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REDUCTION OF GRAPHENE OXIDE USING EXTRACTS AND NATURAL PRODUCTS: A REVIEW

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Abstract: Graphene and its derivatives, such as graphene oxide (GO), are materials that, at room temperature, have excellent electrical, thermal and optical properties. In the GO reduction process, it is necessary to add reducing and stabilizing agents such as hydrazine (N2H4), hydrogen sulfide (H2S), sodium borhydride (NaBH4), ascorbic acid (AA) and others. Although they present excellent graphene deoxygenation conditions, they are highly toxic. The toxicity of these agents directly affects the user with a risk to health and the environment, especially when discarded in inappropriate places for waste disposal. In this sense, natural products are being used as a viable alternative to avoid the use of these toxic reducing agents and contribute to sustainable development. This article aims to present a review of the materials and methods used to reduce GO using natural extracts. Scientific research on the process of reducing graphene with natural products is a growing area and has proven to be a sustainable solution for production. Among the raw materials used, açaí, piquiá and tucumã stand out, which in addition to reducing costs due to their much lower purchasing value, present an alternative route to the use of conventional reducing agents.
Keywords: Green reduction, graphene, plant extract, natural extract.

INTRODUCTION

Graphene-based products are of industrial interest as they enable the development and innovation of materials that have electrical and thermal conductivity, mechanical resistance and a series of applications. Due to this, great attention has been paid to methods of obtaining and producing mass and low-cost graphene (EDWARDS and COLEMAN, 2013; MOHAMED MAHMOUD IBRAHIM et al., 2014; BAI and SHEN, 2012).

One of the most promising alternatives for obtaining graphene is the liquid-phase exfoliation process of graphite oxide using graphene oxide (GO), defined as "return-to-graphene synthesis" (SINGH et al., 2016). In this process, GO becomes reduced graphene oxide (RGO) with structural characteristics distinct from pure graphene (KUILA et al, 2012).

Graphene presents a two-dimensional form of carbon organized in a hexagonal structure. As a characteristic, it has interesting properties, such as high electrical and thermal conductivity, mechanical resistance and, due to its spatial organization, an extremely large surface area. When properties similar to those of pure graphene are required, it is necessary to reduce the GO to mitigate the oxygenated groups and restore the network of carbon atoms with sp^2 hybridization. Therefore, RGO presents properties similar to pure graphene (FENG et al, 2013; MOON et al, 2010; MORIMOTO et al., 2016).

The reduction of GO can be carried out using several methods and the selection of this process will define the specific properties and applications for each of them (PEI and CHENG, 2011; ALAZMI et al., 2016; BOTAS et al., 2012; SHAMAILA et al., 2016).

In a historical itinerary of GO and RGO productions, the timeline is represented in Figure 1. Where the first synthesis of graphite oxide was in 1859, carried out by Brodie. And from this, many other methods were created and improved with the aim of carrying out graphite oxidation (HUMMERS and OFFEMAN, 1958).

