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CIÊNCIA e NATURA

ISSN 2179-460X
OPEN ACCESS

Ci. e Nat., Santa Maria, v. 46, e86374, 2024 • https://doi.org/10.5902/2179460X86374
Submissão: 11/01/2024 • Aprovação: 12/01/2024 • Publicação: 26/04/2024

Chemistry

Eco-friendly strategies for the graphene oxide reduction

Estratégias ecológicas para a redução do óxido de grafeno

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ABSTRACT

The reduced graphene oxide (rGO) is a nanomaterial derived from graphene, which exhibits a high surface area, chemical stability, and extensive diffusion of π-conjugated bonds. Graphene oxide (GO) can be reduced to rGO through different protocols, however, commonly applied methodologies involving the use of chemical reagents may have disadvantageous effects on the environment. Considering the excellent properties of rGO, this study aimed to reduce GO through sustainable green strategies using carrots, oranges, and beets as reducing agents. The characterization of GO and rGO was carried out by X-ray diffraction spectroscopy (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electronic microscopy (SEM), which revealed a reduction in the spacing between the layers of GO, indicating the formation of rGO. Due to the outstanding results obtained, future studies will explore the properties of this nanomaterial as an adsorbent for contaminants of emerging concern.

Keywords: Reduction; Eco-friendly; Green approach

RESUMO

O óxido de grafeno reduzido (rGO) é um nanomaterial derivado do grafeno, que apresenta alta área superficial, estabilidade química e extensa difusão de ligações conjugadas π. O óxido de grafeno (GO) pode ser reduzido a rGO através de diferentes protocolos, porém, metodologias comumente aplicadas envolvendo o uso de reagentes químicos podem ter efeitos desvantajosos ao meio ambiente. Considerando as excelentes propriedades do rGO, este estudo teve como objetivo reduzir o GO por meio de estratégias verdes sustentáveis utilizando cenoura, laranja e beterraba como agentes redutores. A caracterização de GO e rGO foi realizada por espectroscopia de difração de raios X (XRD), espectroscopia no infravermelho com transformada de Fourier (FTIR) e microscopia eletrônica de varredura (MEV), que revelou redução no espaçamento entre as camadas de GO, indicando a formação de rGO. Devido aos excelentes resultados obtidos, estudos futuros irão explorar as propriedades deste nanomaterial como adsorvente para contaminantes de preocupação emergente.

Palavras-chave: Redução; Ambientalmente amigável; Método verde

1 INTRODUCTION

Graphene is one of the most promising materials of the present time. This nanomaterial consists solely of carbon sp_2 hybridized bonds in a one-atom-thick structure. This carbon compound possesses several characteristics, including high specific surface area, thermal and electric conductivity, mechanical strength, mobility, and chemical stability (Rhoden et al., 2021). Considering these properties, graphene offers a wide range of applications in optoelectronics, supercapacitors, sensors, nanocomposites, biomedical applications, photocatalysis, flexible films for solar panel production, water purification, and other sectors of industry and commerce (Wei et al., 2017, Vargas G. O. et al., 2023, de Oliveira, É.C., da Silva Bruckmann, F., Schopf, P.F. et al.,2022).

Graphene oxide (GO) is a carbon nanomaterial obtained from the oxidation and exfoliation of graphite (Bruckmann et al., 2022). This nanomaterial is an excellent absorbent due to its high specific area with several oxygenated groups capable of interacting with many adsorbates (Barbieri, I. A. et al.,2024;). Moreover, the GO shows high mechanical strength, photo-stability, and easy surface modification (Da Silva Bruckmann, F. et al.,2022). This nanomaterial has numerous applications and possibilities for structural modifications to obtain other compounds, such as your reduced form (rGO). One of the most common methods for rGO production involves the initial oxidation of graphite to oxide form. Subsequently, graphite oxide is exfoliated to obtain graphene oxide, and finally, it is reduced to rGO (Zheng et al., 2015). This material is a graphene-derived nanomaterial with a high specific surface area, chemical stability, and extensive diffusion of π-conjugated bonds, which possible the presence of different properties/characteristics (Ahmed, Aamir et al., 2023).

GO can be reduced to rGO through various methods, including microwave treatment, chemical reduction, laser reduction, photo-reduction, electrochemical reduction, and hydrothermal reduction (Velasco-Soto et al., 2015). The most used methodology is the chemical route, which employs toxic reagents, such as hydrazine and sodium borohydride,

that can have detrimental effects on the environment. These reducers include hydrazine, hydroquinone, and sodium borohydride (Amarnath et al., 2011).

