

Molecular modeling of chlordecone interactions with acidic activated carbons

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We use computational chemistry tools for describing chlordecone interactions with acidic surface groups onto activated carbons (AC), for understanding the adsorption process of pesticide on AC.

The French departments, Martinique and Guadeloupe, in order to prevent the propagation of the banana weevil (*Cosmopolite sordidus*), which attacks the roots of the banana tree, extensively used chlorinated pesticides, such as chlordecone (CLD), until the beginning of the 1990s, resulting in the contamination of soil and surface waters. Recent studies has demonstrated that CLD, has a long-range environmental transport, to lead to significant adverse effects on human health and/or the environment. In 2009, CLD was included in the Stockholm Convention on Persistent Organic Pollutants, which bans its production and use worldwide. To limit CLD exposure of Guadeloupe and Martinique population, drinking water and other production plants has been equipped with activated carbon filter. However, the adsorption process onto activated carbon is a very complex phenomenon driven by multiple factors that range from chemical composition to textural properties of the AC. In fact, the influence of surface groups (SG) content over adsorption properties has been reported and studied to some extent both theoretically and experimentally for AC.

In the present work, the interactions between CLD and acidic surface groups on AC are evaluated under different pH and solvation conditions, considering energetic and geometrical aspects of CLD-SG aggregates, in order to better understand the adsorption process on AC.

Systems under study

The coronene has been chosen as AC computational model [1–4]. The edge of coronene has been modified by carboxyl and hydroxyl groups, and it chemical modifications to obtain the oxygen containing models of AC at different pH conditions. The models provide both, the aromatic character and the SGs at the edges of ACs (Fig. 1). CLD and its *gem*-diol form, also known as chlordecone hydrate (CLDh) were modeled, because at a pH > 9, CLD exist in CLDh form [2, 4].

On the other hand, the maximum water molecules number included in the calculations was set to three, in order to study solvation process, since the adsorption of CLD onto AC occurs from aqueous solution.

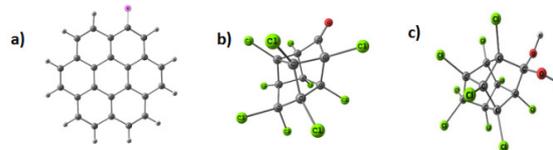


Figure 1: a) AC model consisting on coronene and its oxidized forms: $X = H$ (Coronene), COOH , COO^- , OH , O^- ; b) CLD and c) CLDh.

Computational methods and procedures

The general methodology employed consists of two main steps: first, the semiempirical Minima Multiple Hypersurface (MMH) methodology is utilized to explore the interactions space of the CLD and CLDh with the SGs-AC; second step, the selected distinctive minima structures obtained from MMH are re-optimized using Density Functional Theory (DFT) and the geometries and electronic structure are treated using Quantum Theory of Atoms in Molecules (QTAIM) to more accurately describe the interactions types [4]. MMH calculations were carried out by MOPAC 2016 and using the semiempirical Hamiltonian PM7. DFT and QTAIM were performed by Gaussian09.

CLD interaction with SG-AC

Three distinctive interaction types were obtained as result of MMH calculations, see Fig. 2. The first interaction type was predominant and it was observed between the chlorine atoms of CLD and CLDh with the π -cloud of coronene, indicating a relatively weak interaction (Fig. 3a). The bonding distance was in the range of 2.3 and 3.0 Å, suggesting van der Waals interactions between Cl atoms of CLD and CLDh and the planar configuration of coronene molecule. In fact, QTAIM results showed that the dispersive interactions are mainly due by van der Waals forces between chlorine atoms of pesticide and the graphitic surface in AC [2].

As a second interaction type, a donor-acceptor interaction can be described between the negatively charged oxygen of surface groups (COO^- and O^-) and electronically deficient carbonyl carbon of chlordecone: $\text{O}^- \cdots \text{CO}$ (Fig. 3b). This interaction has not been pre-

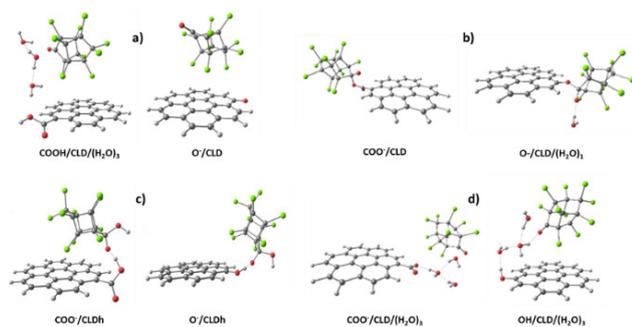


Figure 2: Distinctive interaction types of CLD and CLDh with the acidic surface groups onto AC. a) $\text{Cl} \cdots \pi$ -cloud interaction, b) $\text{O}^- \cdots \text{CO}$ interaction and c) $\text{C} - \text{OH} \cdots \text{O}^-$ interaction. Note in d) how water molecules network are between CLD and SGs.

viously described and it was observed only at slightly acidic and neutral pH conditions and is only present in charged systems. QTAIM calculations showed a few structures with $\text{O}^- \cdots \text{CO}$ interactions with weak to strong covalent bonds. This ratifies the idea of chemical sorption at slightly acidic and neutral pH conditions and reinforced the experimental results [2].

