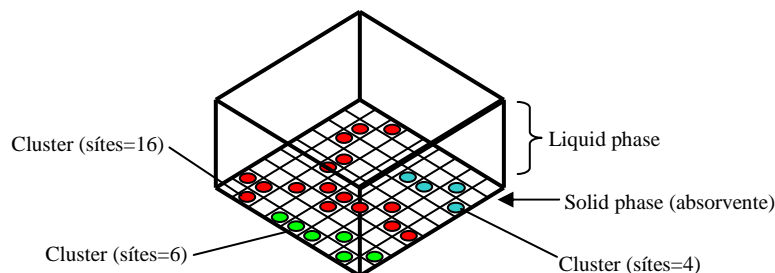


Figure 2 – Representation of the tank in rest where the process of adsorption its reaches a equilibrium acted by a square two-dimensional network.

In the beginning of the simulation, it is chosen a located site in the left border of the network, with the help of a generating routine of uniform random numbers. Like this to each stage of time – discrete variable, a random number (R) it is generated, and used to sort the position of the site in the square two-dimensional network. The chosen site will be marked in case it is busy, that represents the adsorbed molecule. To leave of that first marked site, it will be chosen randomly a busy neighboring site, with the help again of the routine of random numbers. Finishing the choice when there is not more neighbors sites to the last marked site.

Interaction between the adsorbed molecules and processes of superficial diffusion is inconsiderate of this model. We considered a number of stages of time same to 10^5 (a hundred thousand), representing the process of adsorption in equilibrium. Aiming at to represent processes of adsorption sufficiently in times big, or be, processes that reach a equilibrium, we considered a number of stages of time same to 10^5 (a hundred thousand). For each group of parameters we accomplished 2.000 (two thousand) simulations, based on simulated data that showed there to be little variation starting from more simulations Fig. (3).

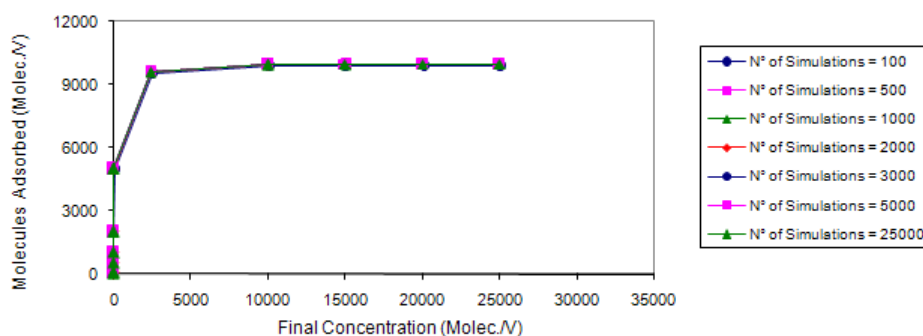


Figure 3 – Results of the simulated data of the simulations.

Forms different from molecules were used in the simulations Fig. (3), looking for to represent the form or the three-dimensional molecular structure of some proteins especially of the insulin (Dodson, 1998), although technically the insulin is just considered a polypeptide, due to its small size.

The form of the proteins can vary from lineal (fibrous proteins) to you form approximately spherical (globular proteins). Those properties are highly influenced by the physical (temperature) and chemical (pH, forces ionic and solvent type and lid) aspects of the atmosphere where its finds the protein.

For physiochemical reasons, the adsorption in a surface can be limited the some directions or senses, or be, there is an only impediment restricting the adsorption in a given direction. We simulated this phenomenon with lineal molecules, allowing its adsorption to happen only in the horizontal direction – Fig. (4 A) – or in the vertical direction – Fig. (4 B). We also accomplished simulations using molecules in form of "L", always restricting the adsorption in one of the directions shown in Fig. (4 - C, D, E ou F), in other words, in four different senses.

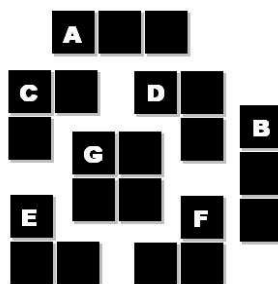


Figure 4 – Different molecules used in the simulations.

