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# Microwave-assisted preparation of a silver nanoparticles/N-doped carbon dots nanocomposite and its application for catalytic reduction of rhodamine B, methyl red and 4-nitrophenol dyes

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In the current work, a silver nanoparticles/nitrogen-doped carbon dots (AgNPs/NCDs) nanocomposite was prepared by a microwave-assisted method that does not require additional reducing or stabilizing agents. Multiple analytical techniques were used to characterize the prepared nanocomposite. The nanocomposite exhibited a surface plasmon resonance (SPR) absorption peak at 420 nm, indicating the development of AgNPs with NCDs. Further, HRTEM results confirmed the formation of the nanocomposite with the appearance of lattice fringes of both materials. Additionally, the nanocomposite did not show any precipitation even after two months of storage. The nanocomposite exhibited high catalytic activity towards the reduction of rhodamine B (RhB, 98.83%), methyl red (MR, 97.14%) and 4-nitrophenol (4-NP, 99.95%) at ambient temperature. Besides, the kinetic analysis revealed that the reduction reaction followed pseudo-first-order kinetics and the calculated rate constants (*k*) for rhodamine B (RhB), methyl red (MR) and 4-nitrophenol (4-NP) were found to be 0.0296 s<sup>-1</sup>, 0.0233 s<sup>-1</sup> and 0.029 s<sup>-1</sup>, respectively. Moreover, it is a reusable and stable catalyst for reduction reactions up to five cycles without significant loss in catalytic activity. Finally, a plausible mechanism for the reduction of pollutants is also discussed in detail. As a whole, the prepared nanocomposite might display stunning behaviour for wastewater treatment applications.

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## 1. Introduction

The organic toxins in wastewater from industries such as the pharmaceutical, paper, leather, textile, and plastics industry are of serious concern because of their adverse effects on the ecological system. These organic pollutants are highly carcinogenic and toxic and can be harmful to human health and the environment.<sup>1-7</sup> Thus, to get rid of this hidden risk, the

development of efficient treatment technology is necessary to fulfill the ever-increasing demand for sustainable water. Several conventional approaches such as chemical, physical and biological processes have been tested to eliminate these pollutants.<sup>8-12</sup> The chemical reduction of these pollutants in the existence of NaBH<sub>4</sub> (as reducing agent) and metal nanoparticles (as a catalyst) is one of the most commonly used techniques.<sup>8,13,14</sup> Noble metal nanoparticles (silver, gold, palladium, and platinum) have attracted significant attention as a result of their unique optical and physical features as well as their large surface to volume ratio, which makes them applicable in different fields such as biomedical, electronics, photonics, sensing and catalysis.<sup>15-20</sup> Among them, mainly silver nanoparticles (AgNPs) have attracted considerable attention because of their high electrical conductivity, cost-effectiveness and antimicrobial activity as well as showing high catalytic efficacy in various chemical reactions such as alkane and alkene oxidation, reduction of dyes, hydrogenation of 4-NP and as intermediates in pharmaceutical reactions.<sup>21-25</sup>

A broad series of methods like chemical, physical, laser ablation, hydrothermal, sol-gel, ultrasonication, microwave

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irradiation and electrochemical have been developed to obtain AgNPs, and additional significant efforts have been dedicated to controlling their shape as well as size that can significantly influence the features of AgNPs.<sup>23,26–28</sup> Among all the synthetic strategies, chemical pathways can govern both the shape and size of the AgNPs, but most of the chemical methods are depending on the reduction of AgNO<sub>3</sub> with a strong reducing agent like hydrazine hydrate, sodium citrate and sodium borohydride.<sup>29,30</sup> These reagents are exceedingly toxic, sensitive and have biological risks. To control their shape and size in nanoparticle synthesis, polymers, DNA and other efficient molecules are used as stabilizers.<sup>31–34</sup> But, these molecules on the surface of nanoparticles always hinder the reactants from approaching the active sites of nanoparticles and restricting their properties and lowering the activities. Hence, some procedures such as thermal treatment and washing have been established to eradicate molecules on nanoparticles' surface. Though, removing the molecules on nanoparticles leads to the agglomeration of nanoparticles, changing their properties.<sup>35,36</sup> To overcome these problems, it is necessary to prepare surfactant-free nanoparticles with controlled size and shape. In recent times, carbon nanoparticles have been proved to retain better advantages compared to the traditional organic surfactants.<sup>37,38</sup> Thus, we have confidence in the phenomenon intended that the nanoparticles fabricated with carbon nanoparticles may have superior features. N-doped carbon dots (NCDs), a new class of carbon nanoparticles have recently been used to synthesize AgNPs and AuNPs. Li-Ming Shen and co-workers reported growth of the AgNPs with NCDs, Peihui Luo *et al.*, described the preparation of gold@carbon dots nanocomposite, B Sinduja and Abraham had prepared silver nanoparticles capped with NCDs.<sup>39–41</sup> From this literature, we understood that the CDs are efficient for preparation of metal nanoparticles with controlled size. Moreover, presence CDs can enhance the adsorption of organic pollutants on the catalyst surface due to their conjugative structure, which leads to the fast reduction of pollutants. From these advantages we have prepared AgNPs/NCDs nanocomposite by using NCDs as reducing and stabilizing agents.

Herein, we report a microwave-assisted synthesis of silver nanoparticles/nitrogen-doped carbon dots (AgNPs/NCDs) nanocomposite. Here, NCDs can directly reduce AgNO<sub>3</sub> to AgNPs in the absence of any harmful reducing and stabilizing agent. These NCDs were prepared from *Lantana camara* fruit extract and ethylenediamine in our previous work. Further, the effect of varying concentrations of AgNO<sub>3</sub> and microwave reaction time on the synthesis was also studied. Various analytical techniques were applied to investigate the optical, structural as well as morphological features of the as-prepared nanocomposite. The catalytic activity of AgNPs/NCDs nanocomposite in the reduction of rhodamine B (RhB), methyl red (MR) and 4-nitrophenol (4-NP) in the existence of NaBH<sub>4</sub> in aqueous media has also been reported. Most importantly, only a slight loss is observed in AgNPs/NCDs nanocomposite catalytic activity even after several recycles. To the best of our knowledge, this is the first report on the fabrication of AgNPs/NCDs nanocomposite by microwave irradiation method and as a catalyst for the reduction of RhB, MR and 4-NP dyes in wastewater.

## 2. Experimental

### 2.1. Materials

AgNO<sub>3</sub>, NaBH<sub>4</sub> purchased from Sigma-Aldrich; RhB, MR and 4-NP from S. D. Fine Chemicals, India. All chemicals were applied as received and double-distilled (DD) water applied for all reactions.

### 2.2. Synthesis of AgNPs/NCDs nanocomposite

NCDs were prepared as per our previously reported method.<sup>42</sup> Then AgNPs/NCDs nanocomposite was prepared by microwave method. In brief, 500  $\mu$ L of AgNO<sub>3</sub> solution was added to the NCDs (1 mL, 1 mg mL<sup>-1</sup>) solution, then the volume was prepared to 4 mL using DD water. After that, the solution was exposed to microwave irradiation for 2 min at 450 W power, and the formed light brown colour solution indicated the successful synthesis of AgNPs/NCDs nanocomposite. Finally, the nanocomposite solution was centrifuged at 8000 rpm for 10 min, and then the collected pellet was dried at 80 °C. Meanwhile, AgNPs/NCDs nanocomposite synthesis was also optimized at diverse concentrations of AgNO<sub>3</sub> (0.1 to 2 mM) with different microwave irradiation times (30 s to 120 s).

### 2.3. Characterization

Several analytical techniques confirm the prepared nanocomposite. Shimadzu, UV-2600 spectrophotometer was used to measure the optical properties. XRD (Rigaku Miniflex 600) was used to find the crystal structure of the nanocomposite. Shimadzu IR Prestige-21 spectrophotometer was employed to detect the functional groups that participated in metal reduction and stabilization. TEM (JEOL JEM 2100) was applied to measure the size in addition to the morphology of the prepared nanocomposite. Besides, XPS analysis was achieved using a Kratos AXIS Ultra spectrometer *via* Al K $\alpha$  (1486.71 eV). DLS (Malvern instrument Ltd, Malvern, UK) was applied to define the zeta potential of the synthesized nanocomposite.

