Facile and Green synthesis of Novel Fluorescent CQD'S from Calotropis Gigantea (blue) Leaves for Photocatalytic Degradation of Dyes

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Abstract

A sustainable, economical, and efficient method for producing biocompatible novel fluorescent carbon quantum dots (CQD's) using the leaves of medicinal plant Calotropis gigantean by using microwave assist method. The obtained CG CQD'S were characterized by UV-Visible spectrophotometer, Fourier Transform Infrared Spectroscopy(FTIR), X-Ray diffraction(XRD), Dynamic light scattering (DLS) and Fluorescence spectroscopy. The synthesized carbon quantum dots (CQD's) are used to study the photo catalytic dye degradation of Bromophenol and Rose Bengal. The photocatalytic degradation of rose bengal by CQD'S with two different concentrations (50µg/ml and 100µg/ml) was 18.5% and 35.33% degradation respectively. The photocatalytic degradation of bromo phenol blue by CQD'S with two different concentrations (50µg/ml and 100µg/ml) was 19.7% and 36.14 % degradation respectively.

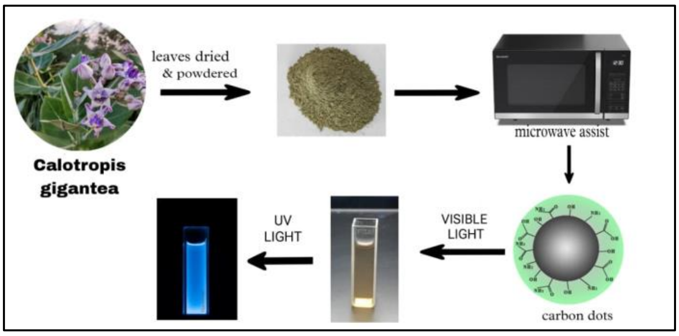
Keywords; Green synthesis, Calotropis Gigantea(CG),Carbon quantum dots, Photocatalytic, Rose Bengal, Bromphenol.

.INTRODUCTION

Carbon dots, or CQDs, are zero-dimension carbon-based nano materials with ultrafine sizes below 10 nm that show promise for a wide range of applications.[1] Comprising discrete, quasi-spherical nanoparticles, carbon nanomaterials (CQDs) are a relatively new class of material. They were initially identified in 2004 during the purification of single-walled carbon nanotubes from the constituents of fluorescent nanoparticles.. Until 2006, these carbon nanoparticles were named as "carbon quantum dots" by Sun et al .[1] Graphene quantum dots (GQDs), carbon nanodots (CNDs), and carbonized polymeric dots (CPDs) are the three main types of carbon dots, which are generally defined as small carbon nanoparticles in aqueous or other suspensions.[2] CQDs exhibit numerous noteworthy benefits, including minimal cytotoxicity, excellent photoinduced electron transfer, stable chemical inertness, good biocompatibility, and efficient light harvesting. As a result, they are promising candidates for a variety of applications in biosensors, bioimaging, optoelectronic devices, solar cells, etc.[2] In particular, carbon-based nanomaterials are receiving more and more attention because of their clear dominance in terms of stability, environmental friendliness, etc.[3] One of the essential fluorescent carbon nanoparticles, CQDs, are becoming more and more valued in daily life due to their useful applications.[4]

In many parts of the world, including India, plants, animals, and other natural objects have had a significant impact on human culture and civilization from prehistoric times to the present. [5] In ancient ayurvedic medicine Calotropis gigantea is known as "Sweta Arka" and Calotropis procera as "Raktha Arka". Both of them usually share same botanical characteristics and have comparable pharmacological effects.

.The present study aims to synthesize the CQD's using leaves of Calotropis gigantean plant using microwave irradiation method [6-13]. The synthesized carbon quantum dots were characterized by using UV visible spectroscopy, FTIR, XRD, DLS, and fluorescence spectroscopy. The CG CQD's are used to study the photo catalytic degradation on Rose Bengal and Bromophenol blue dyes.



Schematic representation of CG CQD's

Materials and Methods

The fresh calotropis gigantea plant (Part) were collected from Government college(A), Rajamahendravaram, Andhra Pradesh India. The plant materials was washed with running tap water followed by double distilled water and subjected to shade drying. After drying, the plant material was made into fine powder using electronic blender. Rose Bengal (Hi media), Bromophenol blue (CDH), Double Distilled water, Miscellaneous: Muslin cloth, Whatman No1 filter paper, Syringes, Quartz and glass Cuvettes, PVDF membrane filters (0.22 µ), Syringes, and eppendorf tubes (2mL).

