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Waste-derived carbon nanodots for fluorimetric and simultaneous electrochemical detection of heavy metals in water†

Viviana Bressi,[ab] Consuelo Celesti,[a] Angelo Ferlazzo,[a] Thomas Len,[b] Kaveh Moulaee,[a] Giovanni Neri,[a] Rafael Luque *[cd] and Claudia Espro*[a]

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A simple and efficient synthesis of carbon nanodots (CNDs) was proposed by using hydrochar obtained through hydrothermal carbonization of beer bagasse (BB), a by-product of the beer industry that possesses several appealing advantages as a lignocellulosic source for carbon material synthesis. Raw materials and produced CNDs were characterized by several techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), FT-IR, CHNS elemental analysis, diffusion light scattering (DLS), and zeta potential, and the optical properties were studied by spectrofluorophotometry (PL) and UV-vis absorption spectroscopy. The synthesized CNDs exhibited small dimensions, interesting fluorescence behaviour, high stability and remarkable water solubility due to the presence of hydroxyl and carboxyl functional groups. Exploiting these properties, CNDs were employed in the development of highly sensitive fluorimetric and electrochemical probes for heavy metal ions, which are of great concern for human health, aquatic life, and environmental sustainability. Hg^{2+} and Pb^{2+} were detected by the fluorimetric probe with a limit of detection of 11.3 nM and 78.8 nM, respectively, while the electrochemical platform allowed the selective and simultaneous detection of heavy metal ions, reaching a detection limit of 124 ng L^{-1} and 551 ng L^{-1}, respectively for mercury and lead ions with high sensitivity, in the range between 11.4 and 34.1 μA nM^{-1} cm^{-2}.

Environmental significance

Prolonged exposure to trace levels of heavy metals in soil and water poses serious health risks, making the use of strong environmental monitoring systems of utmost importance. Carbon nanodots are emerging nanomaterials which, thanks to their exceptional properties such as small size, biocompatibility and high stability, are finding increasingly widespread use in pollutant removal in wastewater. In this work, carbon nanodots are synthesized starting from a waste by-product of the beer industry, demonstrating the ability to convert this waste into useful resources by embracing the circular economy principles. Fluorometric and electrochemical sensors built with these nanomaterials offer a rapid and accurate way to detect low concentrations of heavy metals in water.

1. Introduction

Clean water is an indispensable resource for agriculture, marine ecosystems, human health, and energy production. However, currently, only 40% of European surface water bodies achieve good ecological status.[1] In seawater environments, hazardous substances can accumulate in marine organisms, which are a source of nourishment for humans, leading to harmful effects on human health such as increased disease and cancer risks.[2] Among the hazardous substances, heavy metal ions are a major cause of environmental pollution worldwide, particularly in densely populated urban areas. Heavy metal ions include mercury, copper, cadmium, lead, cobalt, and nickel ions, which can be released from anthropogenic (*e.g.*, industrial or commercial waste, improper disposal of pharmaceuticals) or natural sources (*e.g.*, rock erosion, heavy metal leaching, sediment resuspension), causing toxicity even at low exposure levels.[3,4] The high concentration of heavy metal ions in water is an

[a] *Department of Engineering, University of Messina, Contrada di Dio–Vill. S. Agata, I-98166 Messina, Italy. E-mail: claudia.espro@unime.it*
[b] *Department of Organic Chemistry, University of Córdoba, Campus de Rabanales, Marie Curie (C-3), Ctra Nnal IV-A, Km 396, Cordoba, Spain*
[c] *Universidad ECOTEC, Km. 13.5 Samborondón, Samborondón, EC092302, Ecuador. E-mail: rluque@ecotec.edu.ec*
[d] *Scientific Center for Molecular Design and Synthesis of Innovative Compounds for the Medical Industry, People's Friendship University of Russia (RUDN University), 6 Miklukho Maklaya str, 117198, Moscow, Russian Federation*

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index of several dangerous conditions for the environment and for human welfare. Therefore, the development of simple and rapid methods for the detection of heavy metal ions is of utmost importance.