Considering the excellent potential applications of rGO, this study aimed to reduce GO through sustainable methods using carrots (Vusa et al., 2014), oranges (Mahiuddin & Ochiai, 2021) and beets as reducing agents. These agents contain amino acids, saccharides, organic acids, and microorganisms that reduce the functional groups of GO, allowing the production of rGO (Thakur et al., 2015). Oranges are rich in ascorbic acid (vitamin C) it is a reductant agent (Ferda Mindivan & Meryem Göktaş, 2019) and beet (Siti Kudnie Sahari et al., 2020) how was showed in these studies.

2 METHODOLOGIES

2.1 Graphene Oxide synthesis

Oxide graphene was synthesized through the oxidation and chemical exfoliation of graphite following the method reported by Salles et al. (2020). Initially, 1 g of graphite and 60 ml of 98% sulfuric acid were added to a 1000 ml beaker under magnetic stirring at 150 rpm. The mixture was stirred at 20 ºC for 20 minutes. Subsequently, 6 g of $KMnO_4$ 99% (Synth) was slowly added over 20 minutes.

Next, the reaction was heated to 40 °C for 4 hours and left stirring overnight at room temperature. After this period, 180 ml of distilled water was slowly dripped into the reaction system and maintained at 40 °C for an additional 1 hour. Sequentially, 300 ml of distilled water was slowly added to the solution. Finally, 10 ml H_2O_2 29% (Synth) was added to reduce the chemical species (Mn^{+7}).

For the purification step, the graphene oxide (GO) was washed twice with distilled water and subsequently with a 10% HCl solution to remove any residual metal ions. The final step of the process involved washing the material until reaching a pH around 7 (Peng et al., 2015). Finally, the product was dried in an oven (DeLeo) at 50 ºC for 24 hours (Paulchamy; Arthi; Lignesh, 2015).

2.2 Reduced Graphene Oxide Synthesis

The reduction of graphene oxide started with 200 mg of powdered GO, which was placed in an Erlenmeyer flask containing 100 mL of ultrapure water, with the pH adjusted to 9.5. This mixture was immediately subjected to ultrasonic treatment for 1 hour. Then, 20 g of carrot or beet roots, cut into 1 cm cubes, or alternatively, 20 g of filtered orange juice, were added. The mixture was stirred on a shaker table at room temperature for 24 hours.

Subsequently, the solid parts of the reducing agent were removed, with the help of a sieve, the solid material was washed to remove any part of the GO that had been stuck to the surface. and the solution containing GO was transferred to a round-bottom flask and refluxed at 95 °C for 24 hours (using a reflux condenser to prevent volume reduction). After this period, the reduced material was transferred to a beaker and washed until reaching a neutral pH.

Due to the highly hydrophobic nature of rGO, it settled at the bottom of the beaker, allowing the supernatant to be discarded. Finally, the obtained material underwent a wash with acetone to remove any traces of water and was then dried in an oven (DeLeo), in yields of 90%, 92% and 95% for carrot, beetroot and orange respectively.

