USE OF COMPUTATIONAL CHEMISTRY TO STUDY THE ADSORPTION PROCESS OF CONTAMINANTS USING ACTIVATED CARBON PREPARED CHEMICALLY FROM AGUAJE SEEDS (MAURITIA FLEXUOSA) AND CHESTNUT SHELL

A.L. Paredes-Doig

Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Rímac, Lima, Perú.

E. Doig-Camino

Sección Química, Departamento de Ciencias, Pontificia Universidad Católica del Perú, Av. Universitaria 1801, Lima 32, Perú.

G. Picasso

Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Rímac, Lima, Perú.

A. La Rosa-Toro

Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Rímac, Lima, Perú.

M.R. Sun-Kou

Sección Química, Departamento de Ciencias, Pontificia Universidad Católica del Perú, Av. Universitaria 1801, Lima 32, Perú.

ABSTRACT: In the present study, it was exposed a computational chemistry analysis of adsorption process of the contaminants from wastewaters like metal cations, farmaceutical compounds and organic acids. First of all, the study was focused in the quantum mechanical parameters of the adsorbates and adsorbents. Then, it was explained, calculating the adsorption energy, the method molecular dynamics to predict the mechanism of the adsorption process.

INTRODUCTION

It is very important study computational analysis and molecular dynamics, molecular mechaniscs or Monte Carlo simulation to understand too the mechanism and so optimize treatment process.

This investigation is useful to colect information from the different papers and Works that using DFT calculations and molecular simulations to apply it to the wastewaters treatment.

Many computational methods has been employed to explore a diversity of chemistry phenomenons success as like theoterically as to explain experimental cases (1).

Selecting a Good computational leve lof theory it is possible to simulate the evolution of the adsorption process and to predict the certain of this process (2-7)

Some authors, first, tried to have accuracy with ab initio methos too. Althought, actually, the most used, in DFT calculations, is the DFT theory optimized with the B3LYP hybrid functional.

In the first parto f this review, it is going to talk of DFT calculations. To continue with a approach of interaction of these with molecular simulations- Finally, it is going to show three examples of adsorption with activated carbon from aguaje sedes and chesnut Shell, typical residues from Peruvian amazony.

It is not possible, with human service alone, to monitor water quality for long periods. Therefore, it is important to develop other more intelligent, convenient and less dangerous ways. For example, with computational chemistry it has been possible to predict the behavior of pollutants in nature.

It is known that the identification of the molecular properties of contaminants such as chemical reactivity and biodegradability is a prerequisite for efficient water treatment. Mainly, these molecular properties depend on the molecular geometry and composition. Computational chemistry provides a powerful tool for calculating molecular structures and properties.

Computation methods or molecular simulations can be used to identify materials with high adsorption capacity for wastewater treatment rapidly. They can also provide complementary insights into the dynamics of adsorption processes. In addition, molecular simulations can be used to understand the adsorption mechanism and the interaction between contaminants and adsorbents

Moreover, molecular simulation can provide complementary information regarding the adsorption mechanism and the interaction between the pollutant and the adsorbent. [8-9]

A. ADSORPTION THEORY

II.A.1. ADSORPTION

There is an interaction between force fields between a solid and a liquid or gas when the surface of the solid is in contact with a liquid or a gas. The phenomenon that results from this imbalance of molecular forces present on the solid surface is called adsorption, with the solid being the adsorbent and the fluid (gas or liquid) being the adsorbate.

The adsorption process is the result of two forces, one of attraction towards the surface of the solid and the other of repulsion.

The type of adsorption that occurs in an adsorbate-adsorbent system depends on the nature of both the adsorbate and the adsorbent, the reactivity of the surface, the surface

area of the adsorbate, the temperature and the adsorption pressure .

Adsorption can occur in two types: physisorption and chemisorption. In the case of physisorption, the adsorbate is weakly bound to the surface of the solid by Van der Waals forces.

In contrast, chemisorption involves an exchange or sharing of electrons between the adsorbate molecules and the adsorbent surface resulting in a chemical reaction. Chemisorption is the initial stage of any catalytic process.

