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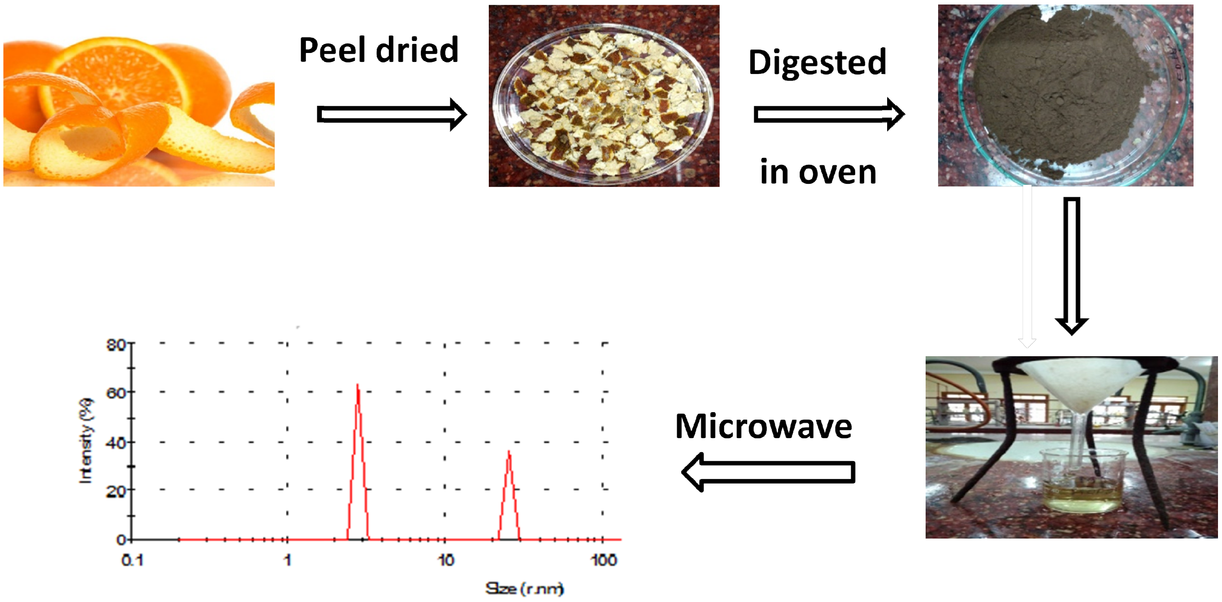
Abstract

The synthesis of water soluble and fluorescent C-dots, a new promising class of biocompatible and multicolor luminescent nanoparticles, from waste such as orange peels through low temperature microwave process has been reported. The prepared C-dots are of 5 nm and they show strong fluorescence. The synthesized C-dots have been characterized by using DLS, UV-Visible, FT-IR, XRD, Fluorescence measurement techniques. The synthesized C-dots are found to be effective catalyst for the reduction of Eosin Y and Methylene Blue with $NaBH_4$ as the reducing agent. A detail pathway for step by step reduction of dyes was established by UV-Vis spectroscopy.



Introduction

Fluorescent nanomaterials have attracted wide attention owing to their wide range of applications as fluorescent probes in chemical and biological sensors, as well as optical elements for sensor designs, in recent years. With the help of rapid advances in nanoscience and nanotechnology, quantum dots (QDs), which are one type of fluorescent nanomaterials, have inspired diverse research interest in recent decades owing to their unique properties, in particular optical and photo-degradation properties in comparison with organic dyes[1]. However, many QDs are expensive, difficult to synthesize and highly toxic which limits their application in environmental monitoring, biosensing and biological imaging[2]. Therefore dedicated efforts are on for the facile synthesis and rational design of other fluorescent nanomaterials with lower toxicity for wide range of applications.

Fluorescent carbon dots, which are a new class of carbon nanomaterials, have attracted many researchers because of their superior resistance to photo-bleaching, low toxicity, high chemical stability and photostability and excellent biocompatibility. Further these are low cost materials with high abundance of raw materials in nature[3-5]. These excellent properties endow the CDs with great potential in many fields, such as environmental monitoring, sensing, catalysis, energy light emitting devices, cell markers, biological imaging, drugs delivery, water remediation. Thus the CDs have attracted widespread attention in recent years.

Carbon is commonly a black material and until recently was generally considered to have low solubility in water and weak fluorosence. The main reason why such tiny carbon dots have recently attracted wide attention due to their strong fluorescence, for which they are referred to as fluorescent carbon[6].

Carbon dots have been acknowledged as discrete, quasi-spherical particles with sizes below 10 nm[7]. They generally possess a sp^2 conjugated core and contain suitable oxygen content in the form of multiple oxygen-containing species represented by carboxyl, hydroxyl and aldehyde groups. Photoluminescence (PL) is the predominant property of C-dots which researchers are mostly interested in. The CNDs exhibit strong quantum effects due to their quantum size and quantum confinement, consequently exhibiting intriguing optical properties[8]. Compared to other carbon nanomaterials (carbon nanotubes, graphenes, fullerenes, etc) the CNDs can be easily synthesized by relatively simpler and faster methods from a wide variety of precursors, without the need for any expensive and sophisticated instruments.

High aspect ratio, defects, and surface functionalities govern the properties of the CNDs, which strongly depend upon the precursor material and synthetic conditions. Cost and availability of precursor material are the prime concerns for commercial production of CNDs with easiness in synthesis. In general carbon quantum dots can be synthesized by both top down (laser ablation, electro deposition, arc discharge) and bottom-up (precipitation, microwave, hydro and solvo-thermal etc) approaches.[8]

Residual dye contents in textile wastewater have complex aromatic structures that are difficult to degrade by a biological treatment. Therefore, over the last few decades considerable attention has been paid to decomposing these textile waste dyes by carbon dots. Several methods have been developed for their synthesis including physical, chemical and biological methods[9-10].

