COMPARATIVE LIFE CYCLE ASSESSMENT OF HIGH-YIELD SYNTHESIS ROUTES FOR CARBON DOTS

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Abstract

Carbon dots (CDs) are carbon-based nanomaterials with advantageous luminescent properties, making them promising alternatives to other molecular and nanosized fluorophores. However, the development of CDs is impaired by the low synthesis yield of standard fabrication strategies, making high-yield strategies essential. To help future studies to focus on cleaner production strategies, we have employed a Life Cycle Assessment (LCA) to compare and understand the environmental impacts of available routes for the high-yield synthesis of carbon dots. These routes were: (1) production of hydrochar, via hydrothermal treatment of carbon precursors, and its alkaline-peroxide treatment into high-yield carbon dots; (2) thermal treatment of carbon precursors mixed in a eutectic mixture of salts. Results show that the first synthesis route is associated with the lowest environmental impacts. This is attributed to the absence of the mixture of salts in the first synthesis route, which offsets its higher electricity consumption. Sensitivity analysis showed that the most critical parameter in the different synthetic strategies is the identity of the carbon precursor, with electricity being also relevant for the first synthesis route. Nevertheless, the use of some carbon precursors (as citric acid) with higher associated environmental impacts may be justified by their beneficial role in increasing the luminescent performance of carbon dots. Thus, the first synthesis route is indicated to be the most environmental benign and should be used as a basis in future studies aimed to the cleaner and high-yield production of carbon dots.

Keywords: Life Cycle Assessment; Carbon Dots; Engineered Nanomaterials; High-Yield Synthesis; Green Chemistry; Fluorescence

1. Introduction

Carbon dots (CDs) are fluorescent carbon-based nanomaterials, with either an amorphous or nanocrystalline core, and a surface on which can be found different functional groups (Esteves da Silva and Gonçalves, 2011; Wang et al., 2017a; Zhou et al., 2017). CDs have several remarkable properties, such as strong luminescence (Xiong et al., 2018; Wang et al., 2013), water solubility (Lim et al., 2015), good physical-chemical and photochemical stability (Lim et al., 2015; Kozák et al., 2013; Sendão et al., 2018), low toxicity (Wang et al., 2013) and biocompatibility (Baker and Baker, 2010; Sun et al., 2006; Vale et al., 2020). Given this, it is not surprising that CDs have been increasingly used in several applications, such as in sensing (Crista et al., 2019; Liu et al., 2021; Mello et al., 2019; Qiu et al., 2020; Simões et al., 2020), bioimaging (Kang et al., 2015; Bogireddy et al., 2020; Ding et al., 2020), photocatalysis (Li et al., 2021), in light-emitting devices (Wang et al., 2019; Wang et al., 2017b; Qiao et al., 2020), drug delivery (Hettiarachchi et al., 2019), solar cells (Yan et al., 2016) and in photodynamic therapy (He et al., 2018; Knoblauch and Geddes, 2020).

Another attractive characteristic of CDs is that they can be produced by using a wide variety of precursors without sophisticated equipment, via simple solvothermal, thermal or microwave-assisted treatment of organic molecules, which are used as a carbon source (Crista et al., 2020a; Zhou et al., 2018a; Crista et al., 2020b; Zhou et al., 2018b; Tripathi et al., 2016; Yang et al., 2016). While CDs can be prepared from a great number of organic molecules, most of them can still be expensive, and their use and/or synthesis can pose significant challenges to the environment and human health (Zhang et al., 2019). Given this, biomass has been increasingly used as a precursor for the synthesis of CDs due to its abundance, low cost, renewability, and sustainability (Algarra et al., 2019; Crista et al., 2020a; Xie et al., 2019; Zhao et al., 2015). However, it should be noted that there is not a consensus about biomass sustainability, namely due to greenhouse gas (GHG) emissions from bioenergy and biobased materials (van der Hilst et al., 2018).

Despite this, one problem that plagues the development of CDs is that their synthesis yields are usually very low (below ~10%) (Christé et al., 2020; Tan et al., 2016; Yang et al., 2012), which hinders their large-scale production and future industrial applications. This low yield is explained by current synthetic strategies generating large amounts of solid carbon material as a major by-product, with the actual amount of CDs in suspension being quite low (Zhang et al., 2018). Thus, as this solid carbon material can be produced by traditional CDs' synthesis in large-scale (as it is the major product), if a strategy could be found to convert it into CDs, the low synthesis yield problem of these nanomaterials could be solved.

Indeed, different authors are already focusing on this topic. Namely, Li et al. (2017) were recently able to generate different CDs in high yield (25.8-66.7%) from different carbon precursors in a two-step process. First, a carbon source and a eutectic mixture of molten salts

were mixed to promote polymerization and then by a carbonization process to generate CDs. In the next step, the mixture was dissolved in water, and by a dialysis process to remove salts as well as products with low molecular weight (Li et al., 2017). In a similar study, Jing et al. (2019) also produced CDs in high yield by first subjecting an aqueous solution of biomass to hydrothermal treatment (at 200 ºC for 6h), resulting in low yield CDs in suspension (less than 10%) and solid hydrothermal carbon (also described as hydrochar). The hydrochar was then converted into CDs by alkaline-peroxide treatment, by dispersion in $NaOH/H_2O_2$ solution for 8h at room temperature. This resulted in the production of CDs with a high yield (~20-40%).

These studies are very important for the development of new CDs, as they show a way for the large-scale production of nanomaterials. Despite their innovative potential, there can be some doubt regarding which type of strategy should be favored in terms of efficiency and sustainability, as there is limited information regarding the potential environmental impacts generated by these synthetic routes. Such information is essential for determining a suitable strategy for the synthesis of nanomaterials, given that the production steps of engineered nanomaterials have been identified as of environmental concern (Pourzahedi and Eckelman, 2015). Namely, previous studies have determined that the reagents and energy required for the synthesis of engineered nanomaterials can contribute significantly to the environmental impacts generated during their life cycle (Eckelman et al., 2008; Bafana et al., 2018). Given this, it is essential that proposals for large-scale synthesis of a given type of nanomaterials should be first evaluated for their environmental impacts and sustainability, to ensure that attempts to devise improved high-yield routes already take into consideration the best alternatives for cleaner production.

Herein, our goal is to assess the environmental impacts associated with the high-yield synthesis of CDs, by analyzing the synthetic strategies proposed by both Li et al. (2017) and Jing et al. (2019). To this end, a life-cycle assessment (LCA) approach will be employed. The aim of LCA is to quantify the environmental impacts of a given system during its life cycle (Ramos et al., 2018a; Ramos et al., 2018b; Hischier and Walser, 2012), making it the most appropriate tool to achieve the goals of the present study. In fact, LCA has already been used with success to evaluate the environmental impacts associated with different types of engineered nanomaterials, such as silver nanoparticles (Bafana et al., 2018; Temizel-Sekeryan and Hicks, 2020), graphene oxide (Deng et al., 2017), copper nanoparticles (Pu et al., 2016), carbon nanotubes (Upadhyayula et al., 2012; Celik et al., 2017; Teah et al., 2020; Temizel-Sekeryan et al., 2021), nanocellulose (Piccinno et al., 2018), TiO_2 nanoparticles (Fernandes et al., 2020), and even CDs (Sendão et al., 2020; Christé et al., 2020). However, a new study about the current state of art in LCA of engineered nanomaterials identifies a scarcity of specific characterization factors regarding the potential impacts related to toxicity, as well as a gap of knowledge about nanomaterial releases into the environment during different life cycle stages, such as their quantities and risks (Salieri et al., 2018).

With this study, we expect to identify the high-yield synthesis route with more sustainability potential, as well as to understand what the most critical parameters are relative to generated environmental impacts. Given this, we expect to provide a basis for future studies to provide a cleaner strategy for the high-yield production of CDs.

