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HETEROGENEOUS CATALYSIS FOR THE SYNTHESIS OF CARBON DOTS (CDs) FROM BIOMASS SOURCE

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Abstract

It has been evaluated the capacity of several phosphate-based acid catalysts of transition metals such as vanadium and niobium in the synthesis of carbon dots (CDs) via a hydrothermal process. For this purpose, two sources of carbohydrates have been used: commercial xylose and liqueur of xylose obtained from the treatment of olive pits. Catalysts were characterized by means of NH_3-TPD, DTA/TG, XRD and XPS. The reaction was carried out at 180 °C and reaction time was varied between 2 and 4h. The properties and characteristics of CDs nanoparticles were analysed confirming the existence of such nanoparticles irrespective the carbohydrate source. In terms of CDs quality, both syntheses produced comparable results. At the same time, N doped CDs with enhanced fluorescence were also synthesized following a kindred hydrothermal process and the photocatalytic activity was studied. With the aim of evaluating the environmental impact of the synthesis from commercial xylose versus the synthesis from biomass, a Life Cycle Assessment (LCA) analysis was carried out for both syntheses. It showed that the most sustainable synthesis route is the one that uses commercial xylose as carbonaceous feedstock. Furthermore, while electricity is the main contributor to all impact categories in both synthesis routes, the main differences that determine their relative sustainability are associated with the identity of the carbon precursor.

Keywords: Carbon Dots; Xylose; Acid catalyst; Biomass; Nanoparticles; Hydrothermal synthesis; Photoluminescence.

Materials and methods

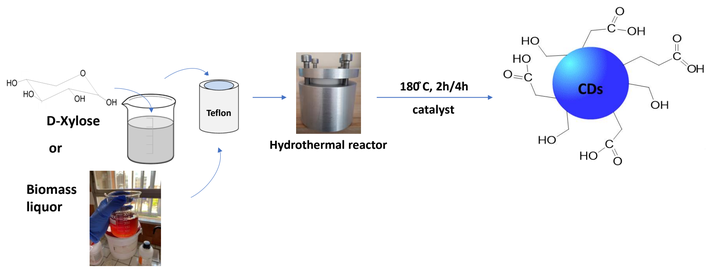

Figure 1. Hydrothermal synthesis of CDs from commercial xylose and biomass liqueur.

Table 1. Chemical composition of biomass liqueur (g/L)

Sugars		Other compounds	
Glucose	4.19	Formic acid	1.10
Xylose	69.97	Acetic acid	17.58
Galactose	8.19	HMF	0.13
Arabinose	9.86	Furfural	0.21
Mannose	0.404		

LCA

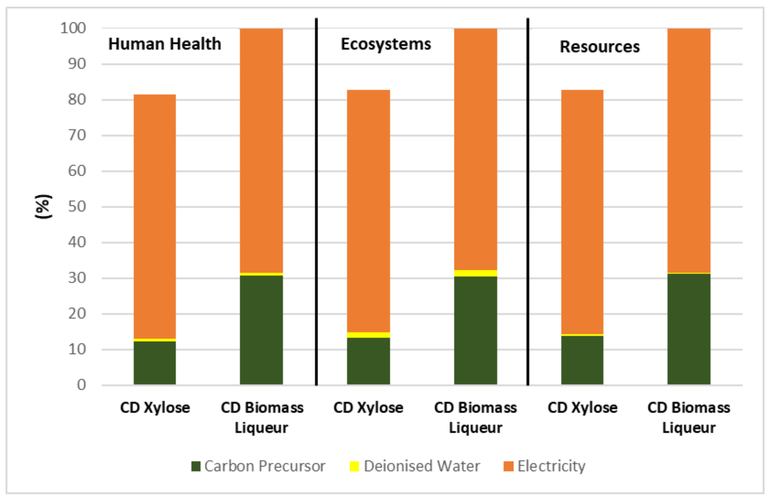

Figure 2. Relative environmental impacts of both syntheses (CD Xylose and CD Biomass Liqueur). This graphic was obtained applying ReCiPe endpoint method.