Green synthesis of carbon quantum dots (CQD's):

The CG CQD's were synthesized by using microwave assist method. In this method 2 grams of plant powder was dissolved in 100mL of distilled water and subjected to stirring at 100^{o}C on magnetic stirrer. After stirring, the reaction mixture was exposed to microwave irradiation at 900W for 10seconds with 30 second interval up to 6 minutes. Then, the reaction mixture cooled down to room temperature, and filtered through muslin cloth to remove the larger particles. The obtained solution was centrifuged at 10,000 rpm for 10 minutes and the pellet was discarded The supernatant was subjected to filtration with Whatman No 1 filter paper and PVDF syringe filters.

Characterization of CQD's:

UV-Vis spectroscopy: The surface plasmon resonance of CQD's was evaluated using A Shimadzu UV-2600 spectrophotometer. A UV-visible spectrophotometer can detect the presence of carbon dots if it exhibits absorbance between 200 and 800 nm in range [14]. In this method, the CQD's were diluted with distilled water in 9:1 ratio and absorbance read from 200nm and 800nm. Based on the obtained peak the formation of CQD's was confirmed. The raw data was further processed with ORIGIN PRO software.

Fourier Transform Infrared Spectroscopy (FTIR): The FTIR analysis was evaluated using Bruker ATR model. FTIR is carried out to determine the functional groups associated with CQD's. The 100 µL of CQD's Was used for the analysis. The transmittance of the CQD's was recorded from 500-4000cm^{-1}. The obtained raw data further processed with ORIGIN PRO software.

X-Ray Diffraction: The powder XRD method was used to determine the crystalline phase and crystalline size of CQD's by using Bruker D8 diffractometer using CuK α radiation (λ=1.54056 Å). The result obtained from XRD analysis cannot be directly utilized in the study. It needs use of additional software packages such as Powder X, MATCH! etc.. The CQD's solidified at 70^{o}C in hot air oven and made into fine powder using Mortar pestle. The CQD's powder further evaluated with X-ray diffractometer with monochromatic Kα1 radiation. The obtained peak and 2θ values were calculated with Bragg's equation to determine the crystalline phase and structure.Bragg's Equation = $n\lambda = 2d.\sin\theta$.

Dynamic light scattering: The particle size distribution and zeta potential were determined using particle size analyser. The particle size measured from 0.1nm to 10000nm. The temperature ranged from 20^{o}C to 120^{o}C.

Fluorescence spectroscopy: The fluorescence was done using Shimadzu RF-6000 Florophotometer. The excitation of CQD's were determined using fluorescence spectroscopy with xenon lamp from 200 to 900nm wavelength range with zero order selectable. The liquid material was observed under 254 and 312nm wavelength filters using UV-trans illuminator

Photocatalytic degradation of dyes: The synthesized CQD's were subjected to photocatalytic degradation of Rose Bengal and Bromophenol blue.

Preparation of dyes The rose Bengal and bromophenol blue dyes are dissolved in distilled water in 10ppm or 10µg/mL concentrations.

Concentrations of CQD's: Two different concentrations of CQD's were dissolved in distilled water 50 µg/mL and 100 µg/mL.

Photocatalytic degradation:

In this method, 50 µg/mL (S1) and 100 µg/mL (S2) of CQD's were added to the 50mL of each dye (10ppm concentration) in a conical flask separately and incubated in a dark chamber with stirring for 30 minutes to achieve the adsorption-desorption equilibrium. After incubation, the samples were exposed to visible light with 100W capacity with distance between conical flask and bulb was 10cm. For every 15 minutes interval up to 90 minutes (Labelled as T1, T2, T3, T4, T5 and T6), a 4mL of each sample was collected in eppendorf tube and centrifuged at 10,000 rpm for 5 minutes at 4°C.