2. Methods

The experimental section of this study is divided into six sub-sections: Scope and system boundaries (2.1), Synthesis Routes (2.2), Life Cycle Inventory Data (2.3), Environmental Impact Assessment (2.4), Sensitivity analysis (2.5), and Scale-Up (2.6), as described below.

2.1. Scope and system boundaries

The present study is a cradle-to-gate LCA that aims to quantify and compare the potential environmental impacts, as well as to evaluate the differences between these two types of CDs syntheses. This study is focused on the laboratory-scale manufacturing stage of target nanoparticles and considers the direct emissions from CDs production and indirect impacts associated with upstream resource extraction and energy generation.

This work uses two different synthesis routes for the high-yield production of CDs (Li et al., 2017; Jing et al., 2019), which are described in detail below (Fig. 1).

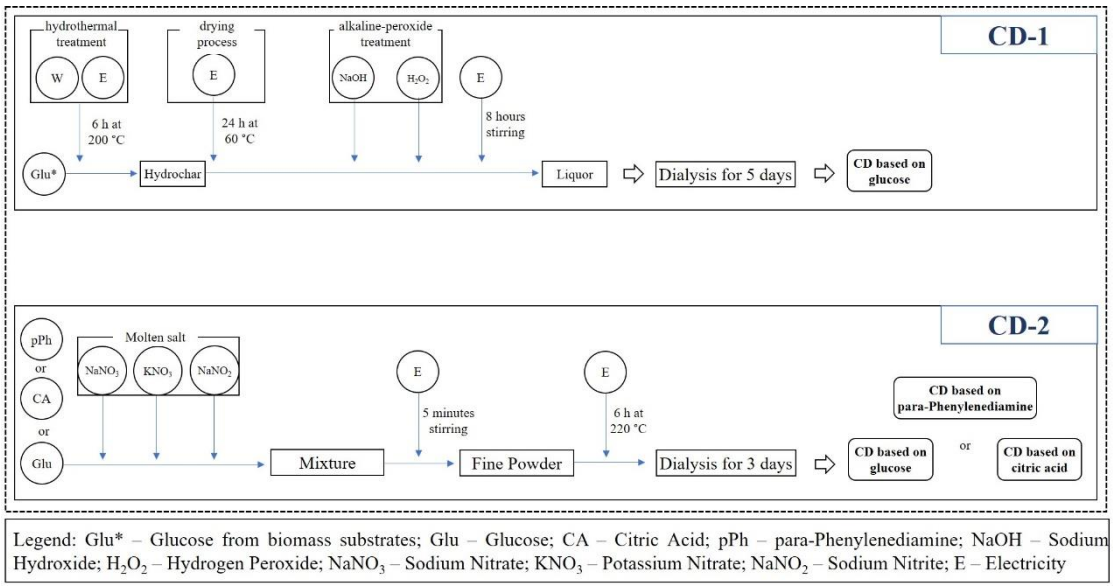

Fig. 1. Diagram for Carbon Dots syntheses.

The synthesis yield and fluorescence quantum yield of the syntheses under study can be consulted in Table 1. Synthesis yield is the amount of nanoparticles formed from the used precursors (in weight, %), while the fluorescence quantum yield is the ratio of photons absorbed to photons emitted through fluorescence.

Table 1. Properties of both syntheses under study (Li et al., 2017; Jing et al., 2019).

	Synthesis Yield (wt.%)	Quantum Yield (%)
Synthesis 1		
CD based on glucose	40.1	22.67
Synthesis 2		
CD based on glucose	45.5	8.0
CD based on citric acid	39.6	20.8
CD based on *para*-phenylenediamine	25.8	5.3

The environmental impacts were analyzed and compared in a first stage by using a weight-based functional unit of 1 kilogram (kg), that is, it was considered 1 kg of produced CDs.

Considering a weight-based functional unit is needed to allow compare an equivalent quantity of nanomaterial (Feijoo et al., 2017; Hischier and Walser, 2012). Later, these impacts were normalized by the fluorescence quantum yield (QY) of the CDs under study. This is needed because weight-based functional units do not consider functional benefits for which the nanomaterials were engineered. Thus, a weight-based functional unit analysis of potential impacts might not account that a more resource-intensive synthesis may be justified later in the use stage. Therefore, the QY was chosen as the normalization factor to consider the fluorescent QY of each CD, since this is a relevant property in most of the several CDs applications. Thus, we have defined a functional unit (FU) related to the highest QY of the studied CDs (CD-1, Glucose, Table 1). Subsequently, we compared reference flows that relate to the FU for each CD under study, according to the expression $\frac{QY_{REF}}{QY}$ (Li et al., 2017; Jing et al., 2019) (Table 2).

Table 2. Functional unit based on Quantum Yield (QY) for each Carbon Dot under study.

Carbon Dot	Quantum Yield (%)	Reference Flow
CD-1 Glucose	22.67	1.00
CD-2 Glucose	8.00	2.83
CD-2 Acid Citric	20.80	1.09
CD-2 *para*-phenylenediamine	5.30	4.28

2.2. Synthesis Routes

For this study, it was compared two different syntheses for the high-yield production of CDs (Li et al., 2017; Jing et al., 2019), with the used materials and electricity being reported in Table S1. The synthesis yields for each route are presented in Table 1.

For the first synthesis route, according to Jing et al. (2019) (from now identified as synthesis 1), glucose was hydrothermally treated for 6 hours at 200 °C, followed by centrifugation to separate the suspension and the obtained hydrochar. The latter was subsequently dried at 60 °C for 24 hours in an oven. The final synthesis step consists of an 8 hours alkaline-peroxide treatment of the hydrochar, at room temperature. Namely, the dried hydrochar was dispersed into diluted NaOH solution, with the subsequent addition of H_2O_2. The mixture was left to stirring for 8 hours at room temperature. Pure CDs were obtained after a 5-days dialysis process, which was employed to remove salts and other molecular impurities (Jing et al., 2019).

In the second synthesis (from now identified as synthesis 2 (Li et al., 2017)), different materials (glucose, acid citric, or *para*-phenylenediamine) were used as precursors in a eutectic mixture of $NaNO_3$/KNO_3/$NaNO_2$ (7:53:40 mass ratio) with a melting point of 140 ºC. The synthesis route was initiated by mixing (1:10 mass ration) and ground (for 5 minutes) the carbon precursor and the molten salt, forming a fine powder. The next step was heating the powder at 220 ºC for 6 hours, followed by dispersion in water and dialysis for 3 days to remove salts and molecular impurities (Li et al., 2017).

CDs obtained by the synthesis 1 procedure are named CD-1, while CDs produced by synthesis 2 are termed CD-2.

2.3. Life Cycle Inventory Data

The assessment of the environmental impacts associated with the syntheses of CDs was based on inventory data from laboratory-scale synthesis procedures found in the Ecoinvent® 3.5 database. The foreground system of the synthesis procedure consists of chemicals used as raw materials and electricity used for the fabrication process (heating plate, oven). The different processes and chemicals included in this study were modeled with the following data present in the Ecoinvent® 3.5 database (GLO standing for global, and RER for regional market for Europe) as described in Table S2.

The amount of chemicals and electricity used are described in Table S1. The dataset used for electricity describes the available electricity data on the medium voltage level in Europe for the year 2014, as described in the Ecoinvent® 3.5 database. As referred above, the electricity considered combined the electricity required for using the heating plate and oven. Given that the authors of the studies under evaluation did not identify the used equipment's, we were forced to use instead standard plates and ovens. By using the same equipment's, we are also ensuring that differences between synthesis routes are not due to equipment-specific issues. Thus, it was considered that the heating and stirring plate used was a Normax Nx1200 Analogical magnetic stirrer with heating, which has a power consumption of 500 W. The

considered oven was DRY- Line® Prime from VWR, with 12 A and a power supply in AC (single phase) of 230 V which can achieve with a maximum power factor (1) a power consumption maximum of 2760 W.

