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Chemical modification of the cocoa shell surface using diazonium salts

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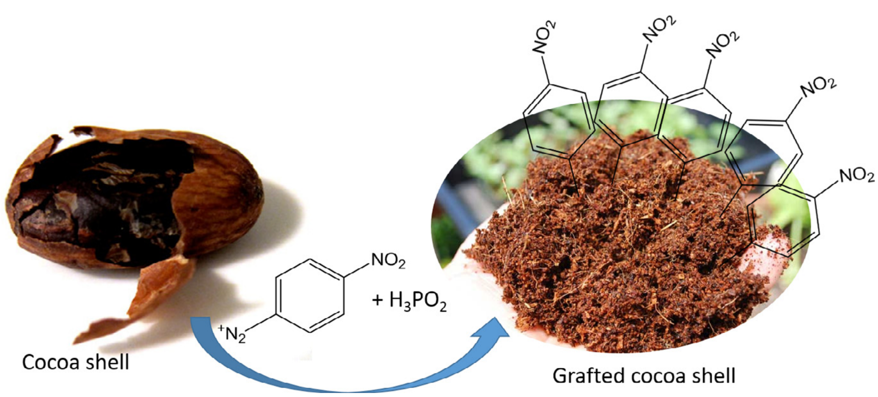
GRAPHICAL ABSTRACT



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ABSTRACT

The outer portion of the cocoa bean, also known as cocoa husk or cocoa shell (CS), is an agrowaste material from the cocoa industry. Even though raw CS is used as food additive, garden mulch, and soil conditioner or even burnt for fuel, this biomass material has hardly ever been investigated for further modification. This article proposes a strategy of chemical modification of cocoa shell to add value to this natural material. The study investigates the grafting of aryl diazonium salt on cocoa shell. Different diazonium salts were grafted on the shell surface and characterized by infrared spectroscopy and scanning electronic microscopy imaging. Strategies were developed to demonstrate the spontaneous grafting of aryl diazonium salt on cocoa shell and to elucidate that lignin is mainly involved in immobilizing the phenyl layer.

1. Introduction

The cocoa industry generates a large amount of waste byproduct each year. The cocoa shell (CS), which is the nonfood part of the cocoa pod represent the main part of these waste materials that are devoid of any marketable value. Mainly employed as a raw biomass material (as food additive, garden mulch and soil

Abbreviations: NBD, 4-nitrobenzene diazonium salt; BBD, 4-bromobenzene diazonium salt; CS, cocoa shell; NaOH-CS, cocoa shell treated with sodium hydroxide; NBD-CS, cocoa shell modified with 4-nitrobenzene diazonium salt; BBD-CS, cocoa shell modified with 4-bromobenzene diazonium salt; ATR-FTIR, attenuated total reflectance Fourier transformed infrared; SEM, scanning electronic microscopy; EDX, energy dispersive X-ray.

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conditioner) or even burnt for fuel, few strategies have been also investigated to further modify and increase its value. One way consists in developing original composite biomaterials using the cocoa shell and a thermoplastic polymer such as polypropylene [1,2]. However, the poor interfacial compatibility is frequently a limit to produce good composites [3]. CS has also been investigated as a biosorbent for the removal of metal ions. Cadmium, zinc and lead ions have been successfully and quickly adsorbed onto cocoa shell [4–6]. Dye molecules are difficult to remove from industrial wastewater. Numerous methods are described in the literature, and adsorption on lignocellulosic material is one of the finest techniques [7]. In general, CS has to be modified to become an interesting adsorbent. For example, Pua et al. treated cocoa husk with sodium hydroxide to modify its porosity and surface roughness, resulting in a good adsorption capacity [8]. Following the example of coconut shells and other agrowastes, both physical and chemical activations to generate CS-derived activated carbons have been the most commonly used post-treatments to prepare efficient adsorbents for dye removal. Different dyes (methylene blue, crystal violet…) have been successfully adsorbed onto activated cocoa shell [9–13]. In some cases, some post-carbonization treatments are required to complete the activation process. For example, CO_2 increases porosity [14,15] whereas HCl [16] or KOH [17] impregnation modulate the chemical composition of the activated carbon. All of these strategies are efficient but the treatment is rather harsh and costly and the selectivity is limited. In this publication, we suggest another simple modification based on diazonium chemistry. Aryl diazonium salts are bifunctional compounds frequently used to modify the surface properties of different materials [18]. They are easy to prepare, and a wide range of reactive functional groups can be synthesized from aniline derivates or nitro precursors. Electroreduction or chemical reduction of aryldiazonium generate an aryl radical that bonds to the surface. Although, aryldiazonium salts are frequently used to modify metallic surfaces, some polymeric surfaces have also been covalently grafted [19–22]. The present work focuses on grafting a phenyl diazonium salt on CS, and characterizing its morphology, chemical composition and porosity. We thus demonstrate that grafting a diazonium salt is a convenient method to selectively modulate the chemical properties of cocoa shell.