The supernatant was taken into the Quartz cuvette and the absorbance spectrum was taken from 500nm-650nm for Rose Bengal and Bromophenol blue using UV-Vis spectrophotometer. The percentage of Inhibition was calculated as follows

$$\% \; of \; Inhibition = \frac{Control \; OD - Sample \; OD}{Control \; OD} \times 100$$

Results and discussion

UV-visible spectroscopy:

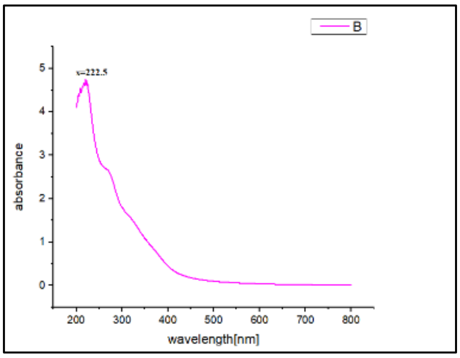


Fig 1: UV-Vis spectra of CQD's

From Figure 1, the UV Visible spectra of carbon quantum dots exihibits two absorption peaks: one at 222.5 nm, which is indicative of the π–π∗ transitions of (C=C), and another at approximately 310 nm, which is associated with the n–π∗ transition of C=O or C-O groups. UV-visible spectra clearly shows the synthesized carbon quantum dots possess both c=c and c=o groups are present on the surface.

Fourier Transform Infrared Spectroscopy (FTIR):

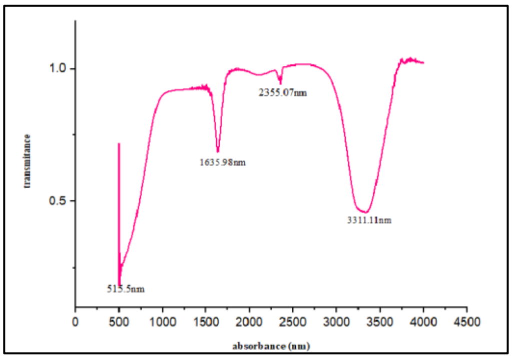


Fig 2: FTIR Spectrum of CQD'S

Fig 2 shows the FTIR spectra of CG CQD's synthesized by using Calotropis gigantea leaves. The peaks are obtained at 3311.11 cm^{-1}, 2355.07 cm^{-1}, 1635.98 cm^{-1},and 515.5 cm^{-1} which correspond to the stretching vibration of N-H stretching, O-H stretching, C≡N stretching , C═O stretching. The FTIR spectroscopy method allows us to analyse the various surface functional groups with ease and with little sample. From the IR spectra of the synthesized carbon quantum dots show that they possess various functional groups that may be hydroxyl group, amine and carbonyl group groups present on the surface of the carbon quantum dots synthesized by using calotropis gigantean.

X Ray Diffraction:

The XRD pattern of calotropis gigantea using carbon dots showed 2 major diffraction peaks at 2ϴ values of 28.58, 31.94, 33.17, 36.06, 38.39,40.77, 45.66,50.4,59.12, 66.57 , 73.93, 88.04, 94.66, 101.92, 108.92 with lattice planes respectively as in clear crystalline size. The results of XRD patterns show a face -centered cubic (fcc) phase for carbon particles

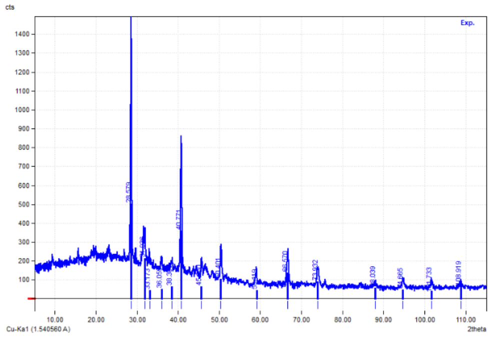


Fig 3 : XRD Spectrum of CQD'S

Dynamic light scattering :

The measured Zeta potential value was around –23.8 mV, indicating the presence of oxygen containing functional groups present negatively charged surface.The functional groups present on the surface of the CG CQD's may be carboxyl group, hydroxyl group, carbonyl group or sulphate group.

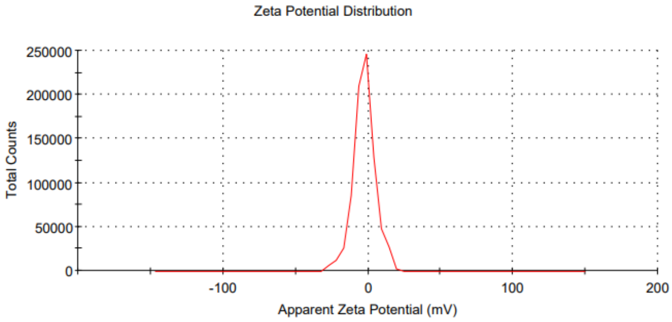


Fig 4 : Zeta size distribution of CQD'S

Fluorescence Spectroscopy:

The fluorescence spectroscopic study revealed that the maximum fluorescence emission intensity of CQD'S was due to excitation at 527.22 nm. CQD's have the highest luminescence in the visible part of the spectrum, with the maximum emission intensity approximately at 450 nm (λex = 370 nm), then it is reduced and shifted at higher wavelengths to approximately 548 nm (λex = 500 nm), and it is consistent with previous fluorescence analysis[15]

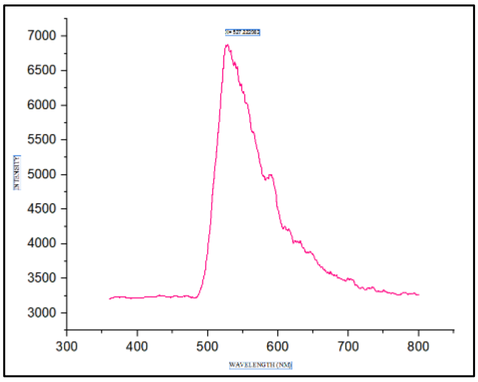


Fig 5 : Fluorscence spectra of CQD'S

Photocatalytic Degradation of Dyes:

Photocatalytic Degradation of Rose Bengal:

In photodegradation experiment 10ppm/µgmml of dye was prepared which was added to two different concentrations of CQD'S. 50µgms/ml and 100µgms/ml respectively then stirred in dark chamber for 30 min to achieve adsorption –desorption equilibrium. The container was then sealed and exposed to tungsten lamp [100watt] with a distance between the light source and sample of 10cm. For every 15 min time interval 3ml of sample was collected in eppendorff tube and centrifuged at 10000rpm for 5 min .then the supernatant was collected and placed in quartz cuvette cells for UV-visible absorbance measurement to determine the amount of dye degraded concentration. The reading were taken at regular intervals and marked asT1,T2,T3,T4,T5,T6.These solutions were absorbed in uv-visible spectrophotometer and of represented in fig. The maximum percentage dye degradation observed was 18.5 % and 35.33% respectively for 50µg/ml and 100µg/ml CQD'S concentrations.

It was observed that the absorbance of Rose Bengal solution decreased in presence of the photocatalyst and light. The plot of 1 + log A versus time was linear and hence, this reaction followed pseudo-first order kinetics. The rate constant (k) for this reaction was determined from the expression k = 2.303 × slope. A value of $k = 1.48 \times 10{-}4\ s{-}1$ was determined for this reaction in its optimum conditions [16].

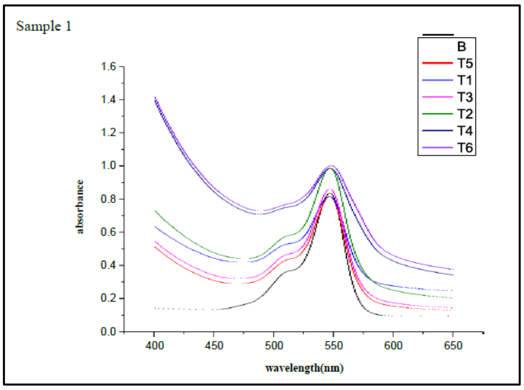


Fig 6: photocatalytic degradation of rose Bengal at conc 50µmg/ml

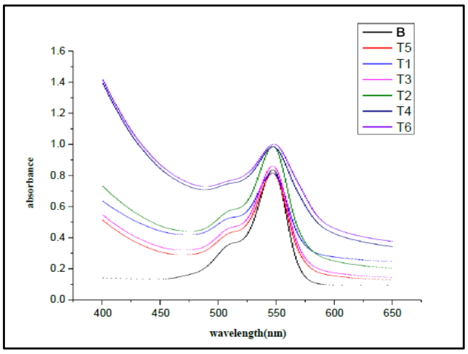


Fig 7: photo catalytic degradation of rose Bengal at conc 100µmg/ml

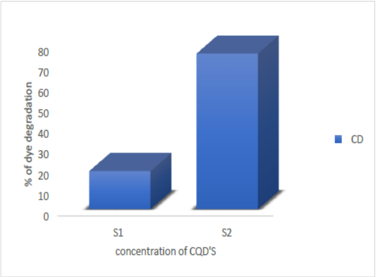


Fig 8: % bromophenol blue degradation for sample 1 and 2.

