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Microwave conversion of *Plantago Psyllium* husk into carbon quantum dots for sensing of heavy metals and removal of organic dyes

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The presence of heavy metal ions and organic dyes in the industrial effluents has toxic effects on human and animal health. There is an urgent growing need for the economic and effective treatment of waste water. The carbon dots (CDs) being a fluorescent zero-dimensional material have active surface area capable of binding with toxic heavy metal ions and organic moieties in water. In this study, the CDs have been successfully synthesized from hemicellulose rich *Psyllium* husk by means of simple green microwave method. The successful formation of CDs and the chemical state of the CDs have been successfully evaluated. The active surface area of CDs arising due to the surface defects contributed by oxygen functionality on the surface has been assessed from FT-Raman and XPS reports. The fluorescence property of the CDs as extrapolated for the sensing of heavy metal ions confirmed the successful sensing of Cr(VI), Fe(II) and Fe(III) ions with a detection (concentration) limit of 0.06 mM, 0.1 M and 0.2 mM, respectively. The photo catalytic performance of the prepared CDs for the discolouration of organic dyes, especially, the cationic dyes is encouraging indicating the successful preparation of negatively charged CDs from the biowaste. Ultimately, the study provides a simple, economical and efficient microwave method for the conversion of biowaste to a smart zero-dimensional carbon material for heavy metal sensing and dye discoloration.

Keywords: Carbon dots, Chromium (VI), Dye degradation, Fluorescence, Microwave synthesis, Sensing

Carbon quantum dots or carbon dots (CDs) are new class of zero dimensional fluorescent nanomaterials discovered in 2004 by Xu *et al.*, during electrophoresis separation of single walled carbon nanotubes[1]. The CDs are biocompatible and soluble in comparison with 1-D and 2-D carbon nanostructures and find applications in various optical, energy and biomedical fields due to the intrinsic fluorescence arising from generation of electron hole-recombination and large active surface area[2]. The sensitivity of the active surface of CDs are due to large number of hydroxyl, amino and carbonyl functional groups. CDs prepared from top-down method have low quantum yield in comparison with CDs produced from bottom-up approach. The sensitivity of the nanostructure and the large surface to volume ratio with intrinsic fluorescence property of CDs enables them as a potential probe for toxic metal ion sensing.[3]

In this study, CDs were prepared from xylose rich biomass called *Plantago Psyllium* husk, which is a pentose rich biomass with the chemical composition of 57% xylose, 22% arabinose, 10-15% uronic acid and small amounts of galactose, rhamnose, glucose and mannose[4]. It consists of highly branched arabinoxylan as backbone with a molecular weight of ~1500 KDa. The pentose sugar xylose has same stereochemistry of glucose from C_2 to C_4 except the CH_2OH in C_6. *Psyllium* is a natural gel reducing material predominantly used in Chinese and Indian traditional medicines to treat blood pressure, bladder problems and skin irritants. *Psyllium* husk is found to have cholesterol reducing property and used in the prevention of colon cancer[5]. The major constituent of *Psyllium* husk is arabinoxylan which is considered to be the important dietary fiber in diet.

The fabrication of efficient CDs by simple economic approach was under taken. The present study aimed in the effective conservation of biomass taking into account its biomedical importance. The present study evolved a new approach for the utilization of husk into a smart carbon material. Among the approaches adapted for the synthesis of CDs, bottom-up approach is very much suitable for practical applications due to economic and large production of materials[6]. Microwave synthesis is a bottom-up approach which is fast and low temperature method for conversion of biomass into emissive small size CDs by means of direct homogenous heating of target molecules. It results in the good crystallinity and the homogeneity of the synthesized products. It is one of the green methods for the synthesis of carbon nanostructures.

The CDs have been explored in sensing of metal ions. Carbon being insulator exhibits semiconducting property such as fluorescence due to confinement effects at nano regime. It arises due to the radiative recombination of electron hole pair. Wu *et al.,* 2021 synthesized CDs from hemicellulose for sensitive detection of Fe^{3+} ions[7]. There are limited reports available on the conversion of hemicellulose into CDs. As there are no reports available for the conversion of *Psyllium* husk into a carbon dots, a simple approach has been carried out in this study.