Current knowledge reveals several techniques for detecting heavy metal ions in water, but fluorescent probes and electrochemical sensors still represent the best choice owing to their numerous advantages such as low cost, rapid response time, biocompatibility, and ease of modification.[5,6] Chemical processes including oxidation and photodegradation have associated issues such as high costs and energy consumption, with the risk of undesired by-products.[7] Biological methods, *i.e.* microbial biomass adsorption and decolourization, demand prolonged residence times and lack stability[8] while physical approaches including membrane filtration and adsorption offer cost-effective solutions and exhibit superior efficiency in removal compared to detection analysis.[7] Electrochemical sensors have garnered considerable attention in recent years due to their exceptional versatility in chemically analyzing heavy metal ions.[9,10] In recent years, carbon nanodots (CNDs) have emerged as a promising material for detecting heavy metal ions, owing to their ease of use, low cost, exceptional fluorescence[11,12] and electrochemical and sensing capabilities.[13–16] The small size, low toxicity, attractive optical properties, photostability and water solubility of CNDs make them valuable materials.[17–19] Furthermore, the CNDs derived from natural sources retain many of the characteristics of the starting materials, often resulting in CNDs already doped with N or S.[20,21] Recently, many natural substances, especially crop residues, became interesting starting points in the synthesis of carbon nanomaterials.[21,22] Biomass conversion through green *bottom-up* processes, such as hydrothermal carbonization, gasification, and pyrolysis, followed by size reduction and purification, is the simplest method for obtaining CNDs from natural feedstocks.[23,24] Moreover, to mitigate waste generated by the agricultural industry and to reduce the quantities of harmful chemicals employed, researchers have investigated the potential use of organic by-products from brewing and agriculture for soil disinfection, maintenance of healthy soil microorganisms, and enhancement of crop yields.[25] An important waste fraction is produced during brewing, often used as an energy source and animal feed. The issue of waste management has become more critical in our quickly evolving world since many different types of materials are being disposed daily (ending most of them in landfill sites). The majority of the organic waste among these products is made up of beer bagasse, estimated to be 20 kg per hectoliter of beer produced,[26] commonly dismissed as basic brewing waste. Bagasse beer is a by-product of the brewing industry that arises from the pressing and filtration process of the pulp, which is obtained following the saccharification of the malted barley grain.[26] Bagasse is composed of three significant biological polymers: cellulose (approximately 40%), hemicellulose (approximately 30%), and lignin (approximately 20%). These polymers are abundant in hydroxyl and phenolic groups, which can be chemically modified to generate materials with appealing chemical properties.[25] These materials have different applications due to their biocompatibility and mechanical strength derived from the hydrogen bonds resulting in crystalline structures.

In this study, we developed a straightforward and effective procedure for synthesizing CNDs using bagasse beer-hydrochar as a natural carbon source. The obtained CNDs exhibit good fluorescence and electrochemical behaviours and were applied for the development of probes for the detection of heavy metal ions in sea water samples showing several advantages such as adaptability for on-site measurements, low cost and the ability to detect multiple ions in the same analysis. To the best of our knowledge, this material has never been used for this purpose before. Furthermore, while green carbon nanodots are becoming more common in heavy metal ion detection, notably in fluorescence, there are substantial gaps in the electrochemical sensing. The versatility for both fields, and the stability and selectivity of these green materials underline their use as extremely promising materials.

2. Experimental

2.1 Materials and reagents

All chemicals used in this work were of extra pure analytical grade and were purchased from Sigma-Aldrich. Ultrapure water (18.2 MΩ cm^{-1}) from a Milli-Q ultrapure system was used. The [illegible] provided by the company Solar Wall S.A. (Seville, Spain), was stored in a plastic bag at −10 °C and was defrosted before the experimental tests. All the electrochemical measurements were carried out in acetate buffer solutions prepared using 0.1 M sodium acetate and 0.1 M acetic acid for different pH values. All the stock solutions of heavy metal ions were prepared using nitrate salts of respective heavy metal cations and dissolving them in double distilled water.

The raw BB composition was achieved by organosolv treatment as follows: to recover fats and oil, 30 g of BB was placed in *n*-hexane for 24 h at 50 °C. Lipid-free BB was placed overnight in NaOH (pH: 10) in order to recover proteins, and a surfactant was then ultracentrifuged 3 times. 6 g of bagasse beer (lipid and protein free) was placed in an autoclave in 50 mL of EtOH–H_2O (50–50 wt%) for 90 min at 210 °C and then filtered. The solid part is represented by cellulose and the liquid part is placed in acid solution in order to separate lignin (solid part) from hemicellulose (liquid part). (All the separated components were kept for further applications). The obtained results are reported in the dedicated section.

2.2 Carbon nanodot (CND) preparation

Carbon nanodots were synthesized from beer bagasse-hydrochar as follows: 6 g of beer bagasse was ground in a ball mill at 450 rpm for 10 minutes to reduce the initial size and make the powder uniform. After, the powder was

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