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## Molecular modelling and molecular dynamics studies of HCH and chlordecone adsorption on activated carbon surface

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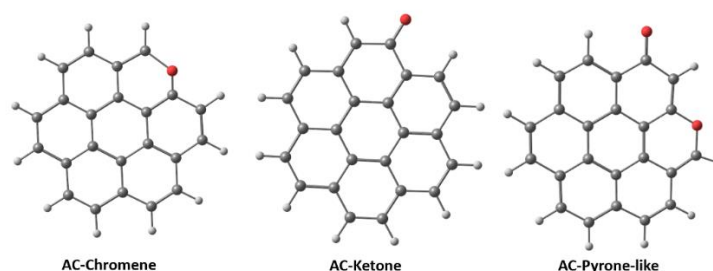
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**Keywords:** chlordecone; beta-hexachlorocyclohexane; water treatment; activated carbon; molecular modeling, molecular dynamics

### Extended abstract:

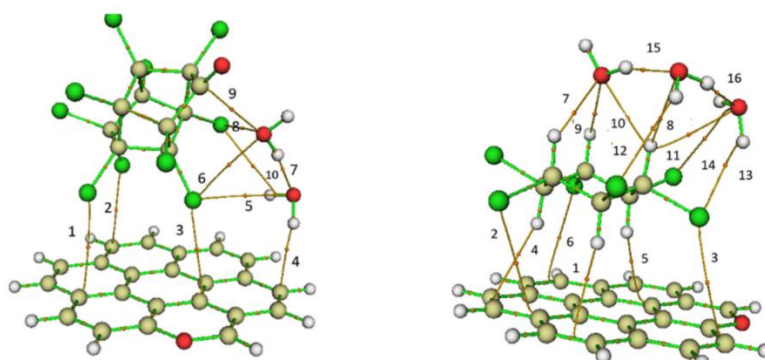
In the 1950s, banana fields in the French West Indies were infested by a parasite called *Cosmopolitan Sordidus*. To face this invasion, farmers had to use organochlorine phytosanitary products. One of them,  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH) (CAS: 58-89-9), usually known under the name of lindane have been massively used to treat banana fields but the parasites developed resistance. Chlordecone (CLD) (CAS: 143-50-0) has been the most common substitute. In 1975, the Life Science Products Company was manufacturing Kepone® (commercialized name of CLD) at Hopewell USA, when many of its workers have been sick [1]. Blood tests have showed a high presence of this pesticide indicating the neurotoxicity of chlordecone [2]. After this chemical disaster, CLD was banned from the United States 2 years later. The use of this pesticide was only banned in 1991 in the French West Indies. For about twenty years, the ground has been soiled with this pesticide causing pollution of various ecosystems such as agricultural land [3], water sources [4], products from agriculture [5], local fishing [6]. Consequently, the local populations have been highly exposed [3-6]. On 22 May 2001, the Stockholm Convention certified that CLD and hexachlorocyclohexane (HCH, the  $\beta$  form being the most recalcitrant isomer) are persistent organic pollutants (POPs). These two organochlorine molecules are toxic to the human organism.  $\beta$ -hexachlorocyclohexane ( $\beta$ -HCH) is an endocrine disruptor [7]. CLD is responsible of the high rate of prostate cancer in the French West Indies [8,9]. One of the most used way for removing these pollutants from water is the utilization of activated carbon (AC). AC wearing basic surface groups (SGs) have been obtained by steam activation whereas AC with acidic (SGs) have been elaborated when phosphoric acid  $H_3PO_4$  has been used as activating agent [12]. The porous structures of AC allows to trap on its surface molecules via a phenomenon called adsorption [13]. It has been shown an enhancing of this phenomenon specially when CLD was in presence of AC with carboxylic acid SGs [14]. From that results, theoretical studies have been led by our team to study the influence of acidic and nitrogen containing surface groups of activated carbon model on the adsorption of CLD and ( $\beta$ -HCH), considering pH and hydration effect. These interactions using acidic SG at neutral pH have revealed a chemisorption whereas nitrogen basic SGs have shown a physisorption. In fact, the interactions were governed by dispersive interactions of chlorine atoms of the pollutants with the graphitic surface and by electrostatic interactions with  $COO^-$  and  $O^-$  acidic groups and water molecules. For nitrogenous basic SGs, the results showed a greater association of both pesticides with the primary amine in comparison with the pyridine, secondary and tertiary amine in the absence and presence of water molecules, and this behavior increase at acidic pH conditions where the amines and pyridine are protonated [15].