After the considerations on restricted impediments, we simulated more general cases, in that the molecules were able to of absolver in any direction of the shown in Fig. (4). Like this, if a molecule was adsorvida in a direction, the other molecules could be adsorbed in any other direction, even in the direction of the previous molecule, even in the direction of the previous molecule. Or better, they were been able to adsorver in a random way. In these random simulations, we used lineal molecules, in "L" and square molecules as display Fig (4 G).

Besides the sense of adsorption, our models allow the variation of the size of each molecule ($Tmol$). In Fig. (4), the molecules A and B possess size "3", while (three) all the other ones, size "2" (two).

4. RESULTS AND DISCUSSIONS

In the Table (1) we see a summary of the results for the different types of molecules and directions presented for the different sizes ($Tmol$). The values act to smallest necessary initial concentration (C_{i0}) to happen the percolation in the network. In all of the simulations initial concentrations were used in the liquid phase same to 35.000 (thirty five thousand) molecules.

Table 1 – Results of the modeled data.

Tmol	Linear			Format "L"					Square
	Random	Vertical	Horizontal	Random	Sense C	Sense D	Sense E	Sense F	
1	3922	***	***	***	***	***	***	***	***
2	1985	2231	2233	***	***	***	***	***	***
3	1204	1407	1409	701	694	697	692	695	699
5	589	950	949	356	372	376	377	373	299
10	313	462	464	95	154	153	153	152	No percolation

Fig. (5) it presents in graph form the data of the Table (1) for the different types of molecules with size ($Tmol$) same to "10". In her we see the amount of adsorbed molecules (q) in function of the types of molecules. As it was already waited, the percolation limited to the horizontal direction is the same that to the vertical direction, due to the square netware model. In other words, as the dimensions of the surface they are same, the percolation conditions are the same ones in all the senses. Likewise it happens with the molecules in form of "L", the amount of adsorbed molecules (q) is the same for the four senses defined previously (C, D, E e F), as we see in Fig. (5) more below.

We noticed that the molecules in form of "L" with sense of adsorption random faster percolation.

We should attempt to the fact that a molecule in "L" is, actually, two molecules orthogonal lineal, what bends its area and that increases in double its probability of finding a busy neighboring site (q).

Still in Fig. (5), we also noticed that the square molecules no percolation, due to great area of those molecules. These are molecules that have more difficulty of adjusting in the net with the increase of its size for its form, forming isolated clusters.

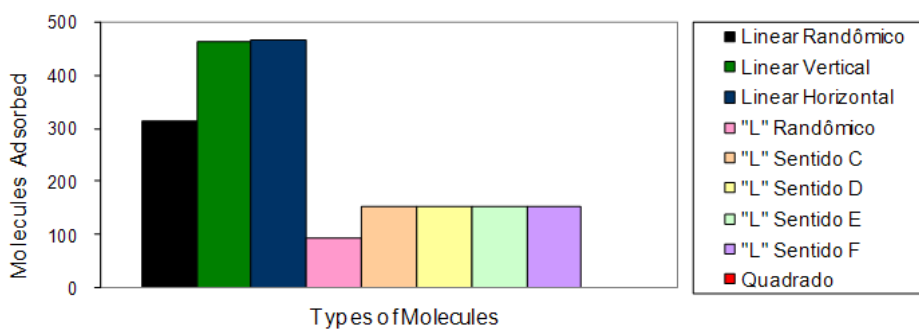


Figure 5 – Results of the simulations with different types of molecules with size same to "10."

In the figures (7), (8) and (9) it is presented in graph form the results of the simulations, using lineal molecules of size same to "10" with ($Tmol$) sense of random adsorption. In all of the simulations initial concentrations were used in the liquid phase same to 1.500 (thousand and five hundred) molecules. We can observe the decrease of the number of the clusters, to each stage of time, however the formation of a cluster of larger size Fig. (6). That resulted was waited already due the system to tend the form a cluster of "infinite" size with the formation of few and small holes, in the course of time.

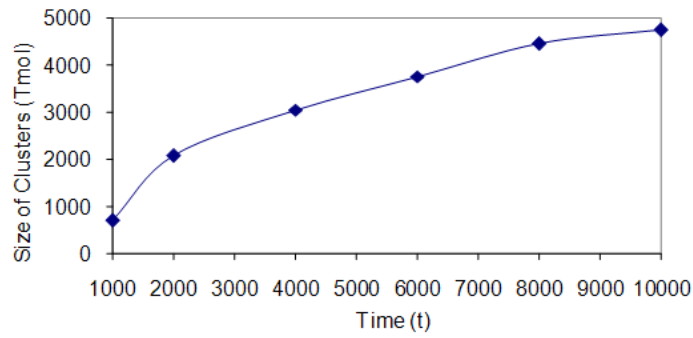


Figure 6 – Result of the simulations with lineal molecules of random sense varying the time (t).

