Green emissive Carbon quantum dots produced from *Plantago Psyllium* by thermal carbonization as heterogenous catalyst

Fairlin Jenitha R. and Sudhaparimala S.*
Department of Chemistry, Ethiraj College for Women, Chennai, INDIA
*sudha92@gmail.com

Abstract

The water retention and metal ion binding efficiency of Plantago Psyllium hemicellulose has been well explored. But there are no reports available on its conversion to carbon quantum dots (CQDs) for potential applications. This study is focused on the correlation of the microstructural features of CQDs with its catalytic and emission properties. The green synthesis of CQDs was explored using hemicellulose rich Plantago psyllium as precursor by a one-step thermal carbonization approach. The functional groups, microstructure, surface and the morphological analysis of CQDs indicate the formation of zero-dimensional carbon material with predominately sp^2 carbon framework with oxygen and nitrogen atoms.

The characterization reports of the carbonized psyllium husk showed that the hemicellulose rich biomass was converted into luminescent CQDs. The CQDs exhibited green emission under the UV lamp. The experimental results of the adsorption study indicate that the CQDs derived from hemicellulose can act as good adsorbent for the removal of Xanthene-based dye. The obtained results promise the effective conversion of biomass and potential application of CQDs as adsorption catalyst for the efficient and economic removal of cationic dyes in waste water.

Keywords: Carbon Quantum Dots, Green Fluorescence, Psyllium Husk, Rhodamine Black, Adsorption.

Introduction

Textile industry uses tremendous amount of water during dying process and the large quantity of waste water is being dumped into river every day. Textile industry effluents containing organic dyes have toxic effects on human health and tend to affect the water and animal ecosystem. The dye under consideration is rhodamine black (RB), ($C_{28}H_{31}N_2O_3Cl$, mol. Wt. 479), a fluorescent based cationic dye. It is a Xanthene derivative with low quantum yield. RB has toxic effects on human health.

Exposure to RB for a long period causes liver disfunction and cancer. It is harmful if swallowed and is used in many textiles and food industries and is found to cause skin and eye irritation. It is found to cause carcinogenic, respiratory tract and reproductive problems. Therefore, the presence of RB in food and water should be addressed. The methods available for the waste water remediation are ultra-filtration, adsorption, coagulation, froth flotation for the removal of organic and inorganic dyes in waste water etc. Among these methods, adsorption is an economic, reliable, easy and conventional method to remove the toxic dyes in water. Adsorption is widely used desalination method due to its versatility.

Scientists have well explored the transition metal quantum dots for catalytic removal of organic dyes. In this study, Carbon Quantum Dots (CQDs) devoid of metal dopants have been explored as an adsorption and photocatalyst for the water remediation in replacement of transition metal quantum dots due to its hazardous, expensive and non-abundance nature.[7] CQDs are fluorescent nanomaterials with excellent optoelectronic, catalytic and biological properties owing to their low-toxicity, hydrophilicity and biocompatibility.[6,17] CQDs are quasi spherical zero-dimensional luminescent carbon nanomaterials with size less than 10nm accidently discovered by Xu et al[19] in 2004.

CQDs are new class of carbon nanomaterial composed of densely packed carbon atoms which can be easily synthesized from carbon rich synthetic and biomass as a source. The top-down approach for the synthesis of CQDs involves breaking down of carbon matrix by arch discharge, laser ablation or chemical oxidation.[4] On the other hand, bottom-up approach involves synthesis of CQDs from small molecules by means of hydrothermal method, thermal method, microwave method and plasma treatment.

In recent years, CQDs have been prepared from waste materials from industrial, agricultural and domestic sectors.[2,8] Water soluble CQDs from coconut husk were prepared and its antioxidant properties were analysed by Avinash et al.[3] Psyllium husk is a soluble fibre and it is a potent antidiabetic and blood cholesterol reducing agent due to its laxative property. Manocha et al[10] had synthesized activated carbon from Psyllium husk. In this study, CQDs were synthesized by simple energy efficient thermal carbonization method using *Plantago Psyllium* as precursor and the product was explored as a heterogenous catalyst for the removal of RB.

India is the largest producer of *Psyllium* and supplies almost 85% of *Psyllium* in the world market.[11] It has the ability to bind metal ions in solution. The polysaccharides in *Psyllium* contains hydroxylic and carboxylic groups which bind with metal containing stable hemicellulose complex. The

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adsorption property of the *Psyllium* was tapped for the removal of toxic pollutants in water by converting it to non-toxic carbon nano material with large surface to volume ratio.