2.4. Environmental Impact Assessment

The present LCA study is based on a cradle-to-gate approach, from the production of precursor materials to the fabrication of CDs. Environmental impacts were modeled using the ReCiPe 2016 V1.03 endpoint method, Hierarchist version (Huijbreagts et al., 2017), which evaluates three categories of potential impacts (Human Health, Ecosystems and Resources). The Hierarchist perspective is a scientific consensus model to deal with uncertainties and assumptions based on the most common policy principles with regards to the time frame and plausibility of impact mechanisms. In Human Health (HH) subsection were assessed Global Warming – Human Health (GW–HH), Stratospheric ozone depletion (SO), Ionization Radiation (IR), Ozone formation – Human Health (OF), Fine Particulate Matter formation (FPM), Human Carcinogenic toxicity (HC), Human Non-Carcinogenic toxicity (HNC) and Water Consumption – Human Health (WC–HH). Ecosystems (E) potential impacts evaluated were Global Warming – Terrestrial Ecosystems (GW–TE), Global Warming – Freshwater Ecosystems (GW–FE), Ozone Formation – Terrestrial Ecosystems (OF–TE), Terrestrial acidification (TA), Freshwater Eutrophication (FE), Marine Eutrophication (ME), Terrestrial EcoToxicity (TET), Freshwater EcoToxicity (FET), Marine EcoToxicity (MET), Land Use (LU), Water Consumption – Terrestrial Ecosystem (WC–TE) and Water Consumption – Aquatic Ecosystems (WC–AE). Resources (R) subsection assessed were Mineral Resource scarcity (MR) and Fossil Resource scarcity (FR). More information about environmental impact subcategories can be found in Table S3. The LCA study was performed using SimaPro 9.0.0.48 software.

2.5. Sensitivity analysis

A sensitivity analysis was performed by considering "What-if" scenarios (Pianosi et al., 2016). These consist of varying the amount and/or identity of the type of materials employed, as well as the amount of required electricity. More specifically, a sensitivity analysis was performed with different scenarios for synthesis 1 and 2, by varying (± 30%) the used amounts of either electricity or the carbon precursor. A hypothetical scenario was considered by replacing the carbon precursor (glucose) of synthesis 1 with either citric acid or *para*-phenylenediamine (types of precursors employed on synthesis 2), considering the same synthesis yield. This was made to evaluate if the variation of the carbon precursors has a relevant impact on the overall environmental sustainability of the synthesis 1, but it should be noted that in "real-life" this sort of substitution would invariably lead to a different synthesis yield. Beyond this, it was also considered a final

scenario related to electricity production from different countries/regions (Brazil, Europe, Japan, and US), to determine how the location of electricity production affects the data and environmental sustainability of the synthesis routes. This is relevant once each country has a characteristic energy matrix that could influence the potential environmental impacts of CDs syntheses.

2.6. Scale-Up

This LCA also aims to help elucidate some uncertainties regarding the large-scale production of these CDs. Thus, we have also modeled the scaling up from laboratory scale to industrial scale. To this end, it was extrapolated the laboratory scale results from the framework developed by Piccinno et al. (2016), by considering a batch reactor with a volume between 100 L and 1000 L to achieve processing quantities of 100 kg and 1000 kg. The amount of materials used (glucose, citric acid, *para*-phenylenediamine, NaOH, H_2O_2, H_2O, $NaNO_3$, KNO_3 and $NaNO_2$) were scaled linearly up to the processing quantity. By its turn, the electricity was scaled based on the framework of Piccinno et al. (2016) that determines the energy required for the heating and stirring.

The heating energy required for the syntheses is determined by Equation (1), in *Cp* is the specific heat capacity of the main solvent (J/K/kg), m_{mix} the mass of the reaction mixture (kg), T_r the reaction temperature (K), T_0 the starting temperature (K), T_{out} the temperature outside the reactor (K), *A* surface area of the reactor (m^2), k_a the thermal conductivity of the insulation material (W/m+K), *s* the thickness of the insulation (m), *t* the time of the reaction (h) and η_{heat} the efficiency of the heating device in % (Piccinno et al., 2016).

$$Q_{react} = \frac{Q_{heat}+Q_{Loss}}{\eta_{heat}} = \frac{C_p \times m_{mix} \times (T_r - T_0) + A \times \frac{k_a}{s} \times (T_r - T_{out}) \times t}{\eta_{heat}} \quad (1)$$

It was considered that the C_p parameter for the solvent in synthesis 1 refers to water, while in synthesis 2 refers to the molten salt ($NaNO_3$/KNO_3/$NaNO_2$). In this sense, the specific heat capacity of the molten salt was estimated according to the C_p of the solid phase of each compound, as obtained in the study of Kawakami et al. (2004) and the ratio of each compound in the synthesis. In this sense, C_p of the molten salt was determined by the expression $\frac{C_{p_{(NaNO_3)}} \times 7g}{100\ g} + \frac{C_{p_{(KNO_3)}} \times 53g}{100\ g} + \frac{C_{p_{(NaNO_2)}} \times 40g}{100\ g}$. The remaining parameters were obtained considering the synthesis in question (CD-1 or CD-2), as well as the values suggested by Piccinno et al. (2016).

On the other hand, the stirring energy was determined by Equation (2), in which *Np* is the type of the impeller (dimensionless number), *ρmix* the density of the reaction mixture (kg/m^3),

N the rotational velocity of stirring (1/s), d the diameter of the impeller (m), t the reaction time (h) and η_{stir} the efficiency of the agitator in % (Piccinno et al., 2016).

$$E_{stir} = \frac{N_p \times \rho_{mix} \times N^3 \times d^5 \times t}{\eta_{stir}} \quad (2)$$

It is noteworthy that, for the heating energy, the reaction time (CD-1 and CD-2: 6 hours) and reaction temperature (CD-1: 200 ºC and CD-2: 220 ºC) remain the same as in the laboratory scale, as well as the duration of the reaction (CD-1: 128 hours and CD-2: 72 hours) for the stirring energy. The parameters of heating energy and stirring energy for the determination of the electricity in the industrial scale for both syntheses can be found in Table S4.

It is worth mentioning that, in addition to heating and stirring energy, synthesis 1 considers the energy required for drying hydrochar. However, it was not possible to model this energy with the framework developed by Piccinno et al. (2016), because of the unknown hydrochar characteristics.

3. Results and Discussion

This section is divided into four subsections, synthesis comparison by weight (3.1), synthesis comparison by QY (3.2), sensitivity analysis (3.3), and scale-up (3.4).

3.1. Synthesis comparison by weight

In a first approach, it was performed a comparison of potential environmental impacts between the syntheses under study by considering a weight-based functional unit of 1 kg of CDs. The results obtained for synthesis 1 are shown in Fig. 2, while the results obtained for synthesis 2 are found in Fig. 3. For this study, our intention was not to make quantitative appreciations of the environmental impacts of each material input, but to compare the contributions to the different impact categories of the input involved in each synthesis and with each other.

It was possible to understand that the major contributor for synthesis 1 is, in almost all the environmental impact subcategories, the electricity (with contributions between 56 to 96%).

However, the subcategories of Marine Eutrophication (ME) and Land Use (LU) are the exceptions, in which the carbon precursor (glucose) constitutes the highest contribution to environmental impacts in those categories (60-61%). As for hydrogen peroxide and water, their relative contributions appear to be quite negligible.

