

From industrial wastes to advanced graphene-like materials: application in wastewater purification

M. González-Ingelmo,¹ Y. Yaque,¹ M. Granda,¹ Z. González,¹ U. Sierra,² A. Mercado,² V.G. Rocha,¹ R. Santamaría,¹ C. Blanco,¹ R. Menéndez,¹ P. Álvarez¹

¹Instituto de Ciencia y Tecnología del Carbono, INCAR-CSIC, C/Francisco Pintado, Fe, 26, Oviedo, 33011, Spain

²Centro de Investigación de Química Aplicada (CIQA) Laboratorio Nacional de Materiales Gráficos, Boulevard Enrique Reyna 140, San José de los Cerritos, C.P. 25294 Saltillo (Coahuila), México

Introduction

Graphene materials exhibit unique properties, such as thermal stability, and have potential application in different energy and environmental areas. In the case of the oxidized graphenes (graphene oxides), they are useful in the removal of **Emerging contaminants (ECs) and toxins in water** (low levels of removal in conventional wastewater treatment processes). However, graphenes are usually produced from natural graphite, and it will be desirable to produce them directly from other more **sustainable carbonaceous sources** as industrial wastes and avoiding their graphitization (thermal treatment at 2500-3000°C). The objective of this work is to develop graphene oxides from a coke residue of the **steel industry** (formed in the upper internal section of the coking oven for the steel production which is stored outdoors causing pollution in the surroundings) and a **biochar** obtained by pyrolyzing macroalgae waste in the **Agar-Agar industry**. **The graphenes obtained will be exhaustively characterized** and the results will be compared with those obtained with a graphene prepared from commercial graphite under the same experimental conditions. Finally, **all GOs will be used to eliminate contaminants in wastewater (diclofenac and uranium)**, at a concentration similar to that reported as a problem for Wastewater Treatment Plants.

Objectives

- ❖ To study the preparation of graphene oxides using, as raw materials, industrial wastes obtained from the steel industry (GO-IW) and from the Agar-Agar industry (GO-AI), avoiding their previous graphitization. Comparison with the graphene oxides prepared from a standard graphite (GO-G).
- ❖ To optimize the processing and to determine the structural differences between the graphenes obtained from the different industrial wastes.
- ❖ To evaluate the capacity of the graphenes prepared to be used in the elimination of contaminants (diclofenac and uranium) in wastewaters.