Material and Methods

Materials: The raw unprocessed *Psyllium* (Plantago Psyllium) husk purchased from the local market in North Chennai was used as biomass for the synthesis of CQDs without any purification. The chemicals used in this study are: ethanol (99%), deionized water, rhodamine black (RB) (Sisco Research Laboratories Pvt. Ltd) and hydrochloric acid (HCl).

Synthesis of CQDs by Thermal Carbonization: *Psyllium* Husk was weighed and transferred into a silica crucible and heated in Muffle furnace at 220°C for 6 hrs. The temperature and duration were fixed based on the thermal characteristic of the chemical constituents in Psyllium Husk. The carbonized solid brown product was then pulverized into fine powder and treated with ethanol and stored in an air tight container at room temperature for further characterization and application.

Characterization: The functional groups, bonding characteristics and structural defects in the synthesized CQDs were analysed using the FT-IR (IR Affinity-1, Shimadzu) and Micro-Raman spectrometer (Bruker, RFS). The micro structural analysis was carried out using Powder X-ray Diffractogram (PXRD) using Cu-Kα1 radiation (PAN analytical model Xpert pro) with the wavelength of 1.540Å. The surface morphology of the as-synthesized samples was studied using Transmission electron microscopic operated with 200kV (HR-TEM) (Fei tecnai G^2-20 Twin). The surface elemental composition and chemical state of the elements were identified using X-ray photoelectron spectroscopy (XPS) (Ulvac-PHI, Inc; Model: PHI5000 Version Probe III). The catalytic efficiency of the samples for the discoloration of xanthene-based dye was studied using UV spectrophotometry (UV -SHIMADZU 1601) respectively. The fluorescence property was analysed using Cary Eclipse fluorimeter.

Adsorption and photo catalytic efficiency of CQDs on the discolouration of RB: The discoloration of RB dye was carried out in both dark and UV media using the synthesized CQDs as heterogenous catalyst. The 5 ppm of RB solution was added with CQDs in the ratio of 1:1 (w/v) (pH 4, RT=±30°C). The catalytic degradation was monitored by measuring absorbance at regular time intervals for the time period of 120mins. The absorbance was recorded and the catalytic efficiency of the sample was estimated:

$$\text{Discoloration efficiency (\%)} = (C_0 - C_t / C_0) \times 100$$

where C_0, is the initial absorbance of the RB dye and C_t, is the absorbance of the RB at time ‘t’.

Cell viability assay: An *in vitro* microculture tetrazolium (MTT) assay was performed to test the cytotoxicity of the CQDs against human leukemia monocytic cell lines (THP-1 cells). MTT assay is a calorimetric assay to quantify the cellular metabolic activity by measuring mitochondrial dehydrogenase. The cells were seeded in wells and incubated for 1 hr. 10μL the CQDs were added to the wells followed by 24hrs incubation. 10μL of MTT solution was added along with 5% Fetal Bovine Serum (FBS) and incubated for 3hrs. Then, 100μL of DMSO was added and the absorbance was measured at 570nm. The wells untreated with CQDs were kept as control. The absorbance of formazon is proportional to the number of viable cells.

Results and Discussion

Functional group Analysis of precursor and CQDs: The FT-IR spectra of CQDs and the Psyllium husk precursor were recorded using KBr pellet method. The FT-IR spectrum of Psyllium husk indicates the presence of hydroxyl, carboxyl, sp^2 aromatic bonds and alkoxy groups. The FT-IR spectrum of CQDs exhibited bands at 3428 cm^{-1}, 1620 cm^{-1}, 1408 cm^{-1} and 1039cm^{-1} ascribed to stretching vibrations of hydroxyl, carboxyl, C=C bond and C-O bond respectively.[16] The spectra strongly indicate the presence of C=O and O-H groups in the molecular structure of CQDs and the groups play a significant role in increasing the hydrophilicity and biocompatibility properties desired for the catalytic removal of organic dyes in water. The absence of symmetric and asymmetric peaks of CH$_2$ bands at 2930cm^{-1} and 2846cm^{-1} in the CQDs indicates less disorderness in the carbon framework.[1]

Determination of Band gap value of CQDs: The absorption spectra of the psyllium husk and the CQDs were represented in figure 2. The psyllium husk shows a broad absorption peak centered at 278nm corresponding to the formation of furfural upon hydrolysis of hemicellulose.