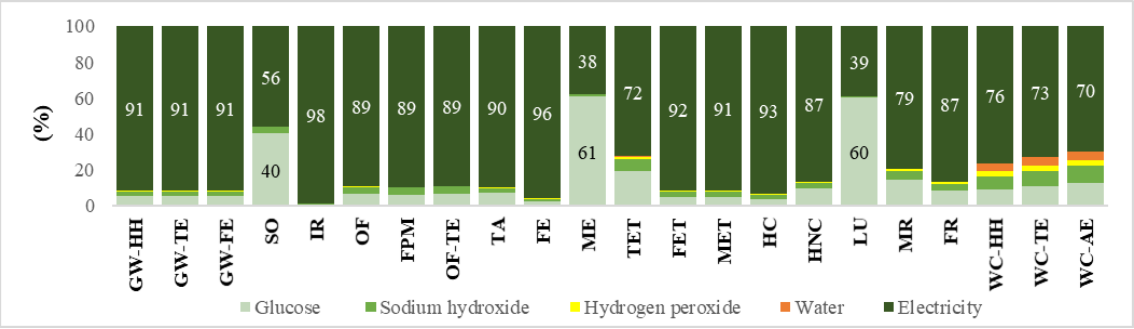

Fig. 2. Relative environmental impacts of synthesis 1 (CD-1 based on glucose). Abbreviations are explained in Section 2.4. This graphic was obtained applying ReCiPe endpoint method.

On the other hand, for the three routes considered for synthesis 2 (each one corresponding to a different carbon precursor), there is not only one major contributor (Fig. 3). For the synthesis routes with either glucose or citric acid (Figs. 3.A and 3.B), sodium nitrite ($NaNO_2$) appears to predominate in many of these categories. For CD-2 based on glucose, the exceptions are: Stratospheric Ozone depletion (SO) and MR with potassium nitrate (KNO_3) as the highest contributor; IR, Freshwater Eutrophication (FE), Freshwater EcoToxicity (FET), Marine EcoToxicity (MET) and Human Carcinogenic toxicity (HC) with a predominance of electricity; ME and LU have a predominance of glucose.

For CD-2 based on citric acid, the exceptions are: the subcategories GW-HH, GW-TE, GW-FE, SO, and MR with a prevalence of KNO_3; IR, FE, and HC show a predominance of electricity; LU and WC-AE show a predominance of citric acid.

Finally, for CD-2 based on *para*-phenylenediamine (Fig. 3.C), the situation is somewhat different as the contributions of the carbon precursor to associated environmental impacts dominate in many categories (thus, replacing $NaNO_2$). Nevertheless, the categories SO and MR have KNO_3 as the major contributor, while electricity is the highest contributor to IR, FE, and LU. Finally, $NaNO_2$ is still the highest contributor in the categories of FET, MET, HC, HNC, WC-HH, WC-TE, and WC-AE.

In conclusion, and for synthesis routes (1 and 2), the results indicate that the environmental impacts of both hydrothermal and thermal procedures are caused mainly by the electricity and the carbon precursor (irrespective of its identity), with water being a negligible contributor. The inclusion of salts, such as $NaNO_2$ and KNO_3, should lead to higher associated environmental impacts, given their significant contribution in several categories. Interestingly, previous LCA studies of low-yield syntheses of CDs did reveal that electricity is a major contributor for hydrothermal synthesis routes, which is a process that typically requires longer reaction times (of several hours) (Sendão et al., 2020). However, when the synthesis route is microwave-assisted (which generally takes minutes), electricity provides only small to negligible contributions (Sendão et al., 2020). It is worth mentioning that, despite the latter

processes potentially being more environmentally sustainable due to low electricity consumption (Sendão et al. 2020), studies show that changing the strategy route (from hydrothermal to microwave), even with the same precursors, can result in significant alterations in synthesis yield, quantum yield and other properties (Crista et al., 2020b). Thus, one should be careful before stating that microwave strategies are indeed more sustainable, as other synthesis strategies could offset some associated environmental impacts by producing CDs with improved/different properties.

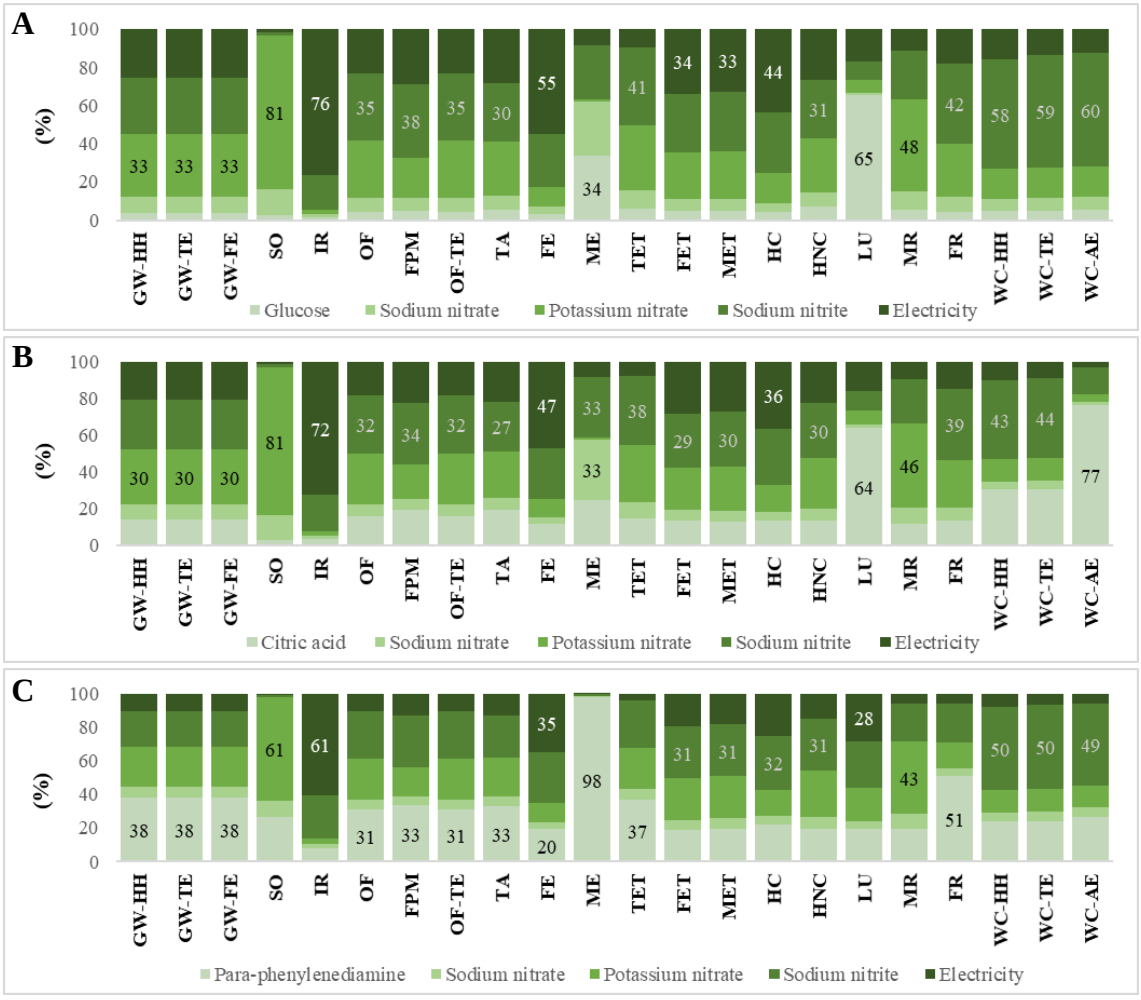

Fig. 3. Relative environmental impacts of synthesis 2 of CD based on glucose (A), CD based on citric acid (B), and CD based on *para*-phenylenediamine (C). The abbreviations are explained in section 2.4. This graphic was obtained applying ReCiPe endpoint method.