Carbon dots prepared by various methods are used for the degradation of dyes in the presence of UV or visible light using $NaBH_4$ as reducing agent. Reduction of dyes (Eosin and MB) by $NaBH_4$ in the absence of a catalyst is kinetically difficult, but thermodynamically favorable. Nanoparticles can achieve this by providing an alternate path by reducing the activation energy, thereby decreasing kinetic barrier, making it kinetically favorable [11-12]. The electron transfer step plays a dynamic role in the degradation of dyes because there may be a large redox potential difference between the electron donor and acceptor species, which can obstruct electron transfer [11-12]. An effective catalyst with an intermediate redox potential between the electron donor and acceptor species can assist in the transfer of electrons, and act as an electron relay system [12-13].

Literature Survey

In the fields of nanoscience and nanotechnology the largest activity has been focused on the synthesis of new nanoparticles with different sizes and shapes which have strong effects on their widely varying properties. Considering the importance of nanoparticles in different fields, various nanoparticles have been synthesized and characterized. Their diverse application also have been investigated.

Carbon dots are new class of fluorescent materials which have attracted many researchers because of their unique properties. Many reports have described efficient synthesis approach to produce the shape controlled, highly biocompatible carbon dots . In general the most common methods including precipitation, hydrothermal synthesis, solvo-thermal synthetic routes can all be directed to the synthesis of high quality of carbon dots nanoparticles.

Dyes are waterpollutant and they are difficult to degrade by biological treatment due to aromatic structure. Therefore, over the last few decades considerable attention has been paid to decomposing these textile waste dyes by metal nanoparticles . Several methods have been developed for their synthesis including physical, chemical and biological methods[9-10]. Some of the papers where metal nanoparticles are used as a catalyst for dye reduction are-

Scope and Objectives

The basic aim of this study is to examine the catalytic properties of the orange peel C-dot nanocomposites, which catalyze the reduction and degradation of dyes. The synthesized powder nanocomposite will be used as a catalyst for the electron transfer reaction to degrade some dyes, especially Eosin Y and methylene blue (MB) by $NaBH_4$ because of their higher stability and relatively well understood physicochemical and electrochemical processes. Therefore, it is important to investigate this type of system where the catalyst is a nanocomposite that relay electrons for the degradation of different classes of dyes with different characteristics into their respective end-products[14].

Herein, we present a simple, facile and economic approach for the synthesis of multicolor fluorescent water soluble carbon nanodots (wsCNDs) based on pyrolytic carbonization of precursor orange waste peel and their potential use as catalyst for dye reduction.

Experimental methodology

***Materials* :** Orange waste peel were collected from house hold waste materials. All the chemicals, such as quinine sulfate, acetic acid, eosin, methylene blue, sodium hydroxide, methanol, sodium borohydride are of reagent grade. Deionised water was used in all the experiments.

***Instrumental facilities* :** Photoluminescence measurements were performed in aqueous solution at room temperature with the help of a Horiba Fluoremax-4c Fluorescence Spectrometer. Fourier Transform Infrared (FTIR) spectra were recorded in solid state and liquid state in a Bruker FTIR spectrometer in the range of 600 to 4000 cm^{-1}. The uv-vis absorption spectra of the wsCNDs were recorded on a LABINDIA 3200 UV-VIS spectrometer in aqueous solution under ambient conditions. Surface charge was analyzed with zeta potential measurements on a Malbein ZS90 zeta potential analyzer. X-ray diffraction spectra have been recorded on a Rigaku Ultima IV instrument, available in the Department of Chemistry, Gauhati University.

Synthesis of water soluble carbon nanodots from orange peel

A simple, economical and green method for the preparation of water-soluble, high-fluorescent carbon dots has been developed via pyrolysis and microwave process using orange peel as a green carbon dot precursor. Prior to pyrolysis orange peels were washed several times with deionised water to remove any contamination and dried in a oven at 160^o - 180^o C for nearly 10 hours. Then the dried pieces were finely powered in mortar and pestle. The finely powered sample was again heated for 2 hours at 200^o C. These were then allowed to cool down naturally to room temperature and the solid carbonaceous CNDs were collected. Such synthesized C-dots were partially soluble in water and in most organic solvents such as acetic acid. The supernatant liquid with intense yellow color was collected. This showed green fluorescence with UV radiation.

Model systems

Eosin Y and Methylene blue dyes were used as model systems for the study of the catalytic reduction of the synthesized C-dots. Eosin Y is used as an acidic red strain for highlighting cytoplasm material in samples. Methylene blue is a basic dye used in biological staining. These dyes possess colour due to the presence of chromophore absorbing in the visible region. Each one has a conjugated system with atoms having non-bonded electrons, thereby showing $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Catalytic reduction of the dyes

The catalytic properties of the synthesized C-dots were explored by recording the change in the absorbance at their corresponding λ_{max} with $NaBH_4$ solution as reducing agents in presence and in absence of C-dots. In a typical procedure 1% Eosin Y, 10^{-5}M methylene blue and 1% $NaBH_4$ solutions were used. 10ml of CNDs solution were dispersed in 50ml of 10^{-5}M dye solution (Eosin Y and MB) followed by rapid injection of .5ml of 1% $NaBH_4$ solution and recording the UV-Vis spectra. The same procedure was applied in absence of carbon dot. The color of the mixture gradually changes and the rate of dye degradation was monitored by recording the UV-Vis spectra at an interval of 5min.

Results and Discussions

The above synthesized Carbon dots were characterized by DLS, FTIR, XRD, UV-Visible, Fluorescence spectroscopy.

The particle size distribution and Zeta Potential can be determined by DLS (Dynamic light scattering) study. The DLS data shows the particle size of C-dots to be 5 nm and a highly negative zeta potential value of -15.5mV for the wsCNDs, suggesting high surface area accumulation due to presence of COO^- which is confirmed from the IR sprectrum of carbon dots which is shown in fig2(a) and (b).