### 2.4. Catalytic activity of the AgNPs/NCDs

Catalytic capability of synthesized nanocomposite was considered to reduce RhB, MR and 4-NP using the NaBH<sub>4</sub> as a hydrogen generator. RhB or MR solution (2 mL of 1 mM) and NaBH<sub>4</sub> solution (1 mL of 10 mM) were taken in a test tube, and then DD water was added to it to make the total reaction mixture 10 mL. After that, 3 mL reaction mixture was transferred into a cuvette, followed by 8 mg of as-prepared AgNPs/NCDs nanocomposite was added to it. Then the UV-visible spectra were recorded at every 1 minute to monitor the reduction reaction. Further, the 4-NP reduction was also accomplished. In a typical procedure, 1.5 mL of 0.2 mM 4-NP solution and 1 mL of 2 mM NaBH<sub>4</sub> was taken in a cuvette, then 8 mg of AgNPs/NCDs nanocomposite was added to it. The absorption spectra were recorded at every 1 minute to monitor the reduction reaction. Without the incorporation of catalyst control experiments were also carried out. However, the reduction reaction kinetics was also studied through observing the depletion in the absorbance.

### 3. Results and discussion

Initially, highly fluorescent NCDs were synthesized by one-step hydrothermal carbonization of *Lantana camara* berries and ethylene diamine; the synthesis and characterization were reported in our previous publication.<sup>42</sup> In this work, the prepared NCDs were mixed with  $\text{AgNO}_3$  solution, and the mixture was exposed to microwave irradiation for 2 min at 450 W. The resulting reaction mixture colour was altered from light yellow to light brown, representing the creation of AgNPs/NCDs nanocomposite (Scheme 1), which is further confirmed by various analytical techniques.

Fig. 1 displays the UV-visible spectra of NCDs and AgNPs/NCDs nanocomposite. The pure NCDs show absorption peaks at 285 nm and 356 nm corresponding to the  $\pi-\pi^*$  and  $n-\pi^*$  transitions.<sup>42</sup> After addition of  $\text{AgNO}_3$ , a new peak appeared at 420 nm consistent with the surface plasmon resonance of AgNPs.<sup>32</sup> However, the absorption peaks of NCDs disappeared. The effects of different concentrations of  $\text{AgNO}_3$  and microwave irradiation time were also optimized on nanocomposite formation (Fig. 2). The concentration range of  $\text{AgNO}_3$  used was 0.1–2 mM possessed the other parameters constant, and the reaction was examined *via* evaluating the absorbance of a reaction mixture. The corresponding absorbance changes were shown in Fig. 2a; it is seen that increasing the concentration of  $\text{AgNO}_3$  resulted in the formation of more number of AgNPs/NCDs nanocomposite. Further, we also examined the effect of microwave irradiation time by keeping other parameters constant. The reaction was monitored between 30 to 120 s at 450 W and the resulted absorption spectra depicted in Fig. 2b; shows that gradual increase in the microwave irradiation time up to 120 s, increased the amount of AgNPs/NCDs nanocomposite formation.<sup>13,23,43</sup> Under these conditions, the yield of the nanocomposite was found to be 5.8%. Besides, Fig. 2c shows AgNPs/NCDs nanocomposite stability, wherein no significant change was observed in peak intensity even after storage for 60 days. This indicates that the NCDs shield and make the AgNPs become stable from accumulation in the aqueous medium.

To identify the surface functional groups of NCDs that are responsible for the reduction and stabilization of the AgNPs, FTIR analysis was accomplished. Fig. 3a demonstrates the FTIR spectrum of the NCDs and AgNPs/NCDs nanocomposite. In NCDs, the broad peak centred at  $3395\text{ cm}^{-1}$  is accredited to the stretching vibrations of O–H/N–H groups. However, the absorption peaks at  $2935$ ,  $1659$ ,  $1411$  and  $1053\text{ cm}^{-1}$  suggest the

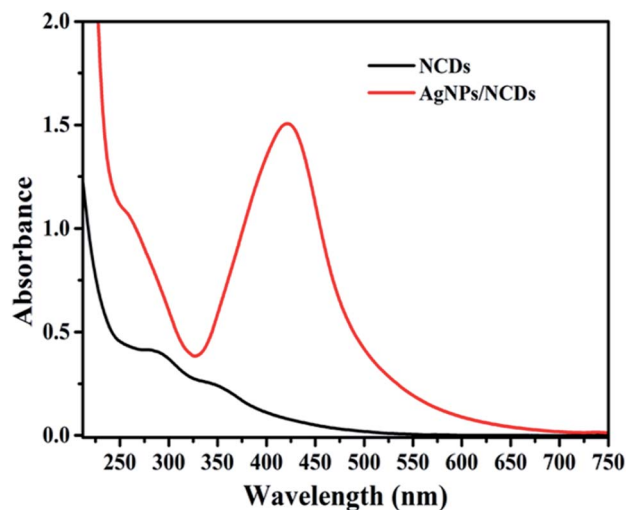
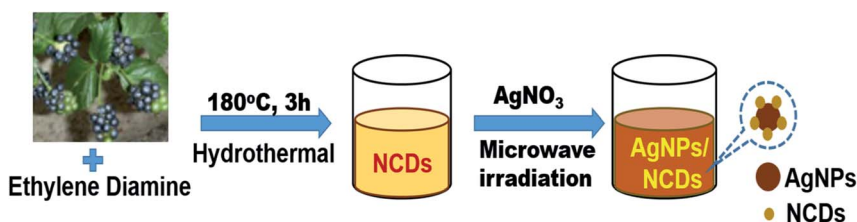


Fig. 1 UV-vis absorption spectra of NCDs and AgNPs/NCDs nanocomposite.

existence of the C–H, C=O, N–H and C–O groups,<sup>42</sup> respectively. In the FTIR spectra of AgNPs/NCDs nanocomposite, absorption bands are observed at  $3547$ ,  $2930$ ,  $1756$ ,  $1604$ ,  $1438$  and  $963\text{ cm}^{-1}$ . Comparison of NCDs and AgNPs/NCDs FTIR spectra, reveals that the peak positions of the nanocomposite were shifted from  $3395$  to  $3547\text{ cm}^{-1}$ ,  $1659$  to  $1604\text{ cm}^{-1}$  and  $1411$  to  $1438\text{ cm}^{-1}$ , and the intensities of peaks were decreased, due to the interaction between the NCDs and AgNPs, confirming the formation of AgNPs/NCDs nanocomposite. Additionally, a new peak at  $1745\text{ cm}^{-1}$  appeared in AgNPs/NCDs spectrum, which corresponds to symmetrical stretching of carboxylate groups.<sup>39,41,44,45</sup> From the FTIR spectrum, we can conclude that NCDs have abundant  $-\text{NH}_2$ , carbonyl and  $-\text{OH}$  functional groups on the surface that acted as electron donors for the reduction of  $\text{Ag}^+$  to elemental  $\text{Ag}^0$ .<sup>46,47</sup>

The crystalline structure of the synthesized AgNPs/NCDs nanocomposite was identified through XRD analysis. As exposed from Fig. 3b, the diffraction peaks located at  $38.14^\circ$ ,  $44.54^\circ$ ,  $64.61^\circ$  and  $77.51^\circ$  can be indexed to the (111), (200), (220) and (311) Bragg's reflection of face centred cubic structure of metallic silver respectively (JCPDS No. 04-0783).<sup>23,28</sup> XRD investigation suggested that the synthesized AgNPs/NCDs nanocomposite was composed of crystalline silver.

TEM analysis was supported to identify the shape in addition to the size of the fabricated AgNPs/NCDs nanocomposite (Fig. 4). As shown in Fig. 4a, the AgNPs/NCDs nanocomposite



Scheme 1 Schematic illustration for the synthesis of AgNPs/NCDs nanocomposite.

