Carbon-dots from vegetable by-products as green antioxidant additives for lubricant oils

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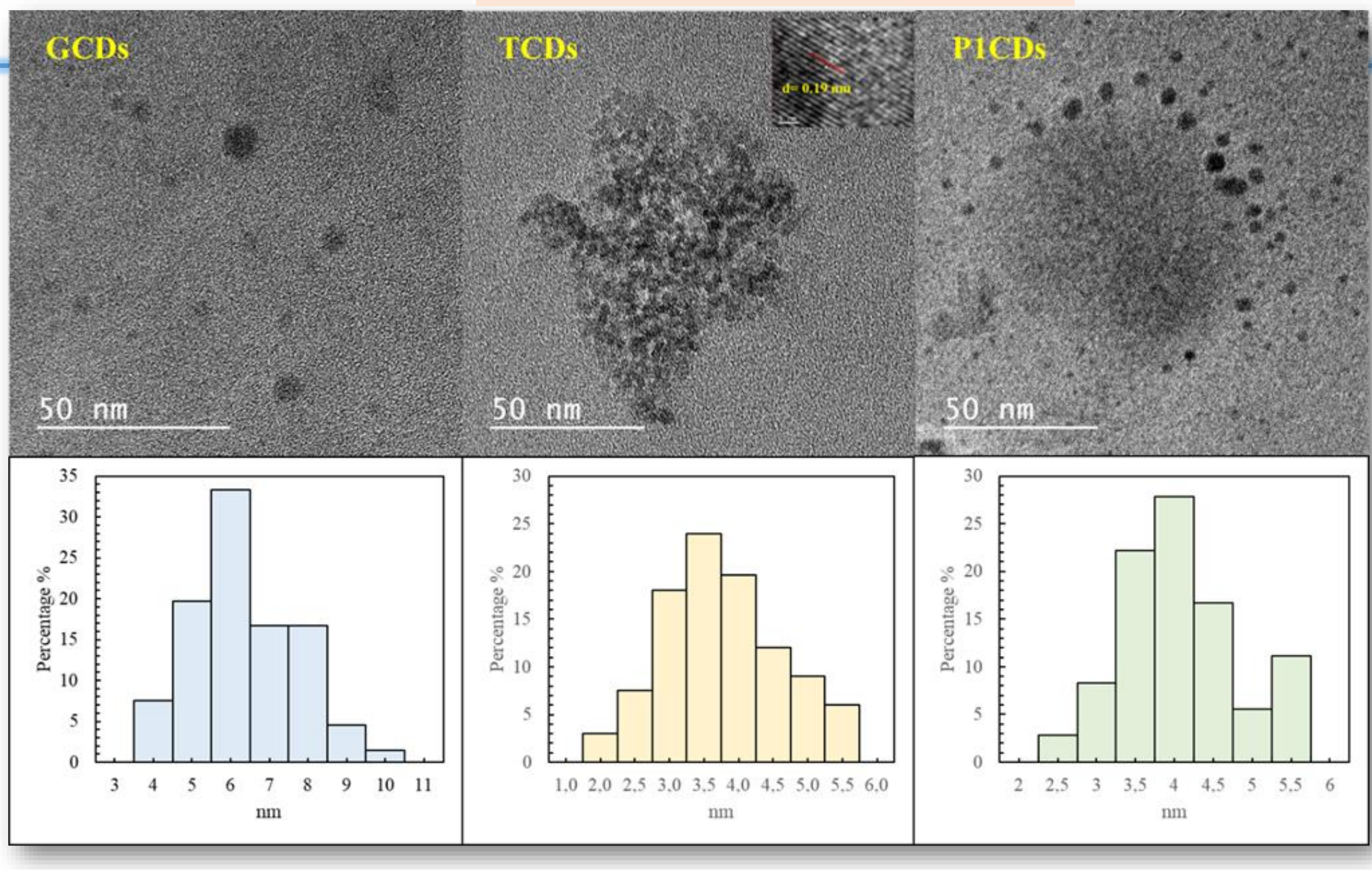
Introduction

Carbon dots (CDs) due to their favourable optical features are applied in different fields such as metal ion sensing, photo-catalysis, bio-imaging and tribology, among others. The aim of the present research was to obtain CDs from vegetable wastes (grape, apple and tea) through an hydrothermal synthesis and also assayed them as antioxidant additives in a mineral lubricant oil for the first time. These CDs have the potential to open new pathways as green additives with improved antioxidant properties that will reduce the capacity of mineral lubricant oils to oxidize and, particularly of biodegradable lubes based on vegetable oils.