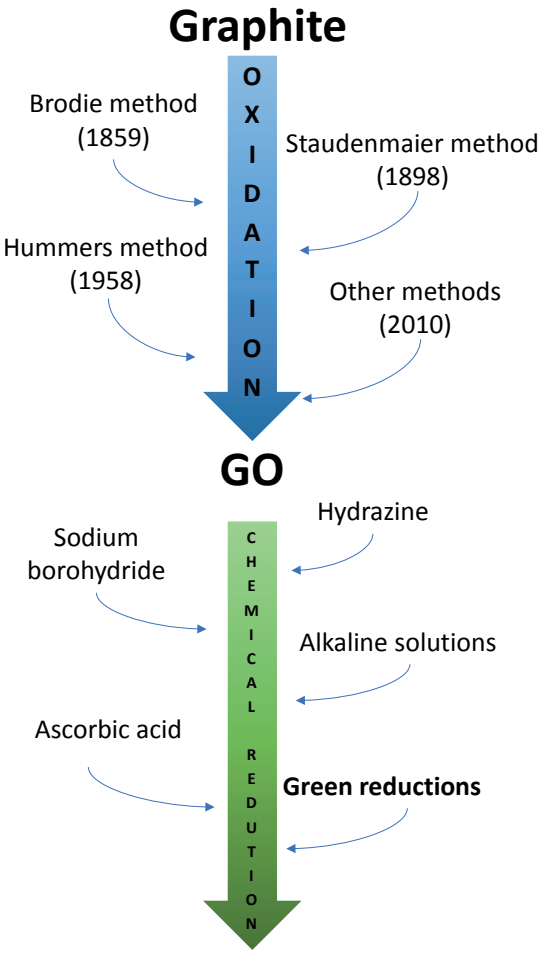

Figure 1: Chronology of GO and RGO synthesis methods.

With the GO produced, the stage of reducing this material begins, that is, the production of RGO. This reduction process will occur through the partial removal of oxygen functional groups and the recovery of sp^2 carbon atomic bonds (PEI et al., 2010). This reduction process can be carried out by chemical, thermal, electrochemical and photochemical methods, with the first two prevailing.

Heat treatment is a method that can be used to reduce GO by efficiently removing oxygen-containing functional groups. However, the system requires a large amount of energy as well as a complicated experimental setup. Electrochemical reduction offers a faster and safer route compared to previous methods, but its reduction efficiency is reported to be lower than hydrazine reduction, for example (LIAO et al, 2011; LI et al, 2017).

Among these methods, reduction by chemical agents is still the most effective technique for producing RGO. The chemical reduction of RGO is considered one of the most promising for the preparation of high-quality RGO (KHAN et al, 2014). Considered the most applicable chemical reduction method in the literature, the agents hydrazine (N2H4), hydrogen sulfide (H2S), sodium borhydride (NaBH4), sulfuric acid and alkaline solutions are highlighted respectively (KHAN et al, 2014; SURESH et al, 2015; GAN et al, 2019; COROS et al, 2020). The chemical reduction route offers an efficient method, enabling large-scale and low-cost application.

However, these chemical agents used often consist of toxic products/by-products that, when discarded incorrectly, can be a problem for the environment (WIJAYA et al, 2020; THAKUR et al, 2013; WIJAYA et al, 2020).

Due to this, scientific research has been seeking alternatives for the use of raw materials that can be efficient to carry out reduction without harming the environment. In this sense, the use of natural products has shown promising results, using green technologies that aim to guarantee quality and promote sustainable technologies. This review article presents scientific research on green reductions applied in the GO reduction process, its characteristics and obtaining methodologies.

GREEN REDUCTION

As a result of the risks mentioned in the previous chapter, researchers have constantly searched for materials that can replace these reducing agents. As we know, the reduction of GO generally involves the application of a toxic

and poisonous substance that, unfortunately, can harm the potential of this process for the mass production of graphene (ISMAIL,2019). When using some of these reducing agents during production, the laboratory worker is exposed to health risks, since the use of these agents, such as hydrazine, is highly toxic in addition to being an explosive material. Furthermore, the use of these products can create serious environmental problems if the solvent applied from a reduction step is accidentally released into a water source or soil without a pre-treatment system with waste disposal (ISMAIL, 2019).

Reducing materials that have shown promising results are environmentally friendly reducers that have a reducing power similar to or greater than hydrazine (KURT et al, 2019; DE SILVA et al, 2017). The ecological synthesis of nanomaterials using "green chemistry" has attracted much attention in recent years due to their easy handling, low cost and biocompatibility (KHAN et al, 2015; ISMAIL, 2019).

The scientific community has strived to replace these non- "green" agents as the remaining amount of these highly toxic agents can have a harmful effect in water filtration membrane applications and especially in biomedical applications (DE SILVA et al, 2017). Because when using RGO in biomedical applications, the body may refuse this material due to toxicity (IRAVANI and VARMA, 2020). Furthermore, the treatment of harmful waste generated in the GO reduction process can obviously increase costs on an industrial scale.