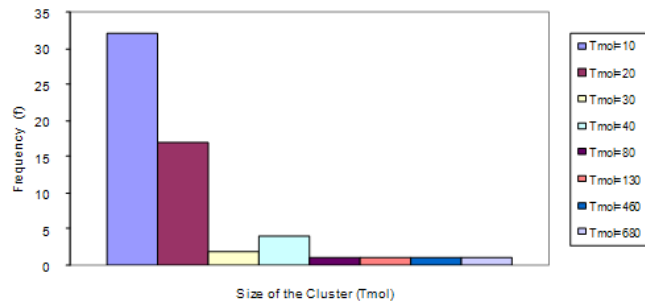


Figure 7 – Result of the simulations with lineal molecules of random sense and time (t) same to 1.000.

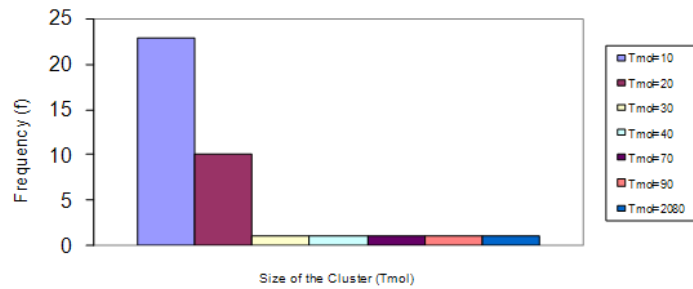


Figure 8 – Result of the simulations with lineal molecules of random sense and time (t) same to 2.000.

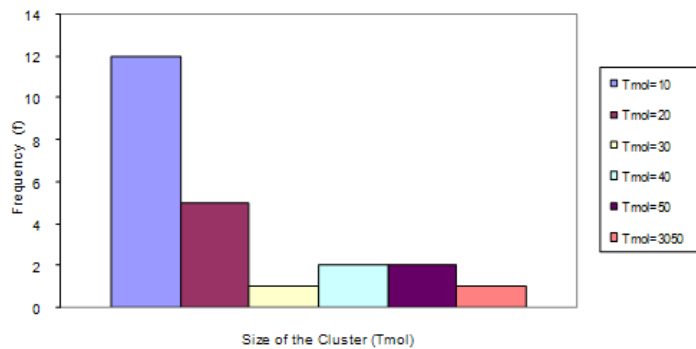
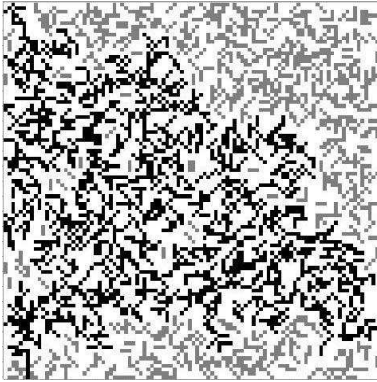


Figure 9 – Result of the simulations with lineal molecules of random sense and time (t) same to 4.000.

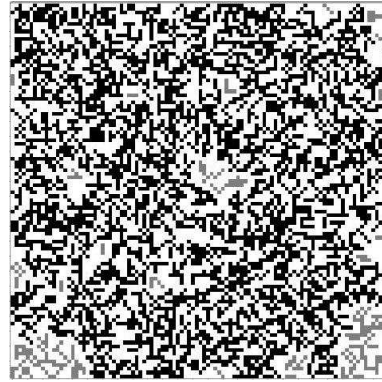
4.1 - Visual results

Besides the numeric results presented above, our simulator allows the visualization of the behavior of the percolation in the surface delimited by the net model.

In the Figures (10) and (11) we noticed the variation of the percolation visually with the increase of the initial (C_{i0}) concentration. Molecules in a lineal way were used with size same to "3" and random sense of adsorption. The initial (C_{i0}) concentrations are 1.209 (thousand two hundred nine) molecules Fig. (10 A), 1.500 (thousand and five hundred) molecules Fig. (10 B), 2.000 (two thousand) molecules Fig. (11 A) and 2.500 (two thousand and five hundred) molecules Fig. (11 B).