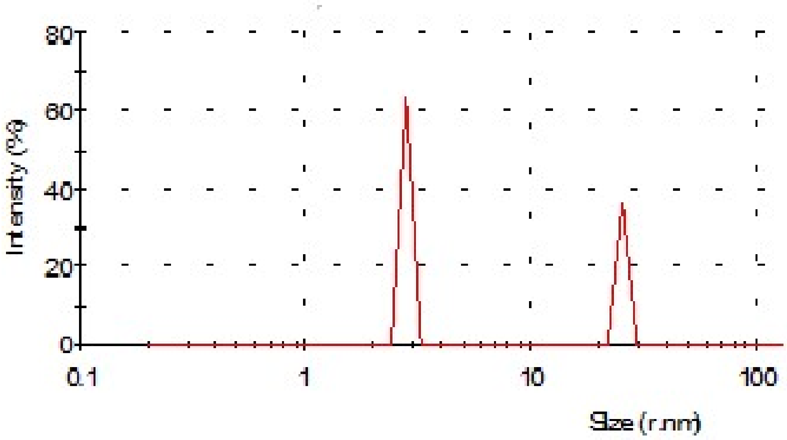


Fig 1(a) : Particle size of the ws Carbon dots

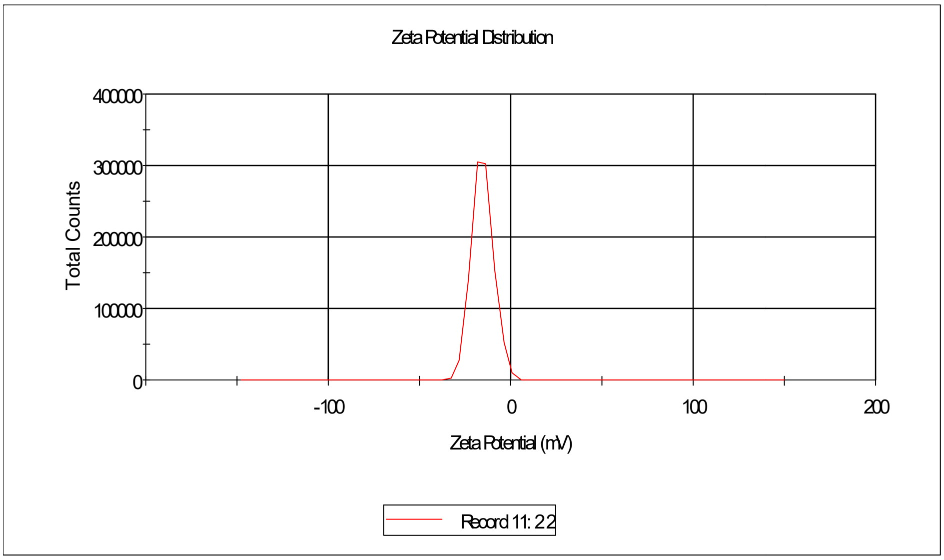


Fig1(b) : Zeta Potential of ws Carbon dots

Fig 2(a) and (b) shows the FTIR spectra of the as synthesized and aqueous solution of the CNDs. The FTIR of the as synthesized product shows sharp peak at 1027cm^{-1}and 697.64cm^{-1} which are indicative of C-O and C-H linkage[38]. The broad absorption band were observed at 1707.3cm^{-1} for stretching vibration of C=O, and band at 1648cm^{-1} and 1454.44cm^{-1} are indicative of C=C moieties. The weak band at 1255cm^{-1}, 2347.92cm^{-1} and 2890.53cm^{-1} indicates stretching vibration of C-O and O-H group. There are weak band around 3206.71, 3614.29cm^{-1} which indicates the presence of hydrogen bonded O-H. The bands due to C=O and hydrogen bonded O-H are retained in the aqueous solution of the CNDs with a broad signal around 2195cm^{-1} which may be due to C=O and C-O stretching vibration, indicating that the surface of C-dots are partially oxidized [39]. Further the band at 765 and 950cm^{-1} suggest the presence of COO^{-} in aqueous solution of C-nanodots.