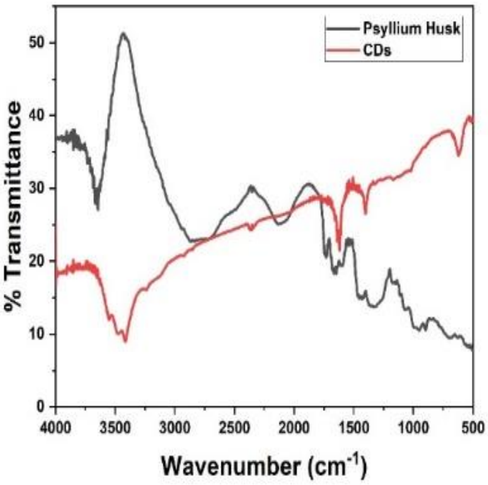
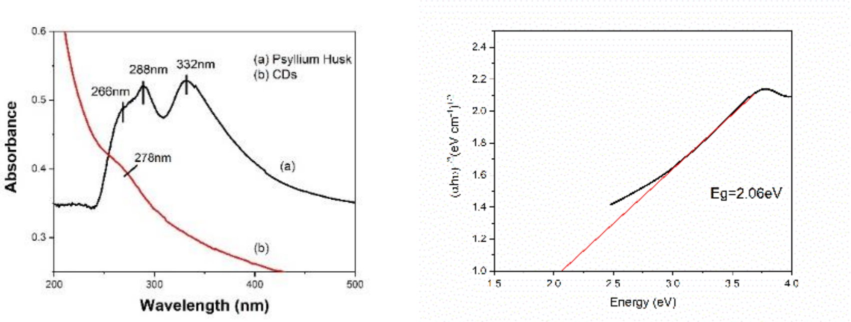


Fig. 1: Fourier Transformed Infrared spectra of (a) Psyllium Husk and (b) CQDs



(a) **(b)**

Fig. 2: UV-Visible spectra of (a) Psyllium husk extract and CQDs and (b) Tauc's plot for CQDs

The UV-visible absorption spectrum of the CQDs (figure 2) exhibited broad peaks at 266nm and 288nm due to $\pi \rightarrow \pi^*$ transition corresponding to C=C group. The peak at 332nm is due to $n \rightarrow \pi^*$ electronic transition of C=O group. This confirms the presence of oxygen functional groups in the structure of CQDs. The band gap (Eg) value of CQDs determined using Tauc's plot was 2.06eV.[18] The reduced bandgap of CQDs suggested the reduction in the dimension due to quantum effect.[12]

Microstructure analysis of CQDs: The micro structural property and the phase purity of CQDs were analysed using Powder X-ray Diffractogram (PXRD) as given in the figure 3(a). The CQDs exhibited broad diffraction peak around 2θ of 19.7° (002) which corresponds to the d-spacing of 0.4503nm with the FWHM of 6.67.[15]

The crystallite size of CQDs was calculated using the Scherrer's equation: $D = (k\lambda)/\beta \cos \theta$ where D represents the crystallite size. Upon assuming CQDs as spherical crystallites, the size of crystallite was found to be ~ 1.2 nm without any peak correction. The peak broadening correlates well with the small size of the CQDs.[13] The broad diffraction peak of CQDs is due to the reduced size and the size induced strain.

The Micro Raman spectrum of CQDs indicates the chemical nature and orientation of crystalline structure (figure 3b). The CQDs exhibited both the D band (1321cm^{-1}) and G band (1561cm^{-1}). The D band arises due to sp^3 hybridized carbon while G band arises due to vibrations of in plane sp^2 domains in aromatic ring. The D band is proportional to the amount of defect which corresponds to A_{1g} symmetry while G band accounts for carbonization and corresponds to E_{2g} symmetry.

The intensity ratio of I_D/I_G of CQDs was found to be 0.6737 which is the characteristic of disorder extent. The low I_D/I_G ratio indicates the low degree of structural disorderliness and high degree of crystallinity as reflected in Micro Raman spectrum of CQDs. The result correlated well with PXRD report and FT-IR results. The low I_D/I_G ratio of CQDs indicates that the fixed synthesis parameter leads to the formation of highly ordered carbon core.

