

# Is cocoa pod shell biochar activation a suitable way for water cadmium removal in the Ivory Coast?

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**Photo 1.**  
Raw biochar from cocoa pod shell biomass (Pyrolysis temperature: 400°C ; degradation time: 1 hour).  
Photo Y. G. L. Koffi.

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## RÉSUMÉ

## ABSTRACT

## RESUMEN

**L'activation du biochar de coques de cabosses de cacao est-elle une solution appropriée pour éliminer le cadmium présent dans l'eau en Côte d'Ivoire ?**

L'objectif de cette étude est de convertir les résidus agricoles, en particulier les coques de cabosses de cacao de Côte d'Ivoire, en bioadsorbants à faible coût. Dans ce contexte, le biochar peut être produit à partir de résidus agricoles pour être utilisé dans l'élimination des polluants de l'eau. La question principale était de savoir si l'efficacité d'adsorption du biochar produit à partir de cette biomasse pouvait être améliorée par une activation physique au dioxyde de carbone (CO<sub>2</sub>). À cette fin, une évaluation a été réalisée afin de déterminer l'efficacité du biochar brut et activé dans l'adsorption du cadmium (Cd<sup>2+</sup>) à partir d'une solution aqueuse dans des conditions proches de celles de l'eau potable (pH = 6 et température = 22 ± 1 °C). Les résultats de l'adsorption ont indiqué que le biochar brut, obtenu par pyrolyse de la biomasse des coques de cabosses de cacao à 400 °C, était plus efficace pour éliminer le Cd<sup>2+</sup> (taux d'élimination = 72,0 ± 1,1 % et capacité d'adsorption = 14,4 ± 0,3 mg/g) que le biochar activé, produit par pyrolyse de la même biomasse à 900 °C, puis activé avec du CO<sub>2</sub> à 800 °C (taux d'élimination = 65,3 ± 1,8 % et capacité d'adsorption = 13,0 ± 0,4 mg/g). L'expérience montre que les propriétés chimiques de surface des adsorbants influencent considérablement l'adsorption du Cd<sup>2+</sup>, tandis que les propriétés physiques ont un impact mineur. Cette étude a révélé que le biochar brut pyrolysé à 400 °C était plus efficace que le biochar activé pour adsorber le Cd<sup>2+</sup>, offrant ainsi un adsorbant facilement disponible, respectueux de l'environnement et peu coûteux pour améliorer la qualité de l'eau potable. Il n'est donc pas systématiquement nécessaire d'activer le biochar pour qu'il soit efficace dans l'élimination des polluants de l'eau.

**Mots-clés :** coques de cabosses de cacao, biochar, activation physique, propriétés physiques et chimiques, taux d'élimination, capacité d'adsorption, cadmium, eau de boisson, Côte d'Ivoire.

**Is cocoa pod shell biochar activation a suitable way for water cadmium removal in the Ivory Coast?**

The objective of this study is to convert agricultural residues, particularly cocoa pod shells from the Ivory Coast, into low-cost bioadsorbents. In this context, biochar can be produced from agricultural residues for use in removing water pollutants. The main question was whether the adsorption efficiency of biochar produced from this biomass can be improved by physical activation with carbon dioxide (CO<sub>2</sub>). To this end, an assessment was made of the effectiveness of raw and activated biochar in adsorbing cadmium (Cd<sup>2+</sup>) from an aqueous solution under conditions close to those of drinking water (pH = 6 and temperature = 22 ± 1 °C). The results of the adsorption indicated that raw biochar, obtained by pyrolysis of cocoa pod shell biomass at 400 °C, was more effective at removing Cd<sup>2+</sup> (removal rate = 72.0 ± 1.1% and adsorption capacity = 14.4 ± 0.3 mg/g) than activated biochar, which was produced by pyrolysis of the same biomass at 900 °C followed by activation with CO<sub>2</sub> at 800 °C (removal rate = 65.3 ± 1.8% and adsorption capacity = 13.0 ± 0.4 mg/g). The experiment indicates that the chemical surface properties of adsorbents significantly influence the adsorption of Cd<sup>2+</sup>, while physical properties have a minor impact. This study revealed that raw biochar pyrolysed at 400 °C was more efficient than activated biochar in adsorbing Cd<sup>2+</sup>, thus offering an easily available, environmentally friendly, and inexpensive adsorbent for improving drinking water quality. Therefore, it is not systematically necessary to activate biochar to be effective in removing pollutants from water.

**Keywords:** cocoa pod shells, Ivory Coast, biochar, physical activation, physical and chemical properties, removal rate, adsorption capacity, cadmium, drinking water.

**¿La activación del biocarbón a partir de cáscaras de bayas de cacao permitiría eliminar el cadmio presente en el agua en Costa de Marfil?**

El objetivo de este estudio es convertir los residuos agrícolas, en particular las cáscaras de bayas de cacao de Costa de Marfil, en bioadsorbentes de bajo coste. En este contexto, el biocarbón puede producirse a partir de residuos agrícolas para su uso en la eliminación de contaminantes del agua. La cuestión principal era si la eficacia de adsorción del biocarbón producido a partir de esta biomasa podía mejorarse mediante una activación física con dióxido de carbono (CO<sub>2</sub>). Con este fin, se llevó a cabo una evaluación para determinar la eficacia del biocarbón crudo y activado en la adsorción de cadmio (Cd<sup>2+</sup>) a partir de una solución acuosa en condiciones similares a las del agua potable (pH = 6 y temperatura = 22 ± 1 °C). Los resultados de la adsorción indicaron que el biocarbón crudo, obtenido por pirólisis de la biomasa de las cáscaras de cacao a 400 °C, era más eficaz para eliminar el Cd<sup>2+</sup> (tasa de eliminación = 72,0 ± 1,1 % y capacidad de adsorción = 14,4 ± 0,3 mg/g) que el biocarbón activado, producido por pirólisis de la misma biomasa a 900 °C y posteriormente activado con CO<sub>2</sub> a 800 °C (tasa de eliminación = 65,3 ± 1,8 % y capacidad de adsorción = 13,0 ± 0,4 mg/g). La experiencia demuestra que las propiedades químicas de la superficie de los adsorbentes influyen considerablemente en la adsorción del Cd<sup>2+</sup>, mientras que las propiedades físicas tienen un impacto menor. Este estudio reveló que el biocarbón crudo pirolizado a 400 °C era más eficaz que el biocarbón activado para adsorber el Cd<sup>2+</sup>, lo que lo convierte en un adsorbente fácilmente disponible, respetuoso con el medio ambiente y económico para mejorar la calidad del agua potable. Por lo tanto, no es sistemáticamente necesario activar el biocarbón para que sea eficaz en la eliminación de contaminantes del agua.

