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# NITROGEN DOPED CARBON QUANTUM DOTS FROM ANTI-OXIDANT RICH SEEDS OF *CAESALPINIA BONDUCELLA* FOR TUNABLE FLUORESCENCE AND CATALYTIC DEGRADATION OF DICHLOROPHENOL

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**ABSTRACT** There is a growing demand for a simple, economical and energy efficient process for synthesizing functionalized Carbon Quantum Dots (CQDs) with multi functional activity. The present study deals with tapping the antioxidant property of the seed of *Caesalpinia bonducella* (as precursor) for the synthesis of Nitrogen (self) doped Carbon Quantum Dots (N-CQD)through a simple hydrothermal process. The microstructure, surface morphology and chemical composition of the assynthesized sample was confirmed by analytical tools. The influence of the radical quenching ability of the precursor, is being considered for its potential application as an adsorption and photo catalyst with tunable emission property upon conversion to N-CQD. Based on the concept, the as prepared sample of N-CQD was screened for its efficiency as an adsorption and photo catalyst in the degradation of dichlorophenols and decoloration of organic dye of methylene blue. The observed tunable fluorescence efficiency more in the greenish region of the spectrum offers wider scope for further exploration for bioimaging of cancer cells and for waste water treatment. The reports of the study add more value to the simple, energy efficient synthesis and the multi functional applications of solid state N-CQDs for water purifications, safer bio imaging of cells and electronic research.

**KEYWORDS :** Carbon Quantum Dots, Caesalpinia Bonducella, Tunable Fluorescence, Adsorption, Photo Catalyst, Anti Oxidant.

## INTRODUCTION

Today there is a wide exploration of research in the Carbon based nanomaterials viz:-Graphene, Graphene Oxide, reduced Graphene Oxide, Single Walled Carbon Nanotubes (SWCNTs), Multi Walled Carbon Nanotubes (MWCNTs) and Graphene Quantum Dots (GQDs), Carbon Quantum dots (CQDs). Among the CBNs, Carbon quantum dot (CQD) is one the emerging fluorescent nanoparticles in the field of bioimaging due to their beneficial properties like low-toxicity, tunable fluorescence emission and biocompatibility. CQDs are electron rich materials predominantly used in the fields of bio imaging, drug delivery, light-emitting diodes, capacitors, catalysis, solar cells and sensors due to its electronic properties. On doping CQDs with non-metals such as nitrogen, sulphur and phosphorus found to increase the hydrophilicity, electronic and photoluminescence property.

As water pollution is increasing drastically with an increase in industrialization, innovative non-toxic catalyst for water treatment is a requirement and of significant step of global concern. Carbon nano materials (CBNs) being photosensitive and having large surface area can be well utilized for the waste water treatment.

Photocatalytic activity is governed by a catalyst which is usually semiconductor and commonly used semiconductor catalysts are $TiO_2$, ZnO and $Fe_2O_3$. Catalytic activity is also governed by the stability of catalyst in water and its particle size.

Nagamalai Vasimalai *et al.* have synthesized C-dots from spices by means of hydrothermal method and the C-dots prepared from spices are employed for bio imaging and tumor cell growth inhiibition[1]. The C-dot emitting blue light was synthesized from hydrothermal treatment of L-Citrulline which was used for metal ion detection and *HeLa* cell detection by Qianchun Zhang *et al* and C-dots synthesized from natural products are not toxic to normal cells[2].

The elemental composition of CBN made out of plant sources varies depending on the chemical constituents of the plant species and method of synthesis. The plant source taken as a precursor for the CQD synthesis is the seed kernel of *Caesalpinia bonducella* (CB). It (CB) contains starch, saponins, terpenoids, sugar and flavones. Bonducin is a homoisoflavone present in CB is responsible for its medicinal properties. In ancient medicinal systems such as *Siddha* and *Ayurveda*, the seed of *Caesalpinia bonducella* (CB) has proven anti-diabetic, anti-carcinoma, anti-diarrheal, anti-filarial properties. Totally six out of twelve of the principles of Green Chemistry were followed successfully in the current work. The method is renewable, inexpensive, non toxic and environmental friendly. The synthesis and application of the assynthesized product is intended for environmental protection that is, degradation of pollutants of the type of amino based organic dyes and dichlorophenols. As a facile and economic method is needed for the degradation of water pollutant, preparation of CQDs from biomass leads to surface functionalization or self-passivation leading to catalytic activity. The study explores the influence of the radical quenching ability of the precursor on the catalytic and green emission property of the product sample of the carbon quantum dot. As there are no reports available on the synthesis of N-CQDs in the solid state, the results will provide key points on the synthesis and application of self-doped carbon quantum dots.

