Utilization of a macroalgae-based industrial waste to prepare graphene derivatives suitable in water filtration systems

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Graphene materials are rapidly gaining attention across various research fields due to their remarkable properties. These characteristics are largely attributed to graphene's unique structure as a single monolayer of carbon atoms. The presence of a free pi (π) electron for each carbon atom, resulting from the sp^2 hybridization in graphene's structure, contributes significantly to these properties (Low et al., 2021). These free π-electrons enable graphene to exhibit outstanding electrical conductivity and unique electronic and optical behaviours, making it an excellent conductor of both electricity and heat. Additionally, graphene's mechanical properties—such as its strength and flexibility—are equally impressive. This combination of conductivity, durability, and flexibility positions graphene as an ideal material for numerous energy and environmental applications, including water remediation (Bykkam et al. 2013).

In this context, graphene-based materials are emerging as a promising alternative to traditional adsorbents like activated carbon, particularly for recalcitrant contaminants that conventional materials struggle to remove effectively. This is especially relevant in industrial wastewater treatment, where pollutants such as oil, grease, and radionuclides present significant environmental challenges. However, issues such as scalability and cost remain key concerns, along with the need for complex separation techniques, such as ultracentrifugation or membrane formation, to extract the graphene material along with the contaminants from the water.

Graphene has traditionally been derived from graphite or fossil fuel-based sources. However, increasing attention is being given to biomass-based feedstocks as a sustainable alternative. Numerous studies have demonstrated the feasibility of this transition, underscoring its potential to make graphene synthesis more environmentally friendly. (Somanathan et al. 2015) This innovative approach not only mitigates the ecological footprint of graphene production but also provides a renewable solution to meet the rising demand for this versatile material in water treatment and other environmental applications (Roy et al. 2014).

In this study, we report the successful synthesis of graphene-like materials from macroalgae waste generated by the Agar–Agar industry. We demonstrate that biochar obtained at 750 °C—the optimal temperature for maximizing bio-oil production—serves as a sustainable precursor for graphene oxide synthesis via the Hummers method, without the need for further temperature increases at any stage of the process.

The graphene oxide (GO-Algae) layers exhibit characteristics similar to those of graphene oxide prepared from graphite (GO), but with the presence of nitrogen atoms in its carbonaceous structure. This nitrogen incorporation, likely due to the biochemical composition of the algae precursor, may influence the material's electronic properties and surface chemistry, potentially enhancing its reactivity and adsorption capabilities. The average lateral size is more than 200 nm, forming a few layers, as confirmed by HRTEM, which suggests that the exfoliation process effectively yields thin sheets suitable for various applications.

Moreover, we demonstrate herein that the graphite oxide obtained from algae waste—i.e., the material obtained after the chemical treatment of the algae waste but before its sonication (GrO)—exhibits characteristics more similar to few-layer graphene than to conventional graphite oxide. This distinction is crucial, as it implies that the oxidation and exfoliation process of algae-derived graphite oxide results in a material with a more ordered structure, possibly due to differences in the starting precursor and oxidation dynamics. This is exemplified by the visualization of this material via HRTEM (Figure 1), where the presence of a few-layer structure with an aromatic spectrum is observed.

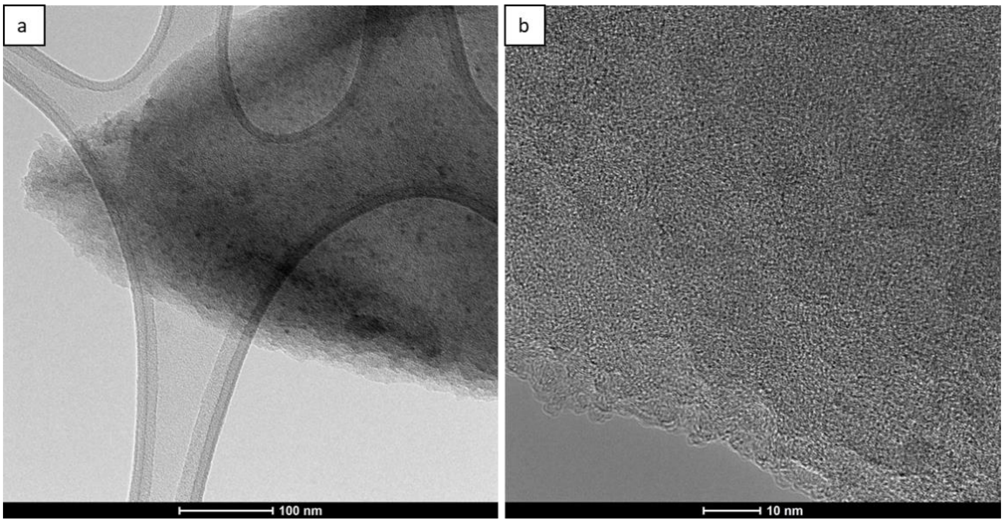

Figure 1. Graphite oxide a) TEM and b) HRTEM analyses.

The materials prepared (GrO-Algae and GO-Algae) were tested for the removal of radionuclides (i.e., uranium) from water, alongside graphene oxide prepared from commercial graphite. The removal efficiency of uranium was studied as a function of radionuclide concentration (ranging from 100 to 1500 ppb) and graphene concentration (ranging from 40 to 160 ppm) at neutral pH. Additionally, adsorption kinetics and isotherms were analyzed to evaluate the adsorption capacity and interaction mechanisms between the radionuclides and the graphene-based materials. The quantification of uranium in water was determined using ICP-Ms analysis. After ultracentrifugation of the mixture

The results obtained indicate that all algae-derived graphene materials exhibit adsorption capacities comparable to those observed for graphene derived from graphite. Our findings also suggest that the most defective graphene exhibits the highest sorption performance, with a possible influence of nitrogen in the graphene layer acting as an active site for uranium adsorption. Moreover, the results for the graphite oxide prepared from algae (GrO) are similar to those of the same material after exfoliation (graphene oxide, GO), with the notable advantage that the suspension can be filtered instead of ultracentrifuged to separate the graphite oxide with the adsorbed uranium from the water.

This work not only demonstrates the potential of macroalgae waste as a biomass source for high-performance water remediation sorbents but also represents a technological breakthrough in the water purification sector.

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