PREPARATION OF BIOCHAR AND ACTIVATED CARBONS FROM INVASIVE SARGASSUM ALGAE FOR THE REDUCTION OF CHLORDECONE IN CONTAMINATED SOIL

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Abstract

The aim of this work is to valorise an invasive brown macroalga, Sargassum (consisting of two species, Sargassum Fluitans and Sargassum Natans), by producing biochar (BC) and activated carbon (AC). Over the past nine years, its frequent and massive appearance along the Caribbean, Florida and Gulf of Mexico coasts has triggered human health problems and had a negative impact on the local economy, ecology and environment. In this paper, BC and CA were developed to study the reduction of chlordecone (CLD) in contaminated artificial and tropical soils. This innovative approach was proposed to limit the presence of CLD accessible to wildlife and outdoor livestock. The BCs were prepared by pyrolysis at 700 °C, while the ACs are collected by chemical or physical activation. Through textural characterisation, it was shown that bimodal structures, with micro- and meso-pores, and various high surface and pore volumes, were successfully obtained. Finally, the environmental presence tests showed various abilities of BCs or CAs to significantly sequester CLD from contaminated artificial soils and from a natural nitisol. In particular, BCs prepared with a pyrolysis time of 3 hours show the highest porosity properties, and are the best candidates to effectively sequester CLD in soil samples.

Introduction

Since 2011, in the islands of Guadeloupe (French West Indies) and other Caribbean islands, strandings of tons of pelagic sargassum (Sargassum Natans and Sargassum Fluitans, a co-occurring complex of two species of floating brown macroalgae), have occurred regularly [1]. These events are most likely due to global warming and anthropogenic activities. For example, Guadeloupe faced one of its worst strandings on record in 2019, with seaweed accumulating dramatically on the windward beaches of the coast. The decomposing sargassum produces hydrogen sulphide and ammonia gas, which has adverse health effects and indirect impacts on tourism, fishing and recreational activities [2,3].

There is currently a growing trend in the Caribbean to transform this Sargassum into value-added material. We propose here to use this local and highly available resource to produce biochar (BC) and activated carbon (AC), thus contributing to solving the environmental problem of chlordecone contamination of soils (CLD) [4–6].

Indeed, CLD was used for more than two decades (from 1972 to 1993) in the French West Indies, Africa and other Central and South American countries to treat banana plantations against the weevil Cosmopolites Sordidus [7]. While its toxicity has been recognised since 1975, CLD was only identified as a persistent organic pollutant in May 2009 and as such was included in the Stockholm Convention on Persistent Organic Pollutants. This molecule has a high molecular weight (490.64 g mol-1), very low solubility in water (2.7 mg L-1 at 25 ◦C), high affinity for organic compounds (log Kow 4.5) and high stability due to its chlorinated structure [8, 9]. As a result, CLD can easily bind to soil particles, and residues have been found in sediment layers as well as in various living organisms (i.e. humans, animals and plants) in terrestrial and coastal areas [10].

Unfortunately, the presence of CLD in water, soil and sediment in banana production areas is expected to persist for at least several decades, up to seven centuries (for the most polluted Andosols) [11]. Therefore, in this work, the development of BC and CA derived from Sargassum was studied to propose an eco-responsible opportunity for "biomass waste valorization" and an innovative strategy to limit the presence of CLD accessible to wildlife and outdoor livestock.

We have produced and characterised BC and CA with different textural and physico-chemical properties, to assess their potential for sequestering CLD in artificial and natural soils. While previous work has focused on the use of BCs to limit pollutant transfer [12-14], to improve soil water retention [15], for microbial activities [16], or to limit the volatility of nitrogen compounds required for plant growth [17, 18]; few have examined the strategy of using BCs to prevent pollutant transfer to livestock. Recent papers [19-21] have reported the great potential of CA and BC to sequester CLD in West Indian soil.

In our previous work, amendment of Nitisol with lignocellulosic CA, such as coconut husk or oak wood, resulted in significant reductions in CLD [21]. However, to our knowledge, no sequestration studies with BC or CA derived from Sargassum are currently available.

1. Materials and method

Raw Sargassum was collected along the Guadeloupean coast in July 2017. The samples were first dried at room temperature and then in an oven at 105 °C for 48h to remove all moisture. They were then crushed and finally sieved into several fractions [22]. The fraction with a particle size of 0.4 to 1 mm was chosen as the basis for producing activated arbon and biochar. In this work, biochar was obtained from the pyrolysis of sargassum. Activated carbon was obtained either by physical activation of biochars or by chemical activation [22].