II.A.2 Surface chemistry of the adsobent material: activated carbon

The surface chemistry of the material is determined by the chemical composition of its surface. In the case of activated carbons, disturbances in the microcrystalline elemental structure due to the presence of imperfections give rise to a variation in the arrangement of the electronic clouds of the carbon skeleton, which creates unpaired electrons and incompletely saturated valences. These characteristics are what define the adsorption properties of activated carbon, especially with polar and polarizable compounds.
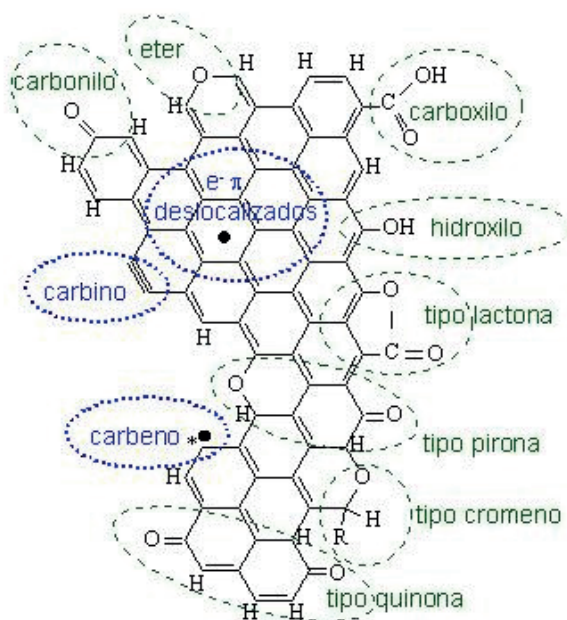

Figure 1. Schematic representation of the acidic character of some oxygenated groups and the basic character of the electrons delocalized in the basal plane and of other oxygenated groups (taken from Ménendez) [28]

II.B. COMPUTATIONAL METHODS

Computational Chemistry, although it goes hand in hand with Theoretical Chemistry, the former includes a mathematical evaluation of Chemistry. Computational studies are used

to predict key properties of even unknown molecules or to explore reaction mechanisms of what has not yet been studied experimentally.

II.B.2. Descriptios of Methods

a) Ab Initio method [11-16]

Fundamentally assuming the Hartree-Fock theory where each electron allows tremendous progress for the calculation of molecular orbitals.[17]

The development of semiempirical theories was motivated in part by parameterization forces that were able to compensate for this feature of Hartree-Fock. Of course, the ultimate rigor is achieved, so the error energy associated with the HF approximation for a given system is called the electron correlation energy Ecorr.

Ecorr=E-Ef

Methods that do not include any empirical or semi-empirical parameters make up the so-called Ab Initio methods.

This is understood in that the programs used in Computational Chemistry are based on different quantum mechanical methods that are solved with Eq. of Schrodinguer associated with a Hamiltonian.

Ab Initio methods try to define a novel theory and a "Basis Set". These "Sets" are used to describe molecular orbitals through the Linear Combination of Atomic Orbitals.

The best-known type of Ab Initio calculation is Hartree-Fock, an extension of molecular orbital theory. This method does not take into account the electron-electron repulsions in the molecule.

Later, the port-Hartree-Fock method emerged, which presents a correction for this repulsion.

b) Density Functional Theory (DFT) Method

The difference between these methods and Ab Initio methods is that DFT uses parameters derived from experimental data. Furthermore, it represents an alternative way to conventional Ab Initio methods by introducing the effects of electronic correlation in the resolution of eq. by Schrödinguer.

What forms the basis of DFT is the fact of using electron density instead of a wave function to calculate energy [BOOK 1, 18]

This function, depending on a spin, and three spatial coordinates for each electron, is particularly intuitive for systems with more than one electron.[17]

b) Semi-empirical Methods [19,20]

They are based on the Hartree-Fock theory; however, they make many approximations and obtain parameters from experimental data.

According to Semi-Empirical primitives, these were designed where a Hamiltonian electron pair is not explicitly included. For this pi electron system, Huckel's method is used.

1. DFT-based descriptor model

(1) First, it is necessary calculate some quantum global parameters like energy gap (ΔE), electron affinity (EA), ionisation potencial (IP), electronegativity (χ), global hardness (η) and global softness (σ):

$\Delta E = E_{Lumo} - E_{homo}$

$EA = -E_{Lumo}$

$IP = -E_{Homo}$

$X = (IP + EA)/2$

$\eta = (IP - EA)/2$

$\sigma = 1/\eta$

This is useful to predict the adsorption mechanism. For example, several authors use the HOMO-LUMO energy such a s indicator: a large HOMO-LUMO energy gap indicates chemically hard molecules interact les with other systems. A more reactive molecule has a moderate value of HOMO-LUMO (11)

Normally, the compounds are firstly optimized with B3LYP hybrid functional within DFT framework (21-22)

(2) Adsorption energy

a) Molecular Mechanics [23]

Use a classical expression for the energy of the compound as the harmonic oscillator.