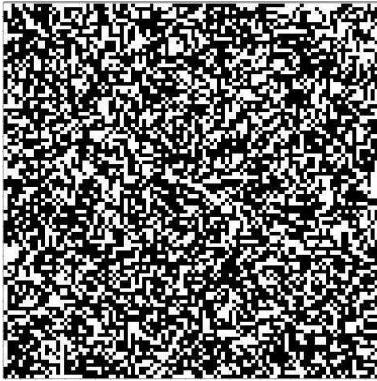


(A)

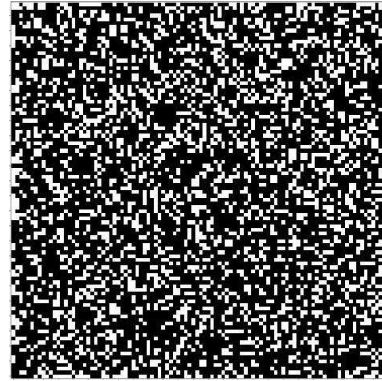


(B)

Figure 10 – Surface of the percolation with initial (C_{i0}) concentration same to 1.209 (A) and 1.500 (B).



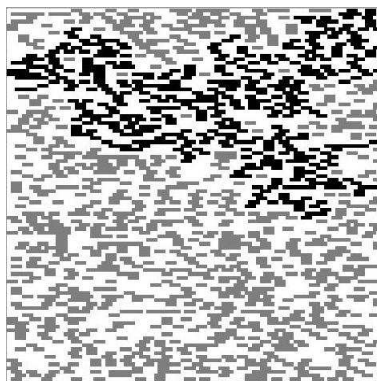
(A)



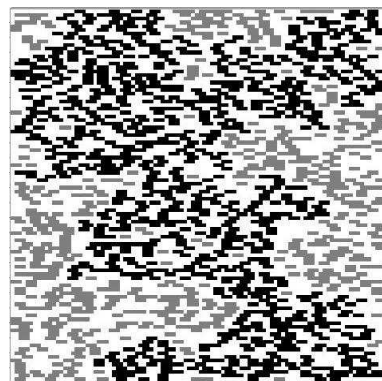
(B)

Figure 11 – Surface of the percolation with initial (C_{i0}) concentration same to 2.000 (A) and 2.500 (B).

In the figures (12) and (13) we see molecules in a lineal way with size same to "3" and horizontal sense of adsorption. The initial (C_{i0}) concentrations are 1.409 (thousand four hundred nine) molecules Fig. (12 A), 1.500 (thousand and five hundred) molecules Fig. (12 B), 2.000 (two thousand) molecules Fig. (13 A) and 2.500 (two thousand and five hundred) molecules Fig. (13 B).

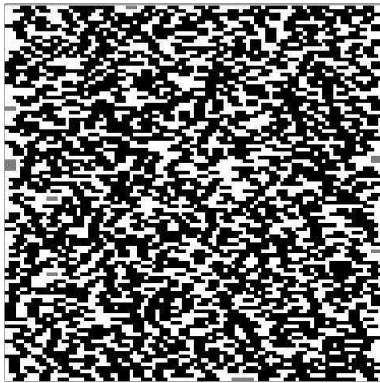


(A)

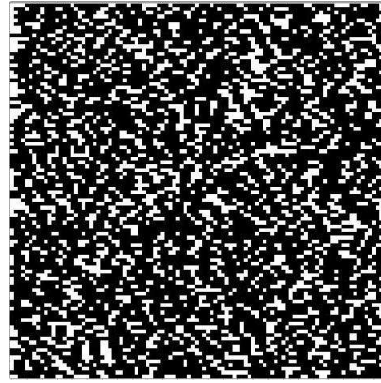


(B)

Figure 12 – Surface of the percolation with initial (C_{i0}) concentration same to 1.409 (A) and 1.500 (B)



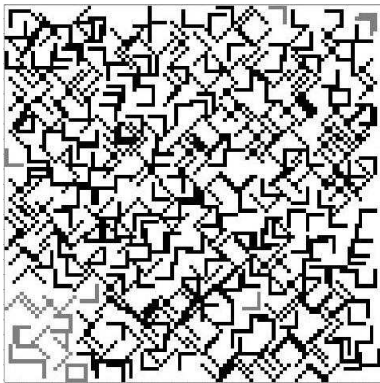
(A)