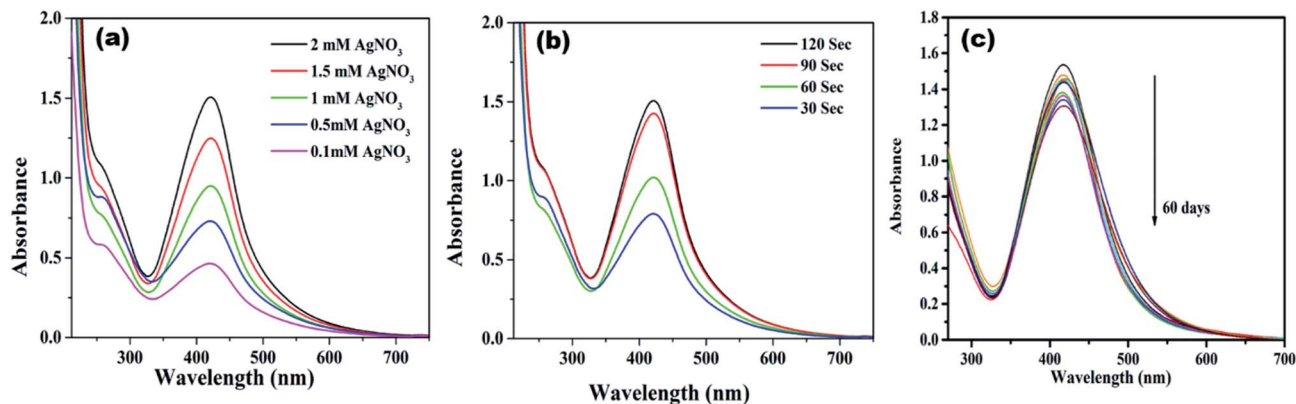


Fig. 2 UV-vis absorption spectra of AgNPs/NCDs nanocomposite synthesized at (a) different concentration of  $\text{AgNO}_3$ , and (b) different microwave irradiation time; (c) UV-vis spectra of AgNPs/NCDs depicting their stability for 2 months.

has a spherical shape and is well dispersed. The dark spots appeared in the TEM image mainly due to high crystallinity of AgNPs, but NCDs combined with AgNPs did not appear clearly in TEM image, because of the amorphous nature and low contrast of NCDs. Therefore, further we provided the HRTEM image for confirming the formation of composite between NCDs and AgNPs. In HRTEM image (Fig. 4b) the characteristic lattice fringe spacing of 0.24 nm and 0.34 nm was observed, which is ascribed to the (111) plane of AgNPs and (002) plane of NCDs, respectively.<sup>48,49</sup> In addition, NCDs are clearly found on the surface of AgNPs that confirmed the formation of AgNPs/NCDs nanocomposite. Moreover, for comparison we provided TEM image of NCDs (Fig. 4c) and its HRTEM image (shown in inset). From Fig. 4c it was observed that the NCDs appear as low contrast spots and from the inset NCDs have lattice fringe spacing of 0.34 nm (002). The size distribution histogram (Fig. 4d) demonstrates that the nanocomposite's average diameter is  $9 \pm 3$  nm.

XPS measurement was checked to ascertain further the surface composition of the as-prepared AgNPs/NCDs nanocomposite (Fig. 5). As found in Fig. 5a, the XPS survey spectrum of the nanocomposite; it clearly displays the peaks at around

285, 370, 400, 531 and 580 eV, which are corresponding to C 1s, Ag 3d, N 1s, O 1s and Ag 3p state, respectively.<sup>48</sup> The strong C 1s, N 1s and O 1s peaks were corresponding to the NCDs prepared from the *Lantana camara* and ethylenediamine as reported in our previous article.<sup>42</sup> Furthermore, the high-resolution spectrum of Ag 3d (Fig. 5b) displayed two different peaks at 368.2 and 374.2 eV, which were accredited to the binding energies of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ , respectively. It is indicating the metallic state of formed silver nanoparticles.<sup>48</sup>

Zeta potential gives information about the state of the surface charge and predicts the colloidal system's long-term stability.<sup>44</sup> To further confirm AgNPs/NCDs nanocomposite formation, the zeta potential values of NCDs and AgNPs/NCDs were measured (Fig. 6). NCDs zeta potential was  $-11$  mV, and AgNPs/NCDs composite was  $-22.1$  mV, respectively. The negative charge on NCDs surface was due to nitrogen and oxygen functional groups.<sup>42</sup> In the case of AgNPs/NCDs nanocomposite, the increased zeta potential was due to the attachment or binding of more than one NCD on AgNPs surface. Thus, the increase in the zeta potentials indicates that the AgNPs/NCDs nanocomposite was relatively stable and NCDs assist as reducing and capping agents for AgNPs/NCDs.<sup>41</sup>

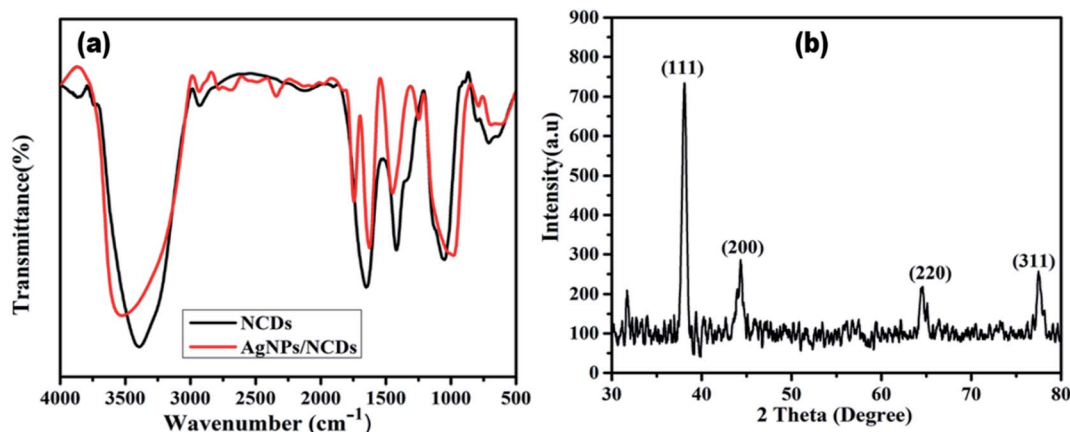


Fig. 3 (a) FTIR spectra of NCDs and AgNPs/NCDs nanocomposite. (b) XRD pattern of AgNPs/NCDs nanocomposite.