### Experimental Materials

CB seeds were purchased from north Tamil Nadu local market, Deionized (DI) water, Ethanol (assay 99.9%), Dichlorophenol (CentralDrug House(P) Ltd), 2,2 Diphenyl-1-picrylhydrazyl (DPPH) (Sisco Research Laboratories Pvt Ltd, Assay 95%), Methylene Blue (MB) stain (Merck Life Science Pvt Ltd), UV-Visible light (Hg vapor lamp, 125W, Bajaj electronics Ltd).

### Preparation of CB water extract:

CB seed kernels were shadow dried and mechanically ground into a fine powder. Finely powdered seed kernel was mixed with DI water in the ratio of 1:5 (w/v). The mixture was sonicated for 10 minutes for homogenizing the mixture and then stirred at 50°C for 30 minutes for extraction. Then, the mixture was filtered. Pale yellowish-white filtrate was refrigerated and stored to avoid the fungal growth.

### Hydrothermal synthesis of Nitrogen self doped CQDs (N-CQDs)

CB water extract was transferred into a Teflon-lined autoclave for hydrothermal treatment and heated at 180°C for 5 hours. The resultant Brown solid residue obtained from hydrothermal treatment of CB water extract was treated with ethanol. The mixture was ultrasonicated for ten minutes and then dried to remove ethanol. The collected sample was used for further application and characterization in this current study.

### Degradation Of Dichlorophenol

Dichlorophenols are the intermediates in the formation of pesticides, antiseptics, and preservatives, etc. Dichlorophenols are corrosive, irritant and toxic to living cells. N-CQDs were screened for degradation of dichlorophenol as both adsorption and photocatalyst. The solid (CQD) catalyst was added to 80ppm solution of dichlorophenol solution in the ratio of 1mg/1mL and the reaction mixtures was incubated in both dark and UV medium separately. The absorbance values were recorded by UV-Vis spectrophotometer after 120mins.

### Discoloration Of Methylene Blue Dye

Methylene Blue (MB) is a commonly used dye in leather, paper and clothing industries and it is found to cause nausea, vomiting, diarrhea and even chronic diseases with prolonged usage. MB dye solution was prepared with DI water (2mg/1L). The N-CQDs were added to MB solution in the ratio of 1mg/1mL.Thereactionmixture wasincubatedinbothdarkandUVlight. The discoloration efficiency of N-CQDs was measured by recording the absorbance of MB solution incubated with N-CQDs for 120mins after the addition of N-CQDs.

**Antioxidant Assay**

DPPH was used to determine the antioxidant property of CB (kernel of raw seed) used as precursor in the study and the as synthesized product of N-CQDs. The solution of DPPH was prepared by using ethanol as a solvent (0.025mM). CB and N-CQDs were added with DPPH solution separately in the concentration of 1mg/3mL. The reaction mixture was incubated in dark for 120 mins and the measurements were recorded using EPR (modulation frequency - 100kHz, sweep time - 2min, field center - 337mT).

**RESULTS AND DISCUSSION**

The FT-IR spectrum of N-CQD shows the vibrations of hydroxy, epoxy, alkoxy, carbonyl, amino and graphitic Carbon nitride functional groups at 3414cm$^{-1}$, 1238cm$^{-1}$, 1157 cm$^{-1}$, 1448cm$^{-1}$ and 2356cm$^{-1}$ respectively. The results are supportive of the fact that hetero atoms of oxygen and Nitrogen have been introduced into the carbon moiety.

The UV spectrum of N-CQDs exhibits a sharp peak at 212nm (n-π* transition) due to the presence of Carbon bonded with a hetero atom having lone pair of an electrons (C-N or C-O) and a less intense peak (hump) at 278 nm (π-π* transition). This peak is due to −C=C− bond. The direct band gap energy corresponds to 278nm and 212nm are 4.4eV and 5.8eV respectively.