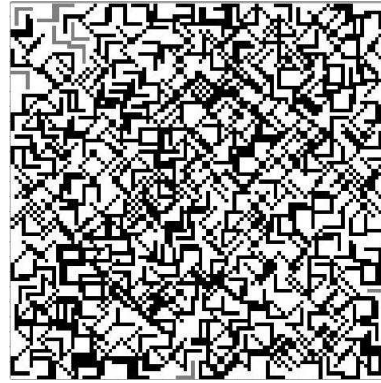
(B)

Figure 13 – Surface of the percolation with initial (C_{i0}) concentration same to 2.000 (A) and 2.500 (B).

The figures (14) and (15) they exhibit percolation surfaces with molecules in way of "L" of size "5", random sense. The initial (C_{i0}) concentrations are 356 (three hundred and fifty six) molecules Fig. (14 A), 500 (five hundred) molecules Fig. (14 B), 1.000 (a thousand) molecules Fig. (15 A) and 2.000 (two thousand) molecules Fig. (15 B).

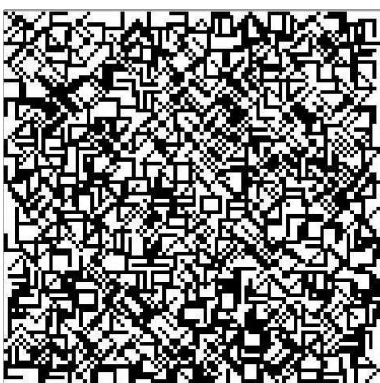


(A)

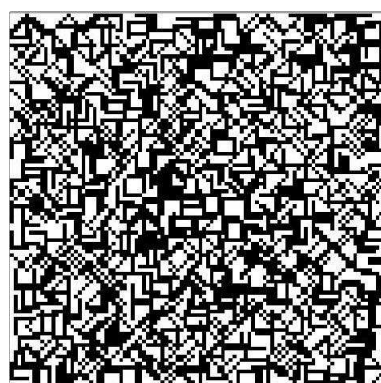


(B)

Figure 14 – Surface of the percolation with initial (C_{i0}) concentration same to 356 (A) and 500 (B).



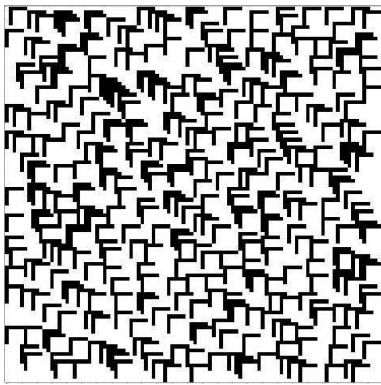
(A)



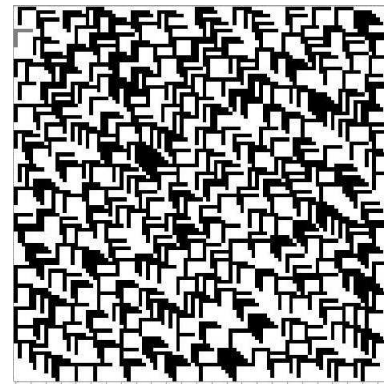
(B)

Figure 15 – Surface of the percolation with initial (C_{i0}) concentration same to 1.000 (A) and 2.000 (B).

In the figure (16) and (17) we see molecules in way of "L" with size same to "5" and sense defined previously (C) of adsorption. The initial (C_{i0}) concentrations are 372 (three hundred and seventy two) molecules Fig. (16 A), 500 (five hundred) molecules Fig. (16 B), 1.000 (a thousand) molecules Fig. (17 A) and 2.000 (two thousand) molecules Fig. (17 B).