Fluorescent sensing is gaining significant place due to simplicity, efficiency and fast response time. It is found that heavy metal ions are toxic soluble pollutants with great mobility and alarming health issues. Chromium is a widely used element in metallurgy, electroplating, tanning industries and in the production of pigment dyes, plastics, protective coating and ceramic[8]. In general, Chromium (Cr) exists in Cr(III) and Cr(VI) oxidation states in aqueous form. Chromium (VI) is a non-biodegradable toxic metal found in industrial effluents. The development of real time sensor for the detection of metals in living systems and in environment is still being researched[9]. The ions of Cr(VI) being highly soluble has an adverse effects on living beings due to its mutagenic property. There are several methods[9,10] available for the detection of Cr(VI) in environmental and living systems such as atomic adsorption spectroscopy, X-ray fluorescence spectrometry and UV-visible spectrophotometric techniques[11]. Mengyin *et al.,* has synthesized $BiPO_4$/BiOI as a photoelectrochemical sensor for the detection of Cr(VI) [12]. Zhan *et al.*, has synthesized CuS nanoparticle for the detection of the Cr(VI). Many metal based nanoparticle and metal organic frameworks have been used by scientists for the detection of Cr(VI) [13].

Among the other metal ions Iron plays an important metabolic activity in human body. The excess or deficit of iron in living system leads to major health concerns. The excess of iron can cause severe health problems such as liver damage, kidney damage or even death. It is considered to be the abundant indispensable element present in aquatic systems.[14]

Even though methods are available for detection, the removal of these metals from the effluents is crucial. In this era, scientists are focusing more on CDs replacement of metals-based materials by carbon-based nanomaterial in all fields due to metal toxicity. There are no reports available on the conversion of *Psyllium* husk to surface passivated carbon quantum dots using microwave irradiation. CDs can provide remarkable advantages such as fast response, simplicity and economic sensing and removal of metals as they CDs possess excellent hydrophilicity, greater photostability which are crucial for practical implementation. Fluorescence sensing is gaining advantage since it does not need laborious technique.

As it is known the CDs being a zero-dimensional material with large surface area and active oxygen functional groups enables them as a potent material in field of catalysis. The exploration CDs for discoloration of of organic dyes such as methylene blue (MB), methyl orange (MO), malachite green (MG), acid red (AR) and rhodamine black (RB) was carried out. The CDs in the degradation of toxic dyes is opening up as a novel approach. The CDs being active carbon-based nanostructure highly reactive surface was used as adsorbent for toxic dissolved pollutants in water.

The effluents from the textile industry cause inherent damage to potable water. It becomes imperative to heat the water using simple approaches and materials. In this regard the present study widens the scope of carbon quantum dots as effective catalyst in the degradation of toxic textile dyes also.

Experimental Details:

Materials required

The husk of *Plantago Psyllium* was purchased from the local parts of India for the synthesis of CDs. The chemicals used in this study are deionized Water, Acetic acid (Polychem), Potassium Dichromate (Spectrum, AR), Ferrous sulphate, Ferric Chloride. All the chemicals used in the study are analytical grade and was used without any further purification.

Microwave synthesis of carbon dots

The raw material of *Psyllium* husk was hydrolyzed in acetic acid. For acid catalysed hydrolysis, about 1 g of *Psyllium* husk was mixed with 30 mL of acetic and 10 mL of deionized water. The mixture was then heated at 60°C for 30 mins and the hydrolyzed biomass was subjected to microwave radiation using domestic microwave oven at 420 W for 10 mins. The resulting brown solid was collected as the sample of quantum dot for further analysis and application.

The chemical composition of CDs was identified through FTIR and UV-visible spectrophotometer (SHIMADZU, UV 3600 PLUS). The microstructure was characterized using X-ray diffractometer (PANalytical, Netherlands) using Cu Kα radiation as source and FT-Raman analytical tool. The chemical state of the elements was determined using X-ray photoelectron spectroscopy (XPS) (PHI Versaprobe III).

Fluorometric sensing of Cr(VI)

The fluorescence sensing capability of the prepared samples of CDs for the Cr(VI) ions was screened. The fluorescence screening of Cr(VI) ions was carried out by adding 3 mL of CDs with 1 mL of $K_2Cr_2O_7$ solution of different dilutions ranging from 33 µM to 650 µM.

Fluorometric sensing of Fe(III) ions

The fluorescence sensing capability of the CDs for ferric ion was screened. About 1 mM ferric chloride solution was prepared and diluted into different concentrations. The fluorescence sensing of Fe(III) ions was done by adding 3 mL of CDs with 1 mL of $FeCl_3$ solutions of different dilution ranging from 250 µM to 1 mM.

Fluorometric sensing of Fe (II) ions

The fluorescence sensing capability of CDs for ferrous ion was screened. About 1 mM ferrous sulphate solution was prepared and diluted into different concentrations. The fluorescence sensing of Fe(II) ions was carried out by adding 3 mL of CDs with 1mL of $FeSO_4$ solutions of different dilutions ranging from 1 mM to 100 mM.

Discoloration of organic dyes

The efficiency of CDs for adsorption and photocatalyst for the discoloration of dyes viz:- methylene blue, methylene orange, malachite green, acid red, rhodamine black were carried out. For the study, the 5 mg of catalyst (CDs) was added to 10 mL of 2 ppm organic dyes and incubated in dark and UV light separately. The reaction kinetics was studied at a time interval of 30 mins at pH of 5 for 2 h in the presence and absence of sunlight.