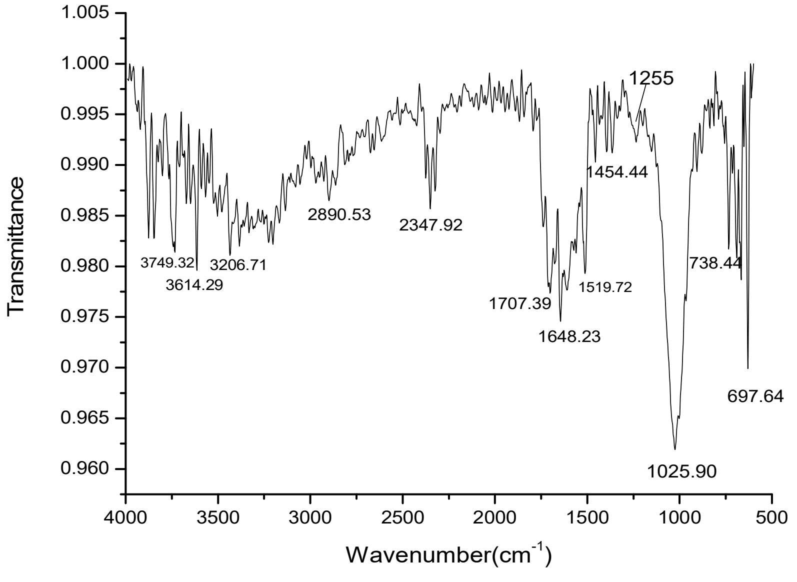


Fig 2(a) FT-IR of carbon dot

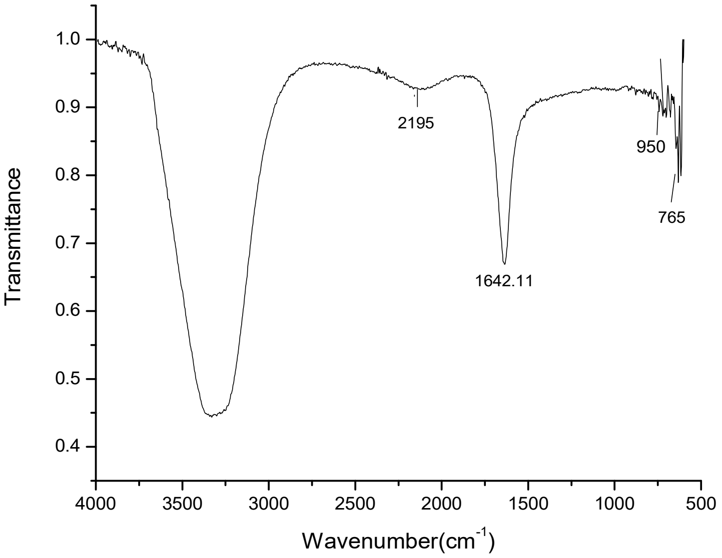


Fig2(b) FT-IR of ws Carbon dot

The X-ray diffraction pattern (Fig 3) of the C-dots, shows an intense and broad peak at 2θ = 23.8⁰ which is due to graphite lattice spacing. This arises due to the presence of highly disordered (sp^3) carbon atoms.

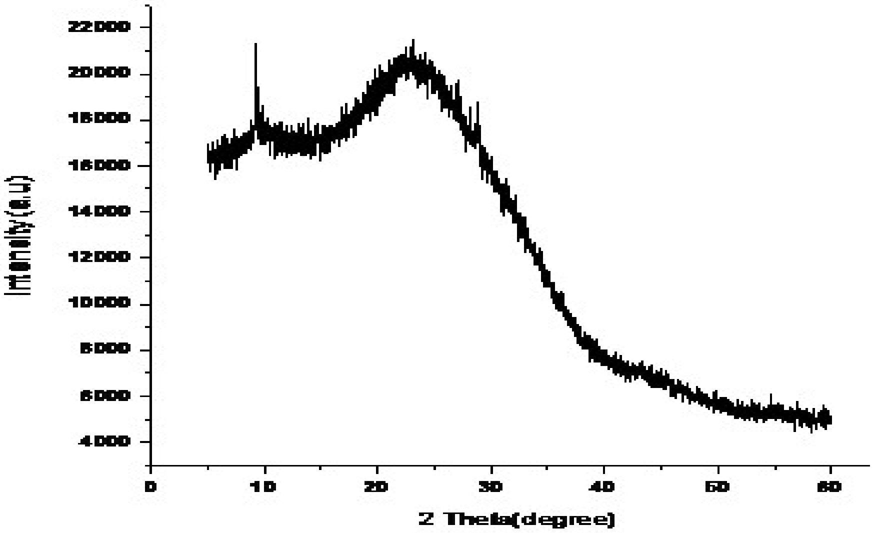


Fig 3 XRD pattern of the wsCNDs

UV Visible absorption spectrum of C-dots

Absorption spectrum of the wsCNDs is shown in Fig 4. The wsCNDs exhibits maximum absorption peak at 340nm and it can be attributed to $\pi - \pi^*$ and $n - \pi^*$ transition of the C = C and C = O bonds respectively. UV-Vis spectrum indicates the absence of any other morphology of nanocarbons or amorphous carbon, as resulting from partial carbonization of precursor, since there is no sign of background absorbance in the visible region(15). Aqueous solution of the wsCNDs after several weeks of storage at room temperature did not result any visible aggregation, demonstrating the excellent stability of the wsCNDs in solution.

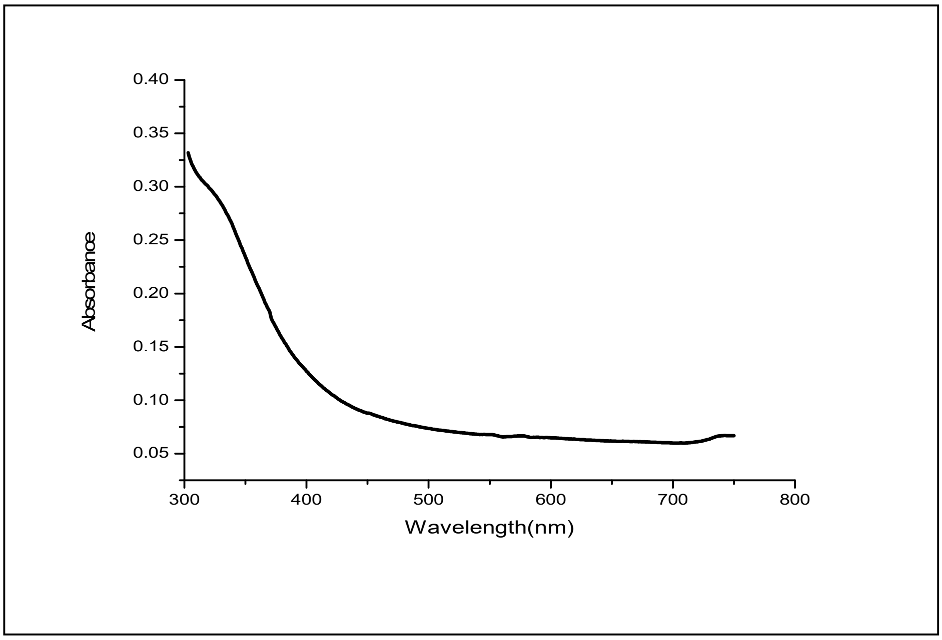


Fig4 Absorption spectra of ws CNDs

Fluorescence emission spectra of C-dots

The photoluminescence study with different excitation wavelengths (λ_{ex}) within the range 300 – 350 nm was carried out in order to explore the optical properties of the synthesized wsCNDs.