The third interaction type consists on an electrostatic interaction between the di-alcohol group of CLDh molecule and the negatively charged oxygen of SGs, represented as $\text{C} - \text{OH} \cdots \text{O}^-$ (Fig. 3c). QTAIM results confirmed this kind of interaction, but is important to explain that this interaction was found only at vacuum, (absence of water molecules). The interaction of CLDh with the acidic SG is favored through a dispersive (governed by van der Waals interactions of chlorine atoms of CLDh with the graphitic surface) and electrostatic interactions (H-bonding interactions of CLDh with SGs on AC in presence of water molecules [4].

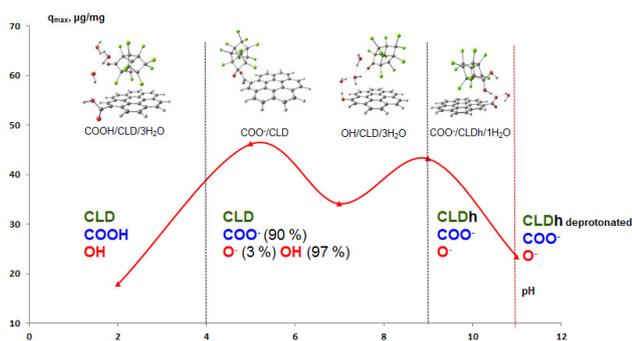


Figure 3: Relationship between experimental and theoretical results. The red line represents the absorption capacity of CLD on BagP0.5 with pH. (BagP0.5 is an AC obtained from sugarcane bagasse collected in Guadeloupe)

The formation of H-bonds and H-bond clusters of water molecules, when one or two molecules of water are close to the interaction site, has been also described through $\text{C} - \text{OH} \cdots \text{OH}_2$ hydrogen bonds (Fig. 3d).

The DFT optimization of the selected structures using CAM B3LYP/6-31+G(d,p) and M06-2X functional, showed in most of the cases that the structures conserved their geometry and the interaction type.

Taking into account the association energy, ΔE_{Assoc} , of the $\text{SG/CLD}/(\text{H}_2\text{O})_{n=1-3}$ and the $\text{SG/CLDh}/(\text{H}_2\text{O})_{n=1-3}$ systems, it was confirmed that there is no significant difference between obtained values of ΔE_{Assoc} at acidic, neutral and basic pH.

Summary

Theoretical and experimental results are in agreement [1, 2, 4], suggesting that the mechanism of adsorption of CLD on acidic surface groups of activated carbons at $\text{pH} \approx 5 - 7$ occurs through a chemisorption and a physisorption and at basic pH conditions through a physisorption. However, at $\text{pH} \approx 2 - 4$ and $\text{pH} > 9$, a very little dependence of the adsorption process of CLD on the SGs composition is observed (Fig. 3). The $-\text{COO}^-$ surface group have a higher influence over the contaminant adsorption than $-\text{O}^-$ group, confirming that an increase in carboxylic SG content is expected to enhance CLD adsorption onto AC, which are in agreement with experimental results [1].

Notes

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References

- [1] A. Durimel, S. Altenor, R. Miranda-Quintana, P. Couespel Du Mesnil, U. Jáuregui-Haza, R. Gadiou and S. Gaspard, *Chemical Engineering Journal*, **229** (2013) 239-349
- [2] J.J. Gamboa-Carballo, K. Melchor-Rodríguez, D. Hernández-Valdés, C. Enríquez-Victorero, A.L. Montero-Alejo, S. Gaspard and U. Jáuregui-Haza, *Journal of Molecular Graphics and Modelling*, **65** (2016) 83-93
- [3] C. Enriquez-Victorero, D. Hernández Valdés, A.L. Montero Alejo, A. Durimel, S. Gaspard and U. Jáuregui-Haza, *Journal of Molecular Graphics and Modelling*, **51** (2014) 137-148
- [4] K. Melchor-Rodríguez, J.J. Gamboa-Carballo, A. Ferino-Pérez, N. Passé-Coutrin, S. Gaspard and U. Jáuregui-Haza, *Journal of Molecular Graphics and Modelling*, **81** (2018) 146-154