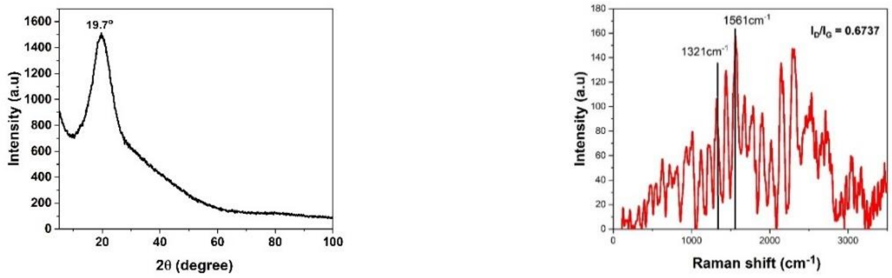
Elemental and functional group analysis of CQDs using XPS: The wide and narrow scan XPS spectra of CQDs were analysed and represented in the figure 5. The C(1s) spectrum of as-synthesized sample shows the binding energy value of alkane (284.6 eV), alkene (285.9 eV) and hydroxyl (285.6 eV), epoxy (286.3eV), carbonyl (287.3eV) and carboxyl (289.1eV) groups suggesting the presence of oxygen functional groups on the surface of the as-synthesized samples. The narrow scan of N1s spectrum (Figure 5d) shows two peaks at 399.2 eV and 408.4 eV corresponding to cyanide and nitrate groups on the surface respectively.

The functional group existing on the surface of CQDs was analysed using C(1s) (Figure 5b) spectra. From C1s spectra, the percentage of C-C and C=C carbon in the surface CQDs was found to be 16.2% and 22.2% which indicated less surface defect. The results correlated well with Micro Raman, PXRD and HR-TEM analysis of CQDs. The percentage of hydroxyl, epoxy, carboxyl groups on the surface is 19.2%, 13.7% and 10.5% respectively. The C-N group present in CQDs is found to be 5.3%. The surface functional group observed in XPS was correlated with FT-IR analysis.

The elemental composition of CQDs calculated from wide scan XPS spectrum (Figure 5a) was found to be carbon (56.21%), oxygen (37.90%) and nitrogen (5.87%). No other trace elements were detected which indicate the purity of Psyllium derived CQDs.[1]

Surface Morphology of CQDs: The surface morphology of CQDs was determined using TEM and represented in the figure 5(a). The TEM image reveals the presence of quasi spherical structure of CQDs. Thus, TEM images of the carbonized sample confirm the formation of CQDs with zero dimension and size less than 10nm.

Therefore, it is evident that the synthesis parameters were able to govern the conversion of hemicellulose biomass into CQDs via one step thermal carbonization method. The diameter of CQDs ranges between 0.6nm to 1.8nm with an average size of ~1.04nm indicating the poly crystallite nature. The size of the CQDs calculated by PXRD using Scherrer equation is in good agreement with TEM image.



(a) (b)

Fig. 3: Microstructure analysis (a) X-ray diffraction Pattern and (b) micro Raman spectrum of CQDs

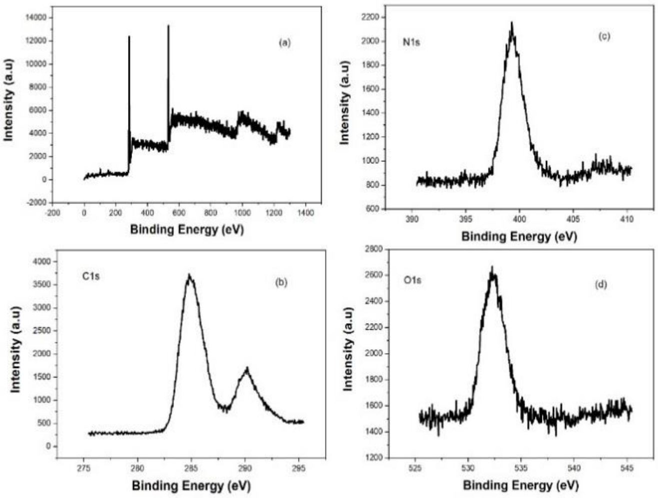
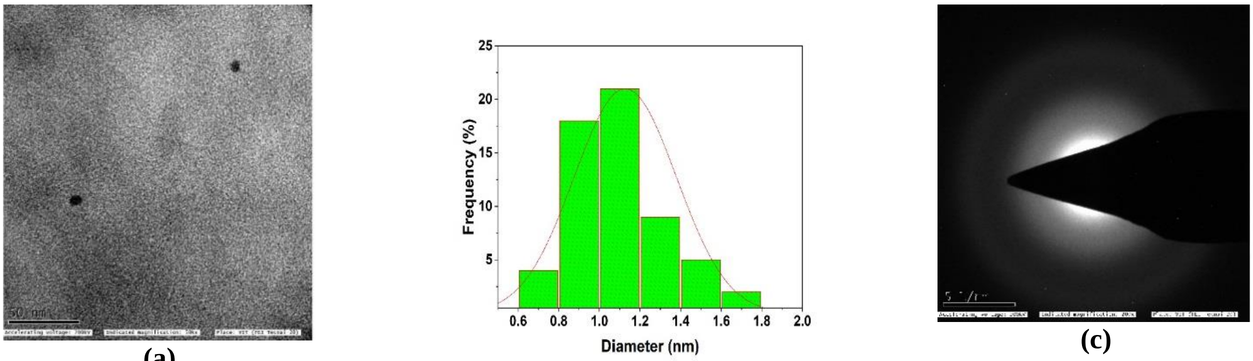