**Palabras clave:** cáscaras de bayas de cacao, biochar, activación física, propiedades físicas y químicas, tasa de eliminación, capacidad de adsorción, cadmio, agua potable, Costa de Marfil.

## Introduction

Access to drinking water is a universal need and a fundamental human right. This is why target 6.1 of the Sustainable Development Goals (SDGs) states: “By 2030, ensure universal and equitable access to safe and affordable drinking water for all” (Guterres 2023). To help advance this objective, this work aims to produce, through thermochemical transformation, a low-cost bioadsorbent capable of effectively removing chemical pollutants from drinking water consumed without prior treatment, using agricultural residues available in the Ivory Coast (a West African country). However, drinking water remains a luxury for some populations living in developing countries. For example, among the 86% of the population that uses at least basic drinking water services in the Ivory Coast, 56% do not use a safely managed drinking water supply service (41% in urban areas and 73% in rural areas) (WHO/UNICEF 2024<sup>1</sup>). Indeed, several chemical pollutants (Cu, Cr, As, Hg, CN, Fe, Pb, Cd) have been identified in drinking water sources (wells, boreholes, backwaters) in the Ivory Coast (Akessé et al. 2022; Kouassi et al. 2022; Sanou et al. 2022). This situation exposes populations who consume water without prior treatment to health risks (OMS 2017). Among these pollutants is cadmium ( $\text{Cd}^{2+}$ ), a toxic heavy metal that is highly problematic in the Ivory Coast because it is recurrently present in surface and groundwater, and it is also found in soil and food (Diaby et al. 2017). To provide sustainable and adaptable solutions to developing countries, priority should be given to the use of accessible and economical local resources. Furthermore, the Ivory Coast has significant biomass potential, including agricultural residues such as agro-industrial waste, forest residues, and urban waste (Zanli et al. 2022). In 2020, the biomass potential for certain agricultural sectors shows that the official estimate of 15 to 17 million tonnes of available biomass is underestimated. According to the International Cocoa Organisation (ICCO), the Ivory Coast is the world’s leading cocoa producer, with 1.95 million tonnes in 2024, accounting for 39% of the global supply. Generally, one ton of beans corresponds to approximately two tonnes of pods. It is worth noting that dry pods account for about 30% of the weight of wet pods. As a result, the Ivory Coast has about 4.4 million tonnes of recoverable dry pod residues. A few recovery initiatives (direct combustion or the production of briquettes or biogas; composting) exist on a small scale. Most of these cocoa pod shell residues are currently left on plantations, often to be incinerated. Leaving pods on plots encourages the spread of swollen shoot disease, which attacks cocoa plants (Global Business Network Programme 2020). The recovery of these pods, therefore, has a significant impact. However, the material recovery of this biomass could also be an interesting and sustainable option for addressing local issues, such as producing biochar from this biomass as a filter material to improve drinking water quality. Nevertheless, preliminary studies on the potential use of biochar derived from these agricultural residues for water filtration of drinking water are necessary before any recommendations can be made.

Moreover, the development of efficient, modified bioinspired materials for heavy-metal adsorption is currently at the forefront of environmental remediation research (Nworie et al. 2022). These studies have shown that functionalised biochar for heavy metal removal is highly advantageous due to its striking properties, including regenerability, high efficiency, mechanical stability, chemical inertness to many organic solvents, surface polarity, functionality, chelation properties, and decreased hydrophobicity, which are absent in raw biochar. Most studies have shown that agricultural waste, in its improved form, is very effective in removing cadmium metal ions (Younas et al. 2023). For example, Kukowska et al. (2025) have also developed new activated carbons derived from fruit waste with a high cadmium adsorption capacity from water through the use of microwave-assisted and conventional electric tube furnace activations, consuming carbon dioxide ( $\text{CO}_2$ ). These authors prepared biochars (BC) and activated carbons (AC) with fruit waste from aronia seeds (*Aronia melanocarpa*) (AB), orange peel (*Citrus sinensis*) (OB), and blackcurrant seeds (*Ribes nigrum*) (RB). To obtain biochars, the biomass was pyrolysed at 400 °C. The activated carbons were produced by direct and indirect activation at a temperature of 700 °C and 800 °C in a  $\text{CO}_2$  atmosphere at a flow rate of 250 mL/min. It was noted that direct activation of biomass led to higher microporosity compared to indirect (two-step) activation. In contrast,  $\text{CO}_2$  consumption activation (direct and indirect) increased the aromaticity and hydrophobicity of the solids. However, the most effective and environmentally safe adsorbent was the one produced from orange peel through direct microwave-assisted activation at 800 °C in a  $\text{CO}_2$  atmosphere, achieving a  $\text{Cd}^{2+}$  removal rate of 46.8% for an initial  $\text{Cd}^{2+}$  concentration of 100 mg/L. Since the aim is to produce biochar (a highly carbonaceous material with the lowest organic or volatile matter content possible) from cocoa pod shells under low-cost conditions, it is worth investigating whether non-activated biochar is always less effective than its modified form in cleaning up water. To answer this question, this study aims to determine the adsorption capacity of cadmium by raw biochar and biochar physically activated by carbon dioxide ( $\text{CO}_2$ ) in an aqueous solution.