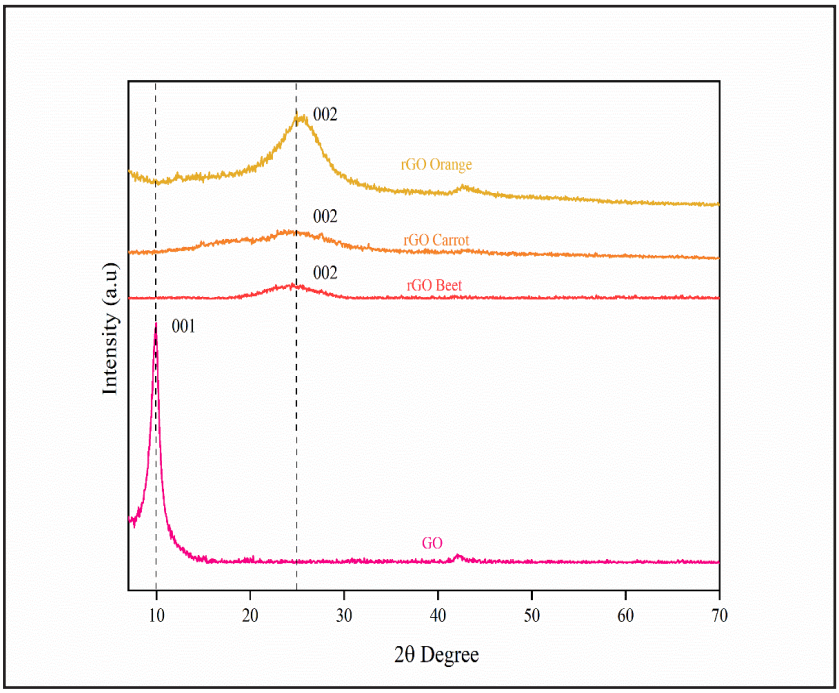
3.RESULTS

3.1 X ray diffraction XRD

The X-ray diffraction (XRD) patterns for graphene oxide (GO) and reduced graphene oxide (rGO) are demonstrated in Figure 1. In the case of GO, a sharp and distinctive diffraction peak is observed at 2θ ≈10.5º, corresponding to a layer spacing of approximately 8.69 Å. This spacing indicates the presence of epoxy, hydroxyl, and carboxyl functional groups, which is attributed to the low temperature in synthesis, favoring the addition of these groups (Harres, A. et al, 2023).

Analyzing the XRD pattern of rGO derived from orange, beetroot, and carrot, the presence of a narrow peak at 2θ ≈25º is evident, attributed to the reduction of GO (Manikandan, Velu; Lee, Nae Yoon.,2023). Additionally, a reduction in the interlayer spacing of rGO is observed, now measured at 3.65 Å, suggesting an effective reduction of GO (Cui et al., 2011).

Figure 1 – XRD GO,rGO carrot, rGO beet and rGO Orange results

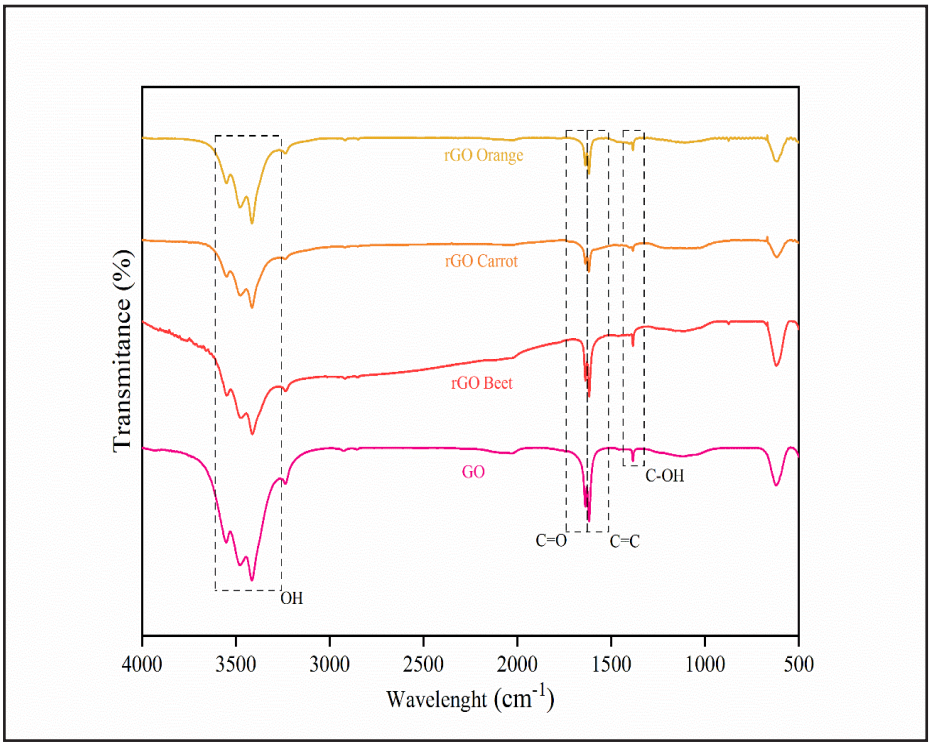


Source: Author's creation

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 displays the Fourier Transform Infrared Spectroscopy (FTIR) spectra of GO and rGO, derived from orange, beetroot, and carrot. In the graphene oxide spectrum, the absorption peak at 3416 cm^{-1} corresponds to O-H stretching vibrations (Nunes, F.B. et al., 2023). The peak at 1640 cm^{-1} refers to the stretching vibration of C=O bonds in the COOH group, and at 1619 cm^{-1}. Additionally, there is the vibrational stretching of the C=C bond (da Silva Bruckmann, F.*et. al.*, 2022). The bands at 1385 cm^{-1} correspond to the vibrations of C-OH bonds in alcohol moieties (da Silva Bruckmann, F.*et. al.*, 2022.