Fig. 4: (a) Wide scan XPS spectrum of CQDs and core level XPS spectra of (b) C1s(c) N1s and (d) O1s



(a) (b) (c)

Fig. 5: (a) TEM image of CQDs (b) size distribution graph of CQDs and (c) SAED pattern of CQDs

Energy Dispersive X-ray Analysis (EDAX) of CQDs: The elemental composition of CQDs was determined using EDAX analysis. The relative % of carbon, oxygen and nitrogen is 96.68, 1.56 and 1.76 respectively. The lower amounts of nitrogen and oxygen heteroatoms correlate with the low surface defects and high degree of carbonization resulted via thermal treatment of Psyllium husk. The C/O ratio increases with decrease in oxygen functionality and indicates the presence of high degree of sp^2 hybridized carbon. This observation is in fair agreement with FT-IR, Raman and XPS results of CQDs. It can be confirmed that the experimental parameters of synthesis were able to govern the formation of CQDs with highly ordered carbon network.

Photoluminescence spectra of CQDs: Emission profile of CQDs was obtained using PL spectrophotometer. The PL emission spectra were recorded by exciting the CQDs at different wavelength (λ_{ex}) ranging from 320nm to 380nm. Upon increasing the excitation wavelength, the emission peak slightly shifts to longer wavelength which confirms the excitation dependent emission nature. The as synthesized CQDs can be inferred to be green nanomaterials and are considered to be safe for bioimaging since it does not cause damage to soft tissues and deoxy ribonucleic acid. The degree of carbonization, non-uniform size distribution and oxygen functionalities of CQDs are the key factors for the excitation dependent PL behavior. This emission behavior is due to the distribution of different surface band gap states of the CQDs.[18]

From TEM (figure 5) and PL results (figure 6), it is evident that the synthesized CQDs have uniform size distribution and narrow surface states. The fluorescence nature of CQDs is due to the electronic transition of n-π^* and almost all excited electrons return to ground state via emission of radiation. Unlike the amorphous CQDs, crystalline CQDs have better photostability.[1] The low intensity of PL emission of CQDs is due to low oxygen functionalities and low surface defects as indicated by EDAX analysis. The emission behavior is due to the combined effect of the heteroatoms and the sp^2 hybridized carbon which acts as chromophore.

Cell viability assay of CQDS: Cytotoxic analysis of CQDs was analyzed and represented in the figure 8. Low cytotoxicity is the critical requirement of the material for the practical applications. Cell viability was measured by means of *in vitro* MTT assay. This method considers the reductive ability of the enzymes present in the mitochondria of the living organism.[9] The CQDs are potential probe for bioimaging due to their biocompatibility and photostability. It is evident that CQDs did not exhibit any significant toxicity towards human leukemia monocytic THP-1 cells. The cells retain viability of 95.73%. Thus, it is evident that CQDs can be explored for further biological applications.