## Material and Method

### Biomass preparation

The biomass used in this study to produce biochar consists of cocoa pod shells and comes from the Ivory Coast. After being collected in the fields, this biomass was dried in the open air for about a week before being stored in bags. It was transported by boat to France, where it was taken to the CIRAD (International Centre for Agricultural Research for Development of tropical and Mediterranean

<sup>1</sup> <https://data.worldbank.org/indicator/SH.H2O.SMDW.ZS>



**Figure 1.**  
Lignocellulosic biomass of dry cocoa pod shells before grinding.  
Photo Y. G. L. Koffi.

regions) Lavalette site in Montpellier. Upon arrival, the dried shells were placed in a dryer for 24 hours at a temperature of 60 °C to eliminate any microorganisms that could contaminate the biomass between collection in the fields and arrival at CIRAD. After leaving the dryer, 100 kg of biomass (figure 1) was stored in a warehouse and used for biomass characterisation analyses and biochar production.

#### Characterisation of cocoa pod shell biomass

The moisture, volatile matter, and ash contents were determined following standard NF EN ISO 18134-3 (ISO 2015d), NF EN ISO 18123 (ISO 2015c), and NF EN ISO 18122 (ISO 2015b), respectively. The element analysis (C, H, and N) was performed in accordance with the standard NF EN ISO 16948 (ISO 2015a) using the Vario Macro Cube elemental analyser. The macromolecular composition of cellulose, hemicellulose, and lignin in biomass was determined by adapting the standard procedure of the National Renewable Energy Laboratory (NREL) (Sluiter et al. 2008).

#### Production of biochar and activated biochar

The biochars were prepared by a pyrolysis process using a vertical tubular resistance furnace (ROK 300/1200/11-3Z) manufactured by Ceradel Industries (1,200 mm heated height, 280 mm internal diameter) and with a maximum power of 20 kW for a maximum temperature of 1,100 °C. It is equipped with three independent 400 mm heating zones, ensuring even heating of the reactor wall. One kilogramme (1 kg) of biomass cocoa pod shells with a particle size of less than 6 mm (figure 1) spread over 10 trays (100 g per tray with a height of 37 mm and 240 mm internal diameter) was heated in the absence of oxygen at 10 °C/min to temperatures of 400 °C and 900 °C for 1 hour. At the end of the heating stage, the biochars were left in the furnace until the room temperature ( $26 \pm 1$  °C) was reached for cooling. This operation was duplicated for each pyrolysis temperature in order to obtain the necessary quantity of biochar for the continuation of the study. The yield of biochars produced, corresponding to the mass loss of biomass during pyrolysis, was calculated using Equation 1.

The biochar produced at a pyrolysis temperature of 400 °C, referred to as “raw biochar”, was used directly for the adsorption experiments. The biochar produced at a pyrolysis temperature of 900 °C was physically activated under CO<sub>2</sub> in another smaller furnace to ensure the homogeneity of the process and the final product. Thus, 10 g of this biochar was placed into a vertical tubular resistance furnace manufactured by Ceradel Industries (40 mm in diameter and 40 mm high) and heated at 10 °C/min in a nitrogen atmosphere under a flow rate of 2 NL/min up to 800 °C. At 800 °C, the volume of nitrogen was reduced to 1.5 NL/min, and 0.5 NL/min of CO<sub>2</sub> (25% of the total volume of gas) was injected into the gas stream during 1 hour. At the end of the heating stage, the activated biochar was left in the furnace until it reached room temperature (26 ± 1 °C) for cooling. The activation temperature of 800 °C was chosen to remain focused on our objective, which is to use a low-cost, energy-efficient process, in case this study demonstrates that biochar activation is necessary to obtain an effective bioadsorbent from the biomass studied. The physical CO<sub>2</sub> activation method will be adopted for the production of activated biochar, as it has been proven that physical CO<sub>2</sub> activation produces microporous activated carbon (Chang et al. 2000; Lee & Roh 2020) and makes it possible to obtain good uniformity of the pores in the biochar (Abioye & Ani 2015). Additionally, the use of CO<sub>2</sub> is a viable option for environmentally friendly research, given its nature and its minimal impact on the ecosystem. The biochar obtained was named “activated biochar”. The activation process was carried out eighteen (18) times to obtain the required quantity of activated biochar for future analyses. The degree of activation, usually referred to as burn-off, which is an important quantitative characteristic for activated carbons and indicates the loss of mass during activation, was determined by equation 2 (Lee & Roh 2020). The raw biochars and activated biochars produced under the same conditions were mixed at the end of production and used as a single sample for the rest of the study.

The samples of raw biochar and activated biochar were ground to a particle size less than 0.2 mm for characterisation analyses and to a particle size of between 0.2 and 2.0 mm for adsorption experiments.

$$\% \text{ Yield} = \frac{M_{BC}}{M_{BM}} \times 100 \quad (\text{equation 1})$$

$$\% \text{ Burn-off} = \frac{M_{BC} - M_{AB}}{M_{BC}} \times 100 \quad (\text{equation 2})$$

where  $M_{BC}$  = mass of biochar,  $M_{BM}$  = mass of biomass, and  $M_{AB}$  = mass of activated biochar.

