Environmentally friendly methods for the synthesis of reduced graphene oxide

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1 INTRODUÇÃO

Orange production in Brazil is an important activity for the country's trade relations. According to an annual report by the United States Department of Agriculture (USDA), Brazil is the largest orange producer in the world and produced 14,712 thousand tons in the 2020/21 harvest. Records indicate that this scenario has been repeated over the last few years, which also occurs for products derived from oranges, such as, for example, processed fruit juice, which accounts for about 73% of world exports of the product (USDA, 2022).

Among the varieties of oranges cultivated in the country, the pera rio orange (Citrus sinensis) stands out, a species belonging to the group of common sweet oranges, whose acidity level is around 1%. This gives it relevant projections in the juice processing industry and also in the fresh consumption market. In addition, it is worth mentioning that the pear orange is easily adaptable to climatic conditions and the particularities of the soil, thus contributing to the production of this fruit during a good part of the year (COELHO, 2019). As a result of these factors, this species has a significant share of cultivated areas and high production volume: it accounts for about 35% of the total cultivated hectares destined for plantation. With this, it is estimated that, for the 2021/22 harvest, production is around 84.66 million boxes, with 40.8 kg each, which indicates an increase of 9.51% compared to the previous harvest.

One of the main uses of oranges is the production of juice for sale, and it is characterized as the most consumed flavor among the varieties of natural fruit juices, accounting for 43.8% of the market, followed by orange juice. Apple accounts for 16.9% of consumption (USDA, 2022). The activities inherent to the production and processing of oranges are, sometimes, outlined by the exacerbated generation of solid organic residues, of which stand out pomace, peel, seeds, leaves, and even whole oranges that did not reach the required quality indexes. In general, such waste is considered inappropriate and is therefore improperly disposed of in the environment (JENA, 2022).

This scenario contributes to the triggering of numerous impacts on nature, as they are associated with the generation of a large volume of waste, which can be cumulative, slow, and/or difficult to degrade in certain cases, or even toxic (CORDEIRO, 2020). In addition, the improper disposal of these by-products results in negative socio-environmental implications, such as soil contamination, eutrophication of water sources, and proliferation of vectors and pathogens (DAI, 2018; GAVAHIAN, 2019). Given this, it is noted that the inadequate management of waste constitutes a socio-environmental problem, while it compromises the quality of life and the integrity of society, as well as the balance of ecosystems and the dynamics of biological systems (CORDEIRO, 2020).

The reuse of biowaste presents itself as a promising and economical alternative since it makes it possible to circumvent the socio-environmental impacts generated and provide potential economic benefits and scientific-technological advances (CORDEIRO, 2020) In the field of citrus fruits, some studies show the reuse of waste generated for the production of biofuels (FAZZINO, 2021), as well as for the extraction of substances with high added value, such as fibers, enzymes, flavonoids, vitamins and sugars (GHASEMI, 2017; BAJKACZ; 2018; CYPRIANO, 2018; ISA, 2019; LACHOS-PEREZ, 2020; AYALA, 2012). These inputs are also reused by the food industry to manufacture bread, cakes, flour, and jams, among others (AMARAL, 2021; DASSOFF, 2021).

Dentre as substâncias isoladas presentes em resíduos agroindustriais, têm-se os flavonoides, os quais se configuram como antioxidantes naturais para o organismo (LU, 2021). Essas biomoléculas são encontradas em uma gama de fontes naturais, dentre os quais têm-se os frutos cítricos, como, por exemplo, a laranja, a toranja e o limão (BARONI, 2021). As cascas da laranja podem conter cerca 13,5 g de flavonoides por quilograma de matéria seca (BARBOSA, 2018).