One of the most interesting properties of a phase point that has not yet been recognized is that it is defined by the positions and momenta of all the particles. This determines the location of the next phase point in the absence of external forces acting on the system.[17]]

b) Molecules Dynamics

It also uses quantum mechanics, molecular mechanics or a mixture of both. Calculate the trajectories by solving Newton's equations of motion for the set of particles.[21]

For a computational chemist, the Surface Energy Potential is a surface that can be generated point by point using some computational methods, which determine a molecular energy for the structure of each point. The first Surface Energy Potential (SEP) was built by people studying molecular spectroscopy.[17]

c) Monte Carlo

It generates configurations of a system that makes random changes to the positions of its particles, along with their orientations and conformations where appropriate.

More generally, it does not provide dynamic system information; However, it can be extended to quantum systems much more easily. [24]

One can imagine entailing a stochastic approximation to extreme logic, in which the event has no equations of motion to integrate.[17]

d) Quantum Mechanics/Molecular Mechanics (QM/MM) [25]

It is a hybrid that combines the precision of quantum mechanics with the speed of

molecular mechanics.

To determine low energy adsorption sites, the adsorption locator uses the Monte Carlo (MC) simulation approach, wich calculates preferential adsorption sites of mixes adsorbate components. This use a geometry optimization.

It is important to note that also is posible to use molecular dynamics or molecular mechanics.

The paper cited (1) that uses Monte Carlo (MC) simulation explained too that the adsorption energy calculation are compute dina a vaccum and ground state environment. Therefore, effects such as kinetic energies, environment surrounding, concentration, pH-dependency and solubility are not included in the calculation (1)

In this paper, the addsorption energy indicates the energy required by the conyaminant to more towards the Activated carbon.

ΔEadsorption=E(complex)- E(adsorbate)-E(adsorbent)

Where E(complex) is the electronic energy of the complex formed by the interaction of the adsorbate and the adsorbent separately (26)

In paper (23), it was calculated interaction between dyes and Graphene oxide and their structures were optimized at the PW6B95-D3/deQ-1ZVP leve lof theory.

In others investigations (27) utilized computational chemistry. They used Hartree-Fock as oppoed to DFT, with a 6-31G basis function using GAUSSIAN 09.

In another cluster atom, calculated semi-empirical approach was used to understand the cyanide adsorption on graphite. A relative reactivity is calculated by comparing the difference between cyanide's HOMO and graphite's LUMO with or whitout magnetite. The smaller the absolute difference between these frontier orbitals, the more reactive is cyanide towar the substrate (28)

III PART: EXAMPLES

a) The interaction of metallic ions onto activated carbon Surface using computational chemistry software

First, it was modeled a reaction site of Activated carbon with the results of Surface acidity (Boehm). For example, AC presented more lactonic groups and AC-OX has more phenolic and carboxilic groups. This can observed in the next table:

	Carboxilics mmol H+/g	Lactonics mmol H+/g	Phenolics mmol H+/g	Total mmol H+/g	pH$_{PCZ}$
AC	1,12	3,08	0,03	4,22	2,450
AC-OX	4,10	0,05	0,67	4,82	2,014

Table 1. Characteristics of surface chemistry of AC and AC-OX

It was used electronic density to observe what AC showed a big negative charge to

attract metal ions.

Like the metal ions are considered Lewis acid, this contributed qith their LUMO orbitals. Whereas the ACs act such a Lewis base, by clasifying Pearson and Alfarra (29) give electrons from their HOMO's orbitals. The order showed of metal ions adsorption was Pb(II)> Cd(II)>Cr(III).

The energies of frontier orbital is shown here.

	HOMO	LUMO	ΔE
Cr (III)	-49.78	-27.81	**18.49**
Cd (II)	-38.92	-14.71	**5.39**
Pb (II)	-37.52	-13.55	**4.23**
AC unoxidized	-9.32	-2.24	
Cr (III)	-49.78	-27.81	**18.7**
Cd (II)	-38.92	-14.71	**5.6**
Pb (II)	-37.52	-13.55	**4.44**
AC-OX	-9.11	-1.82	

Tabla 2. Frontier orbital values obtained using Hyperchem

With these results its possible t osee that, oxidizing, **ΔE** is few greater, although the electronic densities (Unoxidized: -1.38; Oxidized: -2.81) are bigger with the oxidized carbon and indicate the adsorption order.

