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pH dependence of chlordecone adsorption on activated carbons and role of adsorbent physico-chemical properties

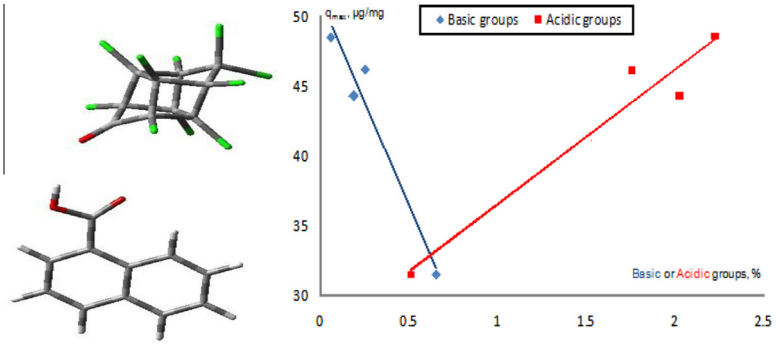
A. Durimel [a], S. Altenor [a], R. Miranda-Quintana [b], P. Couespel Du Mesnil [c], U. Jauregui-Haza [b], R. Gadiou [d], S. Gaspard [a,*]

[a] Laboratoire COVACHIMM, EA 3592 Université des Antilles et de la Guyane, BP 250, 97157 Pointe à Pitre, Guadeloupe, French West Indies, Cedex, France
[b] Facultad de Medio Ambiente, Instituto Superior de Tecnologías y Ciencias Aplicadas, Salvador Allende y Luaces, La Habana, Cuba
[c] Institut Pasteur de Guadeloupe, Morne Jolivière, 97183 Abymes, Guadeloupe, French West Indies, France
[d] Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, 15 rue Jean Starky BP 2488, 68057 Mulhouse, Cedex, France

HIGHLIGHTS

- Chlordecone adsorption isotherms on activated carbons are well described by the Fowler–Guggenheim/Jovanovic–Freundlich model.
- Carboxylic groups at AC surface plays a major role for CLD adsorption.
- Higher amount of CLD is adsorbed at pH = pH_{pzc}, when the surface is not charged.
- Model structures of molecular interactions of chlordecone with the surface functional groups are shown.

GRAPHICAL ABSTRACT



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ABSTRACT

From the 1960s to the 1990s, the large-scale production of banana in the French West Indies required an intensive use of chlorinated pesticides, such as chlordecone (Kepone), resulting in the diffuse contamination of soil and surface waters in the banana-producing areas. For this reason, drinking water plants were equipped with filters containing commercial activated carbons, being one of the challenges to find local adsorbents for the sustainable management of water treatment plants. In this paper, the adsorption of chlordecone (CLD) on activated carbons (ACs) prepared from sugar cane bagasse is studied, aiming to understand the mechanism of CLD adsorption on the AC surface. First, textural, acido-basic and chemical characteristics of the ACs were determined by thermal desorption, X-ray photoelectron and Boëhm studies. Adsorption isotherms of CLD show that the adsorption capacity increases with the amount of carbon and acidic groups at the AC surface whereas basic groups, hydroxyl and ether groups are detrimental to adsorption. The adsorption capacity is maximized at a solution pH level equal to the pH_{pzc} of the considered AC. From temperature programmed desorption studies, it is proposed that chlordecone adsorption mechanism onto ACs is mainly governed by interaction with carboxylic groups. These results were correlated to molecular modeling studies of CLD interactions with surface functional groups of AC. The models of preferential positions, corresponding to minimal value of association energy, of interactions between CLD and AC functional groups were obtained.

* Corresponding author. Tel.: +33 590 590 48 33 79.
E-mail address: sgaspard@univ-ag.fr (S. Gaspard).

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1. Introduction

Since the 1960s, the French departments of Guadeloupe and Martinique have based their economy on two major agricultural productions: banana and sugarcane crops. To prevent the propagation of the banana weevil (*Cosmopolite sordidus*), which attacks the roots of the banana tree, chlorinated pesticides, such as chlordecone (CLD), hexachlorocyclohexane (HCH) and dieldrine were extensively used until the beginning of the 1990s, resulting in the contamination of soil and surface waters [1,2].

Chlordecone was used since 1972 and then definitely banned in early 1993. In 2009, kepone was included in the Stockholm Convention on persistent organic pollutants, which bans its production and use worldwide [3].

Chlordecone ($C_{10}H_{10}O$, is the common name of decachloropentacyclo[5.3.0.02.6.03.9.04.8]decan-5-one (CAS 143-50-0) (Fig. 1) has a high molecular weight (490.64 g/mol), a low solubility in water (2.7 mg at 25 °C) and its vapor tension is less than 2.25×10^{-7} mmHg at 25 °C [4]. Its partition coefficient K_{oc} varies from 2000 to 2500 L/kg, depending on soil physico-chemical properties [1]. Due to its strong persistence in natural environments, its high resistance to chemical reactions and microbiological degradations, around 8–9% of the cultivation areas of Guadeloupe contain CLD concentrations higher than 1 mg/kg in topsoil, and some banana fields exhibit CLD content higher than 9 mg/kg [1]. CLD may be bound to soils for several decades to half a millennium, depending on soil type [1]. CLD has a strong affinity for lipids, accumulates in the food chain [5,6] and is known for its endocrine-disrupting character [7,8] and its carcinogenic potential [9–11]. In order to limit impregnation of the population by CLD in Guadeloupe and Martinica, drinking water and production plants were equipped with activated carbon filters.