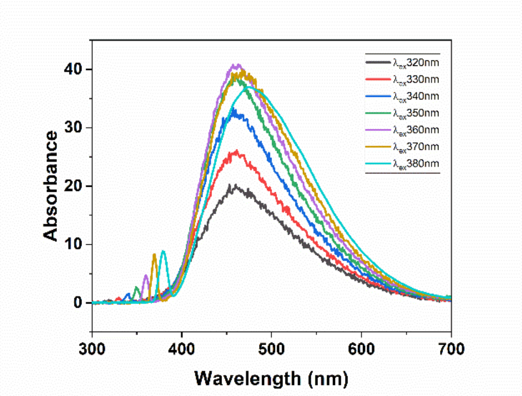
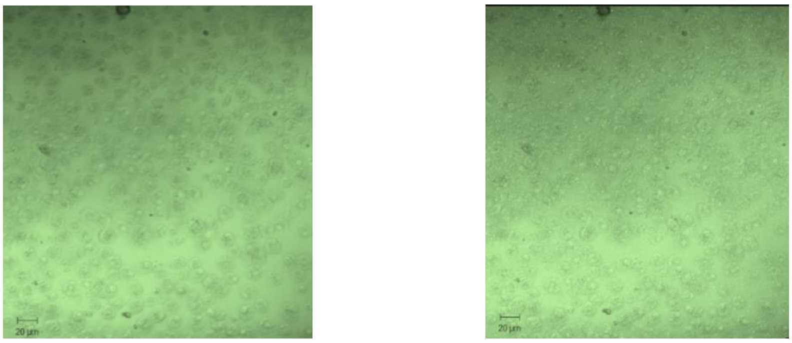


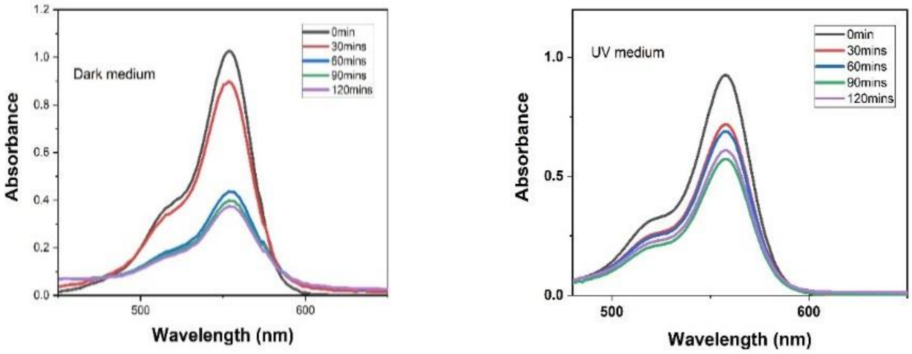
Fig. 6: Photoluminescence spectra of CQDs

Catalytic discoloration of RB at pH 4: The catalytic efficiency of CQDs for the discoloration of RB at pH 4 was studied in the presence and absence of UV light for the time period of 2 hrs and the results are represented in figure 8. The decrease in absorbance of RB was monitored at regular intervals.[5] The discoloration efficiency of 34.1% and 63.4% was obtained in UV light and dark medium respectively. From the results, it is clear that CQDs are better adsorption catalyst than the photocatalyst.



(a) **(b)**

Fig. 7: Cell viability assay of CQDs using THP-1 cells



(a) **(b)**

Fig. 8: Catalytic discoloration efficiency of RB at pH 4 in (a) Dark and (b) UV medium

It can be accounted by the fact that the presence of oxygen containing functional groups on the surface of CQDs makes the active surface area which tends to interact with the nitrogen atoms in the RB leading to the enhancement in their adsorption efficiency. Thus, upon increasing the contact time of catalyst (CQDs) with the RB, the adsorption rate increases until the active surface area of the CQDs is depleted. After depletion, due to non-availability of active sites, the discoloration efficiency reaches saturation. At the acidic pH (pH 4), the surface of CQDs become more negative which increases the adsorption efficiency of the catalyst[13].

The adsorption is an effective way and economic way of removing pollutants from water and the synthesized CQDs with large surface and heteroatoms can serve as an efficient adsorption catalyst than the photocatalyst at pH 4. The low discoloration efficiency of CQDs in presence of UV light is due to the process of electron hole recombination.

Conclusion

A simple, effective, economic and green method was developed for producing CQDs without using any toxic chemicals by means of thermal carbonization of hemicellulose rich Psyllium husk. The presence of low oxygen and nitrogen functional groups in the quasi-spherical structure induced low level surface defects. The chemical state of CQDs surface was evaluated with XPS. The optical profile of CQDs showed the presence of green luminescence under UV light with excitation dependent emission behavior.

The synthesized CQDs have excellent adsorption property and low cyto toxicity which enables their potential in the commercialization of CQDs as efficient adsorbent in waste water remediation. The biocompatibility and the luminescence property can be further explored towards *in vivo* bioimaging.

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