Results

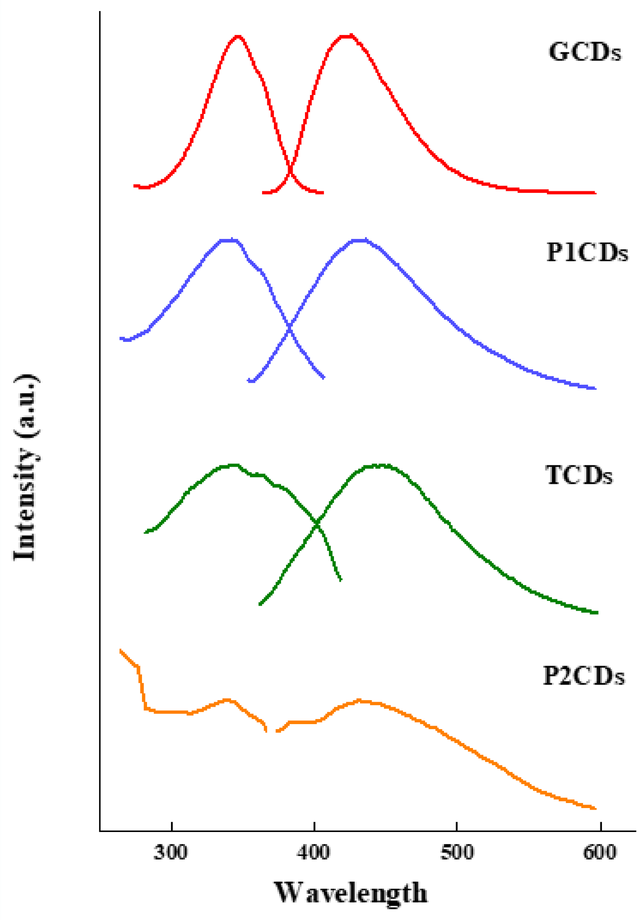
Characterization



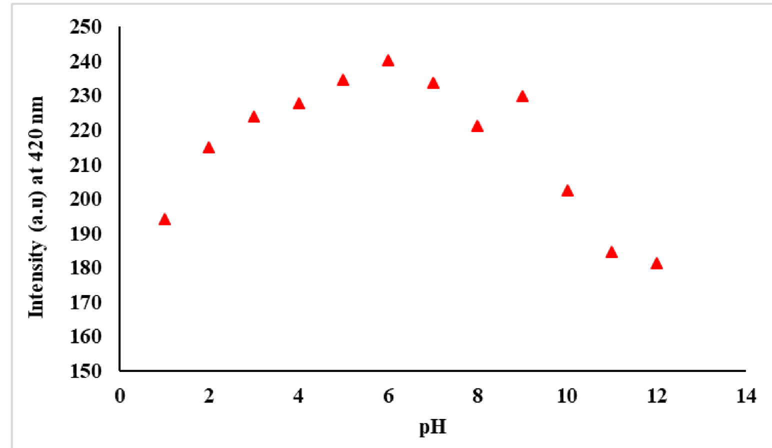
HR-TEM images size distribution histograms.

All the CDs are mostly monodispersed, with average diameters of 6±0.8 nm (gluthatione, GCDs), 3.5±0.6 nm (tea, TCDs) and 4±0.8 nm (grape pomace, P2CDs). TCDs HRTEM image shows both an amorphous phase and a crystalline graphite phase with a lattice spacing of 0.19 nm.