Results and Discussion

FT-IR spectrum of CDs

The CDs obtained after microwave radiation was found to be crystalline solid. The FT-IR spectrum of CDs exhibited bands corresponding to O-H, C-H, C=C and C=O at 3329 cm^{-1}, 2915 cm^{-1}, 1618 cm^{-1} and 1720 cm^{-1}, respectively. The bands at 1245 cm^{-1} and 1034 cm^{-1} are due to C-O bond and the band at 1367 cm^{-1} is due to C-N, respectively. From the FT-IR spectrum of the CDs, it is evident that the CDs possess both C-C and C=C in the structure. The presence of hydrogen bond was indicated by a broad peak at 3329 cm^{-1} indicates the presence of O-H group in closer proximities and in larger amounts[15]. All the IR bands indicate the presence of oxygen and nitrogen functional groups on the Carbon frame work which confirms self-doping and self-passivation of the biomass derived CDs.

Elemental analysis

The elemental analysis of *Plantago Psyllium* husk was done using CHNS analysis. The elemental composition of the husk as provided by the CHNS analysis indicates that the *Psyllium* husk precursor contains hetero atoms such as nitrogen and sulphur and it also provided rich carbon source required for the synthesis of CDs. The presence of heteroatoms of N, O and S is strongly indicated by the reports of CHNS analysis (Table 1).

Absorption spectra

The UV-visible absorption spectrum of CD exhibited a broad hump centered around ~270 nm (Fig. 1a) which corresponds to π-π* transition of C=C group. Also, the small hump at the 320-360 nm indicates the n-π* transition corresponding to C=O group. The determination of the band gap energy of the CD is crucial for optoelectronic. Tauc plot was used to find the band gap energy of the as prepared CD which showed the characteristic of the semiconducting material. Tauc plot was plotted using the Tauc and Davis-Mott relationship: $(\alpha h\nu)^{1/2} = \beta(h\nu\text{-}E_g)$, where α is the absorption

Table 1 — Elemental percentage of *Psyllium* husk precursor from CHNS analysis

Elements	%
Nitrogen	1.359
Carbon	36.123
Hydrogen	3.847
Sulphur	0.169
Oxygen	41.3

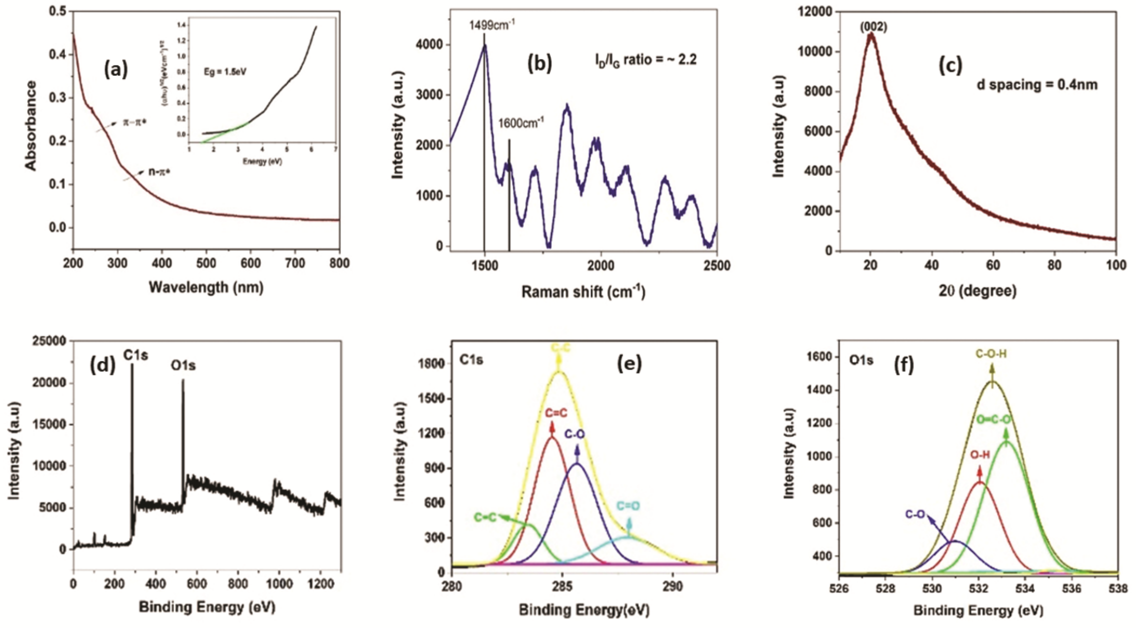

Fig.1 — Structure property analysis of CDs using (a). UV-Visible absorption spectra with the inset of Tauc plot, (b) FT-Raman, (c) PXRD, (d) Wide scan XPS spectrum, Narrow scan XPS spectra of (e). C(1s) and (f). O(1s) respectively