### Characterisation of raw biochar and activated biochar

The proximate analysis was conducted by determining the moisture, volatile matter, and ash contents according to the standard AFNOR NF EN 1860-2 (AFNOR 2005). The pH of the zero-point charge (pH<sub>ZPC</sub>) of a solid material is the pH at which its net surface charge is zero. If both the adsorbent and adsorbate are charged, electrostatic-type

interactions may exist and explain the preferential or disadvantageous adsorption (Cañizares et al. 2006). In a solution, if the pH of adsorption > pH<sub>ZPC</sub>, adsorption is favourable for particles with positive charges, or if the pH of adsorption < pH<sub>ZPC</sub>, adsorption is favourable for particles with negative charges. The pH<sub>ZPC</sub> of the biochar was determined by adding 100 mg of dried biochar to 50 mL of a 0.01 M NaCl solution with a pH range of 2 to 12. The pH of the initial NaCl solution was adjusted by adding a 0.01 M HCl or NaOH solution. The mixture was continuously stirred at room temperature (22 °C) for 72 hours, after which the final pH was measured (Kra et al. 2019). The amount of surface acid and base chemical functionality was determined using the Boehm method, as adopted by Kra et al. (2019). The mineral composition was determined according to U.S. EPA SW-846 Method 3015A (United States Environmental Protection Agency 2007) by microwave digestion for ICP analysis. Then, 0.2 g of each solid material, previously dried at 105 °C, was digested in 10 mL of concentrated nitric acid (65%) using a MARS 240/50 EMC microwave oven (model No. 907511). ICP-OES analysis was performed on the digestate to determine the mineral composition of the solid material. The specific surface area was analysed by CELIGNIS Analytical Laboratory using the Brunauer-Emmet-Teller (BET) technique in accordance with the standard DIN ISO 9277 (ISO 2022) procedure. The samples were dried at 40 °C and ground to a particle size less than 3.15 mm, and nitrogen was used as the adsorption gas. Degassing was performed under vacuum at a temperature of 150 °C for 2 hours.

### Batch adsorption studies

The adsorption experiments were carried out by studying the effect of contact time and initial cadmium (Cd<sup>2+</sup>) concentration at an average pH of 6 at room temperature, 22 ± 1 °C. The kinetic study was conducted by adding 0.05 g of each adsorbent material (raw biochar and activated biochar) to water with 5 mg/L of Cd<sup>2+</sup> under continuous stirring. To carry out the isothermal adsorption experiment, 0.05 g of each adsorbent material was brought into contact with seven initial concentrations of Cd<sup>2+</sup> (i.e., 0.2, 0.5, 1, 2.5, 5, 8, and 10 mg/L) during 48 hours. The pH of the adsorption experiments was stabilised at 2 mmol/L of sodium bicarbonate (NaHCO<sub>3</sub>) in the reaction medium. At the end of each experiment, the residual Cd<sup>2+</sup> concentrations in the filtrates were analysed by flame atomic absorption spectroscopy (FAAS) (Perkin Elmer PinAAcle 500). Each adsorption experiment was carried out in triplicate. The removal rate (%R) of Cd<sup>2+</sup> was calculated using equation 3, and the adsorption capacity (q<sub>t</sub>) was calculated using equation 4:

$$\% R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (\text{equation 3})$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (\text{equation 4})$$

where  $C_0$  and  $C_t$  are the initial and equilibrium Cd<sup>2+</sup> concentration (mg/L), respectively; V is the volume of Cd<sup>2+</sup> solution used (L); and m is the weight of adsorbent (g).

## Results and Discussion

The results of each analysis or experimental point presented were obtained by averaging three replicates to validate the repeatability of the results (the standard deviation is approximately  $\pm 5\%$ ). Microsoft Excel software was used to analyse the experimental data.

### Characterisation of cocoa pod shell biomass

The results of the proximate, elemental, and macromolecular analysis of cocoa pod shell biomass are summarised in table I.

**Table I.**

Proximate, elemental, and macromolecular analysis of biomass (based on dry basis).

Biomass	Ash (%)	Carbon (%)	Fixed Carbon (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Cocoa pod shells	7.9 $\pm$ 0.1	41.8 $\pm$ 0.0	24.0	20.7 $\pm$ 0.2	21.1 $\pm$ 0.5	38.9 $\pm$ 0.5

**Table II.**

Yield, burn-off, and ash of raw biochar and activated biochar (based on dry basis).

Adsorbent	Yield (%)	Burn-off (%)	Ash (%)
Raw biochar	43.7 $\pm$ 0.6	—	18.7 $\pm$ 0.2
Activated biochar	32.8 $\pm$ 0.3*	37.1 $\pm$ 1.2	31.9 $\pm$ 0.1

\*The production yield of raw biochar (produced at a pyrolysis temperature of 900 °C for 1 hour) before physical activation with CO<sub>2</sub>.

**Table III.**

Porosity, functional groups, and pH<sub>ZPC</sub> of raw biochar and activated biochar (based on dry basis).

Adsorbent	Porosity			Functional groups		pH <sub>ZPC</sub>
	S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	TPV (cm <sup>3</sup> /g)	ADP (nm)	Acidic (meq/g)	Basic (meq/g)	
Raw biochar	3	0.02	7.7	1.45 $\pm$ 0.01	1.86 $\pm$ 0.01	8.1
Activated biochar	178	0.09	2.06	0.00	$\geq 5^*$	12.1

\*The amount of HCl (0.1 N) used for the acid-base titration can neutralise just 5 meq.g<sup>-1</sup> of basic functions in the biochar.

