



HAL
open science

Hemicryptophane: A viable supramolecular approach to improve chlordecone removal from water

Oriane Della-Negra, Marie Poujade, Delphine Muselet, Sabine Chevallier-Michaud, Jean-pierre Dutasta, Bastien Chatelet, Pierre-Loïc Saaidi, Alexandre Martinez

► To cite this version:

Oriane Della-Negra, Marie Poujade, Delphine Muselet, Sabine Chevallier-Michaud, Jean-pierre Dutasta, et al.. Hemicryptophane: A viable supramolecular approach to improve chlordecone removal from water. *ChemistrySelect*, 2024, 9 (4), pp.e202304107. 10.1002/slct.202304107 . hal-04444017

HAL Id: hal-04444017

<https://hal.science/hal-04444017>

Submitted on 7 Feb 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hemicryptophane: A Viable Supramolecular Approach to Improve Chlordecone Removal from Water

Oriane Della-Negra,^[a] Marie Poujade,^[a, b] Delphine Muselet,^[b] Sabine Chevallier-Michaud,^[a] Jean-Pierre Dutasta,^[c] Bastien Chatelet,^[a] Pierre-Loïc Saaidi,^{*[b]} and Alexandre Martinez^{*[a]}

The persistent organic pollutant chlordecone massively contaminates water resources of the French West Indies. Hemicryptophanes are cages capable of complexing chlordecone in organic solvents. Here we demonstrate that a hemicryptophane cage is not only able to recognize this pollutant in chloroform but is also efficient for the removal of chlordecone from water. This evidences that, beyond our previously reported proof of

concept, this receptor could be apply as a direct and efficient depolluting agent, making it a promising system for applied supramolecular chemistry. A simple pH switch (basic washing) enables the release of chlordecone from the host, under its deprotonated form, allowing the empty supramolecular cage to be recycled and reused. This method for recycling the receptor, is to the best of our knowledge unprecedented.

Introduction

Chlordecone is an organochlorine pesticide, produced and used worldwide in the 20th century, which has been classified as a Persistent Organic Pollutant since 2009.^[1] The perchlorinated bishomocubane structure of the molecule gives it specific physicochemical properties such as a high hydrophobicity (solubility estimated at about 2 mg/L in water at pH 7) and a strong affinity for organic matter.^[2–4] Due to cyclic constraint and electron withdrawing effects, the ketone moiety of chlordecone (C₁₀Cl₁₀O) can readily hydrate to give chlordecone hydrate (C₁₀Cl₁₀O₂H₂), both in the neat form and in organic solution (benzene, acetone, acetonitrile) when exposed to air moisture (Figure 1a).^[5–6] This predominant hydrated form was taken into account throughout this study.

Massively used to control the banana black weevil in the French West Indies from 1972 to 1993, this pesticide is responsible for a long term pollution of the environment (hydric system, soils, sediments and plants),^[1] resulting in the contamination of the food chain and, consequently, the exposure and the poisoning of the French West Indian population. Its well-

known toxicity and persistence are responsible for significant public health, social and economic problems.^[7–10] More specifically, water represents an important vector for the spread of contamination, since chlordecone contaminates groundwaters, and therefore the drinking water pool.^[11–16] Indeed, regular monitoring of the surface and ground waters of the FWI show that chlordecone represents by at least one order of magnitude the main organic pollutant.^[17] Currently, water purification plants are equipped with activated carbons, the most widespread adsorbent material, that allows the retention of chlordecone. However, it has some limitations in terms of pollutant uptake speed (hours), time of use, saturation limit, and recyclability. Indeed, the regeneration of activated carbons is energy consuming and does not fully restore their performance.^[18] Other materials are currently being studied to decontaminate water and remove heavy metals and organic pollutants. These include biochars and biosorbents, known to adsorb chlordecone due to its strong affinity for organic matter,^[19,20,21] and water falling film reactors, which, when coupled with advanced oxidation processes, simultaneously degrade these compounds.^[22] Here, we wanted to address this issue through the prism of supramolecular chemistry. Recent advances have shown that the use of materials with non-covalent interactions is very promising as they can undergo reversible self-assembly and offer advantages in terms of specific recognition properties (by size of chemical structures and functions) and recyclability.^[23–25] Cyclodextrins are one of the most described supramolecular hosts for pollutants encapsulation and remediation. These hosts have a central cavity, relatively hydrophobic, and a hydrophilic exterior constituted of hydroxyl groups coming from the sugar residues (Figure 1b).^[24] They are water-soluble and non-toxic and were found to encapsulate chlordecone. First experiments performed in 2016 showed that γ -cyclodextrin formed an insoluble complex with chlordecone in water that could be removed by filtration.^[26] This cyclodextrin covalently bound to nanoporous carbon was found efficient for the removal of p-nitrophenol and several organochlorine pesticides in water.^[26–27] Other research labora-