Photo catalytic degradation of bromo phenol blue:

In a typical photodegradation experiment 10ppm/µgmml of dye was prepared which was added to two different concentrations of CQD'S. 50µgms/ml and 100µgms/ml respectively then stirred in dark chamber for 30 min to achieve adsorption –desorption equilibrium. The container was then sealed and exposed to tungsten lamp[100watt] with a distance between the light source and sample of 10cm. For every 15 min time interval 3ml of sample was collected in eppendorff tube and centrifuged at 10000rpm for 5 min ,then the supernant was collected and placed in quartz cuvette cells for uv-visible absorbance measurement to determine the amount of dye degraded.The readings were taken at regular intervals and marked asT1,T2,T3,T4,T5,T6 up to 90 minutes .These solutions were absorbed in uv-visible spectrophotometer and represented in figure . The maximum percentage dye degradation observed was 19.75% and 36.14 % respectively for 50µg/ml and 100µg/ml of CQD'S concentration.

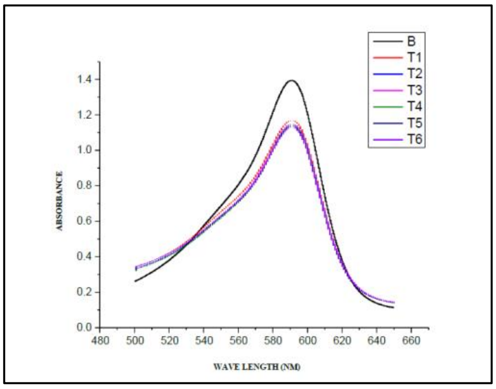


Fig 9 : photocatalytic degradation of bromophenol blue at conc 50µmg/ml

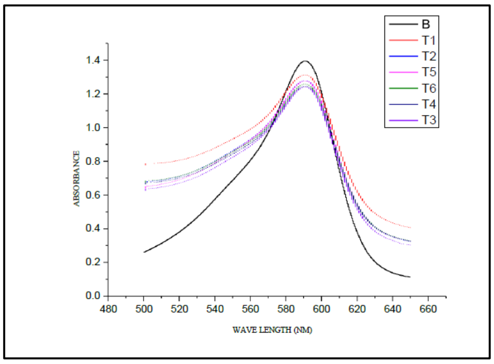


Fig 10: photocatalytic degradation of bromophenolblue at con 100µmg/ml

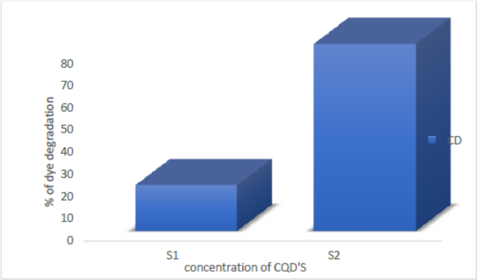


Fig 11: % bromophenol blue degradation for sample 1 and 2.

CONCLUSION

The carbon family assumed tremendous attention in the area of chemistry and biology due to their economical and facile synthesis methods, easy surface modification ,excellent photoluminescence and superior water solubility .In the present study, the CQD'S were synthesized from Calotropis gigantea leaf using microwave assisted method .The UV surface plasmon resonance peak at 222.5nm which is indicative of the π–$\pi*$ transitions of (C=C), and another at approximately 310 nm, which is associated with the n–$\pi*$ transition of C=O or C-O groups and the FTIR analysis of CQD's prepared by microwave irradiation of Calotropis gigantea leaves were 3311.11 cm−1, 2355.07 cm^{-1}, 1635.98 cm^{-1},and 515.5 cm^{-1}which correspond to the stretching vibration of N-H stretching, O-H stretching, C≡N stretching , C═C stretching. The zeta potential of the synthesized CQD'S is - 23.8 mv. XRD analysis of CQD'S revealed the average crystalline nature. The fluorescence excitation was found at 527.22 nm using fluorescence spectroscopy. The photocatalytic degradation of rose bengal by CQD'S with two different concentrations (50µg/ml and 100µg/ml) was 18.5% and 35.33% degradation respectively. The photocatalytic degradation of bromo phenol blue by CQD'S with two different concentrations (50µg/ml and 100µg/ml) was 19.7% and 36.14 % degradation respectively.

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ACKNOWLEDGEMENT

We thank the DST-FIST, New Delhi for providing central instrumentation facility (CIL) in Government College (A), Rajahmundry and also thank the Principal Dr Ramachandra R K for his constant support.