To facilitate the comparison between the four studied synthetic routes (one for synthesis 1, and 3 for synthesis 2), they are compared in the same Figure (Fig. 4), with all environmental impact subcategories being divided into three main categories: human health, ecosystems, and resources. The first conclusion is that synthesis 1 is associated with lower environmental impacts than the routes included under synthesis 2. It should be noted that the amount of carbon precursor

is similar in all syntheses, and the electricity used in synthesis 1 is more than the double used in synthesis 2 (Table S1). Thus, one of the reasons for the higher environmental impacts of the three routes of synthesis 2, especially for the one with glucose as the carbon precursor (the same as in synthesis 1), is attributed to the inclusion of the eutectic mixture of salts (as $NaNO_2$ and KNO_3). This is evident in the SO category where KNO_3 is responsible for 81% of the impacts, and in water consumption categories in which $NaNO_2$ is responsible for circa 60% of impacts.

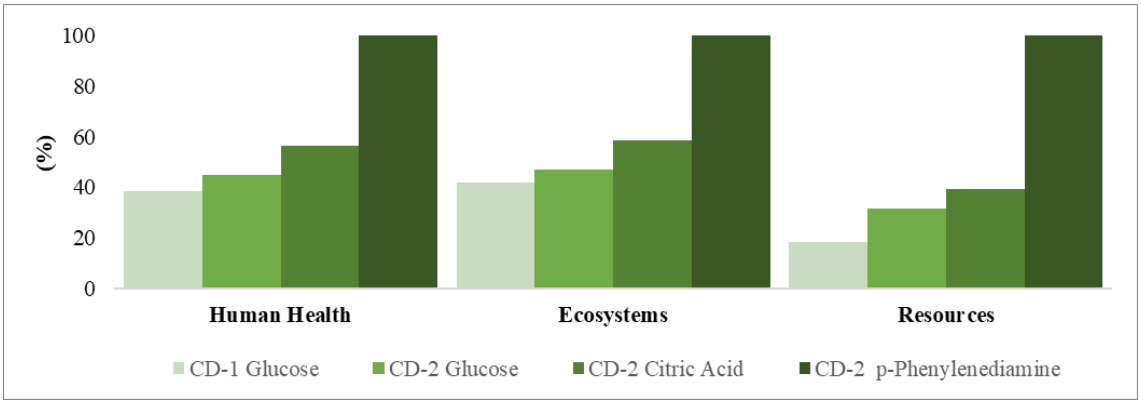

Fig. 4. Relative environmental impacts of both syntheses (CD-1 and CD-2), considering a comparison by weight. This graphic was obtained applying ReCiPe endpoint method.

Interestingly, the environmental impacts associated with synthesis 2 progressively increase when the carbon precursor changes from glucose to citric acid and then to *para*-phenylenediamine. This increase in environmental impacts with different carbon precursors is higher than the difference caused by the addition of the salts (which can be assessed by comparing CD-1 and CD-2 from glucose). Thus, we can conclude that the carbon precursor is a significant contributor to the overall environmental impacts associated with these syntheses, with citric acid and especially *para*-phenylenediamine being responsible for more environmental damages than glucose.

3.2. Synthesis comparison by QY

It was also evaluated the environmental profiles of each CDs by rescaling their environmental impacts according to their fluorescence QY (Table 2). The relative environmental impacts of each synthesis route, according to the QY-based functional unit, are present in Fig. 5.

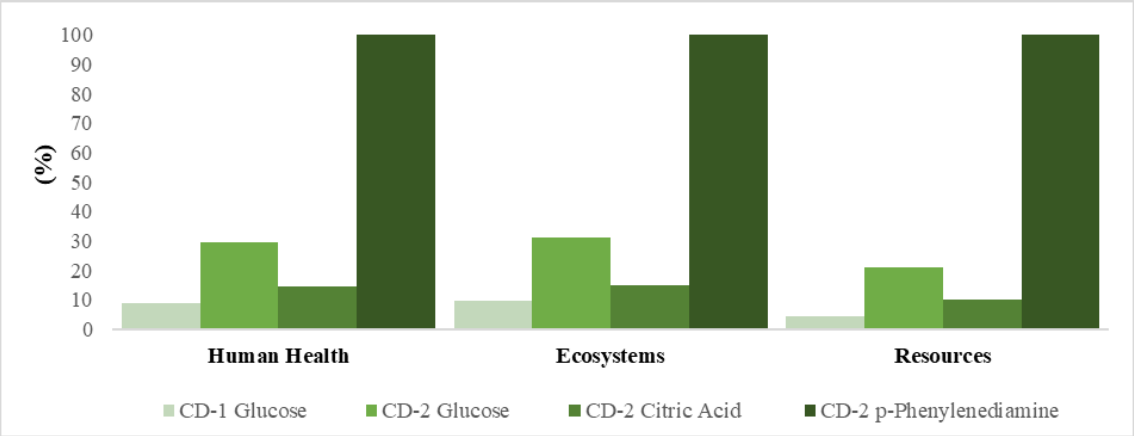

Fig. 5. Relative environmental impacts of both syntheses (CD-1 and CD-2), considering a comparison by QY. This graphic was obtained applying ReCiPe endpoint method.

There is a limited qualitative variation that resulted from the re-scaling, as synthesis 1 is still the one with lower environmental impacts. Also, the route with higher environmental impacts is still synthesis 2 with the use of *para*-phenylenediamine as a carbon precursor. Nevertheless, one qualitative difference among the studied synthesis 2 options, is that now the use of citric acid as the carbon precursor leads to lower environmental impacts than the use of glucose. This is justified by the fact that the use of citric acid led to CDs with higher QY than the ones with glucose. In fact, previous LCA studies on CDs indicated that while nitrogen-doping strategies (typically used to increase the QY of CDs) lead to higher environmental impacts, these are offset by gains in the QY of the CDs (Sendão et al., 2020). The results here obtained indicate that the same can also be said for the identity of the carbon precursor.

Finally, the results showed that re-scaling did lead to a significant quantitative difference. Namely, the environmental impacts associated with synthesis 2 with the use of *para*-phenylenediamine are now even greater than before. This can be explained by *para*-phenylenediamine, besides being the carbon precursor responsible for higher environmental impacts, is also the compound that led to lower QY.

3.3. Sensitivity analysis

3.3.1. Electricity and Carbon Precursor Variation (± 30 %)

Sensitivity analysis was performed for syntheses 1 and 2. The scenarios consisted of (Fig. 6): (1) changing the amount (± 30 %) of electricity used; (2) varying the amount of used carbon precursor (± 30 %).

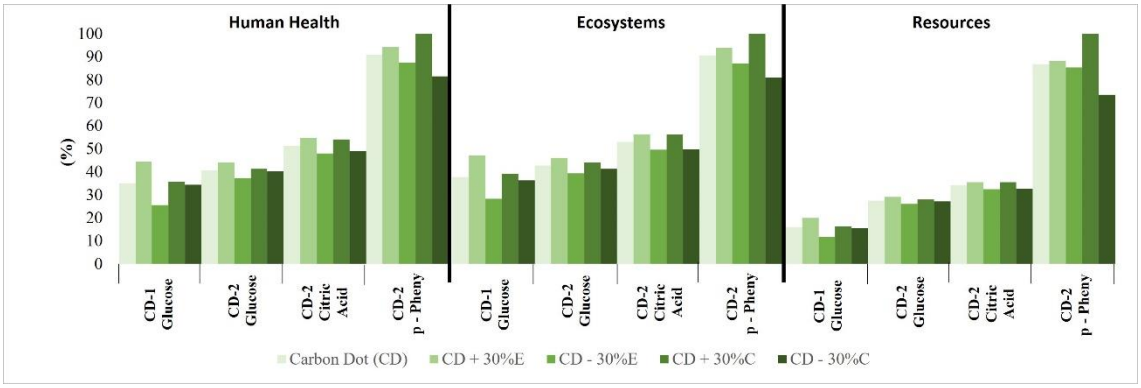

Fig. 6. Relative environmental impacts for sensitivity analysis of both syntheses (CD-1 and CD-2), considering the variation of electricity or carbon precursor. p-Pheny refers to *para*-phenylenediamine, E refers to Electricity and C refers to Carbon precursor. This graphic was obtained applying ReCiPe endpoint method.