Figure 2 – Fourier Transform Infrared Spectroscopy GO,rGO carrot, rGO beet and rGO Orange results



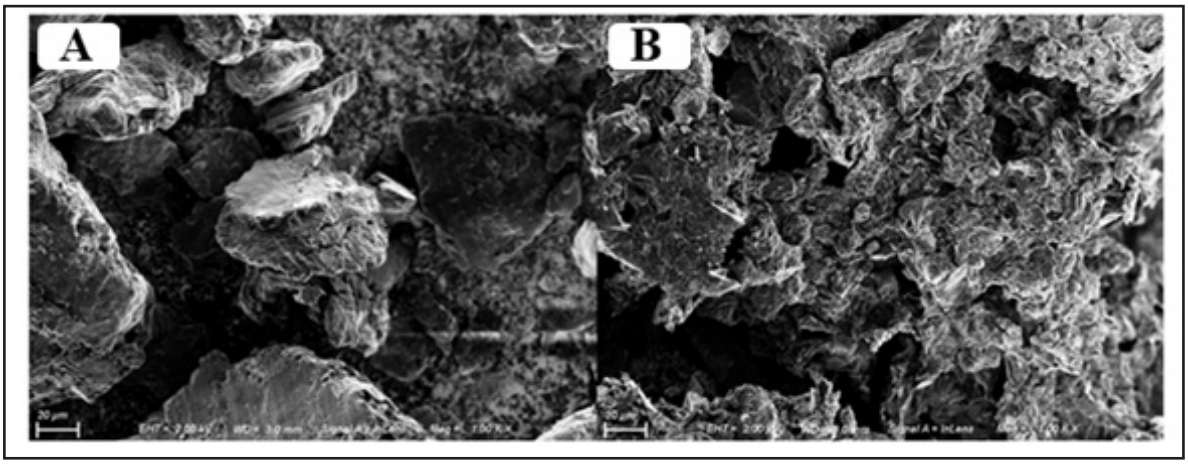
Source: Author's creation

After the GO reduction, it is possible to observe a slight shift in the peaks in the rGO spectrum, indicating the change in functional groups after reduction reactions. For the rGO, it was to observe a considerable decrease in the intensity of bands at 3443 and 1396 cm ^{1}, suggesting the partial removal of OH and C=O groups (reduction process) (Hidayah et al. 2017).

3.3 Scanning electron microscopic

Scanning electron microscopic (Zeiss Sigma 300 VP) was used to show the results of SEM analysis of GO and rGO are presented in Figure 3. As demonstrated in the results, it was possible to note wrinkles and irregular sheets of graphene oxide (Figure 3A) (Kellici et al., 2014). After the reduction process using orange (figure 3B), the reduction form of GO showed an agglomerate structure due to the decrease in the distance between the layers by the oxygen group removal (Pattarith and Areerob, 2020).

Figure 3 – SEM images of (A) graphene oxide and (B) reduced graphene oxide



Source: Author's creation

4 CONCLUSIONS

There has been a significant increase in the use of environmentally friendly reducing agents for the preparation of reduced graphene oxide. In this article, the reducibility capacity of three green reducing agents - Carrot, Beetroot, and Orange - for graphene oxide was comparatively investigated. The process involved the preparation of graphene oxide and its chemical reduction with different reducing agents to obtain reduced graphene oxide. X-ray Diffraction (XRD), FTIR, and microscopy analyses showed that all reducing agents were effective in converting GO into rGO under mild conditions and in high yields, as shown by (Kuila et al., 2012).

Through FTIR, XRD and MEV analyses, it can be concluded that the reduction process from graphene oxide to reduced graphene oxide was successfully conducted. The use of green reducing agents helps minimize defects in the rGO structure, as the reducers employed are not aggressive in slight conditions. Due to the excellent results obtained, future studies will explore the properties of this nanomaterial as an adsorbent for emerging contaminants.

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How to quote this article

Zancanaro, L. V., Salles, T. R., Rhoden, D. S. B., Vincensi, E. C., Mortari, S. R., Zanella, I., & Rhoden, C. R. B. (2024). Eco-friendly strategies for the graphene oxide reduction. Ciência e Natura, Santa Maria, 46, e86374. DOI: https://doi.org/10.5902/2179460X86374.