Experimental Method

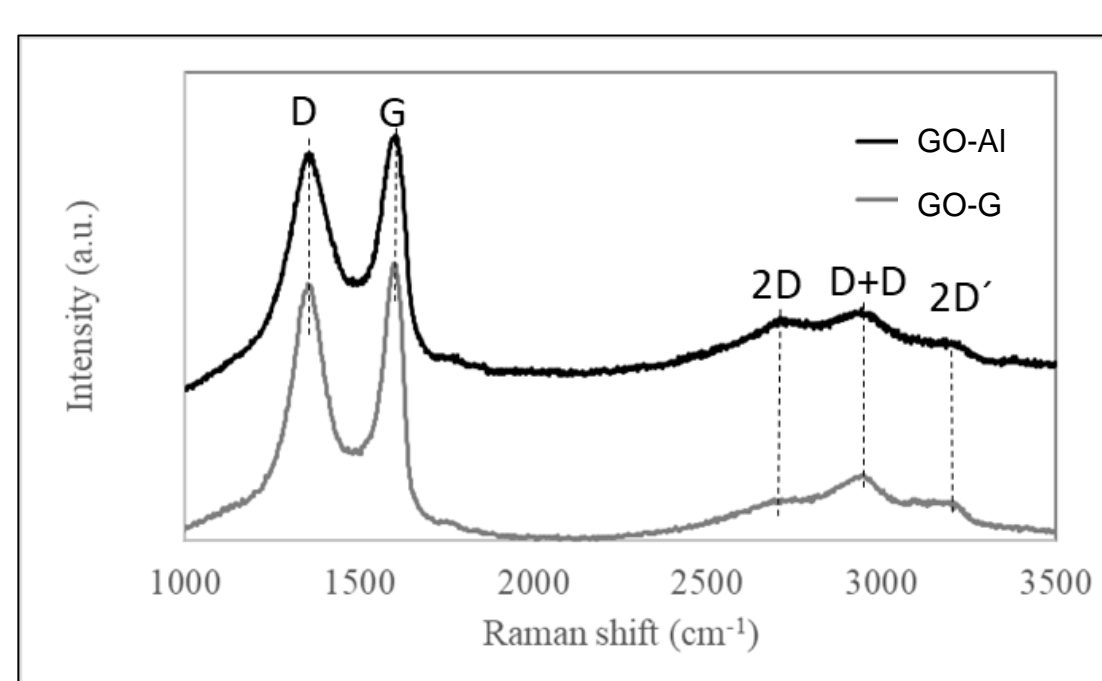
Steel Industry

Agar-Agar Industry

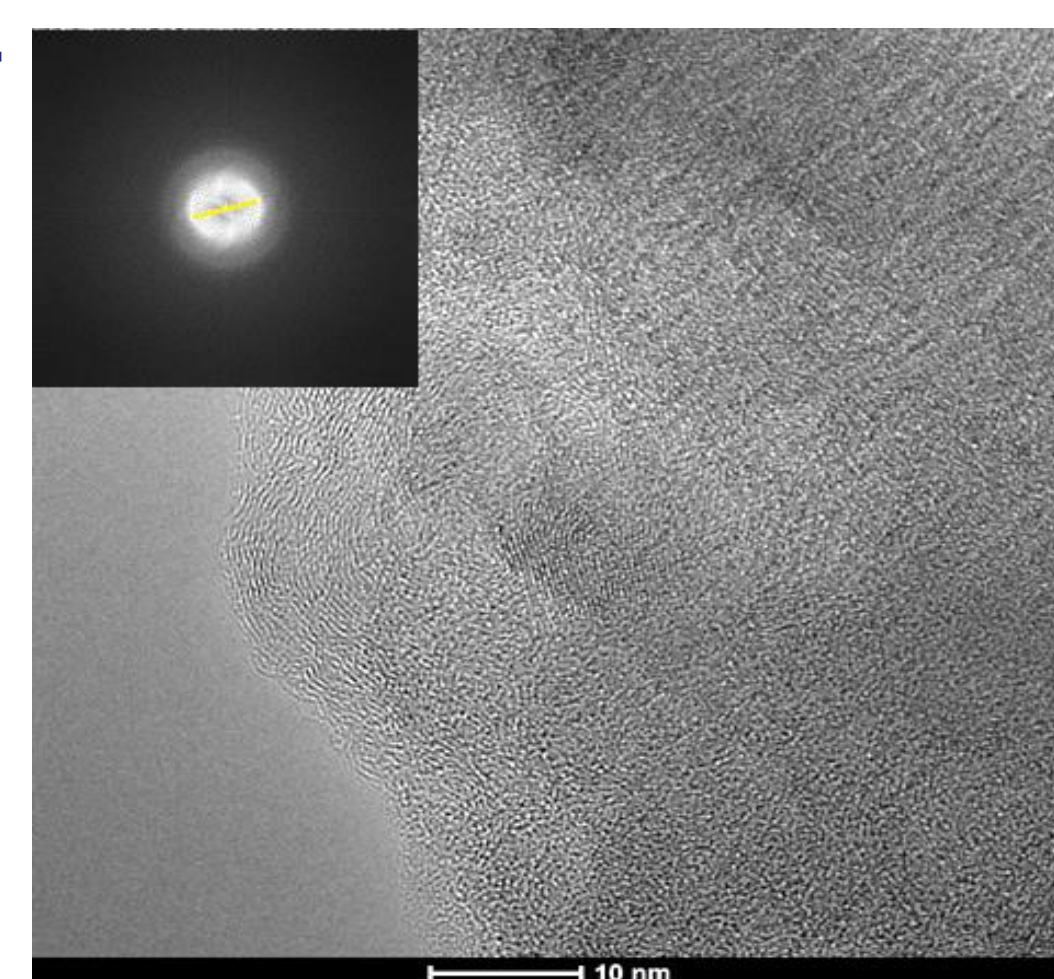


Results & Discussion

Agar-Agar Waste: GO-AI characterization

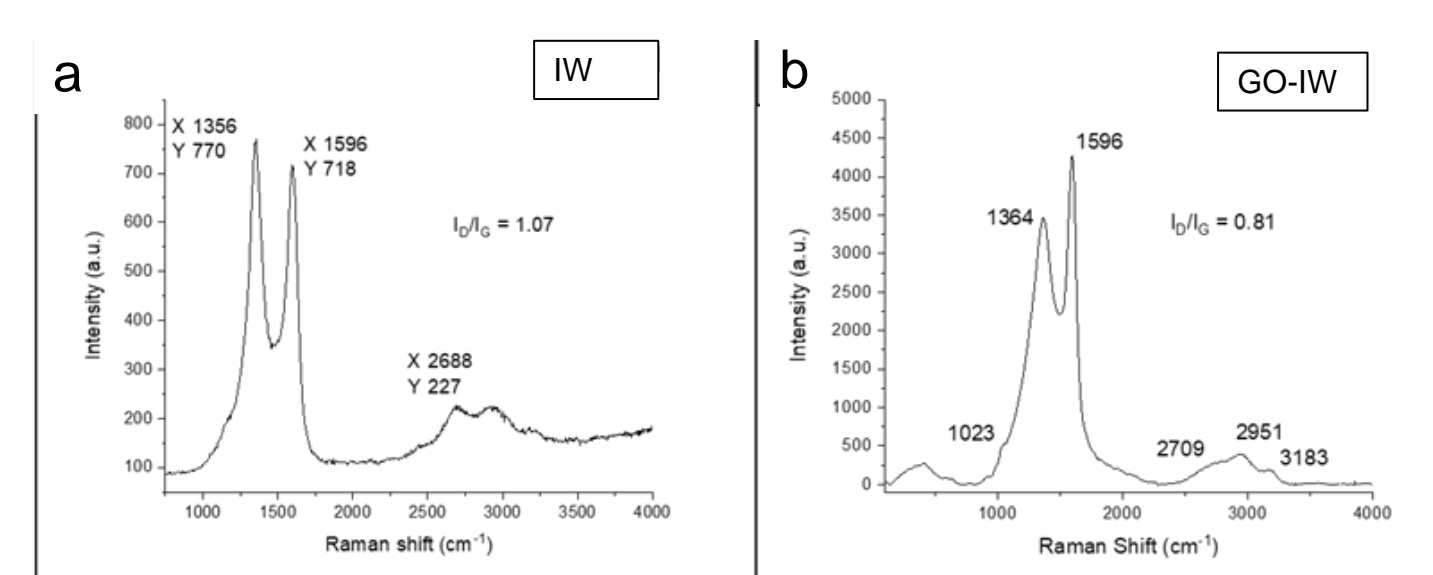


The Raman spectrum of GO-AI shows the typical shape of a graphene oxide, very similar to that of G-GO (from standard graphite). The ID/IG ratio obtained for GO-AI is 0.95, a bit lower than that calculated for GO-G (0.97).

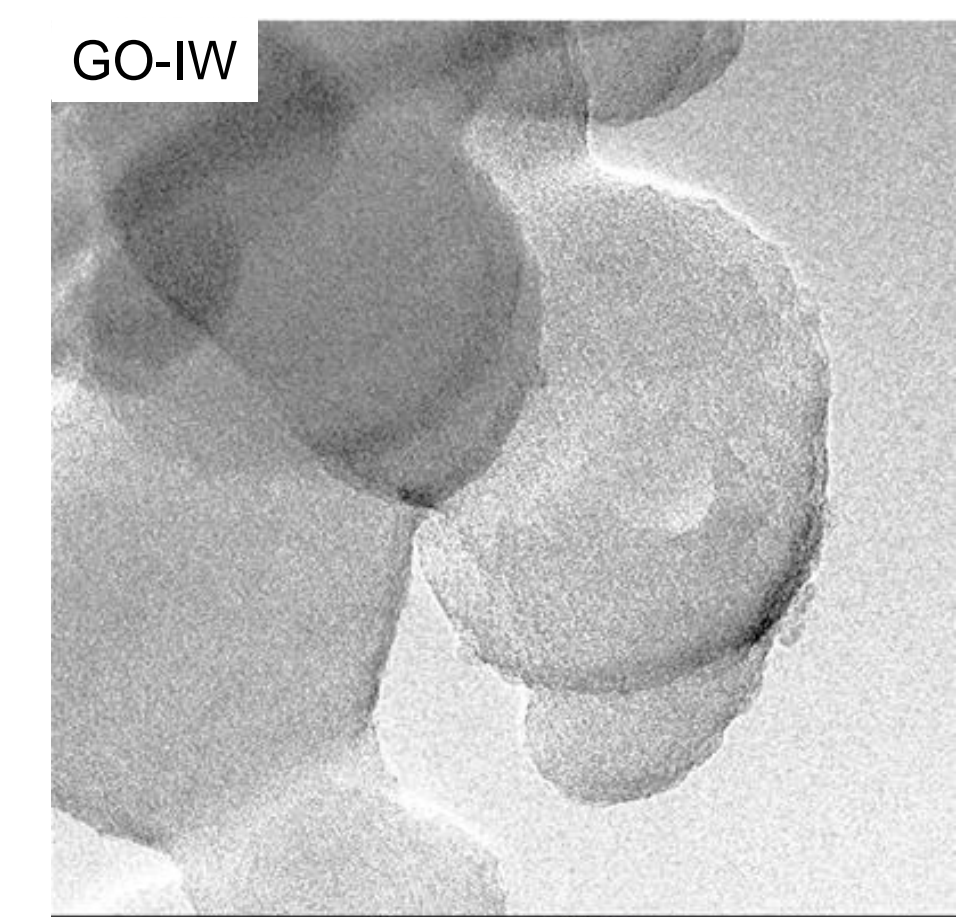


The appearance of more wrinkles and defective edges in GO-AI is noticed by means of HRTEM visualization, in a similar way to other graphene oxide sheets from biomass sources

Steel-industry Waste: GO-IW characterization



The ID/IG intensity ratio for the raw industrial waste (IW) is of 1.07, in accordance with a poor graphitic structure. However, after processing, the ID/IG ratio of the GO obtained without graphitization is of 0.81 in the range of a standard graphene oxide (GO-G, 0.97).