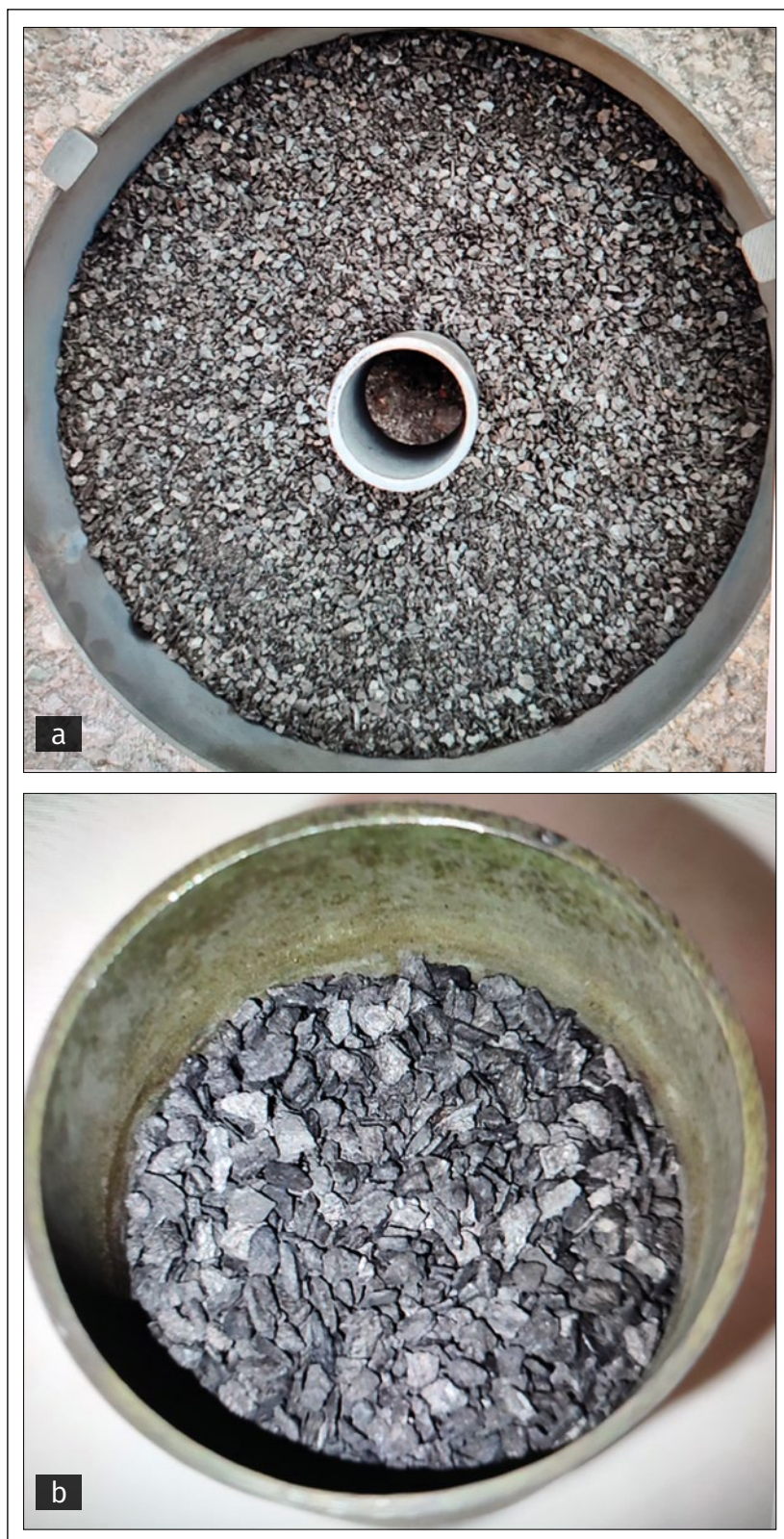
The results of the proximate and elemental analyses of the biomass of cocoa pod shells showed that this biomass contains an ash content of 7.9  $\pm$  0.1%. This ash content can have a negative influence on the specific surface area of the biochars produced from this biomass. Indeed, a high ash content in the biomass results in charcoal with high ash content. Other authors have reported ash contents (10.1%) higher than those in this study, using the same biomass from Malaysia (Tan et al. 2015a; Abbey et al. 2023). This difference may be due to the variety of cocoa and the specific growing environment (including soil, water, etc.). In addition, the biomass has a high carbon content of 41.8  $\pm$  0.0% and 24% fixed carbon, indicating that it is a suitable precursor for charcoal production. Literature studies on the characterisation of cocoa pod shells have shown similar results (ash 10.6%, carbon 53% and fixed carbon 22.9%) (Martínez-Ángel et al. 2015).

The results of the macromolecular composition of the biomass studied showed a high content of total lignocellulosic molecules (80.6  $\pm$  0.2%). This confirms that cocoa pod shells are indeed a lignocellulosic material. There is also a higher proportion of lignin (38.9  $\pm$  0.5%) than cellulose (20.7  $\pm$  0.2%) and hemicellulose (21.1  $\pm$  0.5%) in this biomass. This is advantageous because lignin has a rigid structure (Mohan et al. 2006) and exhibits slow degradation kinetics during thermal processes, which can promote a high solid matter yield (biochar) at the end of a pyrolysis process. Titiloye et al. (2013) obtained the same composition trend (cellulose 30.41%, hemicellulose 11.97%, lignin 33.96%), while Daud et al. (2014) found the opposite for hemicellulose compared to lignin (cellulose 30.41%, hemicellulose 37.00%, lignin 14.70%). These differences in composition may also be related to the variety of cocoa, the growing environment, and the method of analysis used by the authors.

### Characterisation of biochars

Figures 2 show the photos of the raw biochar (figure 2.a) and activated biochar (figure 2.b) produced. The results of the physical and chemical characterisation of the biochars are listed in tables II to III.

The yields, the ash contents of raw biochar and activated biochar, as well as the burn-off of activated biochar, are presented in table II. The yield of biochar decreases when the pyrolysis temperature rises from 400 °C (43.7  $\pm$  0.6%) to 900 °C (32.8  $\pm$  0.3%). After CO<sub>2</sub> activation, there is also a mass loss (burn-off) of biochar of 37.1  $\pm$  1.2%. However, the biochar ash content, which is an important parameter for understanding adsorption mechanisms in aqueous solution, showed the opposite trend to yield. We can see that the ash content of biochar increased considerably from 400 °C (18.7  $\pm$  0.2%) to 900 °C, followed by CO<sub>2</sub> activation (31.9  $\pm$  0.1%). The variation in yield and ash content of raw biochar during pyrolysis is attributed to the release of volatiles, which results in the elimination of non-carbon species and enrichment of carbon (Sekirifa et al. 2013). As for the burn-off and increase in ash content observed after CO<sub>2</sub>



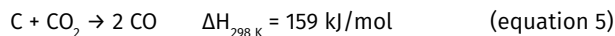
**Figures 2.** Photos of the raw biochar (a) and activated biochar (b); Particle sizes greater than or equal to 0.2 mm and less than 2 mm were selected. Photos Y. G. L. Koffi.

activation, these can be explained by the combined effects of volatilisation of organic matter during pyrolysis and carbon conversion (equation 5) during  $\text{CO}_2$  activation (Sekirifa et al. 2013). These thermochemical transformations promote the densification of raw biochar and activated biochar residues, leading to an increase in their ash content and burn-off, while their yield decreases.