Optical properties: Fluorescence



Excitation and emission spectra of TCDs, P1CDs, GCDs and P2CDs in aqueous solution.



P1CDs fluorescence intensity changes as pH function

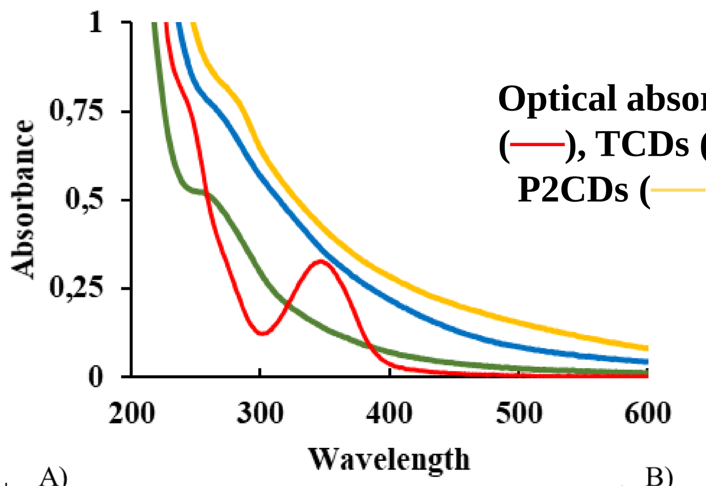
Samples	(Φabs)
GCDs	55.7%
TCDs	4.5%
P1CDs	2.76%
P2CDs	0.65%

Table 1. Quantum yield of the CDs samples.

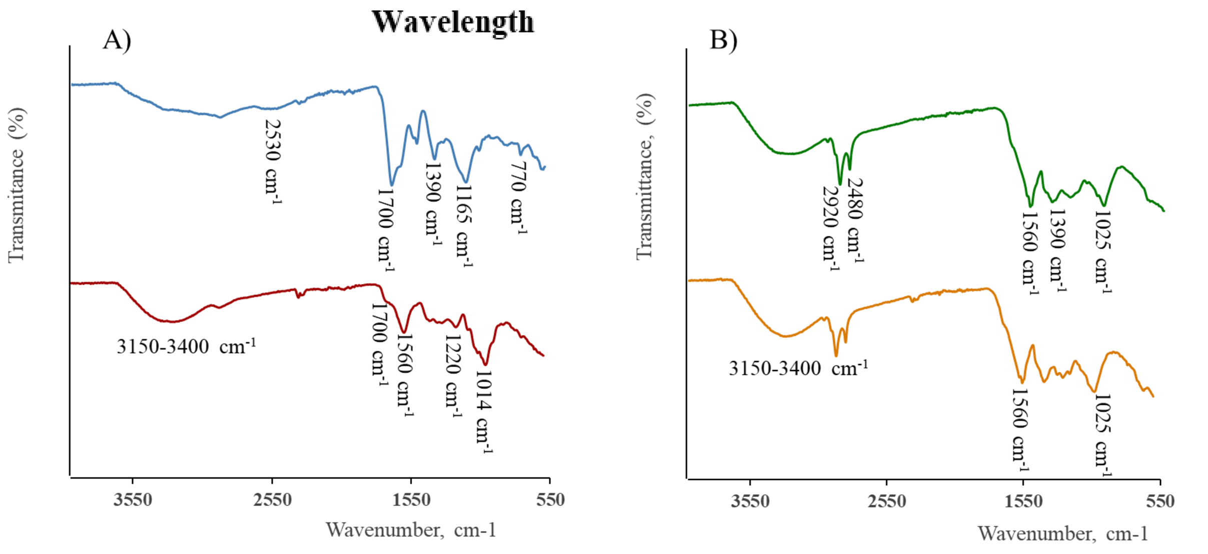
For P1CDs, the fluorescence intensity change upon pH variation depends on the surface groups: $-NH_2$ are protonated at low pH and –COOH groups deprotonated at high pH. This changes made fluorescence to decrease.