coefficient, $h\nu$ is the incident photon energy, β is energy dependent constant and E_g is optical band gap energy. The band gap value calculated using Tauc plot is calculated to be 1.5 eV. Sutantao *et al*. synthesized CDs using microwave radiation energy 300 W to 1000 W and the reported band gap value of CDs ranges from 2 eV to 3 eV. This signifies that band gap value of CDs increases with increase in energy of synthesis[16]. The band gap value of CDs synthesized in this study is lesser than the reported band gap values of CDs synthesized by microwave method. This clearly indicates the drastic reduction in the band gap energy of the CD in this study. The contribution of the biomaterial, processing temperature, other experimental parameters play a crucial role in the band gap energy. From the structural aspect it can be said that the presence of defect structures as induced by the surface passivating groups viz:- -OH, -COOH show a strong influence in the band gap energy. The band gap value confirms the formation of carbon nanomaterial and it correlates with the available reports. But the dimensionality can be finalized by the microstructure and morphology. The oxygen functional groups induce defects on the carbon framework of CDs as determined from the FT-IR results. These defects are significant enough to reduce the band gap value of the CDs due to the formation of sub defect band gap states.

X-ray diffraction and Raman spectra

The microstructure of CDs was studied using powder X-ray diffractometer (PXRD) and Raman analytical tool. The D band in the FT-Raman spectrum arises due to sp^3 carbon and it is the representative of disordered graphite or glassy carbon while the G band arises due to sp^2 carbon. The FT-Raman spectra of the as synthesized CDs (Fig. 1b) exhibited D band and G band at 1499 cm^{-1} and 1600 cm^{-1}, respectively[17]. The I_D/I_G ratio was calculated to be 2.2 suggesting the numerous defects in the core of CDs. The higher value of I_D/I_G ratio indicates large amounts of surface defects induced by sp^3 hybridized carbon[18]. The G band is a characteristic of tangential vibration of sp^2 hybridized carbon corresponding to A_{1g} symmetry while, D band is due to the presence of sp^3 disordered carbon atoms corresponding to E_{2g} symmetry and reduced size. It can be concluded that the low energy synthesis leads to the conversion of biomass into a CDs with extremely small size, large surface defects which synergistically reduce the band gap of the material[16]. The predominance of sp^3 as shown by $I_D/I_G>1$ indicates the formation of low dimensional carbon. Dager *et al.*, reported I_D/I_G ratio of 1.58 for spherical CD obtained by biomass[19].

The PXRD pattern of CDs exhibited a strong intense peak centered around 20.4° (002) and a small hump with comparatively low intensity was obtained around 43.8°(101) as shown in Fig 1c. The d-spacing was calculated to be ± 0.4 nm and ±0.20 nm for 2θ value of 20.4° and 43.8°, respectively. The crystallite size calculated using Scherrer equation was less than unity (0.3 nm) without any peak correction. The size and strain of the CDs correlates with the broadness of the peak.[20] Microwave synthesis is a low energy bottom-up method for the conversion of biomass into CDs which resulted in the formation of CDs with size less than 1nm calculated from PXRD results and the presence of large number of surface defects was found from the Raman spectra of CDs.

X-ray photoelectron spectroscopy

The relative surface composition with chemical state of the elements were analysed using XPS. The wide scan spectrum reveals the existence of carbon (1s) and oxygen (1s) peak at 285.2 eV and 532.2 eV respectively (Fig. 1d). In carbon 1s spectrum of CDs (Fig. 1e), the peak at 284.8 eV corresponds to C-O group. The Oxygen 1s spectrum (Fig. 1f) was deconvoluted into four peaks corresponding to C-O-H (37%), O=C-O (28%), O-H (21%) and C-O(12%). The carbon 1s spectrum was deconvoluted into individual peaks corresponding to C=C (27%), C-O(22%), C=O(7%) and C-C (41%). The relative percentage of C-C is comparatively more than C=C. From the binding energy value of sp^2 and sp^3 Carbon it can be found that the contribution of C-C is greater than C=C by 14%. From the CHNS analysis of CDs, it is evident that percentage of nitrogen in the precursor is 1.3%. The bands corresponding to the C-N is found in FT-IR spectrum of CDs. But XPS spectra of CDs do not exhibit any peaks corresponds to nitrogen functional groups due to the existence of nitrogen beyond the detectable limit. From the results, it is evident that the nitrogen atoms are not present in the surface of CDs. The predominance of sp^3 expected in a spherical CD structure indicated from XPS agrees with FT-Raman results.