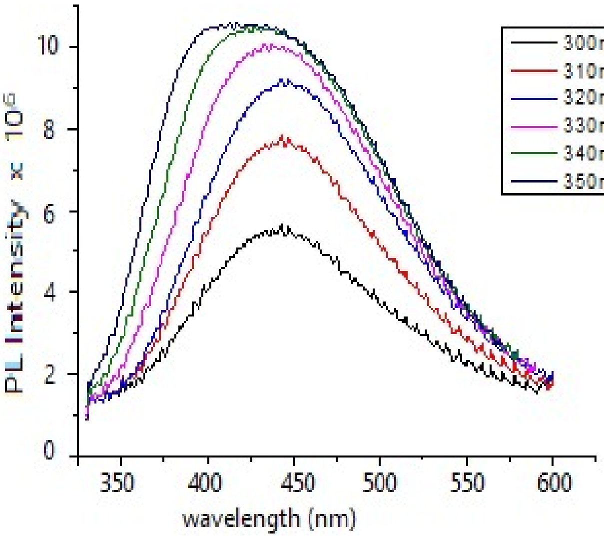


Fig 5 **Tunable fluorescence emission spectra of wsCNDs**

The emission spectrum of the wsCNDs is excitation dependent as shown in Fig 5 and is characterized as a generic feature of nanoparticles possessing carbogenic core(17). When excitation wavelength was varied from 300 nm to 350 nm with a continuous increase of 10 nm, the emission wavelength and the intensity were found to change slightly with simultaneous broadening of the signals. The PL emission of the wsCNDs varied from wavelengths 450 to 600 nm, the maximum absorbance being at 445 nm with the excitation wavelength of 330 nm.

The quantum yield of the wsCNDs was found to be 9% with reference to quinine sulfate, indicating the strong quantum confinement of particles.

Eosin Y and MB degradation

The UV-Visible spectra of Eosin Y degradation by $NaBH_4$ in absence and presence of the synthesized C-dots have been shown in Fig 6(a) and 6(b). Similar degradation of methylene blue with borohydride in presence and in absence of C-dots has been presented in Fig 6(c). The spectra show that $NaBH_4$ alone does not cause much appreciable change in the reduction of the dyes within the specified time of the experiment, which is reflected by small decrease in absorbance in the visible spectra of eosin and methylene blue. The synthesized C-dots act as catalysts to increase the rate of reduction/ decomposition of eosin and MB, as is apparent from the larger decrease in absorbance in presence of the wsCNDs. This suggests that C-dots act as a good electron transfer system that catalyzes the reduction of the two dyes.

The reduction of eosin has been studied for 30 minutes from the addition of borohydride with intervals of 5 minute each at the λ_{max} value of 517 nm in absence [Fig 6(a)] and in presence [Fig 6(b)] of the catalyst. The large difference in the absorbance clearly indicates the effectiveness of the synthesized wsCNDs as catalyst in the reduction eosin Y. Similar result has also been observed in the reduction of methylene blue which is depicted in Fig 6(c) where the decrease in absorbance at the λ_{max} value of 670 nm has been shown after an interval of 15 minute from the addition of borohydride. The synthesized C-dots are found to be a very effective catalyst in the degradation of methylene blue also.