The XRD spectrum of N-CQDs show a broad centred peak at 2θ value of 19.4° corresponds to 100 plane with an FWHM of 9.7 representing higher amounts of Oxygen containing functional groups[3]. The larger FWHM correlates with smaller size of the crystallite. The d-spacing was calculated and found to be 0.4572 nm. Crystallite size of 8.2nm was calculated using Scherrer equation assuming the shape of the crystallites to be spherical. The specific surface area (SSA) was calculated as 7317m$^2$/g. The peak broadening also correlates with the small size of the crystallite. CQDs contain both sp$^2$ and sp$^3$ hybridized Carbon.

The Raman spectrum of N-CQDs shows D and G band at 1291cm$^{-1}$ and 1598cm$^{-1}$ respectively. In Raman, G band corresponds to $E_{2g}$ vibrational mode of aromatic domains and D band arises due to graphitic domains[4]. The ratio of $I_D/I_G$ increases with an increase in disorderness in the morphology. The $I_D/I_G$ ratio of N-CQDs is 1.0555. The value 1 represents the defect in the structure. D band corresponds to sp$^3$ defect Carbon and G band corresponds to sp$^2$ Carbon[5]. These defects generate sub-band gap defect states[3]. The band gap in N-CQD was lowered due to the presence of sub-band gap defect states. This causes the labile movements of electrons between the valance band and conduction band.

The surface defect leads to increased free electrons in the surface of N-CQDs which in turn creates a structure responsible for the degradation, antioxidant, fluorescence and electrical properties[6].

The FESEM image (Fig.1) validates the successful formation of spherical and quasi-spherical CQDs embedded with Nitrogen atoms from the hydrothermal treatment of CB water extract. Poly-crystalline nature of synthesized N-CQD was determined. The FESEM image correlates well with PXRD reports.

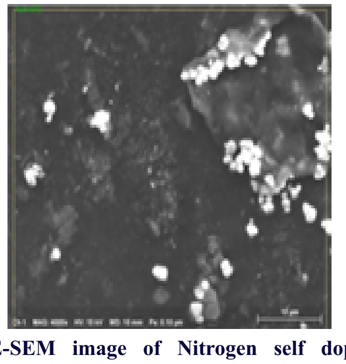

**Fig. 1— FE-SEM image of Nitrogen self doped Carbon Quantum Dots.**

The percentage elemental composition of N-CQD on the surface was found from Energy Dispersive X-ray (EDX) analysis. The relative percentage of elements of Carbon, Nitrogen and Oxygen is 59, 21 and 19 respectively. This confirms the successful doping of hetero atoms like Nitrogen and oxygen onto Carbon core shell.

The antioxidant potential of the as synthesized N-CQD was determined by DPPH assay. In this context the screening for the anti oxidant profile of the raw powder of the seed kernel (CB) and the its converted form to the N-CQD was carried out. From the EPR spectra (Fig.2) it can be found that the N-CQD showed higher level of antioxidant activity than the raw (CB) seed kernel powder. The free radical scavenging activity of CB and N-CQDs are 7% and 30% respectively. This implies that the heat treated CB can exhibit better antioxidant property than the raw CB. The enhancement of antioxidant potential from 7% to 30% is due to enhanced free electrons on the defect surface. It also provides the improved medicinal aspect of the seed kernel upon hydrothermal treatment.

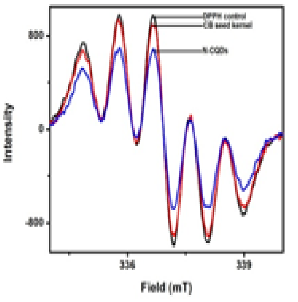


**Fig. 2- Electron paramagnetic resonance spectra of 2,2 Diphenyl-1-picrylhydrazyl quenching.**

The above results also suggest the ability of the defect structure of N-CQD that can provide a basis for its catalytic properties. Hence in the study, the application of the N-CQD as an adsorption and photo catalyst in the degradation of chlorophenols and decoloration of organic dyes are being considered.