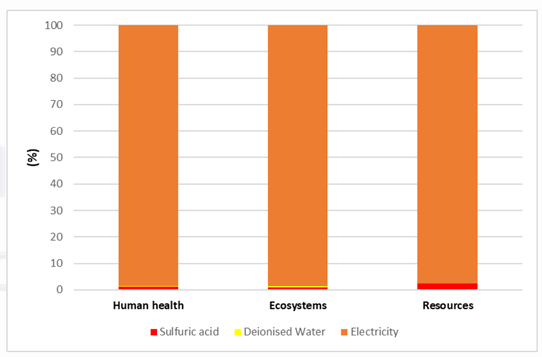

Figure 3. Relative environmental impacts of biomass liqueur. This graphic was obtained applying ReCiPe endpoint method.

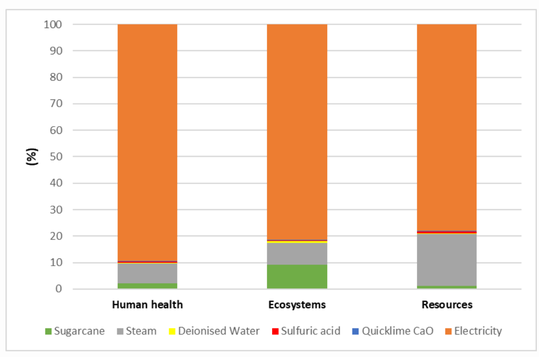

Figure 4. Relative environmental impacts of xylose. This graphic was obtained applying ReCiPe endpoint method.

Results and Discussion

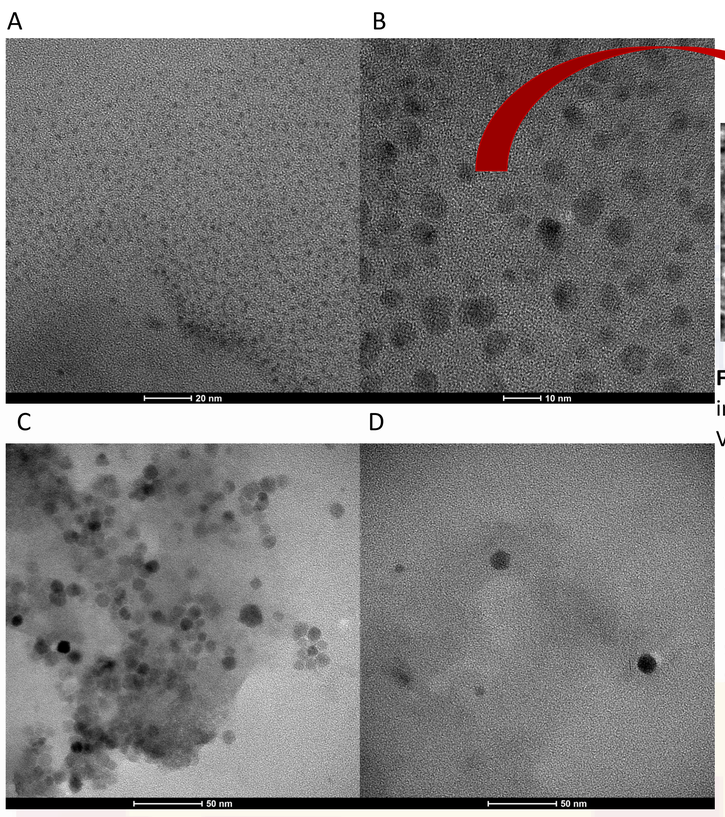

Figure 7. N-CDs from xylose and $VOPO_4$ catalyst (A), pristine CDs from xylose and $VOPO_4$ catalyst (B), N-CDs from biomass liqueur and $NbOPO_4$ catalyst (C) and CDs from biomass liquor and $VOPO_4$ catalyst (D).