Comparing all syntheses, sensitivity analysis shows that lower environmental impacts (for nearly all categories) are obtained for CD-1 with minus 30% of used electricity. However, when increasing the amount of used electricity, the environmental impacts of CD-1 are now higher than all scenarios for CD-2 with glucose, for Human Health and Ecosystems categories. This indicates the importance that electricity has for the overall environmental impacts associated with CD-1. On the contrary, varying the carbon precursor had a limited impact on the environmental impacts of synthesis 1. More specifically (Fig. S1), for synthesis 1, varying electricity (± 30%) represents a variation of 20% in Ecosystems and 21% in Human Health and Resources Categories. On the other hand, considering the carbon precursor for synthesis 1 (Fig. 7), in Human Health the impacts vary 1%, in Ecosystems the variation is 3%, and in Resources vary 2%.

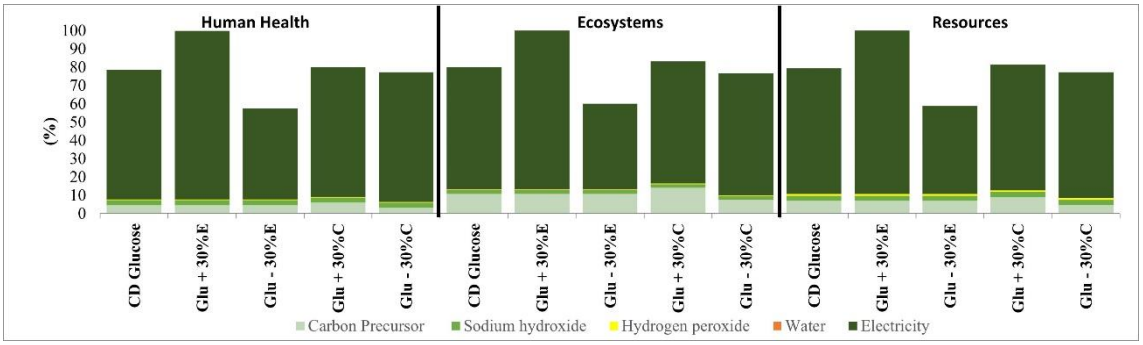

Fig. 7. Relative environmental impacts for sensitivity analysis of synthesis 1 (CD-1 based on glucose). Glu refers to Glucose, E refers to Electricity and C refers to Carbon precursor. This graphic was obtained applying ReCiPe endpoint method.

As seen in Fig. 6, varying the amount of either electricity or the carbon precursor has a limited effect on the overall environmental impacts associated with synthesis 2. In fact, the

main differences between the three routes of synthesis 2 are still explained by the identity of the used carbon precursor.

For synthesis 2 (Fig. S1), the sensitivity analysis of environmental impacts (decomposed by all inputs) revealed some interesting aspects, since there is an alteration of the highest contributor in some categories. Namely, while for reference CD-2 based on glucose, the highest contributor for all categories is $NaNO_2$, the increase of 30% of electricity results in electricity being now the main contributor for Human Health and Ecosystems. For CD-2 based on citric acid, the increase of 30% electricity also results in electricity becoming the highest contributor for the Ecosystem category. Finally, while reference CD-2 based on *para*-phenylenediamine has the carbon precursor as the main contributor in almost all the categories, the decrease of 30% carbon precursor results in $NaNO_2$ being the highest contributor for the category of Human Health.

3.3.2. Carbon Precursor variation in synthesis 1

It was also performed a sensitivity analysis on synthesis 1 that consists in replacing the carbon precursor (glucose) with either citric acid or *para*-phenylenediamine (Fig. 8).

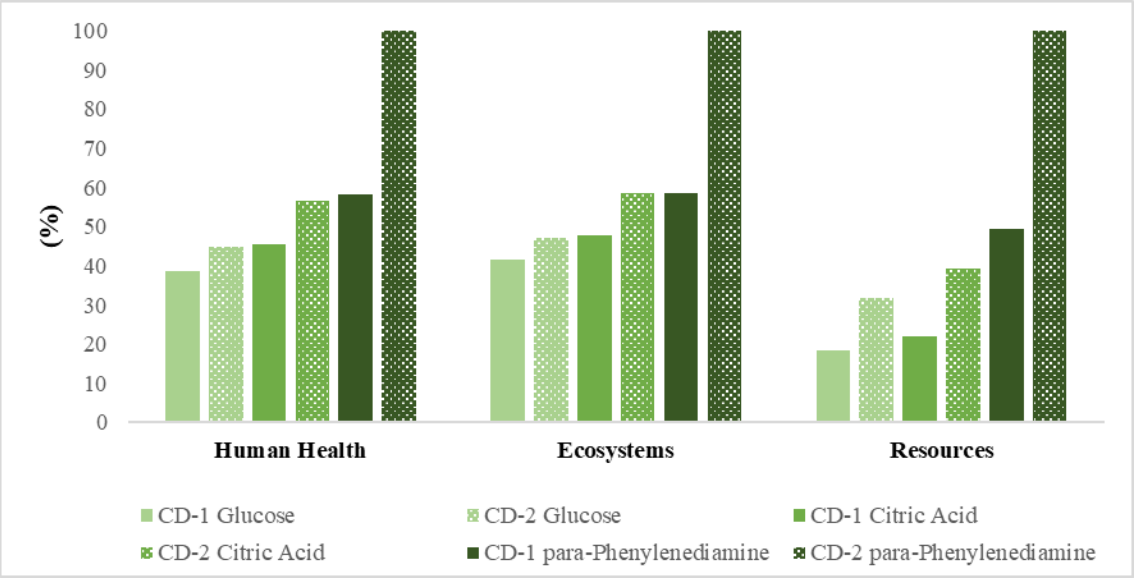

Fig. 8. Relative environmental impacts for sensitivity analysis of both syntheses, with the variation of carbon precursor in synthesis 1. To effects of comparison, all three routes of synthesis 2 are included. This graphic was obtained applying ReCiPe endpoint method.

This analysis shows that reference CD-1 (glucose as the carbon precursor) remains the most sustainable synthesis, having the lowest impacts on Human Health, Ecosystems, and Resources. Changing the identity of the carbon precursor has obvious effects as the environmental impacts of synthesis 1 increase in a relevant manner by replacing glucose with either citric acid or *para*-phenylenediamine. Moreover, the trend observed before is maintained as increasing

environmental impacts are obtained in the following order of carbon precursors: glucose < citric acid < *para*-phenylenediamine. Finally, it should be noted that the environmental impacts of synthesis 1 are always lower than the synthesis 2 route with the same carbon precursor.

3.3.3. Electricity production from different countries

Given that electricity was found to be the main contributor to associated environmental impacts, the final scenario of the sensitivity analysis consisted of varying the region/country in which electricity is generated. That is, a sensitivity analysis (Fig, 9) was performed for the most sustainable CDs of both syntheses (CDs based on glucose), considering other locations for electricity than Europe: United States (US), Japan, and Brazil.

The rationale for this type of analysis comes from the fact that different regions/countries possess different energy matrices, with different ratios of high impact/low impact energy sources. In the US, the energy matrix is basically based on coal and natural gas, while in Japan its main energy source is coal (Vinsentin et al, 2019). In Europe, energy production is also reliant on coal, but many countries also have relevant sources of renewable energy (Vinsentin et al, 2019). In fact, an analysis of energy production of all countries in the European Community (carried out by the Ecoinvent database), found the impacts in European scenarios to be smaller than impacts for scenarios for the US and Japan (Vinsentin et al, 2019). Finally, the energy matrix of Brazil is basically composed of clean and renewable energy sources, such as hydroelectric dams (Vinsentin et al, 2019).