B) Computational modelling of DMA adsorption onto activated carbon prepared from Aguaje sedes

It was studied frontier orbitals (HOMO-LUMO) an their ΔE (eV). The AC reacts as nucleophile and DMA like a electrophile.
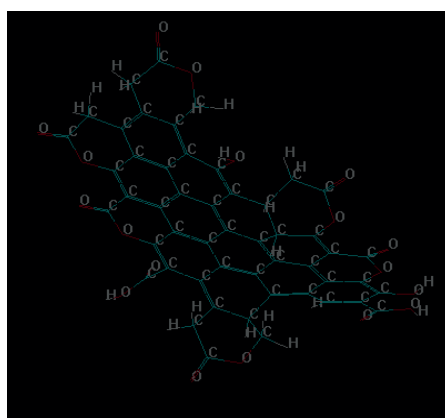

Figure 2. Image of the AC model with its respective functional groups obtained through molecular modeling.

	CA-0,5	CA-0,75	CA-1,0	CA-1,5
HOMO (eV)	-8.21	-8.43	-8.36	-7.18
LUMO (eV)	-3.34	-3.48	-3.41	-2.79
ΔE_{CA} (eV)	4.87	4.95	4.95	4.39

Table 3. Frontier orbitals of activated carbons at different degrees of impregnation.

	DMA	DMAH+
HOMO (eV)	-9.38	-19.10
LUMO (eV)	3.48	-4.99

Table 4. Frontier orbitals of the dimetilamine

	AC-0.5-DMAH+	AC-0.75-DMAH+	AC-1.0-DMAH+	AC-1.5-DMAH+
LUMO $_{adsorbato}$ (eV)	-4.89	-4.68	-4.91	-5.00
HOMO $_{adsorbente}$ (eV)	-9.06	-9.61	-9.23	-7.79
$\Delta E_{adsorbato-adsorbente}$ (eV)	4.17	4.93	4.38	2.79

Tabla 5. Interaction of the molecular orbitals of the adsorbate (DMA) and the adsorbents (AC).

It was prepared many ACs (AC.0.5, AC-0.75, AC-1,0 and AC-1,5 taking account of impregnation ratio of phosphoric acid) It was found that AC-1,5 is the more reactive by the minor frontier orbitals energy difference. This AC has the bigger donor carácter in comparison with the others. The ΔE values reported are les of 7,34 eV. And the adsorption is a chemisorption as conclusión. The order observed by computational chemistry was the same of experimental results: AC-1,5>AC-0,5>AC-1,0>AC-0,75 in relation of their ΔE homo-lumo and their best interaction with DMA. Also, it was compared the adsorption energy of DMA and DMAH+. It could said that the reaction preferred was the ACs with the protonated form. This last análisis a lower pH showed a HOMO and LUMO more negative for DMAH+ species.

C) A study of the adsorption of aromatic compounds using activated carbons prepared from the chesnut Shell

In the last years, agro-industrial wastes has been used as precursors for the AC production. Like the previous examples, these ACs were prepared from Peruvian Amazon residues. The compunds studied were salycilic acid, benzoica cid and phenol. These species interacting with a "π-π" attraction and repulsión.

The frontier orbitals was performed with the Hyperchem 8.

The aromatic compound with major affinity to the carbon (salycilic acid) held minor energetic difference in these electronic densities in the aromatic rings (30).

The adsorption resulted be a reversible process, because ΔE are higher tan 7,34 Ev. But, when it is evaluated a acid pH, the ΔE values observed changed. In this case,

these reached ΔE values lower to 7,34 eV. So in this last case, the adsorption is irreversible (chemisorption). The adsorption order found was salycilic acid>benzoica cid>phenol.

CONCLUSIONS

The method DFT is the most used actually. This allow to calculate quantum global parameters such as computational modelling.

Two factors are important in adsorption process: frontier orbitals and adsorption energy. Taking account results of that, it is possible found the mechanism of adsorption.

Computational chemistry is being applied to adsorption of contaminants onto activated carbon.

It is possible to model activated carbon with Boehm and FTIR characterization. Also, it is possible evaluate factors like concentration, pH, temperatura, etc.

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