[a] Dr. O. Della-Negra, M. Poujade, Dr. S. Chevallier-Michaud, Dr. B. Chatelet, Prof. Dr. A. Martinez
Aix Marseille Univ, CNRS, Centrale Marseille, iSm2, Marseille, France
E-mail: alexandre.martinez@centrale.marseille.fr

[b] M. Poujade, D. Muselet, Dr. P.-L. Saaidi
Génomique Métabolique, Genoscope, Institut François Jacob, CEA, CNRS, Univ Evry, Université Paris-Saclay, Evry, France
E-mail: plsaaidi@genoscope.cns.fr

[c] Dr. J.-P. Dutasta
ENS de Lyon, CNRS, Laboratoire de Chimie UMR 5182, 46 Allée d'Italie, 69364 Lyon, France

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.202304107>

© 2024 The Authors. ChemistrySelect published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

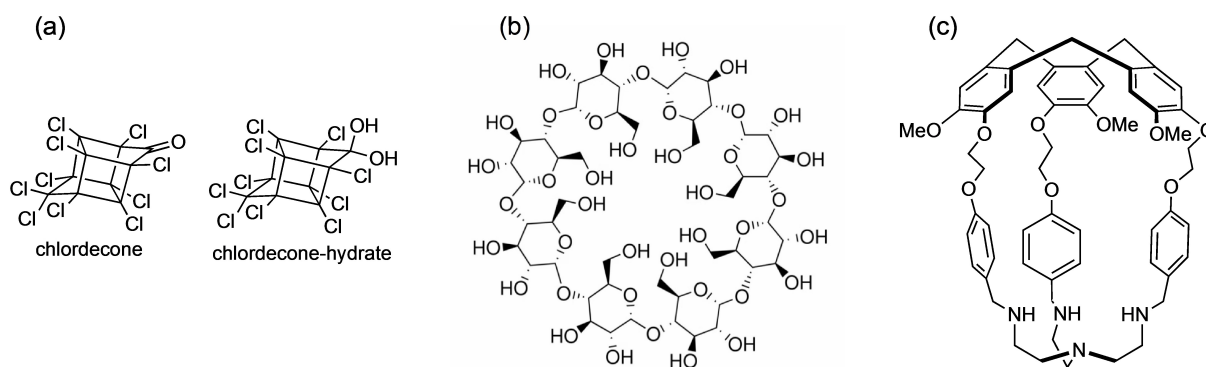


Figure 1. Structures of (a) chlordecone and its hydrated form, (b) γ -cyclodextrin, (c) hemicryptophane used in this study.

studies have also incorporated cyclodextrins within polymers, nanoporous carbons or molecular printed polymers, to improve retention properties toward various water pollutants with great recovery efficiency.^[18,27–30]

In our case, we considered the use of hemicryptophane supramolecular hosts made of a cyclotrimer of 4-aminobenzene (CTV) unit linked to a C_3 -symmetrical platform.^[31] Unlike cyclodextrins, these hosts have the property of being easily modulable in shape and size to specifically recognize well-defined guests.^[32–36] In particular, after a previous study aiming at synthesizing and comparing different hosts of variable size, shape, and chemical functions, we were able to identify a hemicryptophane containing the C_3 -symmetry moiety tris(2-aminoethyl)amine (tren), optimized to encapsulate chlordecone with a good affinity constant (2.1×10^4 L/mol in $CDCl_3$) (Figure 1c).^[33,37] In this context, we have also synthesized fluorescent analogues and showed that the fluorescent properties of some hemicryptophanes changed with chlordecone encapsulation. This allowed us to propose a system of detection and quantification of chlordecone in water by fluorescence monitoring.^[38] In the present study, we took benefit from our exploratory survey in order to propose a novel approach for removing chlordecone from water by filtration. Compared to our previous study that was performed in organic solvents, here chlordecone is directly complexed from a water solution. This demonstrates that the complexation of this pollutant does not only take place in chloroform but can also be directly applied to polluted water. Understanding the specific host-guest interactions between chlordecone and hemicryptophane enabled us to recycle the supramolecular host by means of a simple basic washing, providing an original and unprecedented way to recycle a receptor after chlordecone complexation.

Experimental Section

Chlordecone filtration (monitored by GC-MS)

Chlordecone was solubilised in 100 mL of milliQ water (pH 7.4) at a concentration of 1 mg/L and the selected cage (hemicryptophane or γ -cyclodextrin at 1.1 or 5 equivalents compared to chlordecone) or the material (0.2 mg or 1.3 mg of MCM-41, hemicryptophane

physisorbed on MCM-41 or activated carbon) was added. The resulting mixture was stirred for 30 minutes then filtered either on cotton or sintered glass. 0.1 mg of 10-monohydrochlordecone A1 ($C_{10}Cl_9O_2H_3$) was added as internal standard to the filtrate which was then acidified with 100 μ L of HCl 6 M and extracted with chloroform (3 \times 50 mL). The combined organic layers were evaporated and the residue was solubilised in 1 mL of chloroform prior to GC-MS injection (see supplementary information). Experiments were done in duplicate.