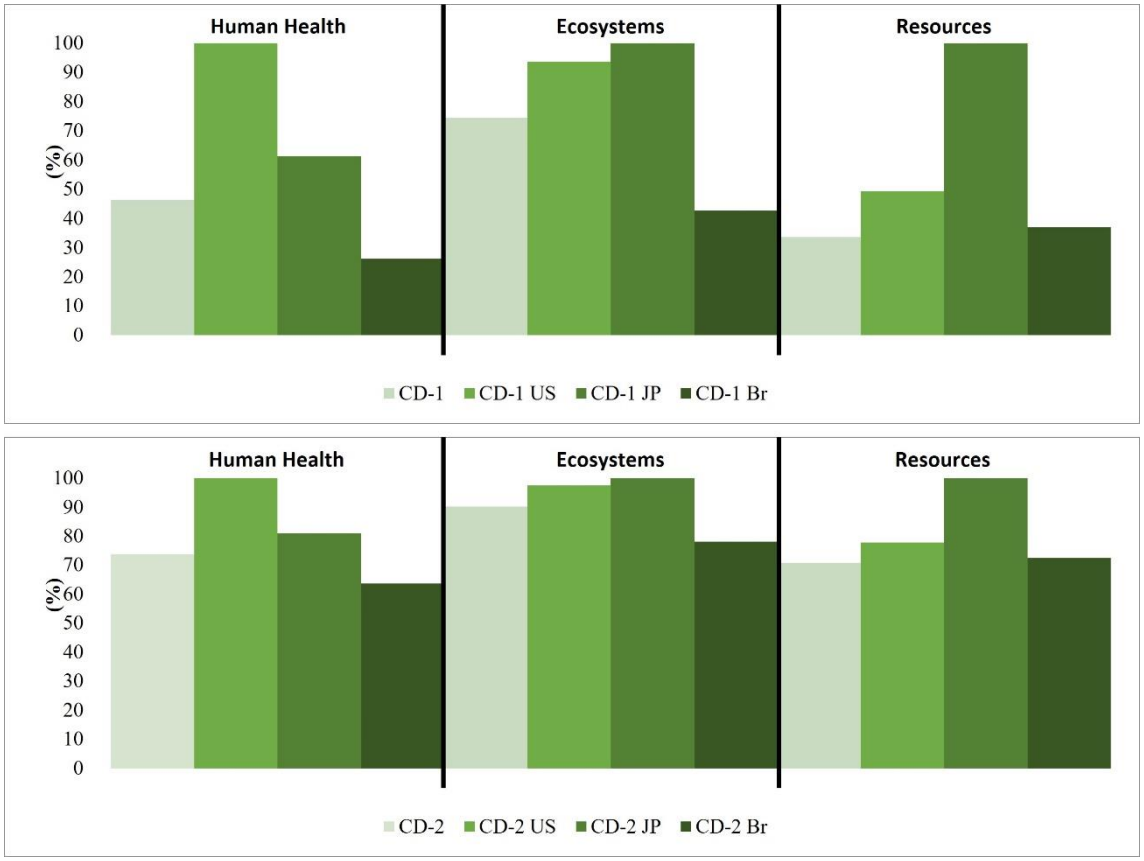

Fig. 9. Relative environmental impacts for sensitivity analysis of CD-1 and CD-2 based on glucose with electricity production from different countries. US refers to the United States, JP to Japan, and Br to Brazil. This graphic was obtained applying ReCiPe endpoint method.

By analyzing the environmental impacts resulting from changing the origin of electricity production (Fig. 9), it is possible to see that using electricity produced in both the US and Japan leads to higher environmental impacts than using electricity produced in Europe or Brazil. More specifically, electricity generated in the US leads to significantly higher impacts in the human health category, while Japan leads to higher impacts in both the ecosystems (in this case comparable with electricity produced in the US) and resources categories. Interestingly, electricity produced in Brazil leads to lower impacts in the human health and ecosystems categories than electricity produced in Europe, while leading to similar impacts in the resources category.

Our analysis also revealed that CD-1 is more sensitive to variations in the country/region of origin of used electricity than CD-2. This is not unexpected as electricity is undoubtedly the main contributor to environmental impacts for CD-1 (71.0-95.5%), while being less relevant for CD-2 (14.9-46.8%) (Table S5).

In conclusion, the country/region where the electricity is generated is a sensitive parameter for the sustainability of these synthesis strategies, particularly for CD-1, with scenarios where

electricity is obtained from a matrix of clean/renewable sources leads to significant environmental gains.

3.4. Scale-Up to Industrial Scale

As explained in section 2.6, results at the industrial scale for both synthesis routes (1 and 2) were extrapolated from the results obtained at laboratory-scale by considering the framework of Piccinno et al. (2016). Table S6 shows the inventory of raw materials to 100 kg and 1000 kg of each CD under study.

This analysis shows (Fig. 10) that, even at an industrial scale, synthesis 1 is still the most sustainable route by a significant percentual margin for all syntheses. In addition, as it is possible to understand by Figure S2, there are no significant differences (<0.1%) between the processing quantity of 100 kg (Fig. S2) and 1000 kg.

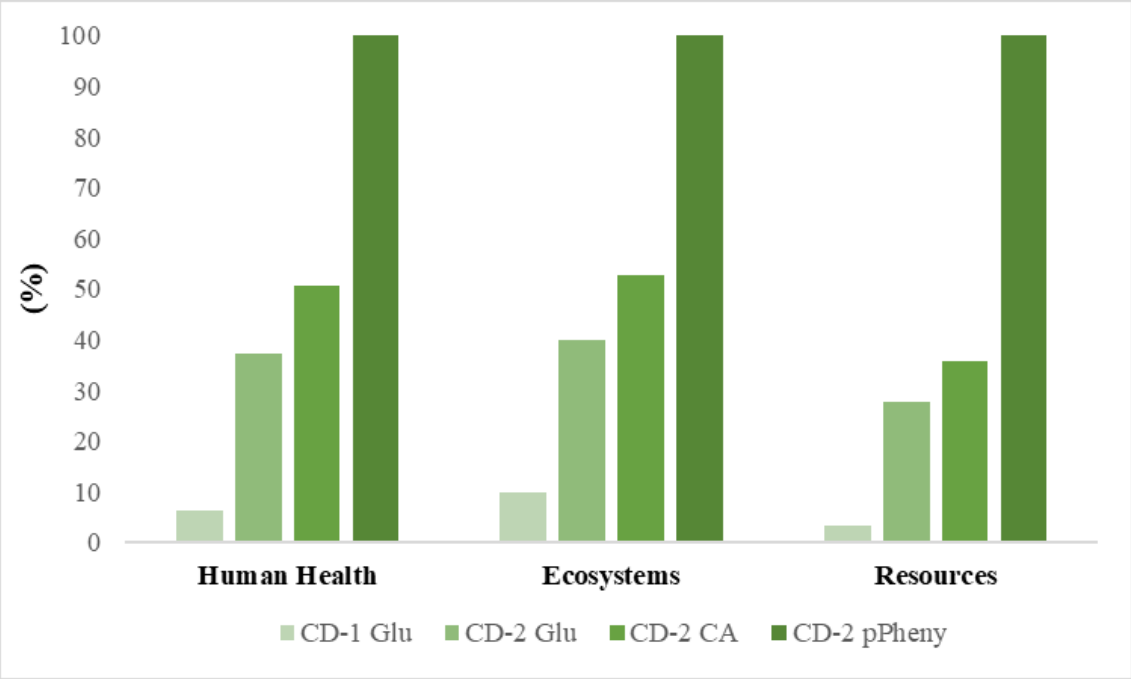

Fig. 10. Relative environmental impacts for scale-up of both syntheses, considering industrial-scale (1000 kg). Glu refers to glucose, CA to citric acid, and pPheny to *para*-phenylenediamine. This graphic was obtained applying ReCiPe endpoint method.