Indeed, activated carbon is commonly used for treating water, especially to remove pesticides from contaminated water [12–16]. There is, however, no available research data on chlordecone adsorption by activated carbons or by other any sorbent. In this research work, sugarcane bagasse activated carbons (SCB ACs) were prepared and used to remove CLD from contaminated water. Preparation of activated carbons from sugar cane bagasse a by-product of sugar industry, has already been the subject of other studies [17–21]. Sugar cane bagasse allowed the production of ACs with interesting textural and adsorption properties [17,20,21]. The use of this renewable resource provides a sustainable cleaning process, because a high value product is obtained from a low cost material, and, simultaneously, it brings, solutions to the problem of wastes and local water pollution. We prepared SCB ACs containing large micropores and small mesopores with different pore size distribution and chemical groups at their surface. Since the size of the molecule is below 1 nm, these kinds of pores are expected to be the most efficient for CLD adsorption. Adsorption isotherm studies of CLD onto SCB ACs were done. The influence of solution pH, activated carbon surface properties and textural characteristics of the adsorption of CLD onto SCB ACs was also investigated. These results were correlated to molecular modeling of CLD interactions with surface functional groups of AC. Overall, the results obtained from this study allow us to bring some understanding to the adsorption mechanism of chlordecone onto ACs.

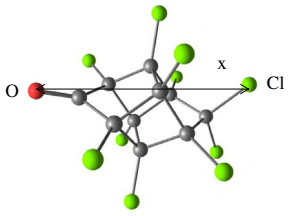

Fig. 1. Structure of CLD molecule. Calculated critical dimensions: $x = 6.52$ Å, $y = 5.89$ Å and $z = 5.30$ Å.

2. Experimental method

2.1. Chemicals

Chlordecone (97.5%) was provided by Cluzeau Info Laboratory. All safety and preventive measures were taken during all experiments. The operator wearied protective equipments, appropriate mask and gloves All CLD containing samples were prepared and handled in a laboratory hood. CLD containing wastes were segregated and disposed in appropriate wastes containers. The structure of the molecule (Fig. 1) was studied with MOPAC software [22].

2.2. Activated carbons: preparation

The ACs were obtained from sugarcane bagasse collected in Guadeloupe, French West Indies. In this experiment, two conventional methods of AC preparation described in [23] were used. Sample prepared by steam activation was denominated BagH_2O. Those prepared by phosphoric acid (H_3PO_4) activation with impregnation ratio, X_P, g H_3PO_4/g precursor: 0.5:1, 1:1 and 1:1.5, are called: BagP0.5, BagP1and BagP1.5, respectively. AC samples with particle size ranging between 0.4 and 1 mm were used for further experiments.

2.3. Activated carbon characterization

The textural characterization of the produced ACs was carried out by N_2 adsorption at 77 K using a Micromeritics model ASAP-2020 analyzer. The total surface area was determined by the BET method (S_{BET}) while microporous surface (S_{micro}), external surface (S_{ext}), total pore volume (V_T) and micropore volume (V_{mi}) were obtained by the t-plot method. The mesopore volume (V_{me}) was computed by applying the BJH method on the desorption branch and the mean pore diameter (D_p) was calculated by the equation $4 * V_T/S_{BET}$ [22].

The percentage of the surface functional groups of the ACs was estimated by X-ray Photoelectron Spectroscopy (XPS). XPS measurements were conducted on an Axis-Ultra DLD Model Kratos, equipped with a hemispherical electron analyzer and Al Kα (1253.6 eV) X-ray exciting source, as described in [23].

The total surface basicity and acidity of the samples and the pH at point of zero charge (pH_{pzc}) were measured as described in [23].

2.4. Chlordecone quantification

Quantification of CLD was carried out using a liquid chromatographer equipped with a mass spectrophotometer (AGILENT LC/MS 1100 series system). Ionization of chlordecone was achieved by electrospray (API-ES) in negative ion mode. The final parameters of the nebulizer chamber were defined as follow: drying gas flow: 12 L/min; temperature of drying gas: 350 °C; pressure of atomizer: 35 psi; capillary tension: 4000 V; and collision energy: 50 eV. The product-ion mass spectra of CLD were m/z 507 and 509. The LC/MS analysis were carried out using a C8 column (2.1 × 150 mm, Eclipse X08-C8). The LC separation was performed at 80 °C using a gradient composed of water and acetonitrile (ACN). The gradient changed as follow: 0–6 min 55% of ACN, 6–7 min increasing to 100%.