The first research considering the method of producing RGO with natural extracts was published in 2011, in which Wang and collaborators carried out the reduction of GO using polyphenol obtained from green tea. These environmentally friendly reducers are also called "green reducers", as they are obtained from natural products (KURT et al, 2019). These natural products can be plant extracts, fruit juices, fruit pulp, seeds, peels, substances and molecules that, in principle, can be obtained directly from nature. All of these reducers are known as "green reducing agents" as they are non-toxic and environmentally friendly (ISMAIL, 2019). However, these reducers may also have some limitations. Table 1 presents some of the reducers investigated and already used. In this table, the divisions are organized: by the types of reducers, the reducing agent itself, the method used to carry out the reduction, the reduction time and the reduction temperature.

In Table 1 it is possible to verify the range of variables in the methodology to reduce GO, where there is no standard for obtaining the material. Furthermore, each research carries out a reduction method, with a different temperature, time and concentration of GO.

Another issue that can be emphasized is the production method of RGOs. The diversity of methods is also addressed in Table 1; The most common methods are reflux, sonication and agitation. These are the methods, cited in the literature, in which GO is reduced through chemical exfoliation. The other methods discussed are less common and in the context of green chemistry are not considered the most appropriate considering the substance being used as a reducing agent. For example, research carried out by Ansari and Siddiqui in 2018 used an ammonia solution to reduce GO with the extract obtained from the fig and stir for twelve hours at 95°C. The difficulty of this work would be to affirm that the reduction was effective because of the natural extract, as it is mentioned in other literature that the presence of ammonia is capable of producing RGO (ZHANG et al, 2020). Therefore, sometimes a natural product may need a supporting chemical compound to accomplish complete reduction. Furthermore, sometimes the natural product may also need

Type of agent	Reducing agent	Method	Reduction time (h)	Temperature (ºC)	GO (mg/mL)	Reference
Plants	Sugar cane bagasse	Unrest	12	60	1,00	GAN et al, 2019
	Eucalyptus	Electro-thermal bath	8	80	0,50	LI et al, 2017
	Sugar cane bagasse	Centrifugation	12	95	0,50	LI et al, 2018
	Eichhornia Crassipes	Sonication	0,5	NI	0,50	FIRDHOUSE e LALITHA, 2014
	T. Chibula	Reflux	24	90	1,00	MADDINEDI et al, 2015
	S. persica L.	Unrest	24	98	0,50	AL-MARRI et al, 2016
	Artemisia vulgaris	Reflux	12	90	0,50	CHETTRI et al, 2016
	Ocimum Sanctum	Reflux	10	100	0,50	SHUBHA et al, 2017
	Cashew leaf	Heating	3 e 5	45, 58, 68 e 75	0,25	MAHATA et al, 2018
	Garcinia indica	Ultrasound	6	NI	1,00	HEGDE e MOHANA, 2020
Fruit	Pomegranate juice	Sonication	12;18 e 24	60	2,50	TAVAKOLI et al, 2015
	Grapes	Oil bath	1; 3 e 6	95	NI	UPADHYAY et al, 2015
	Mangifera indica L.	Reflux and Oil bath	12	60	1,00	SADHUKHAN et al, 2016
	Solanum tuberosum L.					
	Lemon juice	Thermostatic bath	24	95	0,10	HOU et al, 2017
	Honey	Unrest	4	70	0,05; 0,1; 0,2 e 0,3% peso	RAJITHA e MOHANA, 2020
	Indian gooseberry	Autoclave	6	120	1,00	MASCARENHAS et al, 2020
	Coconut	Oil bath	12; 24 e 36	100	0,66	KARTICK et al, 2013
	Pepper	Ultrasound	12	80	0,10	HASHMI et al, 2020
	Fig	Centrifugation	12	95	0,20	ANSARI e SIDDIQUI, 2018
	Sugar cane juice	Autoclave	12	150	1,25	SINGH et al, 2018
Isolated Substance	β- carotene	Reflux	24	95	NI	ZAID et al, 2015
	l-aspartic acid	Sonication	12	80	0,10	TRAN et al, 2014
	Caffeic acid	Unrest	2; 12 e 24	95	0,10	BO et al, 2014
	Gallic acid	Oil bath	24	80	0,20	JIANG et al, 2018
	Curcumin	Unrest	1	NI	4,00	NOWROOZI et al, 2021
	Catechin	Autoclave	2	300	0,34	WANG et al, 2013
	Atenolol	Thermal	5 min	250°C; 300°C; 400°C e 500°C	1,25	COROS et al, 2020

Table 1: Types of reducers used and the parameters used for each reduction and the respective references.