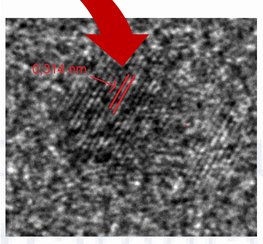

Figure 8. Graphite spacing in CDs from xylose and $VOPO_4$ catalyst.

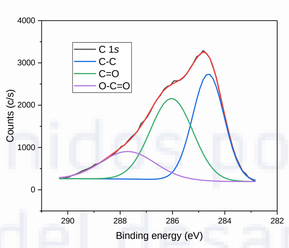

Figure 9. Deconvolution of the binding energy for C 1*s* of CDs after dialysis.

TEM images for commercial xylose derived CDs presented homogeneous quasi spherical nanoparticles whose size range varied from 2 to 6 nm, irrespective of the catalyst they were obtained with and if they underwent doping or not. Biomass derived CDs were notably bigger than the ones synthesized from commercial xylose, presenting an average size of 15 nm.

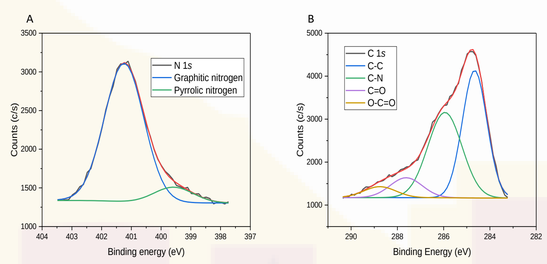

Figure 10. Deconvolution of the binding energy band for N 1*s* of N-CDs (A). Deconvolution of the binding energy band for C 1*s* of N-CDs (B).

Photoluminescence

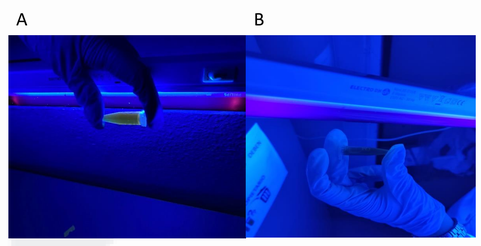

Figure 5. Sample that showed photoluminescence (A). Sample that showed no photoluminescence (B).

CDs show extremely particular photoluminescence properties, thus are very sensitive to irradiation wavelength and its maximum emission peak is highly tuneable.

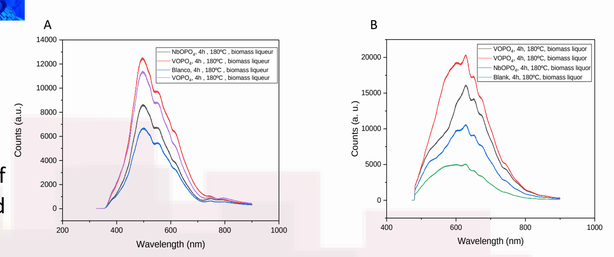

Figure 6. Photoluminescent emission of biomass CDs irradiated with 325 nm (A) and 473 nm (B) excitation laser.

Conclusions

The capacity of both catalysts $VOPO_4$ and $NbOPO_4$ of promoting the synthesis of carbon nanoparticles have been proved, being optimal for $VOPO_4$ according to results obtained for xylose conversion, photoluminescence and TEM that indicated a greater quantity of nanoparticles present in the solution. Reaction time was also a determinant factor in the synthesis of CDs, being 4h the one that showed to be the most fruitful. The slight differences in results established between both carbon sources were almost certainly due to the concentration and composition difference. The synthesized nanoparticles stand out for their size homogeneity. Doped CDs, especially, N-doped CDs showed great potential in photoluminescent applications, since their emissive values exceeded greatly those obtained from pristine CDs. A LCA study was performed considering CD synthesis and carbon precursor production. We have found that the most sustainable synthesis is the one that uses commercial xylose as carbonous precursor. More specifically, while electricity was found to be a major contributor to all categories for synthesis, we have found that the parameters that explain the differences in sustainability between these processes is the identity of the carbonous precursor.

References

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