Suggested reaction pathway for the formation of CDs

The reaction pathway for the conversion of the *Psyllium* to CDs is shown in the Fig 2. The major constituent of the precursor *Psyllium* husk is arabinoxylan which is considered to be the backbone. The chemical composition of *Psyllium* husk is xylose which constitutes about 57%, along with arabinose – 22%, uronic acid – 10-15%, and small amounts of galactose, rhamnose, glucose and mannose[21]. Arabinoxylan is the major non starch polysaccharide found in rice, barley, ragi, and cereals. Based on the composition the biomass can provide as a good precursor for a simple preparation of carbon-based nanomaterial arabinoxylan on hydrolysis breaks down into oligosaccharides and monosaccharides such as xylose and arabinose. The sugar units further undergo series of reaction to form alcohols, aldehydes, ketones and acid[22]. The molecular weight of the precursor has an impact on the size of the CDs. The hemicellulose polymer was broken down into smaller constituents upon hydrolysis. These small molecules produced by acid catalyzed hydrolysis of hemicellulose then condense and carbonized to form CDs. Microwave method is a low temperature energy method for the

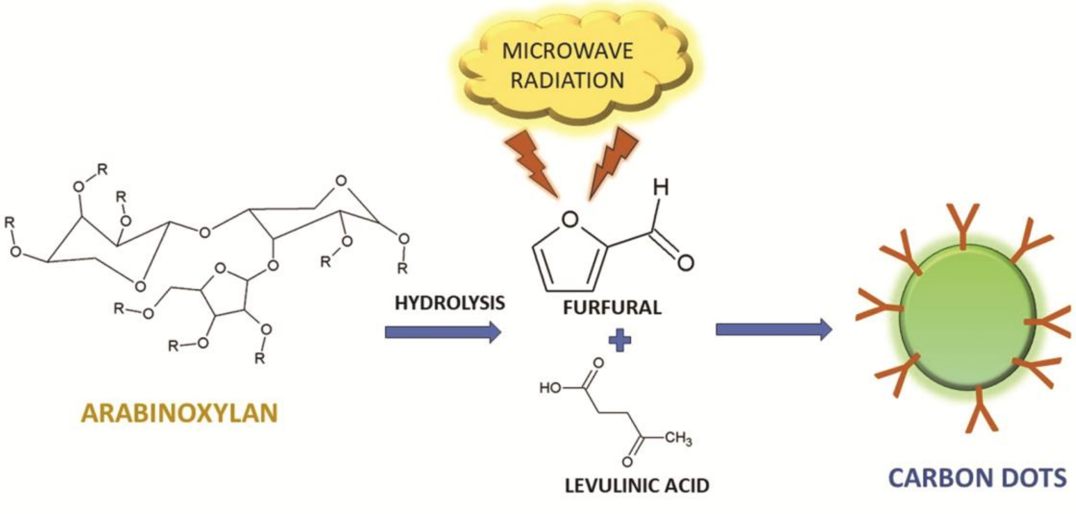

Fig. 2 — Schematic representation of formation of CDs from *Psyllium* husk

production of carbon nanostructures from biomass. *Psyllium* husk contains flexible loose texture hemicellulose favouring hydrolysis and carbonization**.** The molecular weight of the precursor has an impact on the size of the CDs.

The suggested reaction pathway was substantiated using ^{13}C NMR (Fig. 3). The sample was taken from the reaction mixture after the 5 min of microwave irradiation at 420 W. The ^{13}C NMR spectrum was recorded using D_2O solvent. The ^{13}C NMR of the intermediate exhibited signals corresponding to C-C aliphatic carbon, C=C in alkene and C=O in acids or esters at 20.62 ppm, 100-110 ppm and 177.08 ppm, respectively. These peaks correspond to the formation of alkanoic acid as an intermediate during the formation of CDs and it correlates with the suggested mechanism reported in Fig. 2.[23]

Emission behaviour of CDs

The structural aspects of CDs discussed above correlates with the emission behaviour of CD. The emission behaviour of the CDs was obtained by exciting at different wavelengths (Fig. 4). Upon increasing the excitation wavelength from 340 nm to 420 nm, the emission peaks shift from 460 nm to 515 nm indicating the excitation dependent behaviour. The emission in the range of 400 nm -500 nm indicates the formation of zero-dimensional carbon nanomaterial. The presence of oxygen functional groups -C=O, -C-O, -COOH and -OH identified with the FT-IR analytical tool create different surface states leading to excitation dependent emission of the CDs.