In particular, naringenin ((S)-5,7-dihydroxy-2-(4-hydroxyphenyl)-chroman-4-one) is an antioxidant agent that can be widely found in citrus fruits, especially in orange and lemon: its juices may contain 2.13 mg/100 mL and 0.38 mg/100 mL of the substance, respectively (GATTUSO, 2007; CHIN, 2020). It can also be observed in figs of the species Ficus carica (BARONI, 2021), in tangerines, tomatoes, cherries, and cocoa (BHIA, 2021). This flavonoid stands out due to its action as an antioxidant, managing to capture free radicals, such as reactive oxygen species (ROS), and enhancing the activity of other antioxidants, such as superoxide dismutase (NARAKI, 2021). . Due to its anti-inflammatory properties, this flavonoid can be used in the treatment and modulation of diseases related to oxidative stress, such as diabetes and heart disease, for example, and whose derivatives are promising agents in the treatment of Alzheimer's disease (KARIM, 2018).

The use of naringenin is not restricted to biological activities and the balance of the human organism, playing an important role in a variety of chemical processes (LI, 2021). As an example, it is worth mentioning that naringenin is a strong candidate for the graphene oxide (GO) reduction mechanism (PEREIRA JÚNIOR, 2021; PEREIRA JÚNIOR, 2022). Graphene is a two-dimensional material composed of carbons with sp2 hybridization, organized using a hexagonal crystalline structure, like a honeycomb. Thus, it has a very stable structure, is resistant, and has excellent thermal and electrical conductivity, making it the thinnest and strongest nanomaterial so far. Due to such characteristics, graphene has several relevant applications. Such uses include the presence of supercapacitors, participation in the absorption of gases at low concentrations and electrochemical sensors, as well as the ability to enhance the characteristics and performance of composite materials when combined with them (HUANG, 2020).

Although there are already methods for the production of pure graphene, its implementation on an industrial scale to obtain a cheap and high-quality material is still a challenge. Given this, the synthesis of reduced graphene oxide (RGO) is an alternative, which has properties similar to those of graphenes, such as good electrical conductivity and good electrical conductivity, and the ability to absorb light in almost the entire light spectrum. Furthermore, the material can be produced on a large scale by a variety of processes, including electrochemical, thermal, and photo-assisted methods. Thus, new synthesis routes are studied to obtain OGR, implement methods that are viable, safe, and applicable, and produce material with properties that are increasingly similar to graphene (LIN, 2019).

2 METHODOLOGY

To achieve the aforementioned objectives, it is necessary to start with a graphene oxide solution. Thus, the GO was prepared from a solution with pure graphite in an acid medium, based on the Hummers method modified by Marcano. This method consists of subjecting the graphite to oxidative and exfoliative processes in an acid medium, to obtain GO in layers of monoatomic thickness. The product obtained corresponds to a 0.5 mg/mL solution of graphene oxide.

2.1 THERMOCHEMICAL REDUCTION OF GRAPHENE OXIDE SOLUTION

Initially, pear oranges fit for consumption were washed with neutral soap and running water and peeled with the aid of a kitchen knife. Subsequently, the oranges were manually squeezed in the ceramic funnel to obtain the juice and filter out larger residues, such as seeds and any fruit segments. Then, the filtered juice was stored in a 1000 mL beaker. The same procedures were performed with the unsuitable oranges, using other previously sanitized glassware, and both juices were stored separately.

After these methods, in each of the 250 mL glass vials on the bench, 50 mL of graphene oxide solution (0.5 mg/mL) was added. Then, different volumes of suitable and/or unsuitable orange juice were inserted to observe the behavior of the GO solution in the presence of citrus juice. The samples were prepared and identified according to the legend below:

- Sample 1: add 50 mL of natural orange juice;
- Sample 2: add 50 mL of unsuitable natural orange juice.

After preparing the solutions, all flasks were manually shaken and left in the ultra freezer for 72 h. Subsequently, the samples were removed from the ultra freezer and thawed naturally completely at room temperature, and then placed in an oven at 300°C for 4 h, so that the thermochemical reduction could occur. After the specified period, the flasks were removed from the oven for observation and subsequent discussion of the results. After reducing the material, the samples were heated to evaporate the liquid phase. Thus, the OGR was deposited at the bottom of the container and, after scraping, it was possible to obtain powdered OGR.

Figure 1 – Flowchart of the methodology for obtaining reduced GO with suitable orange juice (for reduction with unsuitable orange, an analogous method was used).

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