The degradation of dichlorophenol was carried out in dark and UV light medium by means of the assynthesized N-CQD as a catalyst. The degradation efficiency of N-CQDs was found to be 18% and 40% in dark and UV light medium. The degradation was carried out at pH of 5.8 and a temperature of 25°C for 120 mins. Thus, the degradation of dichlorophenol in dark was achieved due to large surface area of the adsorbate (N-CQDs). The synthesized N-CQDs being zero dimensions with hetroatoms on the surface also tend to favor degradation of dichlorophenol. The degradation in UV light was favored due to trap states and surface defects in N-CQDs.

The adsorption is an important effective phenomenon for water treatment by catalytic properties. It is one of the effective ways of removing pollutants. Decolouration efficiency of 60% and 68% was achieved for 120 mins after the addition of N-CQDs in dark and UV light medium respectively. Thus, the synthesized N-CQDs exhibits the adsorption as well as photocatalyst properties. The higher amount of catalytic degradation was not reported previously for CBNs. N-CQDs can act as both electron reservoirs and photo-sensitizers[4]. The degradation efficiency of dichlorophenol and decolouration efficiency of dye with and without (Blank) N-CQDs in different reaction medium were provided in the Table.1.

**Table1-**Comparison of adsorption and photocatalytic efficiency of N-CQD in both dark and UV light.

| Medium | %Degradation of Methylene blue | | %Degradation of 2,6 Di chlorophenol | |
|---|---|---|---|---|
| | Blanksolution (without N-CQD) | Using N-CQDsas catalyst | Blanksolution (withoutN-CQD) | Using N-CQDs as catalyst |
| Dark | 31 | 60 | Nil | 18 |
| UVlight | 61 | 68 | Nil | 40 |

On photo excitation the valence electron jumps to the Conduction band and leads to formation electron-hole pair. The excited electron comes to the valence band and the electron hole recombination takes place very quickly and it eventually leads to high intense fluorescence emission. It can account for lower degradation efficiency[6].

The Photoluminescence (PL) spectra for N-CQDs were recorded for screening the tunable emission in the visible region especially the green region. The high intense peak as shown in PL spectra (Fig.3) signifies the greater possibility of recombination of photo generated electron-hole pairs and the use of polar solvents (water) in the synthesis[7,5]. In the study, the N-CQDs were excited at different wavelengths and the corresponding emission wavelengths were successfully observed thus tunable emission was confirmed. The PL emission shifts to higher wavelength as the size of N-CQDs increase in size. The red shift in PL is due to increased Oxygen atoms on the surface of N-CQDs[8]. The synthesized N-CQDs have intrinsic tunable fluorescence and photo-stability. Therefore, they can be used for bioimaging.The study indicated that the assynthesized N-CQDs are can be considered as fluorescent nanomaterials with green emission in presence of UV light. Green emission is safe for bioimaging since it doesn't damage soft tissues and DNA.

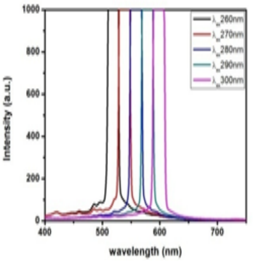


**Fig. 3-Photoluminescence (emission) spectra of N-CQDs at different excitation wavelength.**

The results of the study clearly indicate that N-CQD prepared by the facile method has potential application in bio imaging techniques and degradation of toxic chlorophenols. But a detailed study with varying parameters and optimization techniques is necessary for a successful fabrication of such materials.

## CONCLUSIONS

N-CQDs were successfully synthesised by means of hydrothermal treatment of the seeds of CB. Hydrothermal treatment of biomass leads to formation of solid N-CQDs under uncontrolled pressure and low temperature. So far the reports are predominantly available for the liquid CQDs which limits its use in electronic application and storage. This method leads to successful formation of solid N-CQDs which are superior in application. The synthesised poly crystalline N-CQD was screened for catalytic degradation of phenols and decoloration of dyes in absence of external chemicals. Upon doping the hetero atoms with CBNs, the recombination of electron-hole pair will be hindered. This leads to separation of electron-hole pair and thereby increasing the catalytic efficiency. Further studies are required to fabricate materials. The study widens the scope for solid state applications of Nitrogen doped Carbon Quantum dots especially in the heterogenous catalysis and electronic applications. The electronic properties of N-CQDs will be explored further.

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