*NI – It was not informed

a stabilizer to prevent aggregation of the RGO sheets and there may be a need to repeatedly centrifuge or filter to remove excess reductant or its by-products (DE SILVA et al, 2017).

Some of the main characteristics that can hinder the production of RGO using the "green method" are the different methodologies used and which oppose the concept of optimizing the natural extract within chemistry. In some of these cases, the relationship between time and temperature is emphasized, which can lead to excessive heating and the natural extract can lose its best properties. Therefore, listing the main problems observed in the literature, those presented in the flowchart in Figure 1 stand out and will be addressed in the following items.

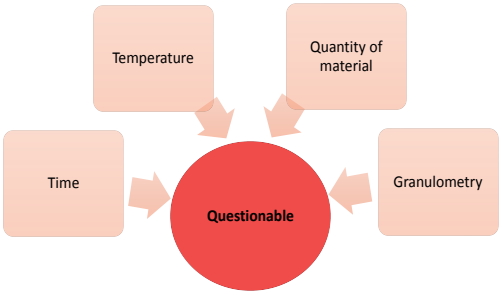

Figure 1: Divergence in literature methodology that can be problematic regarding the use of green reducers. Time and temperature

In many cases, the problems of extract production or graphene reduction are linked to temperature and time. This is because the most widely used and scalable method for producing RGO is through chemical reduction. However, this method can be carried out involving high temperatures and often for a few hours. Although some authors mention that RGOs produced at high temperatures have better electrical properties (PEI et al., 2010). This factor contrasts with natural products, which lose their properties when exposed to high temperatures. Table 2 presents the matrices used and their respective temperatures and RGO production times.

Matrix	Temperature (°C)	Time (h)	Reference
β-carotene	95	24	ZAID et al, 2015
Glucose	60	48	SUNIL et al, 2020
Allium sativum	100	3	SRIVASTAVA et al, 2014
Catechin	300	2	WANG et al, 2013
Ficus carica	80	24	ANASDASS et al, 2018
Platanus orientalis	90	1	XING et al, 2016
Green Tea	80	8	WENG et al, 2019
Lemon Juice	95	24	HOU e LI, 2017
Annona squamosa leaf	100	12	CHANDU et al, 2017
Lignin	90	8	YE et al, 2020
Mangifera indica L.	60	12	SADHUKHAN et al, 2016
Cinnamomum verum	100	12	HAN et al, 2016
Phoenix dactylifera L	80	24	OUSALEH et al, 2020
Cannabis Sativa L			
Citrus Lemon			
Punica granatum			

Table 2: List of the main natural extracts used with the respective temperatures and time for RGO production.

The cases mentioned in Table 2 refer to the reduction of graphene with the natural extract. Although in some cases they can reduce the material in just one hour, the temperature is considerably high for a natural extract. In other cases, they use a temperature of 100°C for 12 hours. Still highlighting work that showed many hours of reduction, there is the work carried out by Sunil and collaborators in 2020, in which there were two days of reduction in GO. In addition to the loss of substances and properties of the

matrices, when applying these materials on an industrial scale, it becomes unattractive due to the high time spent on production.

Still according to Table 2, we can highlight the research carried out by COROS and collaborators (2020) in which the authors carried out a thermal reduction of GO with the substance atenolol. Such research carried out the reduction with temperatures of 250; 300; 400 and 500°C, but it is important to highlight that the substance presents its thermal degradation curve in the range of 150 to 300°C (AMORIM, 2012). That is, when the authors mention that the reduction was carried out with atenolol at the temperatures reported in the article, the characteristics and thermal properties of atenolol are ignored.

