Environmentally friendly methods for synthesis of reduced graphene oxide

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1 INTRODUCTION

Orange production in Brazil is an expressive activity for the country's trade relations. According to an annual report by *the United States Department of Agriculture* (USDA), Brazil is the largest producer of orangein the world, and produced 14,712,000 tons in the 2020/21 crop season. Records indicate that this panorama has been repeated over the last few years, which also occurs for orange products, such as processed fruit juice, which accounts for about 73% of the world's exports of the product (USDA, 2022).

Among the varieties of oranges grown in the country, the orange pear (*Citrus sinensis*), 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 consumer market. In addition, it is worth mentioning that pear orange has easy adaptability to climatic conditions and soil particularities, thus contributing to the production of this fruit for much of the year (COELHO, 2019). Due to these factors, this species has a significant participation in cultivated areas and high production volume: it accounts for about 35% of the total cultivated in hectares destined for planting. Therefore, it is estimated that, for the 2021/22 harvest, production is about 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 jobs of orange is the production of juice for commercialization, and is characterized as the most consumed flavor among the varieties of natural fruit juices, in order to account for 43.8% of the market, followed by apple juice, which accounts for 16.9% of consumption (USDA, 2022). The activities inherent to the production and processing of orange is sometimes delineated by the exacerbated generation of solid organic residues, of which bagasse, bark, seeds, leaves and even whole oranges that have not reached the required quality indices stand out. In general, such residues are considered inappropriate and are therefore disposed of inappropriately in the environment (JENA, 2022).

This scenario contributes to the deflagration of numerous impacts to nature, since they are associated with the generation of a large volume of waste, which can be cumulative, slow and/or difficult to reduce in certain cases, or even toxic (CORDEIRO, 2020). In addition, the improper disposition 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). Therefore, it is noted that inadequate waste management is a socio-environmental problem, while compromising the quality of life and integrity of society, as well as the balance of ecosystems and the dynamics of biological systems (CORDEIRO, 2020).

The reuse of bioresidues is a promising and economical alternative, since it makes it possible to circumvent social and environmental impacts generated and provide potential economic and technological advances (CORDEIRO, 2020) In the citrus fruit business, there are studies that show the reuse of waste generated for the production of biofuels (FAZZINO, 2021), as well as for the extraction of substances of high added value, such as fibers, enzymes, flavonoidres, vitamins and sugars (GHASEMI, 2017; BAJKACZ; 2018; CYPRIANO, 2018; ISA, 2019; LACHOS-PEREZ, 2020; AYALA, 2012). These insums are also reused by the food industry for the manufacture of breads, cakes, flours, jams, among others (AMARAL, 2021; DASSOFF, 2021).

Among the isolated substances present in agro-industrial residues, flavonoids are found as natural antioxidants for the body (LU, 2021). These biomolecules are found in a range of natural sources, among which citrus fruits are, such as orange, grapefruit and lemon (BARONI, 2021). Orange peels may contain about 13.5 g flavonoids per kilogram of dry matter (BARBOSA, 2018).

In particular, naringenin ((S)-5,7-dihydroxy-2-(4-hydroxyphenyl)-croman-4-ona) is an antioxidant agent 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), tangerine, tomato, cherry and cocoa (BHIA, 2021). This flavonoid stands out due to its performance as an antioxidant, managing to capture free radicals, such as reactive *oxygen species* (ROS), and for potentiating 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 stresses, such as diabetes and heart diseases, for example, and whose derivatives are promising agents in the treatment of Alzheimer's disease (KARIM, 2018).

The use of naringenin is not restricted only to biological activities and the balance of the human organism, playing an important role in a plurality of chemical processes (LI, 2021). As an example, it is worth saying that naringenin is a strong candidate with regard to the mechanism of reduction of graphene oxide (OG) (PEREIRA JÚNIOR, 2021; PEREIRA JÚNIOR, 2022). Graphene is a two-dimensional material composed of carbons with hybridization sp^2, organized by means of a hexagonal crystalline structure, like a honeycomb. Thus, it has a very stable structure, is resistant and has excellent thermal and electrical conductivities, configuring itself as the thinnest and strongest nanomaterial to date. Due to such characteristics, graphene has several applications that are relevant. Such uses include the presence in supercapacitors, participation in the absorption of gases at low concentrations and in electrochemical sensors, as well as the ability to potentiate 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 high quality and bara to materialis still a challenge. In view of this, it has as an alternative the synthesis of reduced graphene oxide (OGR), whichhas similar property to graphene, such as good electrical conductivity and good conductivity elétrica and ability to absorb light in almost the entire light spectrum. In addition, the material can be produced on a large scale, by a variety of processes, which include electrokyic, terany and photo-assisted methods. Thenew synthesis routes are used to obtain the OGR in order to implement methods that are viable, safe, applicable and produce material with properties increasingly identical to graphene (LIN, 2019).

2 METHODOLOGY

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

Thermochemical reduction of graphene oxide solution

Initially, pear oranges suitable for consumption were washed with neutral soap and running water, being peeled with the aid of a kitchen knife. Subsequently, the oranges were manually squeezed into the ceramic funnel to obtain the juice and filter larger residues, such as seeds and eventualfruit gums. Then, the filtered juice was stored in a 1000 mL bécher. The same procedures were performed with unfit oranges, using the other previously sanitized glasstiles and both juices werestored separately.

After these methods, in each of the250 mL v idro vials on the bench, 50 mL of the grafeoxide solution (0.5 mg/mL) was added. Then, different volumes of anjaand/or inapt apt apt alar juices were inserted, in order to observe the behavior of the GO solution in citrus juice. The samples were prepared and identified according to the caption below:

- Sample 1: add 50 mL of apt natural orange juice;
- Sample 2: Add 50 mL of natural orange juiceinapt to.

After the preparation of the solutions, all the vials were shaken manually and left in the ultrafreezer for 72 h. In sequence, the samples were taken from the ultrafreezer and naturally thawed at room temperature, and then placed in an oven at 300°C for 4 h, in order to reducethermochemistry. After the determined period, the vialswere removed from the oven for observation and subsequent discussion of the results. After the material is reduced, the samples areheated to evaporation of the liquid phase. Thus, the OGR was deposited at the bottom ofthe r ecipiente and, after scraping, it was possible to obtain the OGR powder.

Figure 1 – Flowchart of the methodology for obtaining the reduced OG with apt orange juice (for reduction with inapt orange, an analogous method was used).

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