HRTEM visualization of GO-IW indicates the presence of few layer graphene material with low lateral size

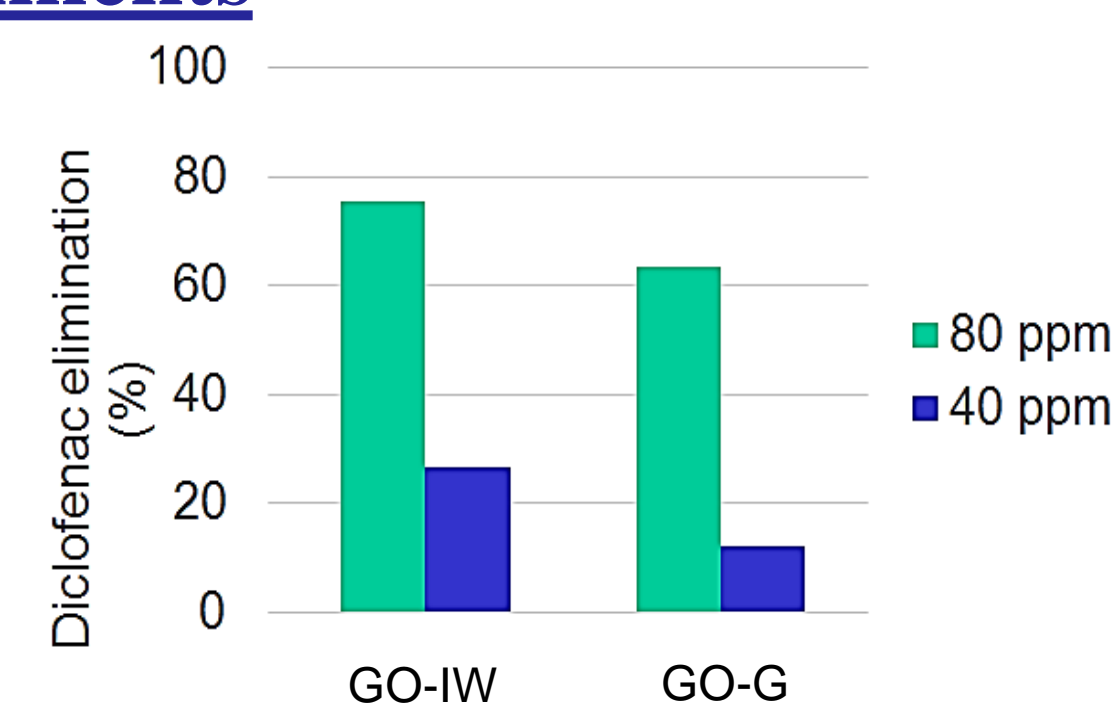
GO-AI: Uranium adsorption experiments

The uranium adsorption capacity of GO-AI is even slightly higher than that of the standard GO-G. Likewise, the process is more effective when a higher concentration of GO is used.



GO-IW: Diclofenac adsorption experiments

In the diclofenac water adsorption experiments, GO-IW exhibited a more effective performance than a standard GO (GO-G), probably as a consequence of their higher defective structure. It was also proven that a higher concentration of GO is more effective in eliminating diclofenac.



Conclusions

*The two industrial wastes, without being graphitized, can be effectively used to prepare graphene oxides (GOs). The properties of the GOs are similar to that of a GO prepared from a standard graphite. The GO from the algae residue has more wrinkles and edge-defects and the GO from the Steel industry appears as few layer with low lateral size

*The graphenes obtained can be used very effectively to remove DCF and uranium from contaminated waters. This represents an important application for the revaluation of residual material.

Acknowledgement

These results are part of the project PID2022-139478OB-100 funded by MICIU/AEI/10.13039/501100011033 and for FEDER, UE, and Spanish National Research Council (ICOOP program, COOPB22006). Mrs. M-González-Ingelmo acknowledges his fellowship from the Asturias Regional Government (FICYT, Severo Ochoa Program BP20-168).



MINISTERIO DE CIENCIA E INNOVACIÓN