In many cases, the literature uses the extract production process through maceration (GIJARE et al, 2021; AHAMED et al., 2022). The production of the most effective natural extracts is known as green chemistry, it has two methods that can extract the substances in the best possible way and without degrading the material. These methods are carried out using microwaves or ultrasound; they are faster, more efficient methods that can be carried out at room temperature (DAI and MUMPER, 2010; AZMIR et al, 2013). This way, the technique becomes attractive for producing extracts in just a few minutes and at room temperatures.

QUANTITY OF MATERIAL AND GRANULOMETRY

The concentration of GO placed to react with the natural extract for reduction was highlighted in Table 1. Most of the studies in the table present a concentration of 0.5 mg/mL, however it is possible to find cases in which they use reductions of 0.1; 1.0; 2.5 and 4.0 mg/mL (HASHMI et al, 2020; TAVAKOLI et al, 2015; NOWROOZI et al, 2021). This raises the question of whether the best procedure for working with GO is in lower or higher concentrations? Furthermore, it is necessary to pay attention because in many cases when the natural extract liquid comes into contact with GO, the concentration, even instantly, becomes lower.

Another extremely difficult item was the concentration or quantity of GO used in the research. Kurt and collaborators 2019, carried out research on the reduction of GO with cloves, white mulberry, black cumin seed, blackthorn, dark grape and rosehip, however they did not specify the amount of GO used in the research. Still according to this same work, the extract reduction process reported by them involves a solid/liquid ratio of 1:10 and the extraction was carried out at 100 °C under reflux for 5 h with a constant stirring speed. In other words, the extract production temperature for 5 hours again causes the loss of properties and substances obtained in natural extracts. Another very common item that can be correlated to this research is the particle size, size or shape of the particle used. It is very common in several works that the natural product source was cut into small pieces, but the size of the particles used is not specified. However, it is possible to find research that addresses in detail the granulometry of the raw material for the production of the extract, one research that can be highlighted is the research carried out by Al-Marri and collaborators in 2016 that specified the granulometry used to prepare the extract. Their production step was first to cut the roots of S. Persica L into small pieces (~5 to 35 mesh). These pieces (1.3 kg) were soaked in deionized water (3000 mL) and refluxed for 4 hours. The aqueous solution obtained after reflux was filtered and dried at 50 °C under reduced pressure in a rotary evaporator to give a dark brownish gum extract (30.0 g) which was stored at −4 °C for later use. This same research also specified the amount of GO, in

which the authors mention that an amount of 200 mg of GO was used and was dispersed in 40 mL of DI water.

In addition to the variable concentration of GO used for reduction, it can also be highlighted that in many cases the literature did not present a certain amount of natural product to make the extracts. Shubha and collaborators (2017) used 15g of dried basil leaves to produce the extracts, while Weng and collaborators used only 5g of green tea to prepare their reducing agent (WENG et al., 2019). There is also research that uses natural extracts in volume, as is the case of research carried out with pine leaf extract and lemon juice (LEE and KIM, 2013; THAKUR et al, 2013). The research used, respectively, the proportion of 20mL of pine leaf extract to 100mL of a homogeneous dispersion of graphene oxide (0.5mg/mL) and 35mg of GO were added to 10mL of lemon juice. Still in accordance with the requirement of sample quantity to produce the extracts, it is possible to highlight the research carried out by Hou and Li (2017), in which they added 45g of dried lemon pieces to produce the extracts, while Hatamie and collaborators (2015) produced the extract with just 5mg of curcumin.

CONCLUSION

The applications and production possibilities of GO and RGO have increased significantly in recent years. The scientific community has been looking for ways to produce low-cost, easy-to-handle and large-scale RGO. The use of abundant materials in each part of the world has been a means of reducing these costs, as each region can present a natural product with antioxidant properties that allow the reduction of GO to RGO. In addition to being a viable means, it seeks application for some materials that are biomass residues. However, as this review article wanted to present, it is necessary to verify that the means of producing RGO is not affecting or losing the properties of the biomass residue.

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