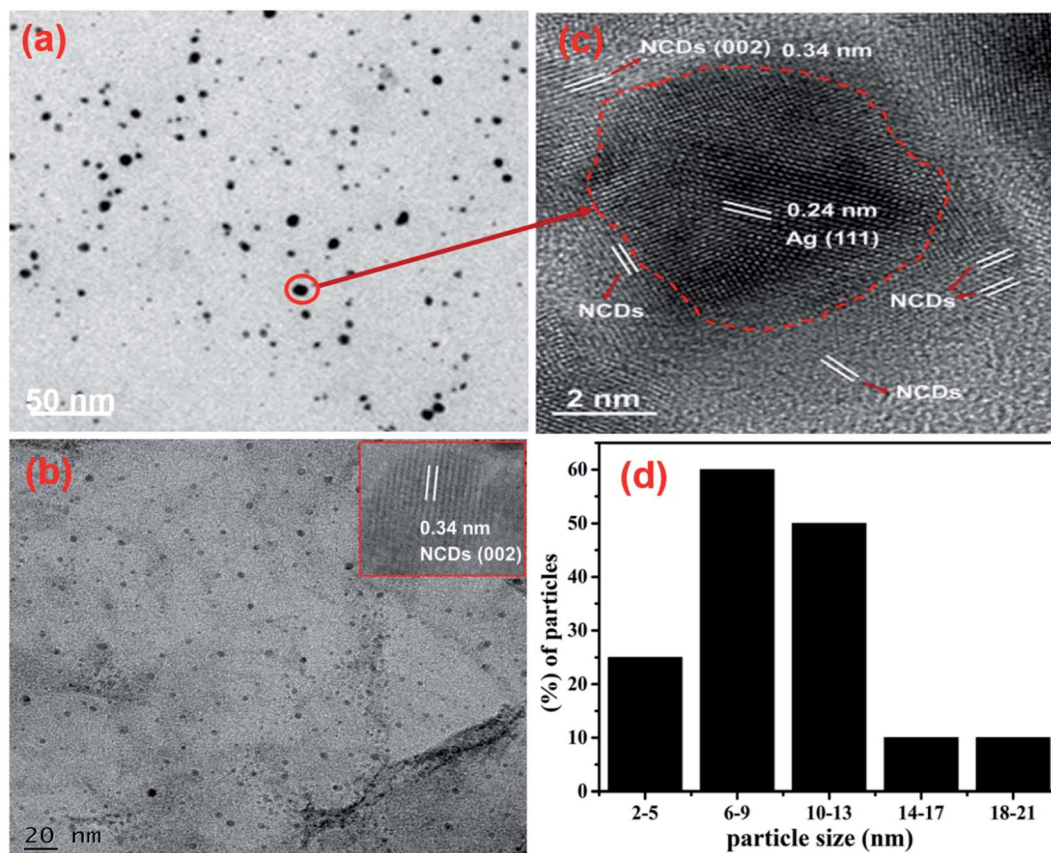


Fig. 4 (a) TEM image and (b) HRTEM image of the AgNPs/NCDs nanocomposite. (c) TEM image of NCDs and its HRTEM image in inset; (d) size distribution histogram of the AgNPs/NCDs nanocomposite.

### 3.1. Mechanism of AgNPs/NCDs nanocomposite formation

Several publications concluded that the plant-based materials are accountable for reducing metal ions into metallic nanoparticles accompanied by capping to inhibit agglomeration.<sup>32</sup> In this work, we used a plant material derived NCDs to reduce and stabilise AgNPs. In our previous publication, we have prepared

NCDs from *Lantana camara* berries and ethylenediamine as carbon and nitrogen sources, respectively. Several analytical techniques characterized the prepared NCDs. According to FTIR and XPS studies, NCDs have numerous functional groups, for instance, hydroxyl, amino, carbonyl and carboxylate groups.<sup>42</sup> Under microwave irradiation, these functional groups combine

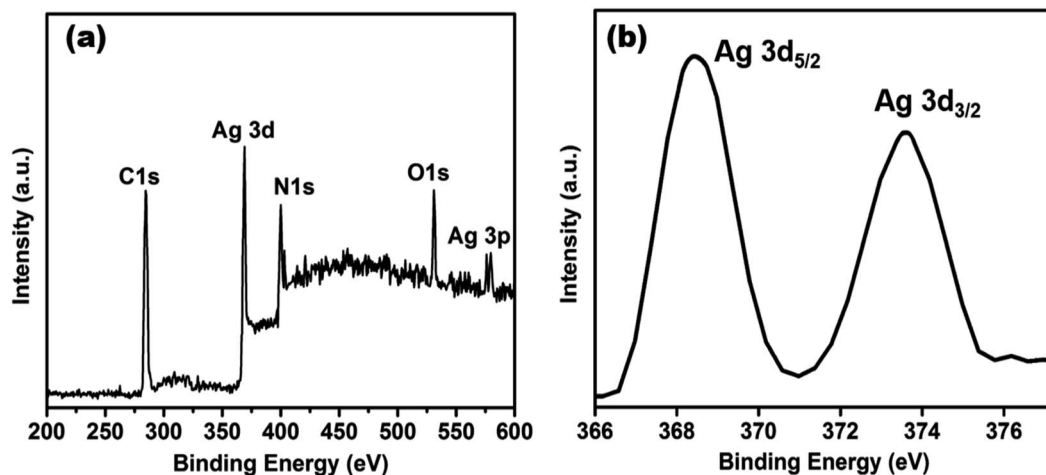


Fig. 5 (a) XPS survey spectrum of AgNPs/NCDs nanocomposite, (b) high-resolution spectrum of Ag 3d of AgNPs/NCDs nanocomposite.

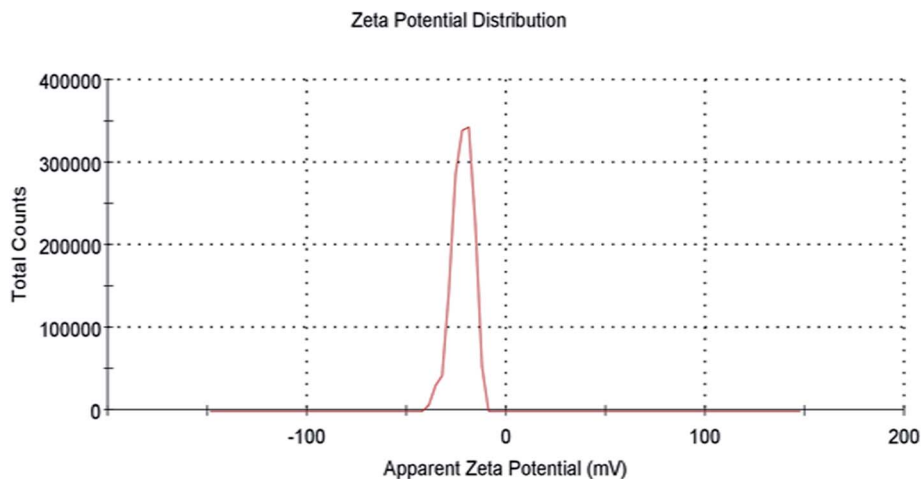


Fig. 6 Zeta potential distribution of AgNPs/NCDs nanocomposite.

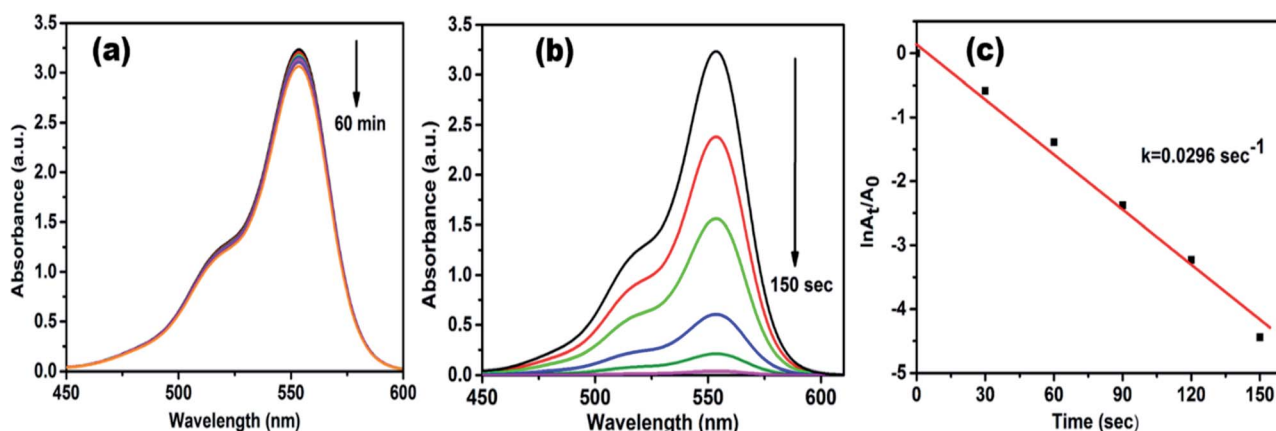


Fig. 7 UV-vis absorption spectra of (a) catalytic reduction of RhB in the presence of  $\text{NaBH}_4$  and in the absence of catalyst; (b) time-dependent absorption spectra of RhB in the existence of both  $\text{NaBH}_4$  and AgNPs/NCDs; (c) plot of  $\ln(A_t/A_0)$  against time for reduction of RhB dye.

with  $\text{Ag}^+$  ions and reduce into AgNPs, which further prevent agglomeration of nanoparticles. MWI generates localized superheating which results in the rapid reaction. In the FTIR analysis, when the AgNPs/NCDs nanocomposite was formed by

using NCDs functioning as the reducing and capping agent, it is depicted that the peak intensities of N-H/O-H and C=O are found to be decreased in comparison with the NCDs and appearance of a new band for  $-\text{COO}^-$  group. The increased zeta