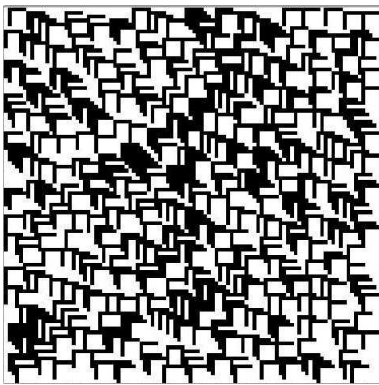


(A)

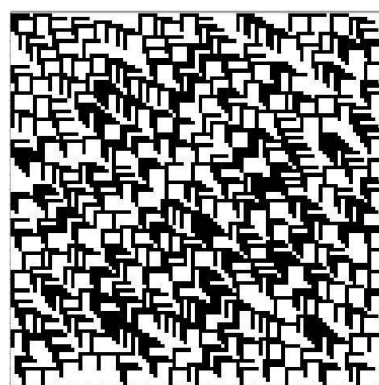


(B)

Figure 16 – Surface of the percolation with initial (C_{i0}) concentration same to 372 (A) and 500 (B).



(A)



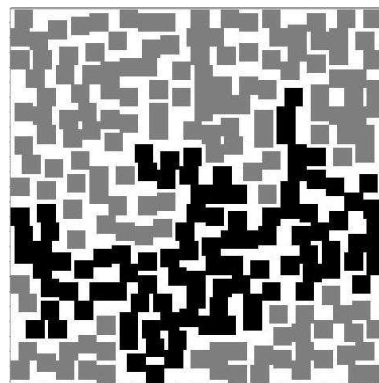
(B)

Figure 17 – Surface of the percolation with initial (C_{i0}) concentration same to 1.000 (A) and 2.000 (B).

In the figures (18) and (19) we noticed the variation of the percolation visually with the increase of the initial (C_{i0}) concentration. Molecules in a lineal way were used with size same to "3" and random sense of adsorption. The initial (C_{i0}) concentrations are 299 (two hundred and ninety nine) molecules Fig. (18 A), 1.500 (thousand and five hundred) molecules Fig. (18 B), 2.000 (two thousand) molecules Fig. (19 A) and 10.000 (ten thousand) molecules Fig. (19 B). We observed that these are molecules that have more difficulty of adjusting at empty sites in the surface for its form.



(A)



(B)

Figure 18 – Surface of the percolation with initial (C_{i0}) concentration same to 299 (A) and 1.500 (B).

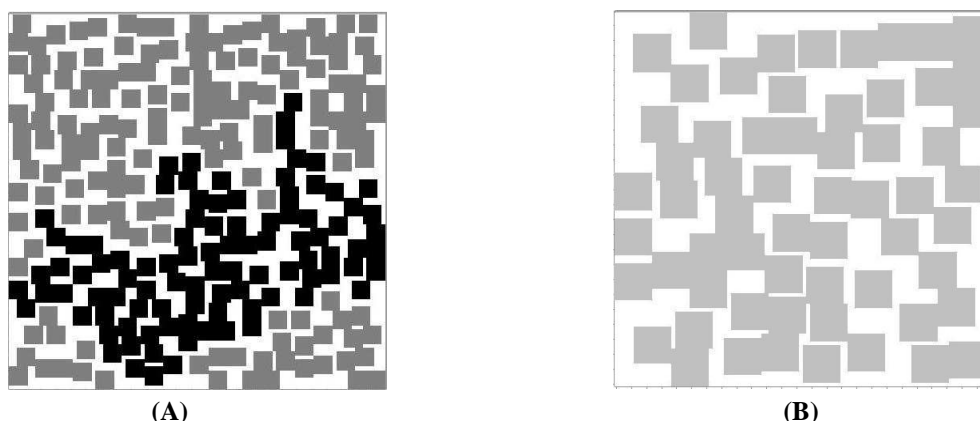


Figure 19 – Surface of the percolation with initial (C_{i0}) concentration same to 2.000 (A) and 10.000 (B).

5. CONCLUSIONS

The study of the Percolation Threshold using different types and sizes of molecules, being observed specific behaviors for each case. This way, it can be obtained parameters of the isotherms related with the types and studied molecular sizes, being observed a strong dependence of those with the size of the molecule, once the selectivity to the adsorption increases with the size of the molecule.

In the simulations of the percolation threshold of the clusters, it was possible to visualize the behavior of the busy sites, as well as the formation and size of the clusters. We noticed that the molecules in form of "L" with sense of adsorption random faster percolation. We should attempt to the fact that a molecule in "L" is, actually, two molecules lineal orthogonal, what bends its area and that reduces its probability in half of finding an empty sites if compared with a lineal one. The square molecules presented larger difficulties to percolation. These are molecules that have more difficulty of adjusting in the network with the increase of its size for its form, forming isolated clusters.

6. ACKNOWLEDGEMENTS

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