The origin of fluorescence is due to the combined effect of quantum confinements, conjugated π-π domains, chemical functional groups and the surface defects[10]. The oxygen and nitrogen self-doping of CDs lead to surface passivation and functionalization of CDs which increase the fluorescence brightness of the CDs[24]. The red shift in emission of the CDs is due to non-uniform size distribution, structural defects and higher degree of surface oxidation as indicated by FT-IR and FT-Raman reports of the synthesized CDs. [25] The excitation dependent emission is a striking feature of CDs and is exploited in various sensing and imaging applications.

Thermal stability of CDs

The thermal stability of the CDs was analyzed using thermal gravimetric analysis (TGA) as shown in Fig 5. The 3% decrease in weight at 100°C corresponds to physical adsorption of water adsorbed on the surface of CDs. The decomposition temperature of CDs was found to be 330°C. The volatile content and the fixed carbon content in CDs are found to be 24% and 10%, respectively. The material becomes completely decomposed and turns

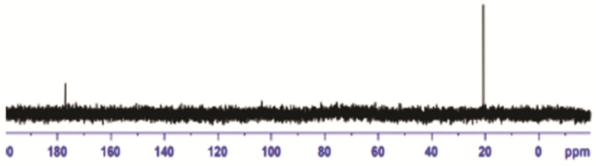

Fig. 3 — ^{13}C NMR spectrum of prepared CDs

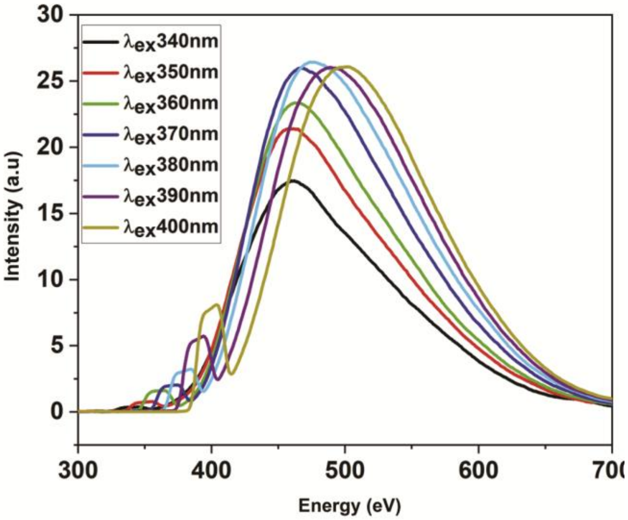

Fig. 4 — Photoluminescence spectra of CDs

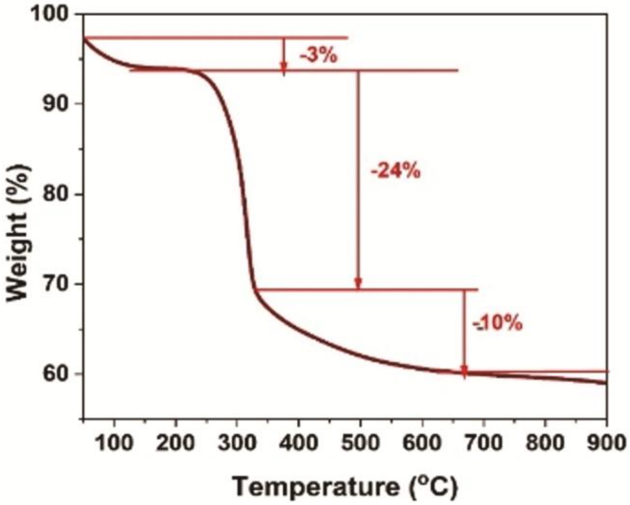

Fig. 5 — Thermogravimetric analysis of CDs

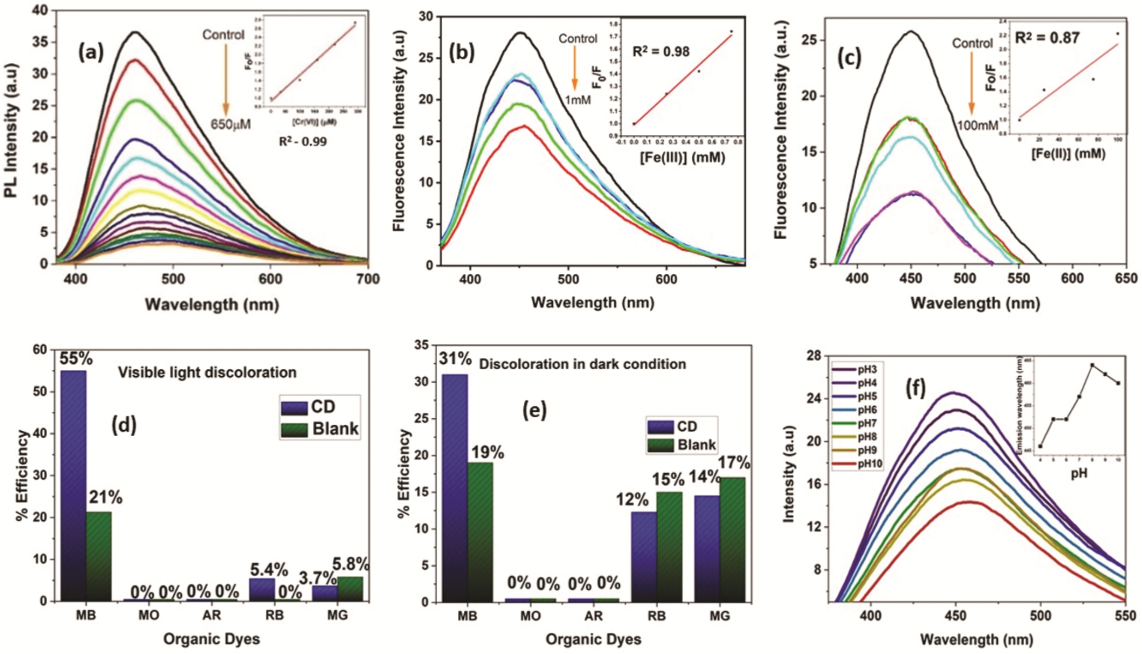

Fig.6 — Fluorescence sensing efficiency of CDs for (a) Cr(VI), (b) Fe(III), and (c) Fe(II) ions respectively. Comparison of catalytic efficiency of CDs for discoloration of organic dyes (d) under visible light and (e) under dark medium and (f) Photostability of CDs

into ash above 800°C. The ash may due to common minerals of arsenic, selenium and silica found in husk.

Fluorometric detection of Cr(VI)

Fluorescence of CDs is due to the radiative recombination of the electron hole pair of the excited molecule. The fluorescence property of the CDs can be explored for the simple, economic sensing, and degradation of metal ions (Fig. 6a). In the study, The CDs were excited at 350 nm and the corresponding emission at 460 nm was analyzed. The decreased in intensity upon increase in Cr(VI) ions concentration. The OH and COOH groups in the CDs act as probe for sensing of Cr (VI) ions. The fluorescence sensing of CDs was monitored and measured using PL spectrophotometer. The results indicated that CD can be explored as fluorescence probe.