Chlordecone filtration (monitored by NMR)

Chlordecone was solubilised in 1 L of milliQ water (pH 7.4) at a concentration of 1 mg/L (2.0×10^{-6} M) and 1.1 equivalent (2.2×10^{-6} M) of hemicryptophane was added. The resulting mixture was stirred for 30 minutes then filtered on cotton. The cotton was washed with 50 mL of chloroform that was then evaporated and the residue was solubilised in 750 μ L of deuterated chloroform prior NMR analysis. Experiments were done in duplicate.

Hemicryptophane recovery (monitored by NMR)

To test hemicryptophane recycling, the steps described in supporting information, section 1.4 were followed until the filtration. The filter was then washed with 100 mL of NaOH 1 M and 50 mL of chloroform. Chloroform was then evaporated and the residue was resolubilised in 750 μ L of deuterated chloroform prior NMR analysis. Experiments were done in duplicate.

Hemicryptophane-chlordecone decomplexation (monitored by NMR)

Chlordecone and hemicryptophane were solubilised in 750 μ L of deuterated chloroform at a final concentration of 7 mM and put in an NMR tube. Successive additions of NaOD 1 M in D_2O were performed and each time a 1H NMR spectrum was recorded.

Results and Discussion

Chlordecone removal from water by filtration using supramolecular hosts and materials

In the present work, we focused on γ -cyclodextrin (Figure 1b) that showed the best encapsulation properties among the

tested cyclodextrins,^[22] as well as on the hemicyptophane depicted in Figure 1c, displaying the greatest affinity constant among the hemicyptophanes previously studied.^[33,37]

We first explored the chlordecone retention properties of these structures according to the protocol already described.^[26] Briefly, chlordecone was solubilized in milliQ water (pH 7.4) at a concentration of 1 mg/L, below its solubility limit estimated at 2.2 mg/L, and the selected cage or material (vide infra) was added. The resulting mixture was stirred for 30 minutes then filtered either on cotton or sintered glass. Convenient and reliable extraction and quantification protocols were developed: the filtrate was acidified with HCl, extracted with chloroform and analysed by GC-MS, using 10-monohydrochlordecone as internal standard (for complete protocol, see SI). In addition to the two selected cages (γ -cyclodextrin and hemicyptophane), three adsorbent materials were compared: activated carbon, MCM-41 mesoporous silica,^[38] and the hemicyptophane physisorbed on MCM-41. MCM-41 was chosen for its specific hexagonal structure, its unidirectional system of pores,^[38] and its properties. In several studies it has been used for its ability to remove highly diluted pollutants from water (organic molecules and heavy metals), and for molecular recognition through adsorption in the nanostructure.^[39,40] In this way it constitutes an economical, efficient, low-cost, easy to use and eco-friendly material which can allow the reuse of the adsorbent and the adsorbate after its removal. Additionally, it is known that parent cryptophane hosts can be physisorbed on this kind of material.^[37] so we wanted to combine the MCM-41 abilities with the specific recognition properties of the selected hemicyptophane.

Figure 2 shows the results obtained using 1 equivalent (compared to chlordecone) of cages: γ -cyclodextrin retained on average $17 \pm 6\%$ of chlordecone, whereas for the hemicypto-

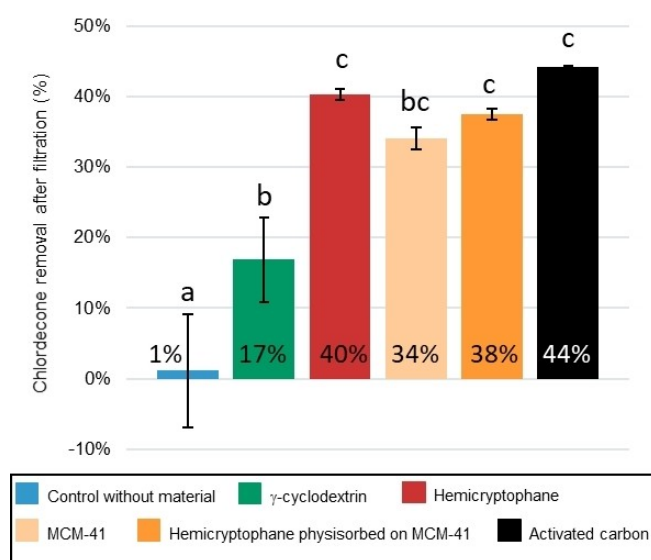


Figure 2. Chlordecone removal (%) after filtration of water (pH = 7.4) spiked with chlordecone at 1 mg/L, in the presence of various cages/materials. Chlordecone removal was determined from GC-MS analyses of the organic phase after liquid-liquid extraction (see details in SI). Letters indicate significant differences between groups (one-way ANOVA).

