Preparation of sustainable graphenes from coke-like wastes with applications in elimination of emergent contaminants in wastewater

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Emerging contaminants (ECs) are chemicals or microorganisms with the potential to cause adverse ecological-human health effects while they are not commonly monitored or cannot be tested for in municipal water systems. They consist of pharmaceuticals, pesticides, industrial chemicals, surfactants, and personal care products that are consistently being found in groundwater, municipal wastewater, drinking water, and food sources. These ECs also last for a long time in the environment. Therefore, how to effectively remove ECs in water has received widespread attention. Diclofenac (DFC) is a human and veterinary medicine widely detected in European surface waters, and which primarily enters these waters in discharges from Wastewater Treatment Plants (WTP). This medicine has also relative low levels of removal in conventional wastewater treatment processes leading to a high exposure of aquatic organisms downstream of the WTP. Its elimination is therefore a requirement. To that end, adsorption is broadly applied in wastewater treatment due to the high simplicity and effectiveness. Regarding this purification method, graphene oxide (GO) shows a better efficiency in comparison to common adsorbents like activated carbon to remove ECs in wastewater. GOs are usually produced from natural graphite, but in order to promote a worldwide use of these materials it would be desirable to ensure a sustainable graphene raw material.

In this work we propose the utilization of an industrial waste as precursor to obtain a graphene-like material. This industrial waste is a carbonaceous residue usually formed at the inner upper part of the coke formation for the blast furnaces for the iron and steel industry (coke-like material). It is usually scraped after several cycles and exhibit not controlled composition. It is therefore discarded leading to solid and water environmental contaminations in the area. The main goal of this work is to prepare two graphene-like materials from this waste to employ them as ECs adsorbents. The first one (G-waste-GO) involves, before chemical oxidation, the typical graphitization step (thermal treatment at 2500-3000ºC) to obtain a graphite-like material. In the other case (waste-GO), the raw coke-like waste is directly oxidized without any pretreatment. In this way, the overall process becomes more sustainable by avoiding the graphitization step. These graphenes will be exhaustively characterized and the results compared with those obtained with a graphene prepared from commercial graphite under the same experimental conditions. Finally, all GOs will be used to eliminate diclofenac in wastewaters, in a concentration similar to that reported to be a problem to the WTP.

Materials and methods

A coke-like waste with and without previous graphitization step (G-waste and waste, respectively) and a commercial graphene (ref) were used as raw materials. Graphene oxides were prepared from them (G-waste-GO, waste-GO and ref-GO) by means of a modified Hummers method (*Sierra* et al. (2015)). Graphenes obtained were characterized by EA, TGA, Raman, XPS and optical methods.
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

According to the elemental analysis, the coke-like waste used as raw material is composed by a 98.5 wt.% of Carbon and less than 1 wt.% of sulphur. Also, its Raman spectra shows a Id/Ig ratio of 0.94, which makes it a good candidate for the preparation of graphene. By means of a Hummer procedure, graphene oxide was prepared from this material (waste-GO), which shows, by TEM analysis, its typical morphology (Figure 1), confirming the feasibility of this material to prepare graphene.

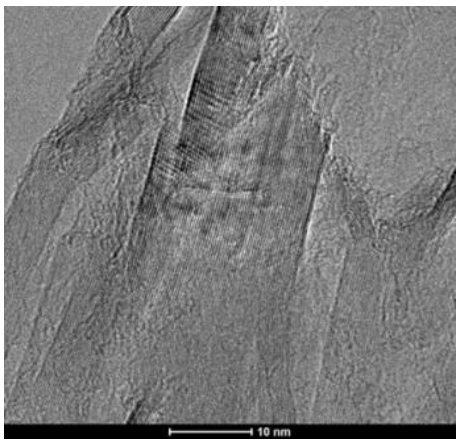

Figure 1. TEM images of waste-GO.

The graphenes prepared were used to eliminate DCF from wastewater (initial concentration of 100 μM). The quantification of DCF after the adsorption experiment (table 1) shows that the capacity of elimination of DCF depends on the type of graphene used. In general terms it is observed that both graphenes prepared from the waste eliminates more efficiently DCF with respect to standard graphene (ref-GO) at the two GO concentrations studied (80 and 40 ppm) and almost reaching a 90% DFC sorbed for G-waste GO. Even the adsorption capacity of waste-GO, despite not having undergone the graphitization step, doubles that shown for ref-GO at a GO concentration of 40ppm. These results represent an important breakthrough in the utilization of an industrial waste in environmental applications.

Table 1. DFC adsorbed quantification by spectrophotometric method.

	[GO] (ppm)	% DFC sorbed
G-waste-GO	80	92.0
	40	52.4
waste-GO	80	75.5
	40	26.6
ref-GO	80	63.6
	40	12.0

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