The drastic decrease in the fluorescence intensity of CDs indicates the sensing efficiency and the affinity of CDs for binding toxic chromium (VI) ions. The Stern Volmer plot (Fig. 6a inset) shows a good linear relation concentration of Cr(VI) fluorescence intensity (F_o/F =0.006x+0.9303) (where F_o and F represents the fluorescence intensity of CDs without and with metal ions respectively). Also, the Stern Volmer plot indicates the molecular interaction of CDs in the excited state and plot provides the information about the dynamic properties of the excited fluorophore and its diffusional interaction with the quencher[26]. The possible mechanism for fluorescence quenching of CDs by Cr(VI) was attributed due to the absorption of the fluorescence emissions of CDs by Cr(VI) as propounded by Stern and Volmer with a limit of detection of 0.066 mM. The adsorption of metal ions by CDs has an impact on the emission intensity of the CDs. From, the quenching efficiency it is evident that the emission wavelength of CDs overlapped with the absorption wavelength of Cr(VI). The electron transfer reactions between the CDs and Cr(VI) results fluorescence quenching as reported by, Bu *et al.*[15] 2016, Huang *et al.*[27] 2021, and Jia *et al.* 2022[28].The functional groups and trap states are the main parameters responsible for photoluminescence quenching. Apart from these factors, size and morphology have impact on selectivity of metal ion sensing[29]. Thus Stern Volmer plot exhibited good linear relationship with a R^2-value of 0.99. The results clearly indicate that the CDs can be utilized as low cost and easily available nanoprobe for sensing of Cr(VI).

Fluorescence sensing of Fe^{3+}

The fluorescence sensing of Fe^{3+} by CDs was represent in Fig 6b. The fluorescence intensity of CDs quenched linearly with increase in concentration of Fe^{3+} ions with regression value of

Table 2 — Fluorometric detection of heavy metal ions using CDs

Metal ions	Limit of detection (LOD)	Regression value (R^2)	Binding constant
Fe(III)	0.2mM	0.98	0.96
Cr(VI)	0.06mM	0.99	0.006
Fe(II)	0.1M	0.87	0.01

0.98 ($F_o/F=0.9655x + 0.9898$) (y=mx+c). From the binding constant is the evident that the efficient FL quenching was attributed to the half-filled d-orbitals of Fe^{3+} ions and the unique interaction of COOH, OH and NH functional groups with Fe^{3+} ions. The COOH, O-H and N-H groups have affinity to bind with Fe^{3+} ions with a detection limit of 0.2 mM.

