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

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Emerging contaminants (ECs) such as Diclofenac, consists of different chemicals, pharmaceuticals, and related materials chemicals consistently found in groundwater, municipal wastewater or different sources of food, which can cause ecological and human health damage. Today, their elimination is a focus of interest to the research community. Diclofenac, a medicine for humans and other animals, has been widely detected in European surface waters and has a low level of removal under conventional wastewater treatment processes. Therefore, it passes through the discharges from Wastewater Treatment Plants (WTP) and enters contact with aquatic organisms. It has been recently reported that the elimination of this contaminant by means of graphene materials (such as graphene oxides –GOs-) is much more efficient that by common adsorbents (*Guerra* et al., 2021), such as activated carbons. The preparation of graphenes has however some limitations. They are usually produced from natural graphite, a finite natural resource or from synthetic graphite, material which requires severe experimental conditions for its preparation (i.e. graphitization temperatures of >2800ºC). However, in order to reduce the costs of the GOs and to promote a more sustainable synthesis, the use of other raw materials avoiding any graphitization step is desirable.

In this regard, authors reported the successful preparation of graphene materials from pregraphitic carbonaceous samples (Sierra et al. 2015). Elaborating in this idea, we report herein the preparation of graphene oxides from an industrial carbonaceous waste from the iron and steel industry. This is a carbonaceous residue formed in the upper part of the blast furnaces and with very heterogeneous composition and morphology. It is usually scraped from the oven walls after several working cycles and discarded. This solid waste is storage outdoors leading to several environmental concerns.

The first objective of this work is to prepare GOs from this industrial residue. For that we will make use of the chemical route to prepare the GOs but the methodology will be adjusted to take into account the heterogeneous structure of the waste. As comparative purposes, the waste will be also graphitized. Additionally, a standard GO obtained from a graphite will be also prepared. The material so prepared will be extensively characterized on order to determine the features promoted by the defects in the graphitic structure of the waste. The ultimate goal is the application of the as prepared graphene oxides in the elimination of diclofenac in wastewaters, in a concentration similar to that reported to be a problem to the WTP. The results obtained will be also related with the strcuctural characteristics of the GOs.

**Materials and methods**

An industrial waste (IW) obtained from a coke industry in Nuevo León, México was used as raw material. As comparative purposes, IW was graphitized and the graphite also used in this work (GW), together with a standard graphite obtained from ALDRIC (G). IW, GW and G were used to prepare graphene materials by chemical methods (*Sierra* et al. (2015)). They wwere named as IW-GO, GW-GO and G-GO respectively. The obtained GOs were characterized by EA, TGA, Raman, XPS HRTEM.

Adsorption experiments were performed to explore the efficiency of the different graphene-like materials at two concentrations removing diclofenac in water solution. Solution containing 200 μM of contaminant is added to 160 and 80 ppm suspension of the prepared carbon-based materials (ratio 1:1). The solution was magnetically stirred for 24 hours. After that time, each solution was filtered using syringe filters (PES 0.1μm). The non-retention of free diclofenac by these filters was checked. For DCF quantification, the spectrophotometric method was selected due to its sensitivity, simplicity, and the little time consumed for analysis (*Guerra* et al., 2021). Absorbance data were recorded at 275 nm with a UV-Vis spectrophotometer (Shimadzu UV-1800) using a quartz cell with a 1 cm optical path. Standard additions were made for each sample to account for the matrix and determine the original concentration of DCF.

**Results and discussion**

The elemental composition of IW reveals that it is composed mainly by carbon (98.5 wt.% ) and less than 1 wt.% of sulphur. After graphitization, the carbon content increases up to 99%.

The laminar structure of both waste-based GOs was further confirmed by their TEM images (Figure 1). However, while GW-GO exhibit the appearance of a single layer of high size (Figure 1 (a)), similar to that of the obtained for the standard G-GO, the GO obtained from the waste at low temperature (IW-GO) is of much lower lateral size and mainly in the form of few layers (Figure 1 (b)). This could be consistent with the previously proposed low oxidation of the basal planes of the graphenic layers, which hinders its exfoliation leading to few layer graphene. This clearly confirms that the utilization of a low temperature waste conditions affects the morphology of the graphene materials obtained from them.

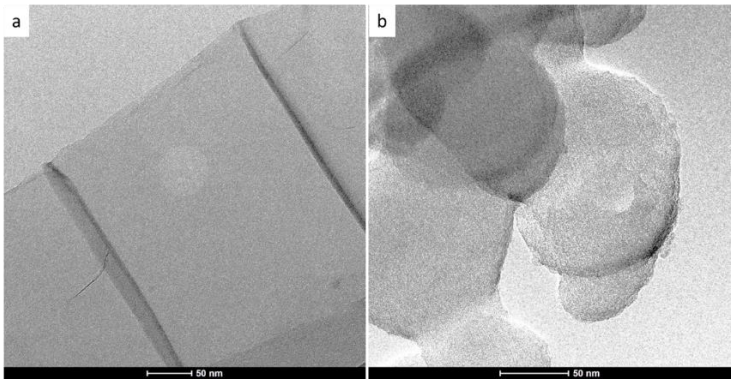


Figure 1: TEM images of a) GW-GO and b) IW-GO

The quantification of DCF after the adsorption experiment showed that the prepared graphenes do not have the same capacity for adsorption of the contaminant (100 μM). Specifically, it is observed that the most effective for removing DFC is G-waste-GO (Table 1). However, the results indicated that waste-H, despite not having undergone the graphitization step, is also better as an adsorbent than ref-GO. This demonstrates that the coke waste can be used very effectively for the removal of DCF in water. This represents an important application for the revalorization of the residual material. On the other hand, the study of two concentrations of GO in the adsorption experiments indicated that for all graphenes, a higher concentration is more effective in eliminating the contaminant. Further research will be carried out to optimize the concentration of the GO suspension.

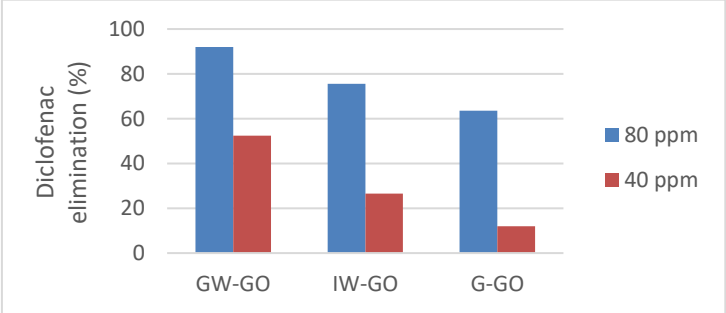


Figure 2: Elimination of diclofenac in wastewater as a function of two different initial diclofenac concentrations (80 and 40 ppm) using GW-GO, IW-GO and G-GO

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