phane the retention rate was $40 \pm 1\%$. Hence, the hemicyptophane cage was found to be more than twice as effective in trapping chlordecone in water than the most efficient cyclodextrin. The complexation of chlordecone by cyclodextrins mainly involved Van der Waals interactions,^[41] whereas hydrogen bonding interactions have also been evidenced when using hemicyptophane hosts.^[33] This could account for the best efficiency of this last cage. The same experiments were carried out using 0.2 mg of the different materials (Figure 2): MCM-41 mesoporous material alone allowed to remove $34 \pm 2\%$ of the pesticide, while the physisorption of hemicyptophane on this matrix increased very slightly the performance (up to $38 \pm 1\%$). A comparable result was obtained with activated carbon, whose retention performance reached $44 \pm 1\%$. The significant adsorption of chlordecone onto the MCM-41 mesoporous silica can be explained by (i) the size of MCM-41 nanochannels (diameters of 20–30 Å),^[40] large enough to allow chlordecone to enter (size estimated at 4–5 Å), and (ii) the formation of hydrogen bonding between the gem-diol function of chlordecone, present in its hydrated form, and the silanol groups of MCM-41. Protonation of the basic tren unit of the hemicyptophane cage, when physisorbed on this acidic silica support, might affect its complexation properties.^[43] Thus, it could account for the lack of significant improvement that was expected from the physisorption of the hemicyptophane on this mesoporous material. Indeed, the complexation of chlordecone by hemicyptophane hosts strongly depends on the size, shape of the cavity and on functional groups located in the lower part of the cage.^[33,37] Using five cage equivalents or increasing the amount of material used to 1.3 mg did not significantly change the results (See SI Figure S1 and Table S1), in agreement with the Le Chatelier's rule related to the addition of an excess of heterogeneous compounds to an equilibrium. The same order of magnitude was obtained in the previously published study (up to 70%).^[30]

Iterative series of hemicyptophane addition and filtration steps were performed. (Figure 3a). The trend observed after the successive filtration steps could be modelled via the following equation (1):

$$\ln\left(\frac{[CLD]_{C,tot,n} - [CLD]_{aq,0}}{[CLD]_{aq,0}}\right) = \ln(|\tau - 1|) + (n - 1) \times \ln(1 - \tau) + \ln([CLD]_{aq,0})$$

where n is the number of successive filtration steps, $[CLD]_{C,n}$ chlordecone concentration which has been complexed by the hemicyptophane at step n , $[CLD]_{C,tot,n}$ the total chlordecone concentration that has been complexed by the hemicyptophane after n filtration steps, $[CLD]_{aq,0}$ chlordecone concentration in the aqueous layer at $n = 0$ (1 mg/L, 2.0×10^{-6} M), and τ a complexation constant estimated at 0.24 (equation (2), see SI):

$$\tau = \frac{[CLD]_{C,tot,n} - [CLD]_{C,tot,n-1}}{[CLD]_{aq,n-1}}$$

More details about the assessment of equation (1) are available in the supplementary information file.

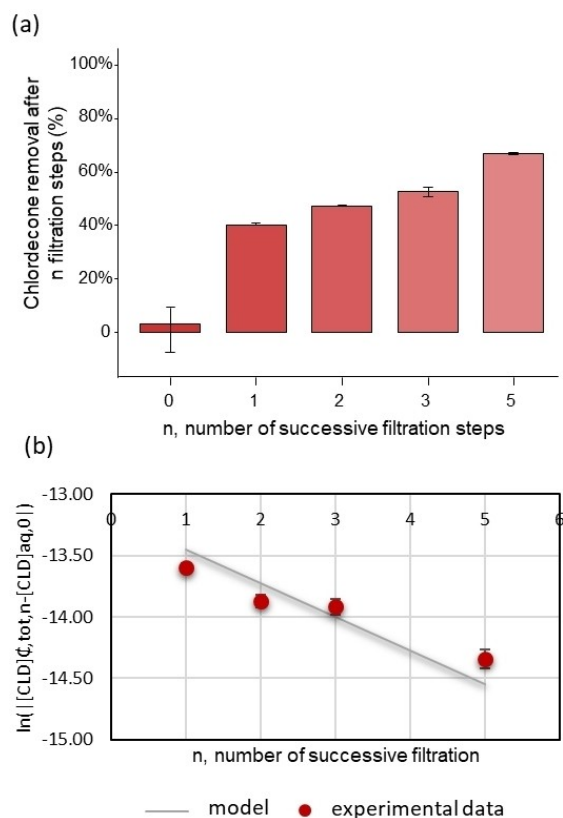


Figure 3. (a) Chlordecone removal (%) after successive filtrations of water at pH 7.4 containing 1 mg/L of chlordecone and hemicryptophane (1.1 eq) at each step. (b) Comparison between experimental data and data obtained from equation (1) of $\ln([CLD]_{C,tot,n} - [CLD]_{aq,0})$ as a function of the number n of filtration steps.