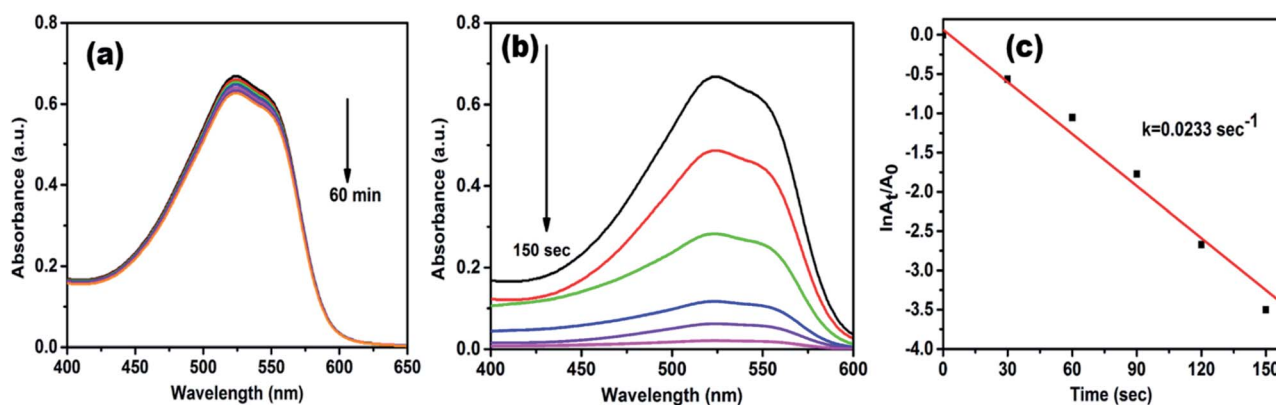


Fig. 8 UV-vis absorption spectra of (a) control experiment of MR (b) time-dependent absorption spectra of MR over AgNPs/NCDs nanocomposite and  $\text{NaBH}_4$ ; (c) plot of  $\ln(A_t/A_0)$  against time for reduction of MR dye.

potential also further confirmed the formation of the nanocomposite. These results demonstrate that the N–H/O–H and C=O groups of NCDs were broken to carboxyl groups after forming AgNPs/NCDs nanocomposite.<sup>50,51</sup>

### 3.2. Catalytic activity of AgNPs/NCDs nanocomposite

The catalytic efficacy of AgNPs/NCDs nanocomposite was evaluated towards the reduction of model contaminants such as rhodamine B (RhB), methyl red (MR) and 4-nitrophenol (4-NP). The reaction was carried out at an ambient temperature and was monitored by UV-visible spectrophotometer.

Rhodamine B (RhB) is a cationic dye, which is widely used in many industries, and it is hazardous as well as mutagenic in nature. The aqueous solution of RhB shows an absorption peak at 554 nm. The variation in the intensity of peak at 554 nm was used to observe the whole reduction process. As shown in Fig. 7a, up to 60 min, a small decrease was observed in peak intensity only in the presence of NaBH<sub>4</sub>, while in the attendance of both AgNPs/NCDs nanocomposite and NaBH<sub>4</sub>, the absorption peak intensity was gradually decreased and finally 98.83% of RhB was reduced in 150 s (Fig. 7b). Here, the taken NaBH<sub>4</sub> concentration was greater than the RhB concentration. Hence,

the rate of the reaction depended on RhB concentration only.<sup>10,13</sup> The linear plot of  $\ln(A_t/A_0)$  versus time indicates that the reduction reaction followed the pseudo-first-order kinetics, and the calculated rate constant ( $k$ ) was  $0.0296 \text{ s}^{-1}$  (Fig. 7c).

Methyl red (MR) is another common water pollutant and widely found in many industrial wastewaters. Hence, removal of it from industrial effluents is a primary task nowadays. MR showed absorption peaks at 524 nm in the aqueous medium, and alteration in absorption intensity was employed to study the whole reduction process. Fig. 8a displays UV-vis absorption spectra of MR with NaBH<sub>4</sub> only, but even after 60 min, there is no noteworthy change in peak intensity, it indicates the reduction process is prolonged. However, in the presence of AgNPs/NCDs nanocomposite in MR and NaBH<sub>4</sub> solution, a gradual decrease in the intensity was detected, and the reduction reaction was accomplished (97.14%) within 150 s (Fig. 8b). Additionally, Fig. 8c shows a linear correlation between  $\ln(A_t/A_0)$  and time and the calculated rate constant ( $k$ ) from the slope was  $0.0233 \text{ s}^{-1}$ .

Generally, 4-NP (light yellow colour) shows absorption peak at 318 nm, when NaBH<sub>4</sub> is added to it, the absorption peak is shifted to 400 nm (Fig. 9a), due to the formation of 4-

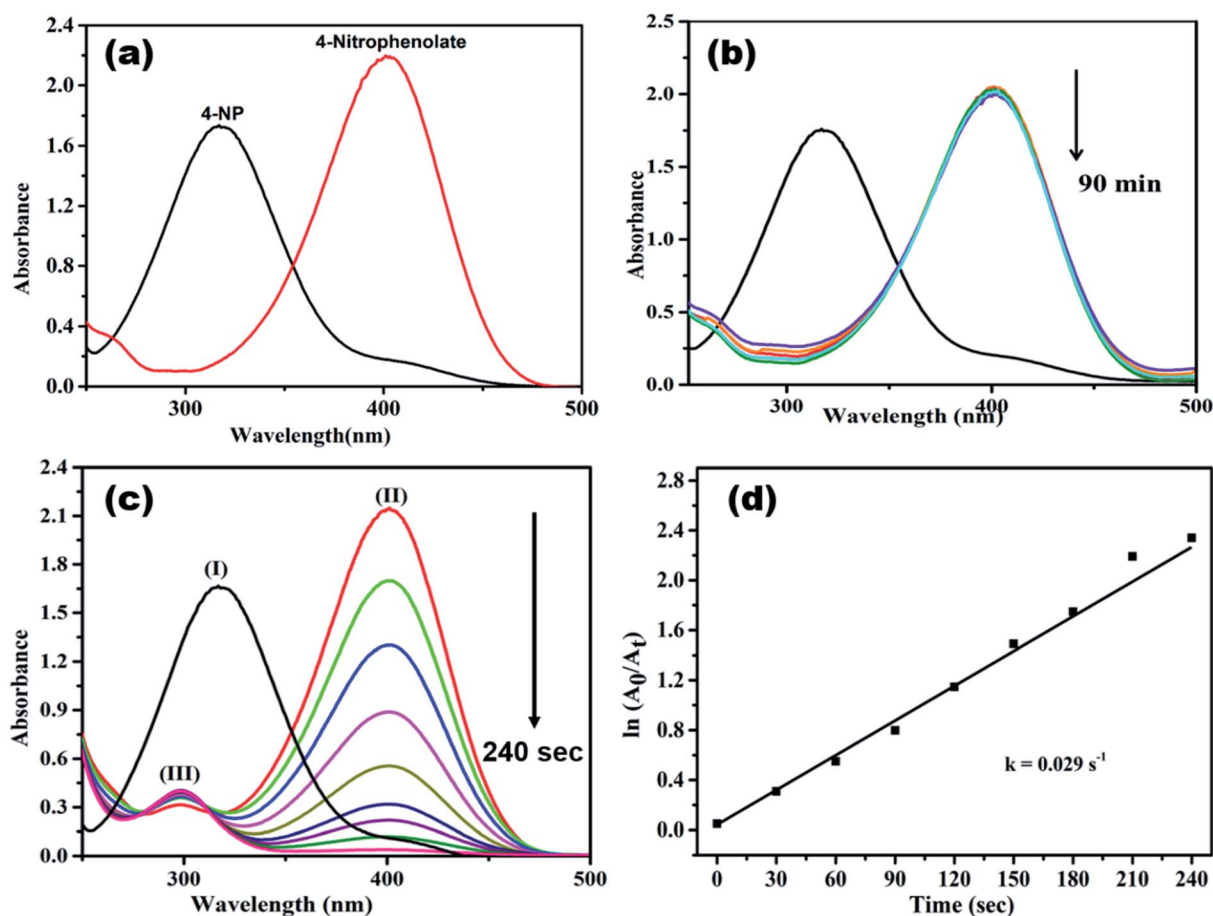


Fig. 9 UV-visible absorption spectra of (a) 4-nitrophenol and 4-nitrophenolate; (b) control experiment of 4-nitrophenol; (c) reduction process of 4-NP in the presence of AgNPs/NCDs nanocomposite and NaBH<sub>4</sub> [(I) 4-NP, (II) 4-nitrophenolate and (III) 4-aminophenol]; (d) plot of  $\ln(A_t/A_0)$  vs. time for the reduction of 4-NP dye.

