# Theoretical study of γ-hexachlorocyclohexane and β-hexachlorocyclohexane isomers interaction with surface groups of activated carbon model

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## ARTICLE INFO

## ABSTRACT

Activated carbon (AC) is employed in drinking water purification without almost any knowledge about the adsorption mechanism of persistent organic pollutants (POPs) onto it. Hexachlorocyclohexane (HCH) is an organochlorinated contaminant present in water and soils of banana crops production zones of the Caribbean. The most relevant isomers of HCH are γ-HCH and β-HCH, both with great environmental persistence. A theoretical study of the influence of AC surface groups (SGs) on HCH adsorption is done in order to help to understand the process and may lead to improve the AC selection process. A simplified AC model consisting of naphthalene with a functional group was used to assess the influence of SGs over the adsorption process. The Multiple Minima Hypersurface (MMH) methodology was employed to study γ-HCH and β-HCH interactions with different AC SGs (hydroxyl and carboxyl) under different hydration and pH conditions. The results obtained showed that association of HCH with SGs preferentially occurs between the axial protons of HCH and SG's oxygen atom, and the most favorable interactions occurring with charged SGs. An increase in carboxylic SGs content is proposed to enhance HCH adsorption onto AC under neutral pH conditions. Finally, this work presents an inexpensive computer aided methodology for preselecting activated carbon SGs content for the removal of a given compound.

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## 1. Introduction

Hexachlorocyclohexane (HCH) is a monocyclic saturated chlorinated hydrocarbon of chemical formula $C_6H_6Cl_6$. HCH is synthesized, by photochemical chlorination of benzene. The synthesis product, a mixture of HCH isomers (67–70% of α-HCH (alpha-HCH), 10–12% of γ-HCH or lindane, 5–6% of β-HCH (beta-HCH), 6% of δ-HCH, traces of ε-, λ-and υ-HCH) is called "technical" HCH. Nearly 600,000 tons of HCH isomers were used in many countries of the world between the 1940s and the 1990s to control a wide range of agricultural, horticultural, and public health pests [1–6]. Indeed, heavily HCH contaminated sites have been reported in several countries such as The Netherlands [7], Brazil [8], Germany [9,10], Spain [11,12], China [13], Greece [14], Canada [15], the United States [15], and India [1,16]. HCH isomers can be detected in all environmental compartments, including water, sediments, air and biota [17], where they accumulate and then enter surface water as a result of runoff from agricultural land. Because of their suspected carcinogenic, persistent, bioaccumulative and endocrine disrupting properties [18,19], the use of Lindane has been banned in at least 52 countries and HCH isomers were then included to the POP Stockholm convention [20]. Lindane is the sole isomer having insecticide properties, nearly 90% of the HCH mixture are inactive isomers [21]. Because of their low vapour pressure ($4.69 \times 10^{-3}$ to $1.25 \times 10^{-3}$ Pa), hexachlorocyclohexane isomers evaporate slowly from soil and surface waters. Their high sorption coefficient to organic carbon ($K_{oc} \approx 3.57$) shows its excellent affinity for organic matter rich soils. The β-HCH is the isomer with the higher mobility and the α-HCH isomer is persistent in soils. The α-HCH and the γ-HCH isomer are the most dispersed in all media (air, soils, water), α-HCH and β-HCH isomers can be

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transported by air [22–25]. Technical HCH was used in banana plantation of the French West Indies Islands, Guadeloupe and Martinica, since 1951 to prevent the development of parasite such as banana weevil (*Cosmopolite sordidus*) which attacks the roots of this plant. Its use was then banned in 1972. Therefore, more than forty years after HCH has been banned the molecule can be found in soils, water and the food chain in Guadeloupe and Martinica [26]. To limit impregnation to pesticides, in the polluted areas of Guadeloupe and Martinica, drinking water production plants were equipped with activated carbon filters.

The adsorption process onto activated carbon (AC) is a very complex phenomenon driven by multiple factors that range from chemical composition to textural properties of the AC. The influence of surface group content over adsorption properties has been reported and studied to some extent both theoretically and experimentally for porous carbons, mainly AC and soot particles [27–32]. In the experimental works, either commercial AC with different SG content have been used in order to correlate this content with the adsorption capacities, or designed and tested AC with different SG contents. Even though, modifying the SGs content can lead to changes in the hydrophilic/lipophilic balance, the modifications should guarantee the specific design purpose. In this regard the computational chemistry can play a major role in designing specific modifications to obtain more efficient and specific adsorbents [31,33].