From what we can observe in Figure 3b, the model depicted as a grey line is close to the experimental results obtained after successive filtrations of chlordecone. Using the same protocol and according to the established model, it would take 20 successive filtration steps to remove 99% of the chlordecone present in the water (at 1 mg/L). Accordingly, one would expect that the use of cages with higher affinity would lead to an improved removal system. The 30-min contact time chosen for water depollution by hemicryptophane in this experiment could also be extended as was done previously for the cyclodextrin system.^[26]

Recovery of the supramolecular host hemicryptophane after chlordecone encapsulation

In a second time, the purpose was to develop a system enabling the hemicryptophane recovery. To do this, we exploited the strong increase in chlordecone solubility under basic aqueous conditions.^[2] Considering the very low water solubility of hemicryptophanes, no titration experiment could be performed directly in water. We thus studied the behaviour of the hemicryptophane:chlordecone 1:1 complex by ¹H-NMR in CDCl₃, upon progressive addition of 1 M D₂O solution of

NaOD to the solution of the complex in CDCl₃. According to Figure 4b, addition of a NaOD solution to the complex led to a reverse shift of the protons of the hemicryptophane (in green) compared to that observed during the encapsulation of chlordecone (in blue, Figure 4a). More specifically, in Figure 4, the encapsulation of chlordecone induced an up-field shift of the aromatic doublets located in the hemicryptophane linkers and the two well-defined doublets at 3.4 ppm, corresponding to the diastereotopic Ar-CH₂-N- protons, gave a broad signal upon addition of chlordecone.^[33,37] Reverse effects were observed upon the addition of the basic solution. Interestingly, addition of 250 μL of NaOD solution to the solution of CDCl₃ (750 μL) containing the hemicryptophane and chlordecone, provided an NMR spectrum similar to that of the free cage (without chlordecone inside). Thus, these results clearly demonstrated a switch from a filled cage to an almost empty cage upon addition of basic water,^[33] chlordecone passing into the basic aqueous phase.

From this experiment, we assessed that the hemicryptophane encapsulating chlordecone could be regenerated by simple basic washing. To test this hypothesis, we modified the previous filtration process and performed two parallel experiments: 1 L of water contaminated with 1 mg/L of chlordecone was stirred with 1.1 equivalent of hemicryptophane for 30 min, then filtered. (i) The filter was washed with 50 mL of chloroform, the organic phase was evaporated and analysed by ¹H-NMR (Figure 5b); (ii) the filter was first washed with 100 mL of 1 M NaOH, then with 50 mL chloroform, the organic phase was then evaporated and analysed by ¹H-NMR (Figure 5c). In the first experiment we could observe that aromatic signals were up-field shifted, indicating the presence of chlordecone, whereas after basic washing, the empty hemicryptophane was recovered.

As it could be observed in Figure 4b and Figure 5, the ¹H-NMR signals of the hemicryptophane cage were not affected by the basic washing. Indeed, these supramolecular hosts are known to be highly stable in basic conditions whether in water^[44] or organic solvents in the presence of strong bases such as Ph₂PLi or Verkade's suberbase.^[44–47]

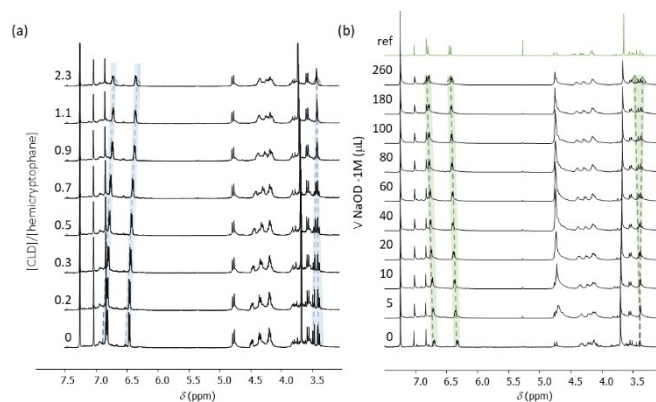


Figure 4. a) ¹H NMR spectra in CDCl₃ of the hemicryptophane upon the progressive addition of chlordecone. (b) ¹H NMR spectra of the chlordecone:hemicryptophane 1:1 complex in CDCl₃ upon the progressive addition of a 1 M solution of NaOD in D₂O (ref: free cage in CDCl₃).