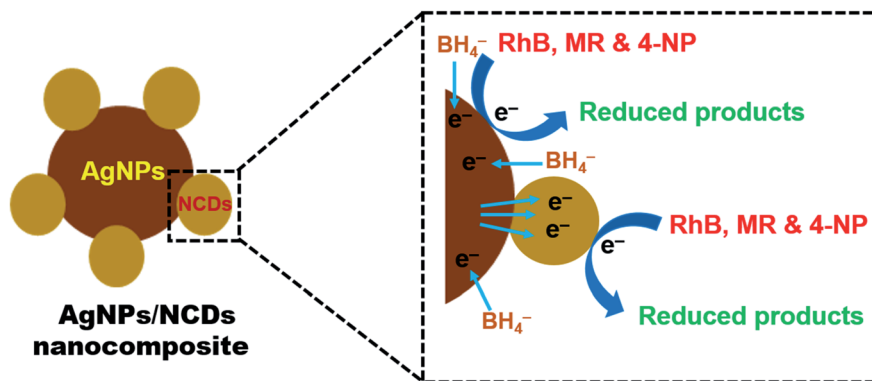


Fig. 10 Schematic representation of a plausible mechanism for the reduction of RhB, MR, and 4-NP dyes in the presence of AgNPs/NCDs nanocomposite and  $\text{NaBH}_4$ .

nitrophenolate ion (deep yellow).<sup>13,15,52</sup> In a control experiment it was noticed that the absorbance peak at 400 nm did not change even after 90 min (Fig. 9b), it indicates the reduction of 4-NP was not proceeded without adding catalyst.<sup>16,18,37</sup> When AgNPs/NCDs nanocomposite was added to 4-NP +  $\text{NaBH}_4$  solution the absorption peak considerably decreased within 240 s, meanwhile a new peak found around 297 nm, and the peak intensity gradually increased with time, it corresponds to the 4-aminophenol (4-AP) product (Fig. 9c)<sup>13,15,22</sup> and about 99.95% of 4-NP was reduced to 4-AP. As shown in Fig. 9d, a linear correlation was found between  $\ln(A_t/A_0)$  and time and the calculated rate constant ( $k$ ) was about  $0.029 \text{ s}^{-1}$ .

### 3.3. Catalytic mechanism of AgNPs/NCDs nanocomposite

From the above results, it was observed that the reduction reaction was completely negligible in the presence of  $\text{NaBH}_4$  only. But in the existence of both nanocomposite and  $\text{NaBH}_4$ , the reduction reaction was taking place and completed within a few seconds. From these observations, it was concluded that the AgNPs/NCDs nanocomposite played a role of catalyst for RhB, MR and 4-NP reduction. Based on this, a reasonable mechanism was proposed for the reduction of these pollutants (Fig. 10). While in the presence of nanocomposite, both  $\text{BH}_4^-$

ions and pollutant molecules co-adsorbed on the surface of nanocomposite. As the pollutants used in the present study have aromatic rings in their structures they get readily adsorbed on the catalyst surface due to the  $\pi$ - $\pi$  interaction between NCDs conjugated structure and aromatic rings of pollutants.<sup>48</sup> During the reduction reaction, the electrons transfer from the  $\text{BH}_4^-$  ion to direct AgNPs and through NCDs to AgNPs, at the same time the formed electrons in AgNPs transfer to surface functional groups of NCDs. Then these electrons transferred to the adsorbed pollutants; further, these pollutants were successively reduced.<sup>13,15,35</sup>

### 3.4. Recyclability of catalyst

Further, we studied the reusability of the catalyst because it is a vital parameter in industries. To explore the stability of formed nanocomposite, recycling experiments were executed by reducing RhB, MR, and 4-NP under  $\text{NaBH}_4$ . After each cycle, the catalyst was recovered through centrifugation and washed and oven-dried for the next cycle. Thus, the recovery and recycling experiments were implemented for 5 cycles. As shown in Fig. 11, little loss in the catalytic activity was detected up to five cycles, which implies the high stability of formed nanocomposite during the reduction process.

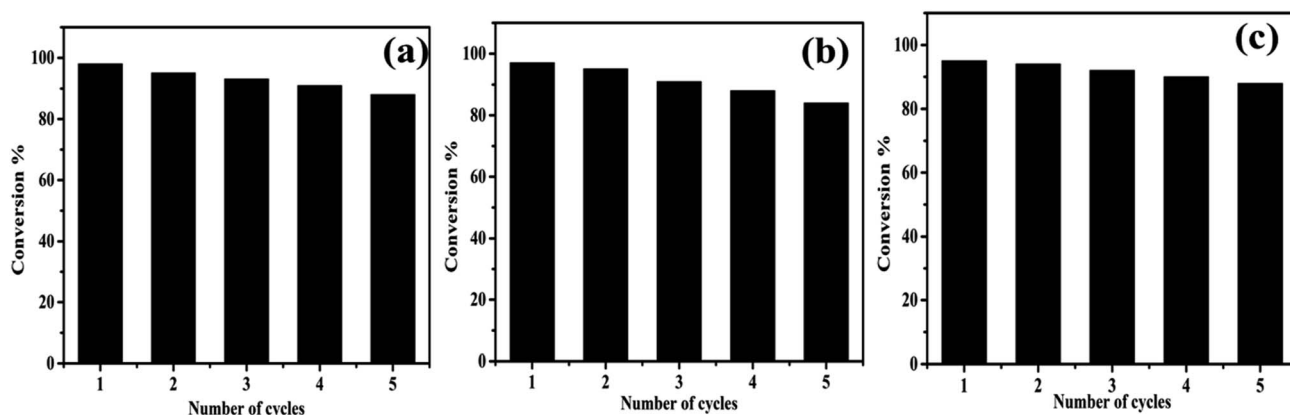


Fig. 11 Reusability of formed AgNPs/NCDs nanocomposite towards the reduction of (a) RhB, (b) MR and (c) 4-NP dyes.



## 4. Conclusion

In summary, we have prepared AgNPs/NCDs nanocomposite by a microwave irradiation method. Characterization results revealed that the formed nanocomposite showed SPR absorption band at 420 nm, it corresponds to the AgNPs, and further HRTEM results confirmed the nanocomposite formation, due to the existence of lattice fringes of both materials. After storage for two months, the formed nanocomposite was not shown in any deposition in the bottom of the test-tube. The catalytic activity of formed nanocomposite was studied by a reduction reaction of various pollutants like RhB, MR and 4-NP under NaBH<sub>4</sub>. These pollutants' reduction reactions followed the pseudo-first-order kinetics, with rate constants 0.0296 s<sup>-1</sup>, 0.0233 s<sup>-1</sup> and 0.029 s<sup>-1</sup>, respectively. Further, the nanocomposite showed good recycling ability for five cycles with only little loss in catalytic activity. Therefore, these AgNPs/NCDs nanocomposites will show promising environmental safety and the treatment of several industrial effluents.

## Author contributions

B. R. G. helps in preparing material, characterized them by different characterization techniques and writing the manuscript. R. D., R. B. and K. S. helps in investigation, methodology, data curation and analytic characterization. K. D. and G. M. K. contributed in the characterization of the obtained materials and discussed the results. Furthermore, B. R. G. and A. E. S. designed the research, contributed to supervising the work, discussed the results and wrote the manuscript. All the authors participated in writing, editing and revising the manuscript.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could appear to influence the work reported in this paper.