2. Material and methods

Chemicals: All the chemicals were purchased from Sigma Aldrich. All the solutions were prepared from double distilled water (Millipore).

Materials preparation: Cocoa shell conditioning: The cocoa shells were collected from a local farm managed by the IRAD (Institut de recherche Agricole pour le Développement) at Yaoundé, Cameroon. The shells were cut, washed with acidic water (HCl, 1 M) to remove the organic impurity, sun-dried for 5 days, and then heated at 70 °C overnight to remove moisture. The latter, they were ground and sifted at 160 μm. The diazonium grafting process wad carried according to a procedure described elsewhere [23]. Briefly, 4-nitrobenzenediazonium (NBD) and 4-bromobenzene diazonium (BBD) salts were dissolved in acidic solution, and then stirred with hypophosphorous acid (H_3PO_2) (90:10 v/v) for 1 h. The products (NBD-CS) or (BBD-CS) were filtered and washed with acetone and double distilled water and then dried at 50 °C for 2 h.

Material characterizations: Infrared spectroscopy (ATR-FTIR): ATR-FTIR spectra were recorded using a Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal. For each spectrum, 20 scans were accumulated with a resolution of 4 cm^{-1}. Cocoa shell samples were drilled before IR analysis and background spectra were recorded on air. The scanning electron microscopy (SEM) images were acquired with a ZEISS EVO 15 electron microscope coupled to an EDX detector for X-ray energy dispersion analysis. CS were metallized by a gold layer at 18 mA for 360 s using a Biorad E5200 device.

3. Results and discussion

To modify a non-conductive material such as CS, diazonium salts have to be chemically reduced to obtain an aryl radical. Therefore, cocoa shell was incubated with hypophosphorous acid and NBD or BBD for one hour. When the experiment began the cocoa shell powder rests on the bottom of the beaker. Herein, a few gas bubbles were generated corresponding to N_2 elimination. As subproduct kept forming, the color of the solution turned from transparent to yellow-orange (Fig. S1).

Also, the cocoa shell powder moved from the bottom of the beaker up to the liquid surface during the reaction, corresponding to morphological modifications at the cocoa shell surface. In parallel, no modification was observed when cocoa shell was incubated with HCl and H_3PO_2. The above results are confirmed by ATR-FTIR spectroscopy, which provides significant details about the presence of all characteristics band assigning to the CS and NBD group (Fig. 1).

To facilitate the FTIR analysis, the IR bands observed in Fig. 1 are listed in Fig. S2. As expected, the cocoa shell exhibits distinguishable peak patterns which are in good agreement with literature [8]. The bands observed at 1334 and 1517 cm^{-1} were attributed to nitro groups attached on the CS surface. Further cleaning by distilled water did not modify the infrared spectra confirming the durable grafting of nitrophenyl layer. Furthermore, the NBD grafting were evaluated by ultrasonic treatment in distilled water and in acetone. As result, no modification was observed on infrared spectroscopy. Chemical resistance was also evaluated by causing the pH to vary from 2 to 9, no modification was observed either.

Fig. 2 showed the SEM images of natural and modified CS. It can be seen that CS is an amorphous material with a smooth porous structure (Fig. 2a). Some components such as polysaccharides, hemicellulose, and lignin are present on its surface. After grafting of NBD, the surface morphology of NBD-CS is strongly modified compared with the natural CS (Fig. 2b and c). Fig. 2d confirmed that acidic solution had no effect on cocoa shell.

As seen, the CS-NBD surface was covered by some films, which suggested that the NBD was grafted into the lattice of the CS and a covalent bond may be formed between NBD and CS. In addition, the chemical grafting provided small cell cavities in the micrograph, producing a developed porosity by activation agent. It is important to note that the whole cocoa shell surface seemed to

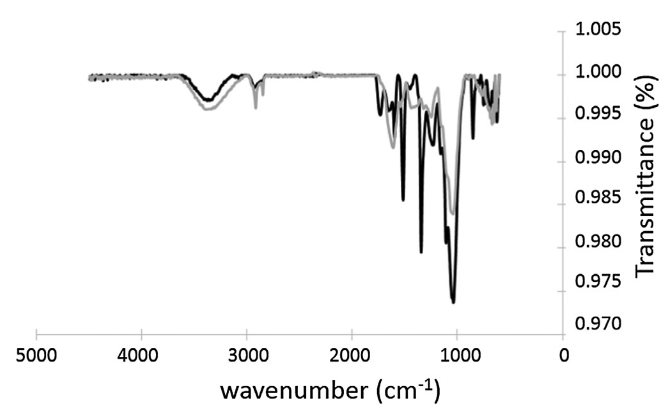

Fig. 1. ATR-FTIR spectra of natural (gray curve) and 4-nitrophenyl-modified cocoa shell (black curve).