The specific BET surface areas ( $S_{\text{BET}}$ ), Total Pore Volume (TPV) and Average Pore Diameter (APD) of raw biochar and activated biochar presented in table III revealed that the very low  $S_{\text{BET}}$  of raw biochar increased considerably ( $3 \text{ m}^2/\text{g}$  for raw biochar to  $178 \text{ m}^2/\text{g}$  for activated biochar), as did its TPV ( $0.02 \text{ cm}^3/\text{g}$  for raw biochar to  $0.09 \text{ cm}^3/\text{g}$  for activated biochar) after raising the pyrolysis temperature followed by  $\text{CO}_2$  activation. Meanwhile, the ADP of biochar decreased significantly ( $7.7 \text{ nm}$  for raw biochar to  $2.06 \text{ nm}$  for activated biochar). This experimental result is strongly linked to the action of  $\text{CO}_2$  on the biochar during activation. As equation 5 shows, when  $\text{CO}$  gas escapes from the carbon matrix, porous structures of carbonaceous materials can form and become well-developed (Zhao et al. 2020), thereby reducing the pore size of the biochars after activation. The activation of biochar by  $\text{CO}_2$  in this study produced mesoporous activated biochar ( $\text{ADP} > 2 \text{ nm}$ ). However, it has been demonstrated in the literature that  $\text{CO}_2$  activation leads to the formation of microporous activated carbon ( $\text{ADP} < 2 \text{ nm}$ ) (Lee & Roh 2020). This may be due to the two-step physical activation method used in this study. Indeed, Kukowska et al. (2025) made the same observation in their study, which aimed to develop new activated carbons derived from fruit waste through physical activation with  $\text{CO}_2$ . These authors noticed that direct activation of biomass led to higher microporosity compared to indirect activation (two-step). The levels of development and widening of microporosity also depend on the activation temperature, activation time, and  $\text{CO}_2$  flow, as well as the burn-off ratio (Chang et al. 2000; Lee & Roh 2020).

Quantitative information on the acidic and basic surface organic functional groups of raw biochar and activated biochar, as determined by Boehm titration, is presented in Table III. The increasing pyrolysis temperature followed by CO<sub>2</sub> activation reduces the amount of acidic functional groups (1.45 ± 0.01 to 0.0 meq/g) in the biochar, while the amount of aromatic functional groups increases (1.86 ± 0.01 to ≥ 5 meq/g). These observations indicate that the pyrolysis temperature and CO<sub>2</sub> activation destroy the acidic chemical functions while promoting the formation of basic functions on the surface of the biochars. Previous studies have also shown that the binding of heavy metals to the adsorbent surface is strongest by complexation with acidic functional groups. In contrast, π-electrons predominate in adsorption on basic surfaces (Wibowo et al. 2007). This means that the capacity of raw biochar to exchange and complex with heavy metal ions is stronger than that of activated biochar. In contrast, activated biochar has more π-electrons that can participate in adsorption via electrostatic attractions.

The pH at zero-point charge (pH<sub>ZPC</sub>) values of raw biochar and activated biochar, presented in table III, show that pH<sub>ZPC</sub> increases with increasing pyrolysis temperature, as well as after CO<sub>2</sub> activation. This increases the pH<sub>ZPC</sub> of biochar (from 8.1 for raw biochar to 12.1 for activated biochar). Both solid materials have pH<sub>ZPC</sub> greater than 7.0. We can therefore conclude that the basic groups dominate the surface of these materials (da Silva et al. 2023).



The inorganic elements of raw biochar and activated biochar are illustrated in table IV. Globally, the quantities of inorganic elements identified in raw biochar and activated biochar are consistent with their respective ash contents. The increase in the ash content of biochar induced by the pyrolysis temperature, followed by activation, leads to an increase in the quantities of its various inorganic elements. Thus, activated biochar, which has the highest ash content, has the highest quantities of these inorganic elements, compared to raw biochar, which has the lowest ash content. In addition, these materials contain higher levels of K, Ca, and Mg (major elements), which, although they limit the specific surface area and porosity, can nevertheless contribute to adsorption via ion exchange (Lian et al. 2020).

## Batch adsorption studies

### Effect of contact time between adsorbents and the cadmium (Cd<sup>2+</sup>)

Figure 3 shows the kinetic profiles for the removal of cadmium (Cd<sup>2+</sup>) using raw biochar and activated biochar. The removal rate of Cd<sup>2+</sup> from both biochars increased rapidly during the first 30 min, followed by a gradual increase up to 48 hours. These spontaneous increases in the Cd<sup>2+</sup> removal rate at the initial stage (0 to 30 min) are likely due to the large number of vacant adsorption sites on the adsorbent surface at the start of the experiment, which gradually become saturated over time (Kim et al. 2013). The values of the Cd<sup>2+</sup> removal rate of the adsorbents (raw biochar: %R = 59.3 ± 3.6% and activated biochar: %R = 32.7 ± 0.9%) show that when the pyrolysis temperature is increased, followed by CO<sub>2</sub> activation, the Cd<sup>2+</sup> removal rate of the adsorbents decreases. Zama et al. (2017) observed similar trends regarding the effect of pyrolysis temperature alone, namely that the experimental adsorption capacity decreased in the adsorption of Cd<sup>2+</sup> by peanut biochars pyrolysed at 350 to 650 °C.