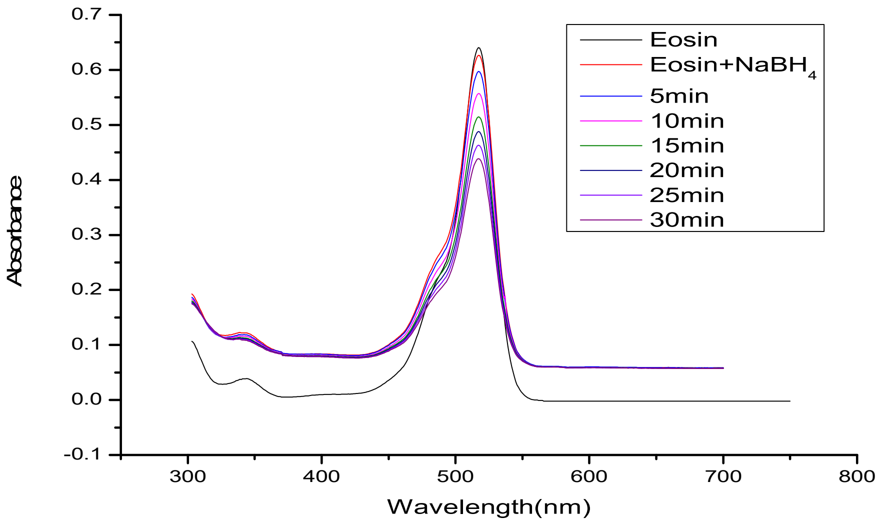


Fig 6(a) UV-visible spectra of Eosin degraded by $NaBH_4$ in absence of C-dots

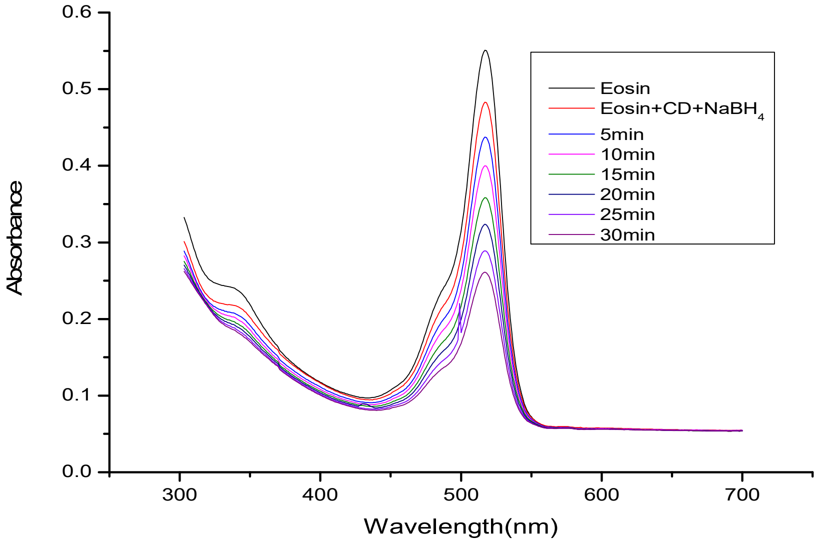


Fig 6(b) UV-visible spectra of Eosin degraded by NaBH$_4$ in presence of C-dots

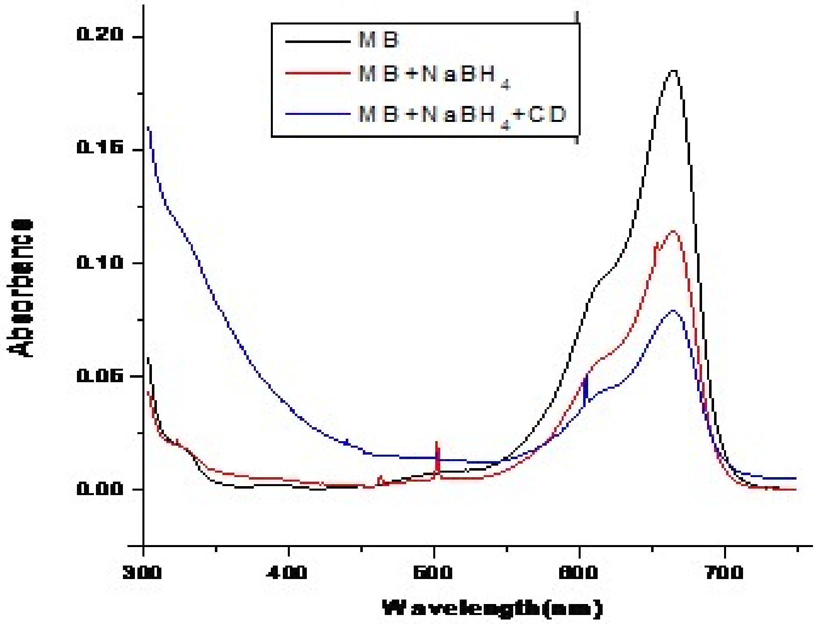


Fig. 6(c) UV-visible spectra of MB, degraded by NaBH$_4$ in absence and in presence of C-dots

The percentage degradation of Eosin Y and MB by $NaBH_4$ in presence and in absence of C-dots has been shown in Fig7(a) and (b) . The initially sharp increase in the percentage degradation of the dyes is probably due to the adsorption of the dyes on the surface of C-dots. The average degradation in terms of the percentage of eosin and MB in solution was calculated using the following formula :

$$\eta = (A_o - A_t / A_o) \times 100\%$$

where η is the rate of degradation of dyes in terms of percentage, A_o is the initial absorbance of dyes solution and A_t is the absorbance of the dyes at time t(18-19). At the end of 30 minutes of the reaction degradation of Eosin Y was found to be 52.61% in presence of C-dots against 31.4% in absence of the catalyst. Similarly 66.30% of methylene blue was found to be degraded in presence of the catalyst while it was only 38.26% in the absence of the catalyst.

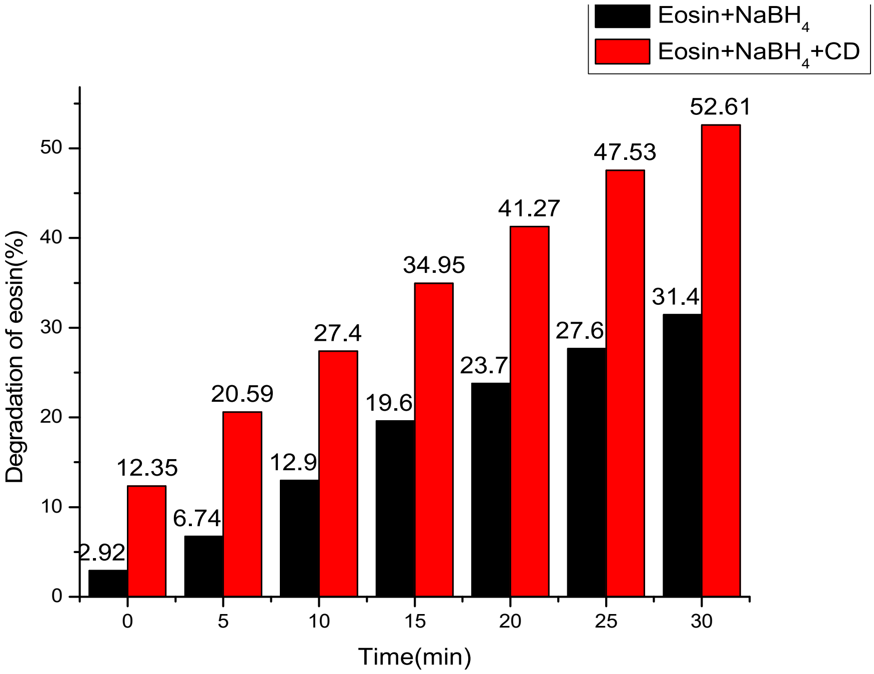


Fig. 7(a) Percentage degradation of Eosin by $NaBH_4$ in presence of C-dots at an interval of 30mins