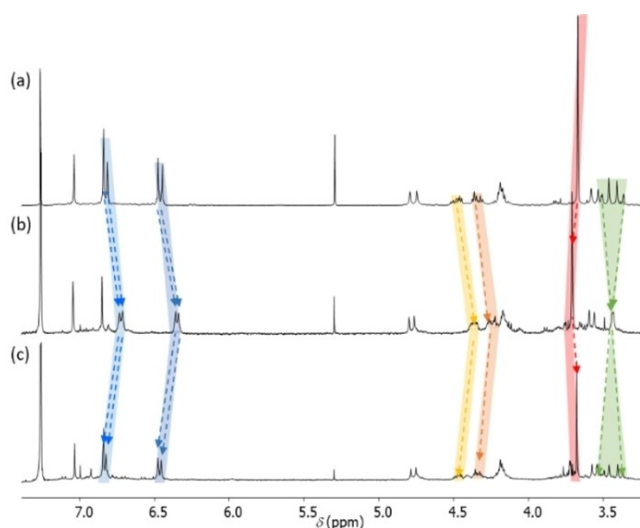


Figure 5. a) ^1H NMR spectrum of the hemicryptophane in CDCl_3 . (b) ^1H NMR spectrum of the residue from cotton filtration of 1 L of water containing 1 mg of chlordecone and 1.1 equivalent of hemicryptophane, washed with chloroform and evaporated. (c) ^1H NMR spectrum of the residue from cotton filtration of 1 L of water containing 1 mg of chlordecone and 1.1 equivalent of hemicryptophane, washed with 1 M NaOH, then with chloroform and evaporated.

As the pH range of environmental water can vary between 6.5 and 9,^[48, 49] the effect of pH was also investigated. Basically, the same protocol described just before was applied to water at pH 6.5 and 8.5. ^1H NMR spectra are available in Figure S3. From these spectra, proton shifts characteristic of chlordecone encapsulation, and more specifically those from the aliphatic area ($\text{Ar-CH}_2\text{-N}$ and $\text{O-CH}_2\text{-CH}_2\text{-O}$) were observed. As expected, broader signals of the hemicryptophane cage were observed at pH 6.5 due to the possible protonation of the tertiary amine. However, it seems that it does not prevent from chlordecone encapsulation, which confirms the application of this method to environmental waters with different pH values.

To confirm the possibility of hemicryptophane reuse, we applied the previously described protocol with the hemicryptophane recovered from a first filtration step (filtration, basic washing and chloroform washing) to a new solution of water contaminated with chlordecone. ^1H NMR spectrum arising from this 2nd use (Figure S4) attested (i) the presence of the hemicryptophane, (ii) the presence of the complex (chlordecone-hemicryptophane), notably through the specific NMR signature of aliphatic protons.

Through these experiments, we therefore confirm the possibility of recovering the hemicryptophane by simple basic washing, allowing to reuse the cage several times.

Conclusions

Through this proof of concept, we have demonstrated that the hemicryptophane cage can efficiently complex chlordecone in water, thus allowing its removal by a simple filtration. Compared to other hosts capable of complexing chlordecone

(γ -cyclodextrin), the hemicryptophane receptor appears to be more efficient to decontaminate water polluted with chlordecone. Furthermore, this study reveals that the hemicryptophane cage can be easily recovered after complexing chlordecone: a subsequent washing of the precipitated host-guest complex by a basic aqueous solution leads to decomplexation of chlordecone which passes into the basic filtrate, regenerating the empty hemicryptophane host on the filter that can be reused in further experiments. This results in a pH-switchable chlordecone receptor, allowing both efficient complexation of chlordecone at neutral pH and recovery of the depolluting cage after basic washing. We thus designed a recyclable system to trap chlordecone in water. Further studies are now required to improve chlordecone retention, and to test this new system on more complex environmental samples.

Supporting Information

The authors have cited additional references within the Supporting Information.^[50,51]

Additional details about experimental data concerning chlordecone filtration with 5 equivalents of cage/material, the model established for successive filtration of chlordecone, ^1H NMR spectra of chlordecone encapsulation at different pH and the reuse of the hemicryptophane cage, analytical procedures and statistical analyses are available in Supporting Information.