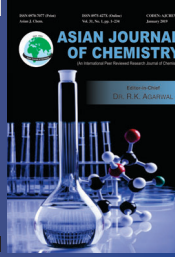
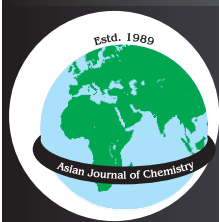
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## Microwave Assisted Synthesis and Optical Properties of Highly Fluorescent N-Doped Carbon Dots

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Herein, a rapid microwave assisted solid state method is reported for the synthesis of highly fluorescent N-doped carbon dots (NCDs) using citric acid as carbon source and guanidine hydrochloride as N-dopant. Synthetic parameters such as microwave power, irradiation time and reactants ratio were optimized to produce high quality N-doped carbon dots. The N-doped carbon dots were well characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), SEM-EDS, FTIR, UV-visible and fluorescence spectroscopies. N-Doped carbon dots exhibited bright emission with a quantum yield of 11 %. Detailed study of their optical properties revealed their excellent property of resistance to photo bleaching, high ionic strength and solution pH. Further they exhibited excitation dependent emission behaviour, high aqueous solubility and a long shelf life of 60 days. This strong fluorescence emission combined with high stability make N-doped carbon dots a promising fluorescent probe for wide range of applications.

**Keywords:** N-Doping, Carbon dots, Citric acid, Guanidine hydrochloride, Fluorescence.

### INTRODUCTION

Luminescent carbon dots (CDs) serendipitously discovered in the year 2004, have grabbed the attention of many research groups with their spectacular properties [1]. They are fool proof and robust materials with unique, versatile and novel properties such as chemical inertness, superior stability against photo bleaching, biocompatibility and low cytotoxicity which made them find wide applicability in various fields [2,3]. They are best known for their strong and stable fluorescence ability. These are the nanoparticles of carbon and considered as raising star of the carbon nanomaterials family with sub 10 nm of diameter. Since their first discovery, several researchers came up with a wide variety of approaches ranging from laser ablation, arc discharge, thermal and electrochemical treatments to ultrasonication, hydrothermal and microwave treatments for the production of carbon dots (CDs) [4-6]. Furthermore, application of CDs to numerous areas including biomedicine, biomedicine delivery, sensing, catalysis and optoelectronic conversion were also widely explored [7-9]. Carbon dots (CDs) can be viewed

as promising alternatives to traditional fluorescent substances with their superior features of good water dispersibility, non-toxic nature, and high tolerance to photo bleaching [10].

Although considerable progress has been made towards the production and usage of CDs to diversified fields, much more research needs to be focused on synthesizing CDs in ways of overcoming the major drawbacks like poor fluorescence quantum yields [7,11]. Doping of heteroatoms particularly N and S into the carbon core is considered to be promising in this regard. Currently, researchers are making several attempts in developing novel strategies for the production of improved CDs with doping [11]. In most of the studies, hydrothermal treatment is successfully applied for CDs production by employing many natural resources, waste materials and various organic small molecules [12]. However, hydrothermal treatments generally require long reaction times. Recently, usage of microwave radiation for the synthesis of carbon dots (CDs) have gained much attention and diverse starting materials including small organic molecules like hydrocarbons, acids, esters and natural resources [6,13]. Microwave radiation assisted fabri-

cation offers advantages such as operational simplicity, cost effectiveness and a rapid reaction times and avoids the traditional harsh treatments like strong acids, elevated temperatures, and lengthy reaction times [14].

Here in this work, we report a simple microwave assisted production of N-doped carbon dots (NCDs) with fluorescent quantum yield as high as 11 %. Citric acid is used as carbon source and guanidine hydrochloride as dopant and various synthetic conditions like microwave power, irradiation time and mole ratio of reactants are optimized. The as-fabricated NCDs were systematically characterized by various analytical techniques and their optical properties are studied.

## EXPERIMENTAL

Citric acid and guanidine hydrochloride were procured from S.D. Fine Chemicals Ltd. Mumbai, India. All the chemicals and reagents used in the present study are of analytical grade and used without further purification. Double distilled water was used throughout the study.

**Synthesis of N-doped carbon dots (NCDs):** Appropriate amounts of citric acid and guanidine hydrochloride (mole ratio of 1:2) were placed in an agate mortar and grounded into a uniform powder. Then the mixture was taken in a glass vial, placed in a domestic microwave oven and heated at 500 W for 5 min followed by the addition of 10 mL of double distilled water to obtained a char like material. The obtained brown coloured solution containing N-doped carbon dots (NCDs) is then centrifuged and filtered to remove large particles. Unreacted reactant molecules and other small molecules were removed by dialysis (MWCO 3500Da).

Fluorescence spectral measurements were carried out using a JASCO spectrofluorometer (FP-8500) set with excitation and emission slit widths at 2.5 nm. UV-visible spectral studies were conducted on Shimadzu UV-VIS-NIR 3600 spectrophotometer. Transmission electron microscopy (TEM) images were acquired on a JEOL 3010 microscope operating at 200 kV by drop casting an appropriate dilution of NCDs aqueous solution onto the carbon-coated copper grids. Fourier Transform Infrared (FT-IR) spectrum was recorded on Shimadzu IR Prestige-21 spectrophotometer. X-ray diffraction (XRD) patterns of NCDs were obtained using an X'pert Pro powder X-ray diffractometer (Netherlands) with Cu K $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ .

**Quantum yield calculation:** Quantum yield (QY) of N-doped carbon dots (NCDs) was determined by comparing the integrated fluorescence intensities and absorbance values

with those of reference compound (quinine sulfate). Quinine sulfate ( $\Phi = 0.54$ ) was dissolved in 0.1M H<sub>2</sub>SO<sub>4</sub> ( $\eta = 1.33$ ) and the NCDs were present in double distilled water ( $\eta = 1.33$ ). To avoid inner filter effect, absorbance values were kept less than 0.1. Finally, quantum yields were calculated by employing the following equation:

$$\Phi = \Phi_R \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

where  $\Phi$  is the quantum yield, I is the recorded integrated emission intensity, A is the absorbance at excitation wavelength, and  $\eta$  is the refractive index. The subscript R denotes reference compound (quinine sulfate).

## RESULTS AND DISCUSSION

**Synthesis of N-doped carbon dots (NCDs):** In this work, a simple, green, microwave assisted solid state synthesis of N-doped carbon dots is reported. Citric acid is used as carbon source and guanidine hydrochloride as dopant. Synthetic conditions such as microwave power, heating time and reactants ratio were optimized by taking quantum yield of the produced N-doped carbon dots (NCDs) as a parameter. Firstly, mole ratio of reactants was optimized by keeping the microwave power at 500 W and heating time at 5 min. As shown in Fig. 1a, the mole ratio of 1:2 (citric acid to guanidine hydrochloride) resulted NCDs with high quantum yield.

Similarly, microwave power was also optimized by keeping other conditions constant. As shown in Fig. 1b with increase in the microwave power from 180 to 500 W, the quantum yield also increased. However, further increase in microwave power resulted in a drastic decrease in the quantum yield and water insoluble char like product was obtained at a microwave power above 900 W. Furthermore, microwave irradiation time was optimized by keeping other parameters constant. Increase in the irradiation time from 1 min to 5 min resulted in a clear increase in the quantum yield and reached the maximum value (Fig. 1c). However, at higher irradiation time, NCDs with relatively low quantum yield were obtained. This can be ascribed to the fact that increased reaction times will lead to the over carbonization of the formed carbon dots which in turn would lead to the decrease in the quantum yield [15]. Thus, the optimized synthetic conditions are 1:2 mole ratio of citric acid and guanidine hydrochloride, microwave power of 500 W and irradiation time of 5 min.