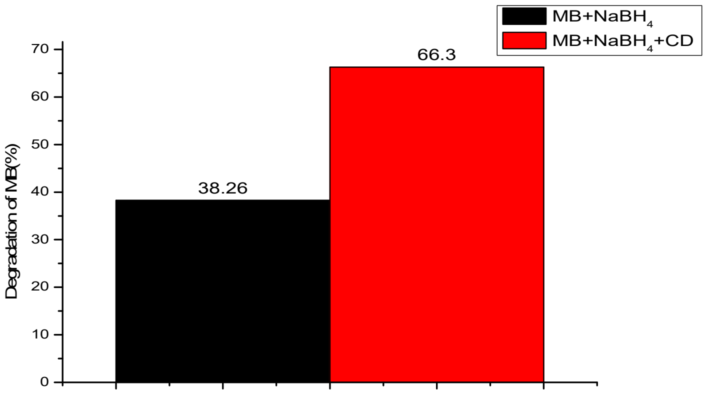


Fig 7(b) Percentage degradation of MB by NaBH$_4$ in presence of C-dots at an interval of 15 mins

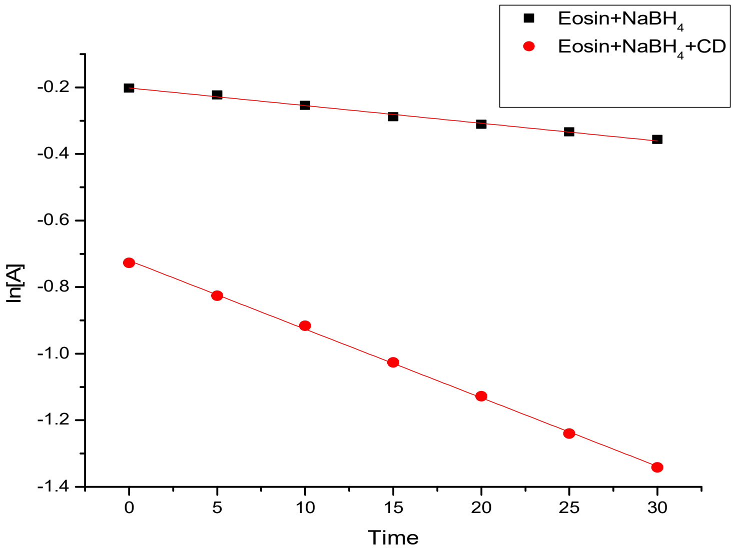


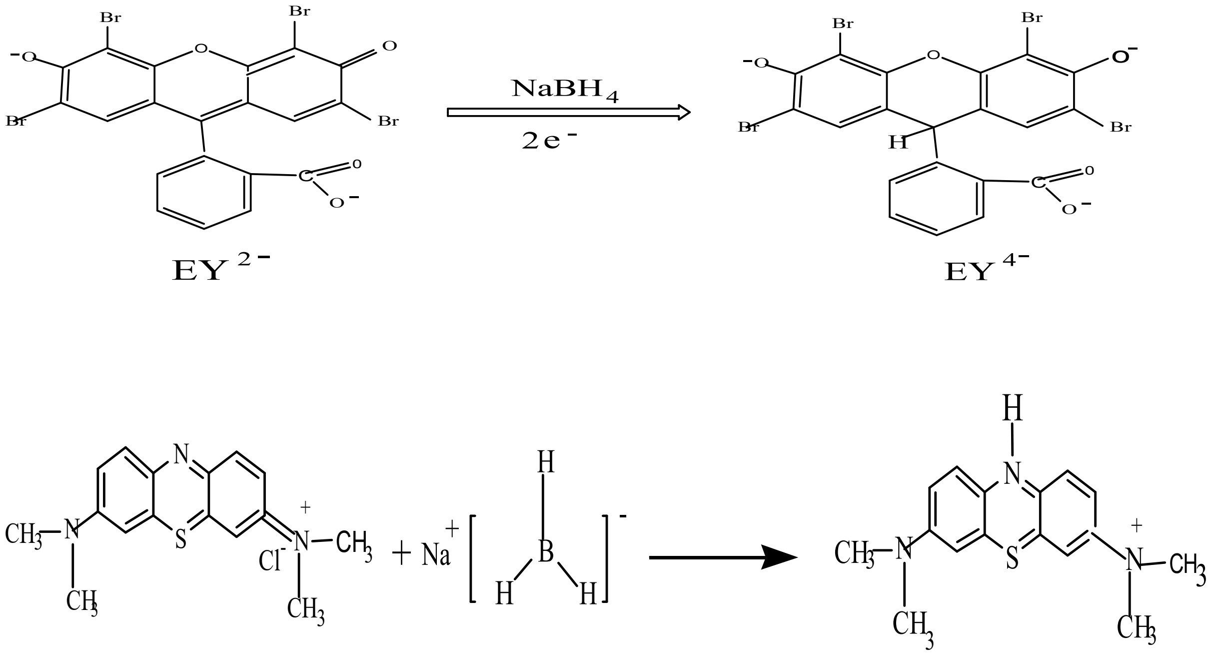
Fig 8 Kinetics of catalytic reduction of eosin by NaBH$_4$ in presence and in absence of C-dots

From Fig 8 ln[A] Vs time graph shows that in presence of C-dots, concentration of eosin dye decreases exponentially with time. The decrease is such that the time required for a definite fraction of the reaction to occur is independent of the intial concentration of the reactant.

The linear regression plots fitted well, from which the slopes of each plot were calculated and used to obtain the first- order rate constants (k). The k for Eosin degradation in absence of CNDs was found to be $k=0.0122 min^{-1}$ and in presence of CNDs, $k=0.0474 min^{-1}$. The k value represents the catalytic activity of the catalyst. The higher the k value, the faster the degradation of eosin, hence, better catalytic activity of the CNDs.

Mechanism of reduction of dyes

In aqueous solution Eosin Y undergoes hydrolysis to form bianion, EY^{2-} [20] and it shows a strong absorption at 517 nm. This species undergoes reduction at the double bond of the heterocyclic ring and as a result a colourless species EY^{4-} is formed [21]. Borohydride can donate two electrons to EY^{2-} for the reduction to take place. This reduction has been shown in Fig 9 which shows time-dependent decrease in absorbance upon addition of a definite amount of borohydride. Since the absorbance (A) is proportional to the concentration of EY^{2-} so the plot of ln A against the time of reaction should be informative about the kinetics of the electron transfer process. This plot has been shown in Fig8. The linear relationship between ln A and the time of reaction suggests that the reaction follows first order kinetics. Thus EY^{2-} is reduced to EY^{4-} by borohydride in a one-step process due to a two- electron transfer reaction [20].