Carbon dots	λ_{exc}, nm	λ_{em}, nm	Spectral shift respect to GCDs
GCDs	350	430	--
TCDs	350	445	Em. 15 nm
P1CDs	350	438	Em. 8 nm
P2CDs	318	440	Ex. 32 nm, Em. 10 nm

Optical properties: UV-Vis and FTIR



Optical absorption spectra of GCDs (—), TCDs (—), P1CDs (—) and P2CDs (—) in aqueous solution.

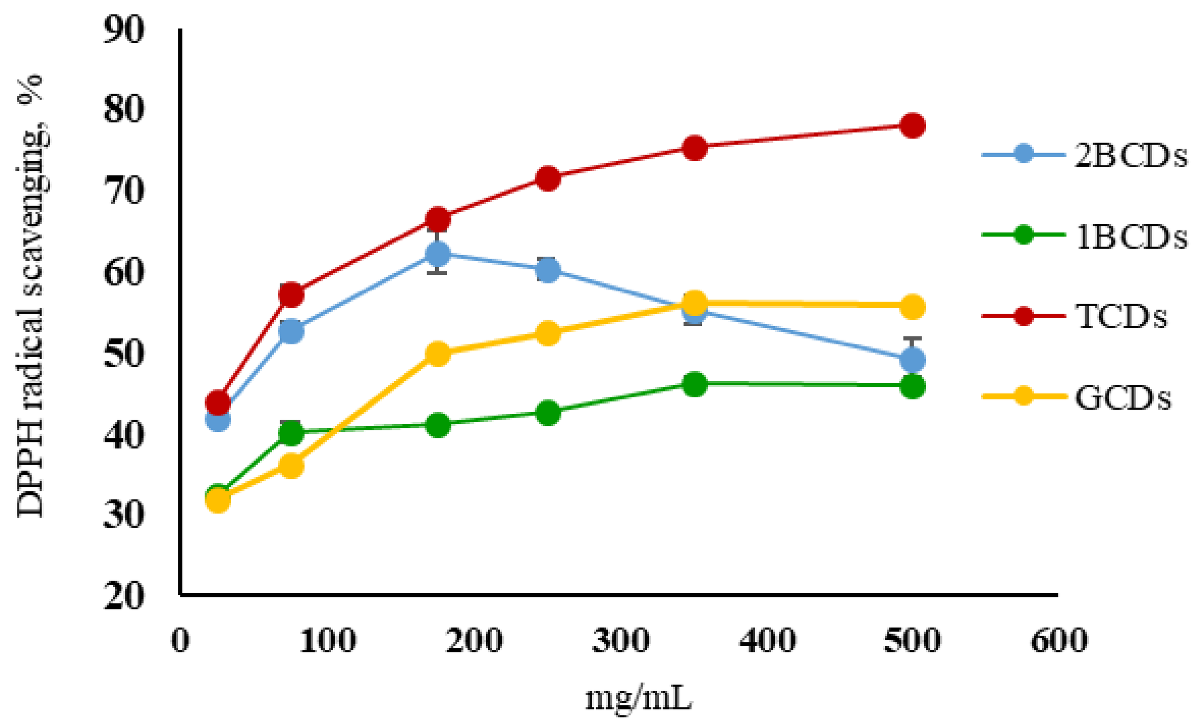


FTIR spectra of: A) GCDs (—) and TCDs (—). B) P1CDs (—) and P2CDs (—)