The biochar samples obtained were labeled BioSarg 1 h and BioSarg 3 h, depending on the pyrolysis time applied to them. Activated carbons (ACs) are named SargCO, SargH2O, SargCO2/ H2O and SargP0.5 according to the activation process used.
In this study, the sequestration efficiency of CLD by each Sargassum BC or AC was assessed by presence tests that determine the proportion of CLD that can be transferred to wildlife or biota. These tests were first applied to artificial soils in order to select the most effective Sargassum BCs or ACs. In a second step, the most effective Sargassum BCs were tested on a Caribbean nitisol contaminated with CLDs.

2. The impact of activated carbon and Sargassum biochar characteristics on CLD sequestration

The present study reveals that a BC (BioSarg 3 h) is capable of effectively sequestering CLD, either in OECD artificial soils or in a CLD-contaminated Nitisol. Contrary to previous results obtained from lignocellulosic precursors, where BCs did not show a high retention potential [21], the 3 h BioSarg used in this study appears to be a viable candidate for this purpose. Indeed, the BC is prepared in an eco-responsible way through a single pyrolysis step, which allows, even if the sample has to be efficiently washed, to obtain on an industrial scale a preparation cost lower than that of a physical or chemical activation.

These retention capacities can be explained by the many interesting characteristics that BioSarg 3 h has compared to other samples. Indeed, its textural characteristics such as specific BET surface area, total pore volume, micro and meso pore volume, and average pore diameter are the highest of all BC and CA samples [21,59]. These physico-chemical characteristics are well known to play a role in chemical characteristics and in the sequestration of organic pesticides [21]. The reduction in presence of CLD is much more consistent than the results obtained for the SargP0.5, SargCO2 samples which also showed high potential.

Textural properties such as micro and meso pore volumes also seem to play a role in this reduction: the sample named SargCO2 had the highest surface area of 968 m2.g-1, but was not able to trap CLD in this study. This may be due to its very low amount of micropores capable of trapping CLD. BioSarg 3h, on the other hand, has a high proportion of microporosity and mesoporosity compared to the other matrices. A similar observation was previously noted in another set of BC and CA [21, 59].

In contrast, SargP0.5, which contains slightly fewer micropores than BioSarg 3h, was not able to significantly retain CLD. Even with a very low surface area and volume of micropores, SargH2O achieves a 32% reduction in the presence of CLD, showing that the textural characteristic is not the only factor affecting the retention of CLD by the carbon material. The chemical groups of carbon samples may also play a role in reducing the presence of CLD in the soil. Indeed, it is known that the chemical composition of the surface plays a major role in the adsorption of chlorinated pesticides to water [60,61], to cite an example that was not analysed in the present work, since here CLD is removed from the soil, not from the water.

Although several surface characterisations were carried out in this work, no conclusions could be drawn at this stage regarding the relationship between surface chemical composition and the presence of CLD.
Overall, these results suggest that a significant reduction in the environmental presence of CLD can only be expected when the condensed material is highly porous, but this also depends on other factors. Therefore, the influence of carbon chemistry, which includes surface group polarity and acid-base character in relation to soil characteristics such as pH, moisture content, etc., requires further investigation.

3. Conclusions

This study revealed that pyrolysis of Sargassum can produce condensed materials with high levels of porosity. In particular, BioSarg 3 h (3 h pyrolysed Sargassum process) displayed both the highest total pore volume, as well as one of the best BET surfaces. Thus, this biochar appears to be the best candidate to effectively sequester Chlordecone from soil samples, suggesting that the textural properties of the materials play a major role. This very promising result indicates that a wider use of this biochar, with a reduced preparation cost and an easy preparation process, could contribute to strongly limit the transfer of Chlordecone to the food chain. Further work (e.g. on the influence of soil pH, effects of Chlordecone loading in soils, contact times, etc.) is underway to better understand the results obtained. Overall, these results can be considered as a first major step towards further bioavailability studies to investigate the transfer of Chlordecone from contaminated soils to plants and food-producing animals.

Declaration of competing interests
The authors declare that they have no competing financial interests or known personal relationships that could have influenced the work reported in this article.

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