Fluorescence sensing of Fe(II) ions

The sensing efficiency of Fe(II) ions by CDs was monitored with decrease in fluorescence intensity (Fig. 6c). To assess the sensitivity for quantitative detection of Fe^{2+} ions, CDs was added with various concentration of Fe^{2+} ions. The CDs without Fe^{2+} ions displayed strong emission peak at 450 nm. The emission intensity progressively decreased upon increase in concentration of Fe^{2+} ions expressing that CDs is sensitive towards Fe^{2+} concentration. The plot of F_o/F versus concentration was not linear and the regression value was found to be 0.87. The detection limit of Fe^{2+} ions was 0.1 M.

The sensitivities of CDs towards Cr(VI), Fe(II) and Fe (III) were summarized in Table 2. Although the CDs can able to react with all three heavy metals ions, their sensitivity is more towards Cr(VI) with the detection limit of 0.06 mM. From the values of binding constant calculated from the slope of Stern Volmer plot (Fig 6c inset), it is evident that the binding affinity of Fe^{3+} ions with CDs is more.

Discolouration of organic dyes by CD

The discolouration of organic dyes was carried out to evaluate the CDs as adsorbent for water remediation (Fig. 6d and 6e). The percentage of discolouration organic dyes such as MO (anionic dye), MB (cationic dye), RB (fluorescent dye), MG (basic dye) and AR (acid dye) were calculated to be 0%, 55%, 5.4%, 3.7% and 0%, respectively, in visible light condition. The discolouration efficiency in dark condition is calculated to 31%, 0%, 0%, 12%, and 14% for MB, MO, AR, RB and MO, respectively. The discolouration efficiency was calculated using the formula

$$\% \text{ Efficiency} =((C_o-C) / C_o) \text{ X } 100$$

Where C_o is the initial absorbance of the dye, C is the absorbance at time ‘t’.

The discolouration efficiency for MB was found to be more in comparison with MO, AR, RB and MG dyes. The discolouration efficiency of the dyes with and without catalyst were calculated and represented in the above Fig 6d and 6e. From the discolouration efficiencies of MB with and without catalysts, it evident that CDs induce better discolouration with respect to blank solution. This is due to the fact that MB being a cationic dye is more susceptible towards negatively charged oxygen functional groups on the surface of CDs. The discolouration efficiency in presence of light is more than the absence of light. This confirms the ability of CDs to absorb the visible light to form electron hole pair which aids the discolouration of organic dyes. The small hump in the near visible region in the UV spectra of CDs (Fig. 1a) confirms the visible light absorption capacity of CDs, which enables them as a potent photocatalyst in presence of sunlight. From these discoloration efficiencies of CDs towards organic dyes it is evident that carboxylic groups of CDs are capable of adsorbing cationic organic substrates in water.

Stability of CDs

The influence of pH on the emission of the CDs was studied in pH range of 3 to 10 (Fig. 6f). The change in the pH of CDs affects the radiative recombination of electron hole pair and thus influences of photoluminescence emission upon excitation at 350 nm. From the emission peaks of the CDs it is clear that that emission wavelengths were red shifted upon increasing the pH. The smaller the size of the CDs, smaller is the emission wavelength observed. It may be accounted by the fact that upon changing the pH of the CDs, the protonation and deprotonation of the oxygen functional groups occur and the corresponding change in the functional group which may alter the band gap of the CDs. It can lead to change in photoluminescence emission wavelength. Also, the red shift and decrease in photoluminescence intensity upon increasing pH, suggest that the CDs agglomerate in the alkaline pH, but CDs with Oxygen functional groups are stable under acidic conditions [31].

Conclusion

In the study, simple and green method for the synthesis of CDs by microwave irradiation of

Psyllium husk as new natural precursor without the use of any toxic chemical, surface passivating agent was successfully developed. The chemical composition, crystal structure and optical properties were characterized using FT-IR, PXRD, UV visible spectrophotometer, Photoluminescence spectrophotometer and TGA. The functional groups viz:- -OH and -COOH groups in CDs improve water solubility and fluorescence intensity. The CDs exhibited fluorescence emission observed at 450 nm is dependent on the excitation wavelength. The emission intensities of CDs were prominently quenched by Cr(VI), Fe(II) and Fe(III) ions. From the results it is evident that the sensitivity of synthesized CDs towards Cr(VI) is more. The CDs were also screened as an adsorbent for wide range of dyes in both presence and absence of light. The CDs possess high selectivity and sensitivity towards Cr(VI) and cationic dye (MB). The synthesized CDs adsorb the metal ions and organic pollutants in water due to COO- and OH functional groups. Therefore, in future CDs can be utilized as environmentally safe nanomaterial for biosensing, bioimaging and catalysis.

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