### Effect of the initial concentration of cadmium (Cd<sup>2+</sup>) in solution

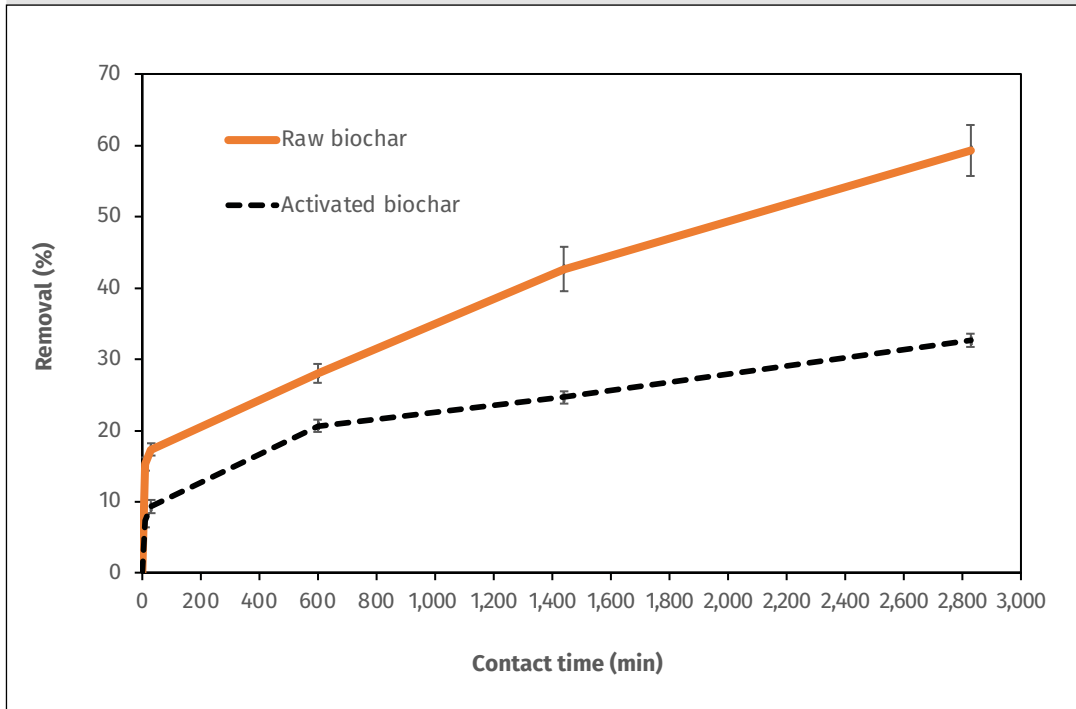
The results of the isothermal study of Cd<sup>2+</sup> adsorption by adsorbents (raw biochar and activated biochar) are presented in figure 4. The adsorption capacity (q<sub>e</sub>) of each adsorbent increased gradually and significantly with the increase in the initial amount of Cd<sup>2+</sup>. This can be attributed to the ratio between the solute (Cd<sup>2+</sup>) in solution and the available adsorption sites on the surface of the adsorbent (Kim et al. 2013). In addition, the q<sub>e</sub> = f(C) curves are sigmoidal, and each shows an inflexion point between initial concentrations of 2 and 8 mg/L. This indicates the probable existence of at least two opposing mechanisms during the adsorption processes (Edeline 1998). The maximum adsorption capacities determined experimentally (raw biochar: Q<sub>max,exp</sub> = 14.4 ± 0.3 mg/g and activated biochar: Q<sub>max,exp</sub> = 13.1 ± 0.4 mg/g) reveal that increasing the pyrolysis temperature followed by CO<sub>2</sub> activation leads to a decrease in the adsorption capacity of the adsorbents. These results show that raw biochar, which has the lowest S<sub>BET</sub>,

**Table IV.**

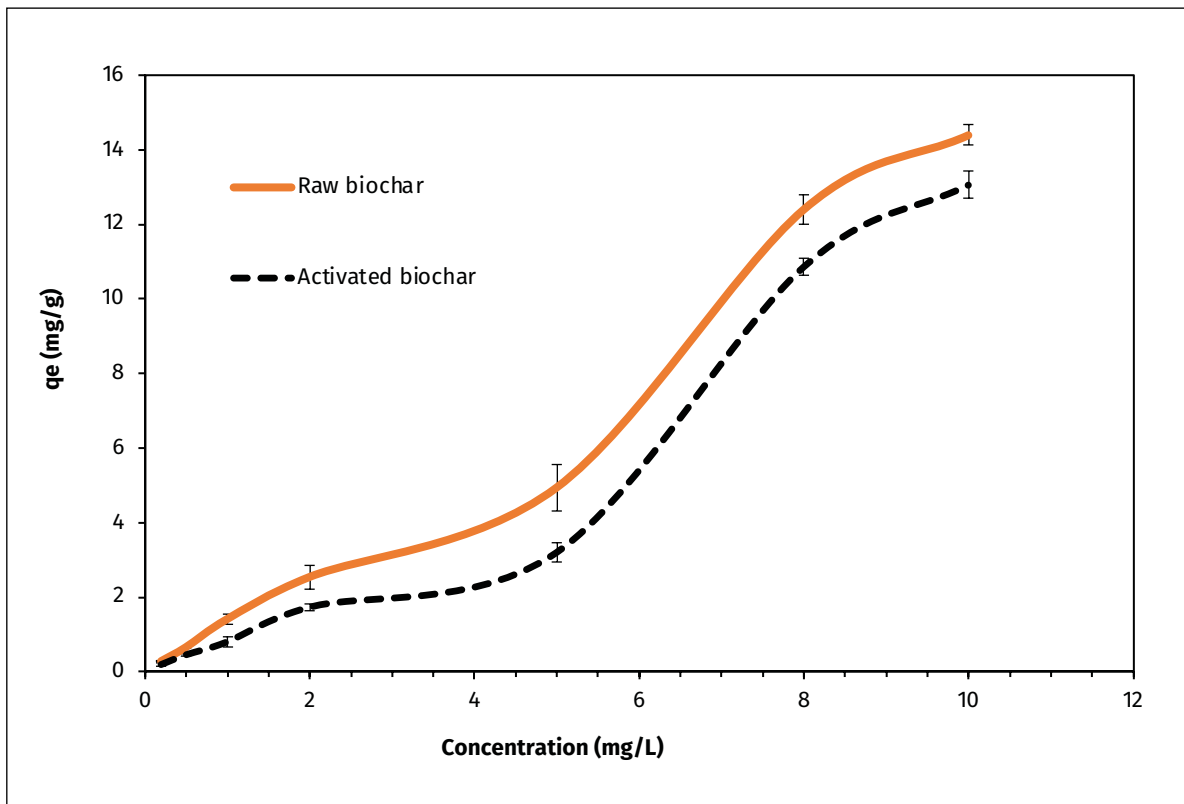
Inorganic composition of raw biochar and activated biochar (based on dry basis).