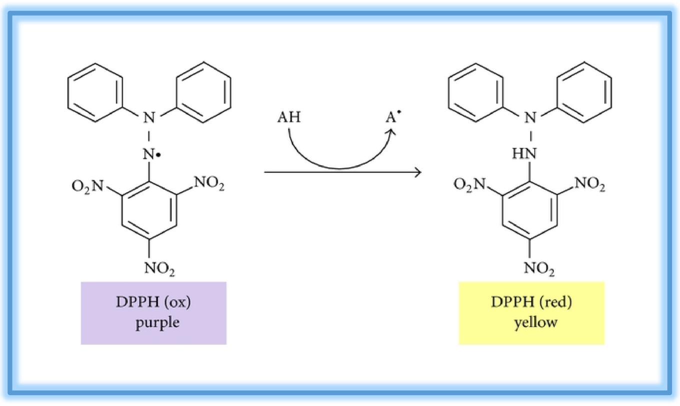
Main IR bands

- 3600 cm^{-1} to 3200 cm^{-1} : O-H and N-H bonds
- 1560 cm^{-1} : O-H bending from phenolic compounds;
- 1390 cm^{-1} : CH_3 out of plane bending (polysaccharide structure)
- 1600 cm^{-1} : amide I (N-H bending)
- 1014 cm^{-1} : C-O groups in polysaccharides;

DPPH scavenging assay



Antioxidant activity of the CDs at different concentrations.

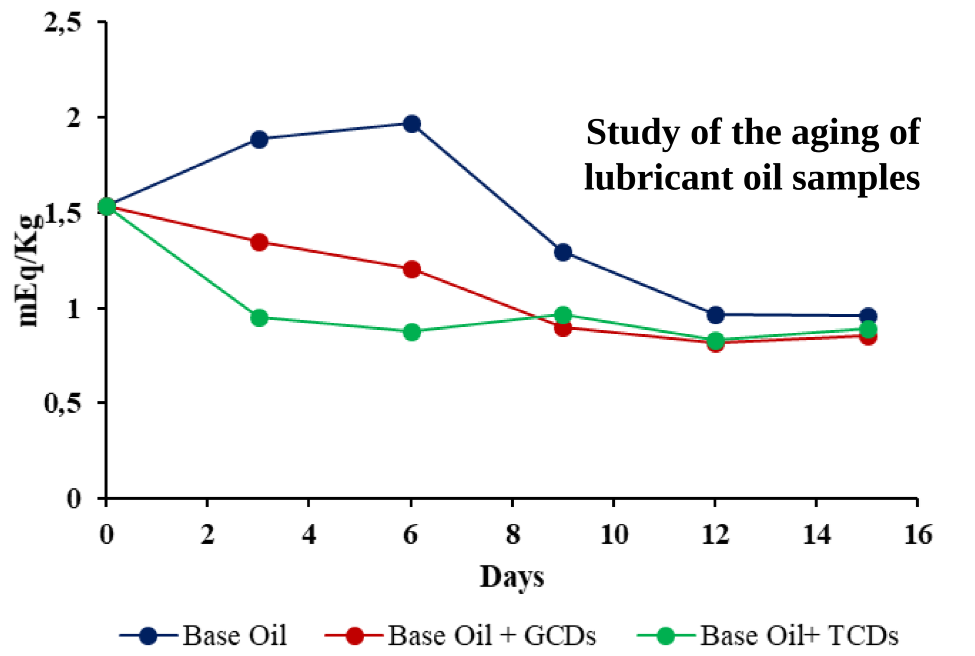


- There is a correlation between the antioxidant capacity expressed as total phenolic content (TPC) and the DPPH radical scavenging activity
- TCDs and P2CDs with a high TPC had also a high DPPH radical scavenging activity
- P1CDs with the lowest TPC had the lowest DPPH radical scavenging activity

Peroxide Value

The peroxide value (PV) is one of the primary indicators used to assess the hydroperoxydes formation. In this work, PV was measured by the iodometric titration method with potentiometric measurement of the end-point.

The samples containing CDs showed more oxidative stability, being those containing TCDs the more stable since the first two hours. Consequently, TCDs and GCDs have potential as antioxidant additives in lubricant oils.



Conclusions

This work is a step forward towards the use of CDs as antioxidant additives in lubricant oils as demonstrated by the oxidative stability provided by TCDs added to a commercial lubricant oil sample In principle, due to its low toxicity, these CDs are expected to be applied in the future as "green" antioxidant additives in bio-lubricants, particularly those based on vegetable oils or in cosmetic products.

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