Here, a theoretical study of the interactions of these pesticides with oxygenated SG of AC is reported. A molecule of coronene with a functional group whether it be pyrone, chromene or ketone in the edge, was used as a simplified model of AC [15–21] (**figure 1**).



**Figure 1.** Structures of basic oxygen surface groups on coronene molecule as activated carbon model (grey: carbon, white: hydrogen, red: oxygen)

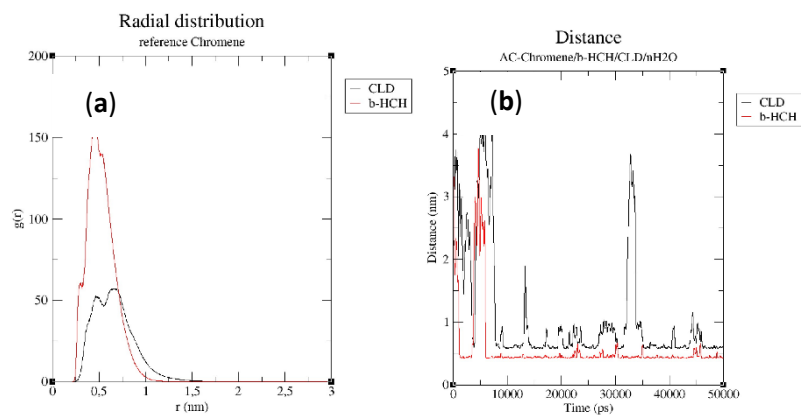
Multiple Minima Hypersurface methodology was employed to study the interactions of CLD and  $\beta$ -HCH with SGs on AC using PM7 semiempirical Hamiltonian. The principal aim of this methodology is to calculate the variation of the association energy  $\Delta E_{association}$  which describe the stability of adsorption of POPs by AC. A further re-optimization of obtained structures was done for pesticide-AC complexes by means of Density Functional Theory. To choose these SGs, the lowest value of association energy was the criteria (MMH-PM7 and DFT results). The Quantum Theory of Atoms in Molecules was used to characterize the interaction types using the Nakanishi criteria. No interactions have been shown at acidic pH for both pollutants whereas dispersive interactions have been found at neutral and basic pH explaining a physisorption process (**figure 2**).



**Figure 2.** Interactions and bond paths obtained by QTAIM for distinctive minima structures of the systems Chromene/CLD/2H<sub>2</sub>O and Chromene/ $\beta$ -HCH/3H<sub>2</sub>O

The two best AC surface groups for adsorption (AC-chromene and AC-pyrone) have been selected and have been performed with the molecular dynamics simulation (MDs) and the same findings have been illustrated (**figure 3**).

This study has shown the possibility of the adsorption of  $\beta$ -HCH and chlordecone by basic oxygen activated at neutral and basic pH means by quantum mechanics calculations and molecular dynamics simulation. In fact, the adsorption of  $\beta$ -HCH is better than CLD with basic activated carbon and joined the previous study about nitrogen basic SG by Melchor *and al.*[19]. MDs confirm the better adsorption of  $\beta$ -HCH on graphitic surface basic oxygen-containing than CLD. Furthermore, MDs was brought information about competition adsorption with the two organochlorine pesticides and has shown repulsive interaction. At the end, the adsorption process of CLD or  $\beta$ -HCH on an AC is enhanced with acidic SG as shown in our previous studies (chemisorption) rather than basic SG.



**Figure 3.** Distance between AC and pesticide molecules as a function of time: **(a)** radial distribution between AC-Chromene with  $\beta$ -HCH and CLD during competition adsorption; **(b)** Distance between AC-Chromene with  $\beta$ -HCH and CLD during competitive adsorption.

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