Considering the contribution of each raw material in synthesis 1 (Table S7), the scale-up to 1000 kg reveals that electricity (main contributor at laboratory-scale) constitutes the second main contributor to potential environmental impacts in all categories (HH, E, and R) and that now the carbon precursor occupies the position of the main contributor (Fig. 11).

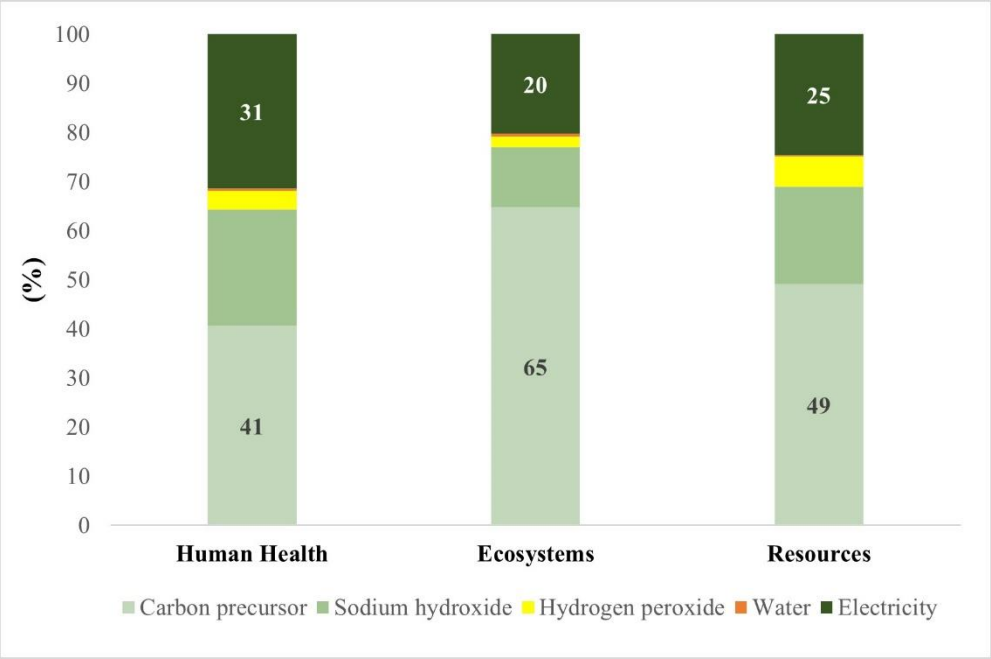

Fig. 11. Relative environmental impacts for scale-up (1000 kg) synthesis 1 in CD based on Glucose. This graphic was obtained applying ReCiPe endpoint method.

In synthesis 2, the scale-up of CD based on glucose (Fig. S3) indicates that the main contributor is still $NaNO_2$. Nevertheless, the magnitude of its contributions is higher at an industrial scale than at a laboratory-scale (Table S8). It is interesting to note that with scale-up, the contribution of electricity to HH, E, and R decreased from 18-28% to 1-2% (Table S8). The scale-up of CD-2 based on citric acid (Fig. S4) also reveals that sodium nitrite is still the main contributor (Table S9), while the contribution from electricity decreased in a similar magnitude as indicated above (Table S9). Finally, for CD-2 based on *para*-phenylenediamine, the scale-up to industrial scale (Fig. S5) reveals that carbon precursor is still the main contributor (Table S10), followed by $NaNO_2$.

In conclusion, scale-up modeling efforts indicate that the relevance of electricity decreases significantly for all routes at an industrial scale, becoming even somewhat negligible for synthesis 2. The impacts associated with the use of carbon precursor (for all synthesis routes) and eutectic mixture of salts (for synthesis 2) are further highlighted.

Our approach is aligned with the principles of green chemistry, as its searches for strategies to prevent waste production during synthetic procedures. Our work focuses on providing researchers with insight toward the development of a more sustainable high-yield synthesis of CDs, in which waste generation is reduced. It should be noted that the typical low-yield synthesis of CDs is associated with the production of ~90% waste. Also, by identifying hotspots of potential impacts toward the environment and human health, we are helping to devise safer synthetic strategies.

4. Conclusions

This work provides the first LCA-based environmental evaluation for high-yield synthesis routes of carbon dots (CDs). Its goal was to understand the environmental performance of two available routes for the large-scale production of CDs, and to provide some considerations that could improve the sustainability of fabricating these engineered nanomaterials of interest.

The studied synthesis routes consist of: (1) hydrothermal treatment of carbon precursors to obtain hydrochar material, which is subsequently subjected to alkaline-peroxide treatment to generate CDs with high-yield; (2) thermal treatment of carbon precursors (in powder form) mixed in a eutectic mixture of salts, which generated CDs with high-yield.

Analysis of the performance of the syntheses, by considering a weight-based functional unit of 1 kg of produced CDs, showed that synthesis route 1 is associated with the lowest environmental impacts, when comparing with the different options regarding synthesis 2 (associated with the possible use of different carbon precursors). In synthesis 1, electricity is the input with the highest environmental impacts in nearly all studied impact categories. The lower relative environmental impacts of synthesis 1 (relative to synthesis 2) were attributed to the absence of the eutectic mixture of salts, used in synthesis 2, which had relevant contributions to several categories of impact.

Analysis of synthesis 2, in which different carbon precursors (glucose, citric acid, and *para*-phenylenediamine) were studied, revealed that the identity of the carbon precursor is a key parameter to determine the sustainability of the synthesis route. More specifically, we have found that higher environmental impacts are associated with different carbon precursors in the following trend: glucose < citric acid < *para*-phenylenediamine.

A performance-based functional unit (based on the fluorescence quantum yield of the studied CDs) was also used, to understand if functional gains could offset some environmental impacts. Its use still identified synthesis 1 as the fabrication route with the lowest environmental impacts, showing that the formation of hydrochar and its treatment into forming CDs, without the use of other inputs (as a eutectic mixture of salts), can offset its relatively high electricity consumption.

A sensitivity analysis was also performed to assess how the environmental impacts of these synthesis routes were affected by variations of the amounts used of carbon precursors and electricity, as well as by replacing the identity of the carbon precursor. Varying the amount of carbon precursor has a not very significant effect on the environmental impacts of the studied synthesis routes. The same can be said for electricity, but just for synthesis 2. However, varying the identity of the carbon precursors led to significant changes in associated environmental impacts for both routes, further showing that this is the most sensitive parameter for the synthesis of CDs, irrespective of the employed synthetic strategy. Scale-up studies

indicated that the relevance of electricity decreases significantly for all routes, while the impacts of the carbon precursor are highlighted.

In conclusion, synthesis routes based on hydrochar formation and treatment should be favored over strategies focused simply on the thermal treatment of carbon precursors (especially if including extra inputs, such as mixtures of salts). Furthermore, the identity of the carbon precursors is shown to be a critical point in terms of environmental impacts for all studied synthetic strategies. Nevertheless, the environmental impacts resulting from the use of a given carbon precursor can be offset if they lead to better performance in terms of fluorescence quantum yield. Thus, the identity and properties of chosen carbon precursors should become the focus of future studies aiming to a cleaner production of CDs.

Acknowledgment

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Supplementary Data

Inventory of used materials and electricity, as well as data inventory from Ecoinvent® 3.5 database. Parameters of heating and stirring energy for the determination of electricity in the industrial scale for both synthesis routes. Relative environmental impacts to the sensitivity analysis of both syntheses (variation of ±30% electricity, carbon precursor, and country/region of where electricity is generated). Scale-up inventory of raw materials for each CD under study. Relative environmental impacts for the subcategories of Human Health, Ecosystems and Resources for syntheses 1 and 2, relative to scale-up studies.

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