In order to get information on structural and textural properties favoring HCH adsorption on AC, Durimel et al. attempted to correlate adsorption studies data to some activated carbons surface functional groups composition. This study demonstrated that β-HCH adsorption was favored by the presence of high amounts of acidic groups at the AC surface, suggesting that hydrogen bonds were involved in adsorption mechanism [34]. To get more insight on the adsorption mechanism of HCH onto AC this work will focus on the most elementary factor i.e. the influence of some different SG over the adsorption energy. In this work, the interactions of both isomers of HCH (γ and β) with two SGs of AC are studied using multiple minima hypersurface (MMH) methodology [35–38]. MMH is a non-dynamical stochastic approach that allows estimating the thermodynamic association functions by means of the internal energy calculations with semiempirical Hamiltonians. In a previous work, exploring the interactions space through MMH methodology has helped to identify the main interactions responsible for chlordecone adsorption in a similar system [39].

This research will permit to design a methodology to evaluate the influence of SGs over the adsorption of small molecules onto AC allowing to help designing the best AC for the removal of a particular compound. It is important to note that focus is on finding the SGs improving the adsorption process.

## 2. System under study

Computational methods have been used widely to investigate the adsorption energies of guest molecules to idealized models of carbon-based materials. However, it is important to bear in mind that the description of the interactions between guest molecules and carbon surfaces is still challenging with current theoretical techniques. For these idealized models of carbon based materials, small polycycles and their oxidized derivatives are a common choice [27,40–50]. In fact, naphthalene [40,42] and coronene [41,45–47] have repeatedly been employed as such idealized models. The use of such small models has both advantages and disadvantages, being the most obvious of the advantages the savings in computational resources allowing either the application of relatively high level calculations or a throughout exploration of the interactions space. Small carbon models such as the naphthalene

allows the use of most quantum chemical methods and the correct description of non-local correlations as well as the evaluation of zero point and thermal contributions to the enthalpy [45] or the application of energy partition schemes to analyze binding characteristics.

Obviously, the use of these idealized models brings alone negative size effects and, in some cases, the oversimplification of the structure. The dramatic reduction in size of these models with respect to the real structures can reduce the non-local contributions to the dispersion energies. In the specific case of AC, the use of oxidized forms of polycycles completely neglects the influence of pore shape, defects, pore size and pore connectivity but in return allows a quantum chemical description of the interactions with the adsorbed molecules.

In a previous work, Durimel et al. showed that lindane adsorption onto the studied ACs is not diffusion controlled [34]. In order to center our attention in the SGs influence over the adsorption process, the selected AC model for the simulations consists of naphthalene with a functional group attached, as shown in Fig. 1 together with γ- and β-HCH structures. As surface groups, carboxylic acid (COOH) and hydroxyl (OH) both directly attached to sp2 carbons were selected since these are the most commonly encountered and abundant oxygenated SGs found on AC surface [34,51,52]. To account for different pH conditions, chemical modifications to the SGs i.e. COO$^-$ and O$^-$ respectively were included. This model for AC does not take into account morphological or topological characteristics of the AC, but focuses on SG interaction with adsorbate, which is the main goal of this work.

The main advantage of this simple model is that it allows a big number of calculations while retaining the main feature of AC we are interested in (i.e. edge surface groups influence over adsorption processes).

## 3. Methods and procedures

In order to explore the conformational space corresponding to the interaction of each SG with water and both HCH isomers, multiple minima hypersurface procedures were applied (MMH) [35–38]. MMH is a very useful and reliable approach for localizing the minima of weakly interacting systems and, therefore, it has been successfully employed in several studies [53–60]. This procedure combines quantum mechanical methods for the calculations of energy with statistical mechanics to obtain thermodynamic quantities related to the molecular association process. The main procedure of this approach will be outlined briefly.

An appropriate construction of several random molecular geometries initially generates a set of n non-redundant cluster configurations, starting from the independently optimized structures of AC, γ-HCH, β-HCH and water. The random structures are optimized, normally following an energy gradient pathway, and a set of clusters of local minima in the configuration space is obtained. The energy, $\varepsilon_i$, of every $i$th cluster of the ensemble is thus obtained.

The partition function of molecular association is calculated by choosing the same set of non-interacting molecules as reference value for the energy scale, which means that the association process is taken as isothermal.

Thermodynamic properties such as association energy ($\Delta E_{assoc}$), entropy ($S_{assoc}$), and Helmholtz free energy ($A_{assoc}$) are then calculated by this procedure [36,37].

The standard MMH procedure [36] put the solute in the center of a cubic box and then generates the solvent molecules in random configurations. By this procedure, the space region for generated solvent molecules cannot be restricted [38]. The above mentioned procedure combined with the model used here, would lead to an inefficient exploration of the interesting interaction