Methylene blue **leuco methylene blue**

Fig 9. Reduction reaction of eosin and methylene blue

Reduction of EY^{2-} by Borohydride in Presence of C-dots

Reports regarding metal nanoparticles, such as Ag, Au, Pt, being used to catalyze electron transfer reactions are in aplenty [22]. The mechanism of this nanocatalysis involves electron transfer from the reducing agent (electron donor) to the nanocatalyst which is followed by an electron transfer from the nanocatalyst to the electron acceptor reactant. In the reduction of Eosin Y (EY^{2-}) by borohydride in presence of Au nanoparticles as catalyst an intermediate species (EY^{3-}) was identified with λ_{max} value of 405 nm [23]. This was not observed in our study involving the same reaction catalysed by the wsCNDs.

The IR spectrum of Eosin Y solution in water shows a strong band at 1634 cm^{-1} which shifts to 1642 cm^{-1} when the dye is added to the aqueous solution of the CDs. Further shifts in the IR bands are also observed in the finger print region, *viz.*, the bands at 608, 638 and 701 cm^{-1} in Water solution are shifted to 620, 630 and 718 cm^{-1} respectively in presence of the CDs. These shifts in the bands suggest binding of Eosin Y to the CDs. Similar results are also observed in case of the borohydride solution. The band at 1641 cm^{-1} of borohydride solution in water splits up into two in presence of the CDs. This may be due to the adsorption the borohydride on the CDs due to which the symmetry of the species is lost and thereby resulting in the splitting of the band. The aforesaid observation suggests that the electron transfer from borohydride to the dye has taken place through adsorption of the two species on the surface of the CDs. Thus the C-dots act as the electron relay, assisting in the transfer of electron from BH_4^- ions to the dyes, thereby causing the reduction of the dyes.

The BH_4^- ions were nucleophilic, whereas the dyes were electrophilic in nature with respect to the C-dots. Nucleophiles can donate electrons to nanoparticles. BH_4^- ions and the dyes were adsorbed simultaneously on the surface of C-dots when they were in close proximity, and electrons transfer from BH_4^- ions to the dyes can occur via C-dots [19,24]. The adsorbed O_2 at the surface of C-dots in the presence of any electrons providing sources (such as BH_4^-) can generate $O_2^{\bullet}$ and $^{\bullet}OH$ radicals [18,27-28,29,30-31,33]. These radicals are quite energetic and can easily mineralize the dyes [22,26-37]. The electons that are captured by the nanoparticles are transferred to the O_2 adsorbed at the surface for the formation of $O_2^{\bullet}$ and later $^{\bullet}OH$ [11,15,36]. Therefore C-dots with the appropriate size are effective for improving the catalytic activity. The size of orange peels were in the range of 5nm, which is effective for the transfer of electrons produced by BH_4^- ions to the dyes, adsorbed O_2 molecules for the formation of $O_2^{\bullet}$ and $^{\bullet}OH$ radicals [29,30,34-37].

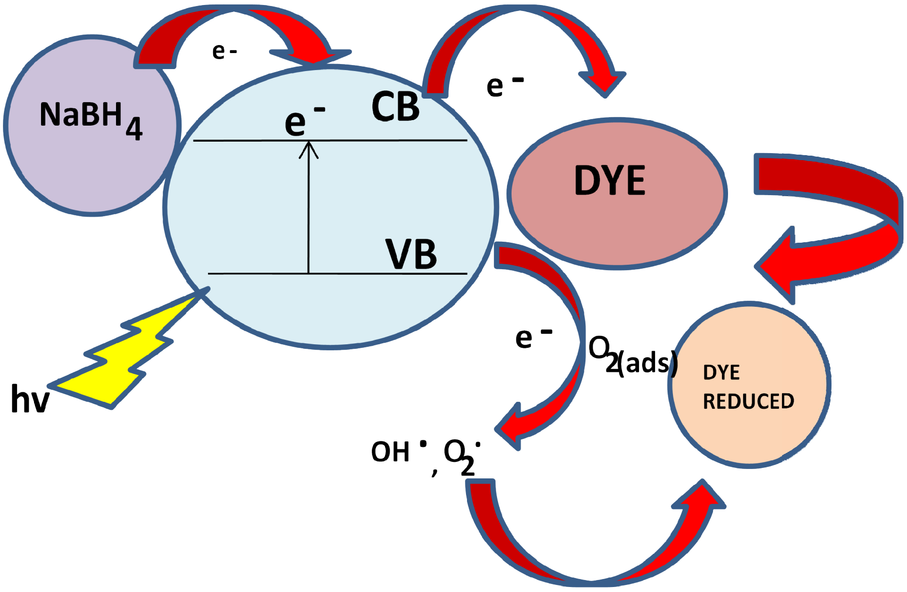


Fig. 10 Proposed mechanism for the catalytic reduction of Eosin Y in presence of C-dots

Further scope: C-dots can be trap in a solid support to remove toxic elements from waste water

Conclusions

In summary, carbon dots with efficient catalytic activity under UV-Vis light irradiation have been successfully prepared by facile pyrolysis and microwave process, which is more biocompatible, ecofriendly, low cost process. The catalytic activity of the green synthesized c-dots was evaluated by choosing Eosin Y and Methylene blue dye. The main absorption peak of the dyes decreased gradually with the extension of the exposure time indicating the catalytic degradation of dyes. Thus from the present study it is found that c-dots exhibits catalytic activity against dye molecules and can be further modified and can be used in water purification systems and dye effluent treatment.

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