Acknowledgements

CNRS, Aix Marseille Université, CEA, Université Paris-Saclay Evry Université are acknowledged for continuous support. This project has received funding from the Préfecture de Martinique, under the auspices of Plan Chlordécone III, action remediation (2019). The authors acknowledge the French National Research Agency (ANR), the Region Guadeloupe and the Collectivité Territoriale de Martinique for their financial support of the CHLOR2NOU project n°ANR22-CHLD-0005-01. M.P.'s PhD work was funded by CEA.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: chlordecone · hemicryptophane · water depollution

- [1] M. Lesueur-Jannoyer, P. Cattan, T. Woignier, F. Clostre, *Crisis Management of Chronic Pollution: Contaminated Soil and Human Health*, CRC Press, Boca Raton, 2016.
- [2] G. W. Dawson, W. C. Weimer, S. J. Shupe, *AIChE Symp. Ser.* **1979**, *75*, 366.
- [3] T. Woignier, P. Fernandes, M. Jannoyer-Lesueur, A. Soler, *Eur. J. Soil Sci.* **2012**, *63*, 717–723.
- [4] T. Woignier, F. Clostre, H. Macarie, M. Jannoyer, *J. Hazard. Mater.* **2012**, *241–242*, 224–230.
- [5] N. K. Wilson, R. D. Zehr, *J. Org. Chem.* **1979**, *44*, 1278–1282.
- [6] R. L. Harless, D. E. Harris, G. W. Sovocool, R. D. Zehr, N. K. Wilson, E. O. Oswald, *Biomed. Mass Spectrom.* **1978**, *5*, 232–237.
- [7] S. S. Epstein, *Sci. Total Environ.* **1978**, *9*, 1–62.
- [8] L. Multigner, F. Rouget, N. Costet, C. Monfort, P. Blanchet, P. Kadhel, H. Bataille, S. Cordier, *Bull. Epidémiol. Hebd.* **2018**, *22–23*, 480–485.
- [9] M. Maudouit, M. Rochoy, *Thérapie* **2019**, *74*, 611–625.
- [10] H. A. Tilson, C. F. Mactutus, *Neurotoxicology* **1982**, *3*, 1–8.
- [11] C. R. Dromard, X. Bodiguel, S. Lemoine, Y. Bouchon-Navaro, L. Reynal, E. Thouard, C. Bouchon, *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 73–80.
- [12] A. Crabit, P. Cattan, F. Colin, M. Voltz, *Environ. Pollut.* **2016**, *212*, 615–626.
- [13] C. R. Dromard, D. A. Devault, Y. Bouchon-Navaro, J.-P. Alléno, H. Budzinski, S. Cordonnier, N. Tapie, L. Reynal, S. Lemoine, J.-P. Thomé, E. Thouard, D. Monti, C. Bouchon, *Environ. Sci. Pollut. Res. Int.* **2022**, *29*, 51–60.
- [14] R. Rochette, V. Bonnal, P. Andrieux, P. Cattan, *Environ. Sci. Pollut. Res. Int.* **2020**, *27*, 41132–41142.
- [15] C. Mottes, L. Deffontaines, J. B. Charlier, I. Comte, P. Della Rossa, M. Lesueur-Jannoyer, T. Woignier, G. Adele, A.-L. Tailame, L. Arnaud, J. Plet, L. Rangon, J.-P. Bricquet, P. Cattan, *Environ. Sci. Pollut. Res. Int.* **2020**, *27*, 40999–41013.
- [16] P. Della Rossa, M. Jannoyer, C. Mottes, J. Plet, A. Bazizi, L. Arnaud, A. Jestin, T. Woignier, J.-M. Gaude, P. Cattan, *Sci. Total Environ.* **2017**, *574*, 1232–1242.
- [17] M. Voltz, P. Andrieux, A. Samouëlian, L. Ponchant, O. Grünberger, T. Bajazet, I. Comte, J.-B. Nanette, G. Onapin, F. Bussière, A. Richard, *Sci. Total Environ.* **2023**, *893*, 164815.
- [18] A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, *Nature* **2016**, *529*, 190–194.
- [19] K. H. Hama Aziz, R. Kareem, *Case Stud. Chem. Environ.* **2023**, 100495.
- [20] R. Ranguin, M. Delannoy, C. Yacou, C. Jean-Marius, C. Feidt, G. Rychen, S. Gaspard, *J. Environ. Chem. Eng.* **2021**, 105280.
- [21] P.-A. Deyris, F. Pelissier, C. M. Grison, P. Hesemann, E. Petit, C. Grison, *Chemosphere* **2023**, 137307.
- [22] K. H. Hama Aziz, F. S. Mustafa, K. M. Omer, I. Shafiq, *Water Resour. Ind.* **2023**, 100227.