Adsorbent	Major elements (mg/kg)			Minor elements (mg/kg)														
	K	Ca	Mg	Na	Sr	Al	Cu	Cr	Mn	Fe	Ba	Co	Cd	Ni	Pb	Zn	As	Ti
Raw biochar	9,377.04 ± 30.84	2,148.91 ± 47.22	1,126.67 ± 18.16	< LD	< LD	6.53 ± 7.70	< LD	< LD	14.99 ± 0.09	36.73 ± 6.95	48.43 ± 0.11	< LD	< LD	< LD	< LD	11.83 ± 2.36	< LD	< LD
Activated biochar	23,110.56 ± 176.14	5,077.63 ± 77.61	2,430.65 ± 36.16	< LD	< LD	10.13 ± 13.32	< LD	< LD	40.50 ± 0.15	26.88 ± 0.10	148.86 ± 0.78	< LD	< LD	< LD	< LD	5.15 ± 0.01	< LD	2.98 ± 0.01

Note: LD: Inductively coupled plasma optical emission spectrometry (ICP-OES) detection limit.



**Figure 3.** Cadmium (Cd<sup>2+</sup>) removal rate by raw biochar and activated biochar as a function of time.



**Figure 4.** Amount of cadmium (Cd<sup>2+</sup>) adsorbed by raw biochar and activated biochar as a function of initial concentration, with q<sub>e</sub>: adsorption capacity.

obtained the highest  $Q_{\max, \text{exp}}$ , while activated biochar, which has the highest  $S_{\text{BET}}$  obtained the lowest  $Q_{\max, \text{exp}}$ . This implies that the adsorption of  $\text{Cd}^{2+}$  on the surface of adsorbents was strongly influenced by the chemical properties of the adsorbents rather than their physical properties. Since the  $\text{pH}_{\text{ZPC}}$  of both adsorbents ( $\text{pH}_{\text{ZPC}}$  of raw biochar = 8.1 and  $\text{pH}_{\text{ZPC}}$  of activated biochar = 12.1) is greater than the pH of the adsorption (pH = 6), their basic functional groups on the surface could not have participated in the adsorption (Cañizares et al. 2006). Consequently, the acidic functional groups (phenolic function) and surface metal ions (K, Ca, and Mg) of raw biochar are likely the primary reasons for its observed  $\text{Cd}^{2+}$  removal efficiency, which occurs through complexation and ion exchange mechanisms, respectively (Tan et al. 2015b). On the other hand, the adsorption of  $\text{Cd}^{2+}$  by activated biochar could be favoured mainly and solely by its surface metal ions (K, Ca, and Mg) via an ion exchange mechanism (Tan et al. 2015b).

## Conclusion

The removal efficiency of toxic cadmium ( $\text{Cd}^{2+}$ ) by raw biochar from cocoa pod shells was found to be high compared to its activated form. The maximum adsorption capacities determined experimentally are  $14.4 \pm 0.3$  mg/g and  $13.1 \pm 0.4$  mg/g for raw biochar and activated biochar, respectively. The adsorption of  $\text{Cd}^{2+}$  on raw biochar pyrolysed at 400 °C can be mainly attributed to complexation mechanisms due to the oxygenated acid functional groups on its surface and to metal ion exchange with its surface inorganic elements. In contrast, the adsorption of  $\text{Cd}^{2+}$  by activated biochar under  $\text{CO}_2$  is governed mainly and solely by a metal ion exchange mechanism with its surface inorganic elements. Furthermore, the basic chemical functions generated on the surface of activated biochar by increasing the pyrolysis temperature, followed by physical activation in the presence of  $\text{CO}_2$  were not beneficial under the conditions studied. Thus, biochar produced from cocoa pod shells at the lowest pyrolysis temperature of 400 °C exhibits the best affinity for monometallic adsorption with  $\text{Cd}^{2+}$ . This demonstrates that it is possible to obtain an efficient and less expensive biochar from cocoa pod shells, thereby improving the quality of drinking water in the Ivory Coast. However, further adsorption experiments should be conducted under the same conditions to improve the process: (1) deeper analysis for a better understanding of the mechanisms that favoured adsorption and desorption tests to evaluate and optimise biochar performance, including investigating how adsorbed molecules can be released and biochar regenerated; (2) commercial activated carbon intended for water purification for comparison purposes; (3) manufacture biochars from cocoa pod shells at pyrolysis temperatures below 400 °C and test them for  $\text{Cd}^{2+}$  removal in aqueous solution; and (4) approaching real-life conditions by evaluating adsorption efficiency and selectivity in systems containing multiple metals.

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## Data access

Data is available on request and can also be found at the following address: Koffi, Y. G. L. (2025). Is biochar activation always the suitable way to produce biofilters? Mendeley Data, V1. <https://doi.org/10.17632/mjh8wtzmvk.1>

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