- [23] E. Krieg, H. Weissman, E. Shirman, E. Shimoni, B. Rybtchinski, *Nat. Nanotechnol.* **2011**, *6*, 141–146.
- [24] K. H. Waris, V. S. Lee, S. Mohamad, *Environ. Sci. Pollut. Res. Int.* **2021**, *28*, 47785–47799.
- [25] D. Zhang, T. K. Ronson, Y.-Q. Zou, J. R. Nitschke, *Nat. Chem. Rev.* **2021**, *5*, 168–182.
- [26] V. K. Rana, R. Kissner, S. Gaspard, J. Levalois-Grützmacher, *Chem. Eng. J.* **2016**, *293*, 82–89.
- [27] G. Zolfaghari, *Chem. Eng. J.* **2016**, *283*, 1424–1434.
- [28] S. I. Kaya, A. Cetinkaya, S. A. Ozkan, *Trends Environ. Anal. Chem.* **2023**, *37*, e00193.
- [29] A. Martín-Esteban, *Separations* **2022**, *9*, 133.
- [30] P. Bosman, A. Combès, M. Lambert, G. Lavison-Bompard, V. Pichon, *Separations* **2021**, *8*, 237.
- [31] D. Zhang, A. Martinez, J.-P. Dutasta, *Chem. Rev.* **2017**, *117*, 4900–4942.
- [32] N. Fantozzi, R. Pétuya, A. Insuasty, A. Long, S. Lefevre, A. Schmitt, V. Robert, J.-P. Dutasta, I. Baraille, L. Guy, E. Genin, D. Bégué, A. Martinez, S. Pinet, I. Gosse, *New J. Chem.* **2020**, *44*, 11853–11860.
- [33] A. Long, S. Lefevre, L. Guy, V. Robert, J.-P. Dutasta, M. L. Chevallier, O. Della-Negra, P.-L. Saaidi, A. Martinez, *New J. Chem.* **2019**, *43*, 10222–10226.
- [34] A. Long, O. Perraud, M. Albalat, V. Robert, J.-P. Dutasta, A. Martinez, *J. Org. Chem.* **2018**, *83*, 6301–6306.
- [35] A. Long, E. Antonetti, A. Insuasty, S. Pinet, I. Gosse, V. Robert, J.-P. Dutasta, A. Martinez, *J. Org. Chem.* **2020**, *85*, 6400–6407.
- [36] D. Zhang, G. Gao, L. Guy, V. Robert, J.-P. Dutasta, A. Martinez, *Chem. Commun.* **2015**, *51*, 2679–2682.
- [37] O. Della-Negra, A. E. Kouassi, J.-P. Dutasta, P.-L. Saaidi, A. Martinez, *Chem. Eur. J.* **2023**, e202203887.
- [38] S. Bhattacharyya, G. Lelong, M.-L. Saboungi, *J. Exp. Nanosci.* **2006**, *1*, 375–395.
- [39] S. Anandan, M. Okazaki, *Microporous and Mesoporous Materials* **2005**, *87*, 77–92.
- [40] D. Wisser, M. Hartmann, *Adv. Mater. Interfaces* **2021**, *8*, 2001266.
- [41] J. J. Gamboa-Carballo, A. Ferino-Pérez, V. K. Rana, J. Levalois-Grützmacher, S. Gaspard, L. A. Montero-Cabrera, U. J. Jauregui-Haza, *J. Chem. Inf. Model.* **2020**, *60*, (4), 2115–2125.
- [42] C. Tao, X. Li, J. Yang, Y. Shi, *Sens. Actuators B* **2011**, *156*, 553–558.
- [43] B. Chatelet, E. Payet, O. Perraud, P. Dimitrov-Raytchev, L.-L. Chepellet, V. Dufaud, A. Martinez, J.-P. Dutasta, *Org. Lett.* **2011**, *13*, 3706–3709.
- [44] A. Schmitt, V. Robert, J.-P. Dutasta, A. Martinez, *Org. Lett.* **2014**, *16*, 2374–2377.
- [45] J.-P. Dutasta, A. Martinez, *ChemPlusChem* **2020**, *85*, 977–984.
- [46] P. Dimitrov Raytchev, A. Martinez, H. Gornitzka, J.-P. Dutasta, *J. Am. Chem. Soc.* **2011**, *133*, 2157–2159.
- [47] B. Chatelet, H. Gornitzka, V. Dufaud, E. Jeanneau, J.-P. Dutasta, A. Martinez, *J. Am. Chem. Soc.* **2013**, *135*, 18659–18664.
- [48] J. B. Charlier, B. Lachassagne, P. Ladouche, P. Cattan, R. Moussa, M. Voltz, *J. Hydrol.* **2011**, *398*, 155–170.
- [49] <https://www.epa.gov/caddis-vol2/ph#:~:text=U.S.%20EPA%20water%20quality%20criteria,decreased%20growth%20C%20disease%20or%20death>.
- [50] M. L. Chevallier, O. Della-Negra, S. Chaussonnerie, A. Barbance, D. Muselet, F. Lagarde, E. Darii, E. Ugarte, E. Lescop, N. Fonknechten, J. Weissenbach, T. Woignier, J.-F. Gallard, S. Vuilleumier, G. Imfeld, D. Le Paslier, P.-L. Saaidi, *Environ. Sci. Technol.* **2019**, *53*, 6133–6143.
- [51] J. Feys, *The R Journal* **2016**, *8*, 367–378.

Manuscript received: October 12, 2023