**TEM analysis:** The structure, morphological features and size distribution of NCDs obtained under optimal synthetic

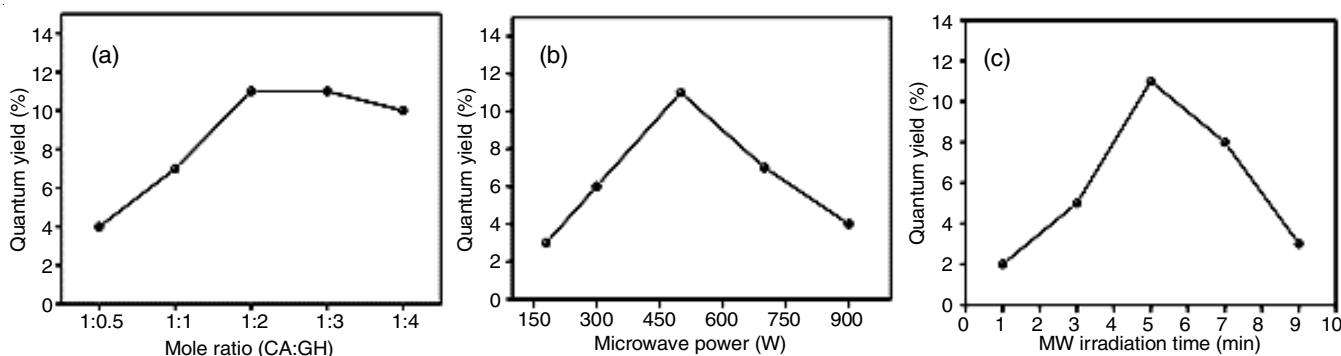


Fig. 1. Optimization of synthetic conditions: QY as a function of (a) mole ratio (b) microwave power and (c) microwave irradiation time

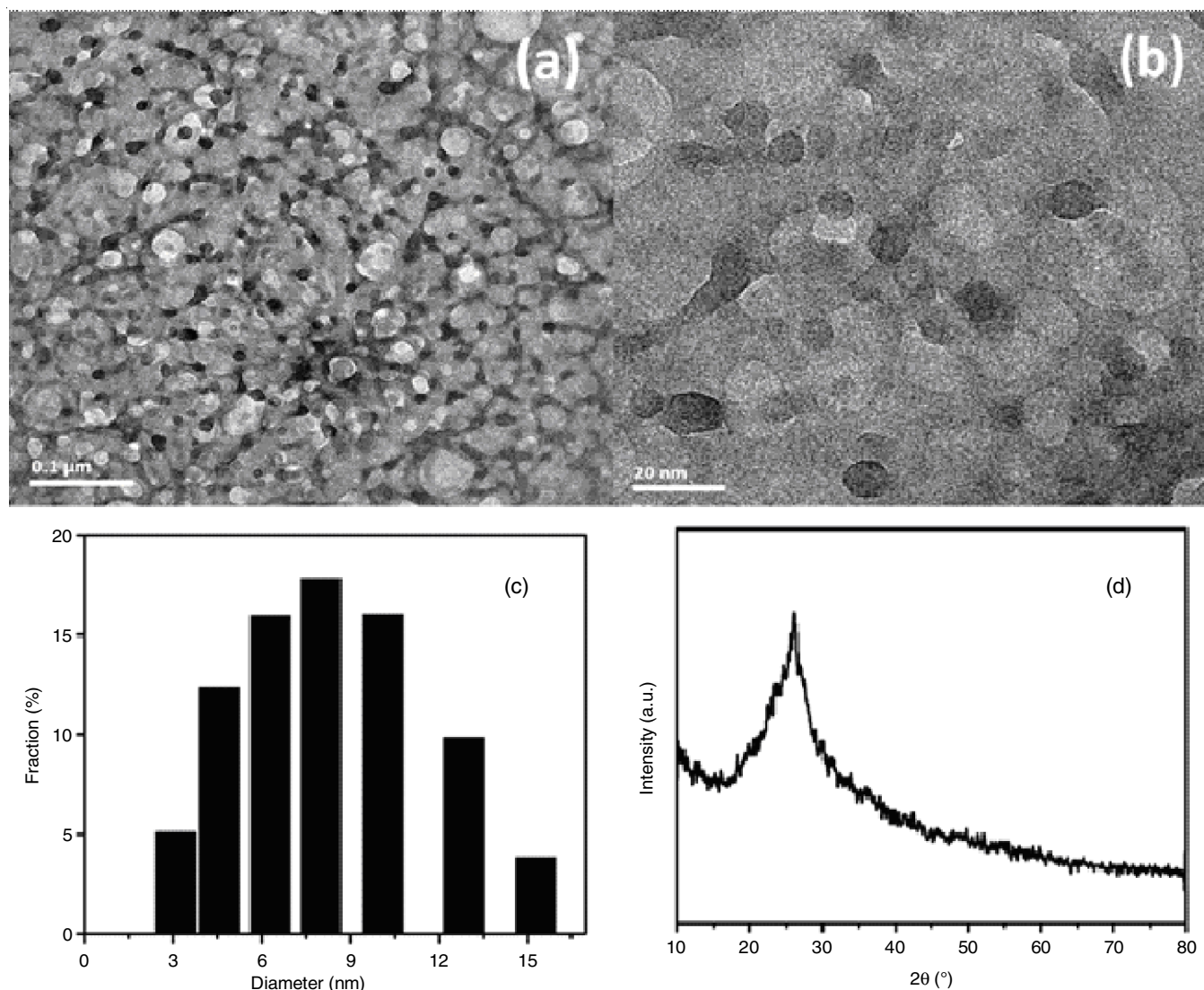


Fig. 2. TEM images of NCDs (a) low magnification (b) high magnification and (c) corresponding particle size distribution (d) powder XRD pattern of NCDs

conditions were studied by using TEM analysis. TEM image shown in the Fig. 2a clearly revealed the spherical morphology of NCDs and the particles were well separated from each other without undergoing any agglomeration.

Corresponding size distribution histogram is shown in Fig. 2b suggested the size of NCDs ranging from 3 to 15 nm with an average diameter of 8 nm. Powder XRD patterns of NCDs (Fig. 2c) exhibited a single broad peak centred at  $2\theta = 26.2^\circ$  indexed to the (002) lattice spacing of graphitic carbon indicating the graphite like structure of NCDs [15]. The interlayer spacing  $d$  (0.37 nm) is larger than that of graphite (0.34 nm) suggesting the incomplete graphitization or amorphous nature and can be attributed to the existence of polar functional groups on the surface [16].

**SEM-EDS analysis:** The chemical composition of NCDs is evaluated by using SEM-EDS analysis. As shown in Fig. 3, the NCDs are composed of carbon (56.57 %), nitrogen (14.55 %) and oxygen (28.88 %).

**FTIR analysis:** In the FTIR spectrum (Fig. 4), the broad vibration band in the range of  $3500\text{--}3200\text{ cm}^{-1}$  can be ascribed to the characteristic -OH and -NH stretching vibrations. The

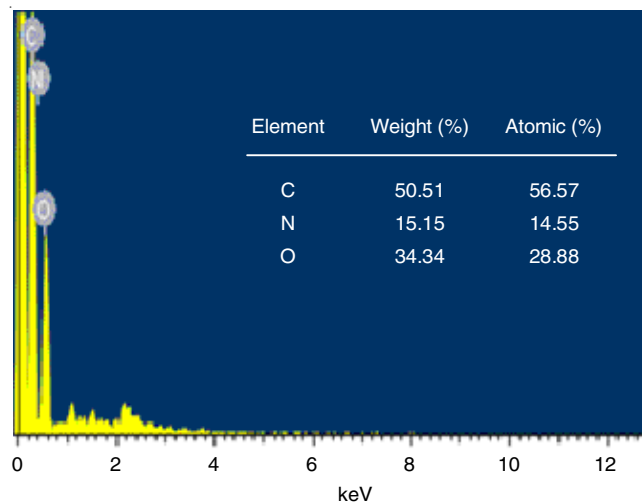


Fig. 3. SEM-EDS analysis of N-doped carbon dots

peak at  $1643\text{ cm}^{-1}$  represents the carbonyl stretching, while the peaks in the range of  $1600\text{--}1400\text{ cm}^{-1}$  can be assigned to C=C stretching vibrations of polycyclic aromatic hydrocarbons

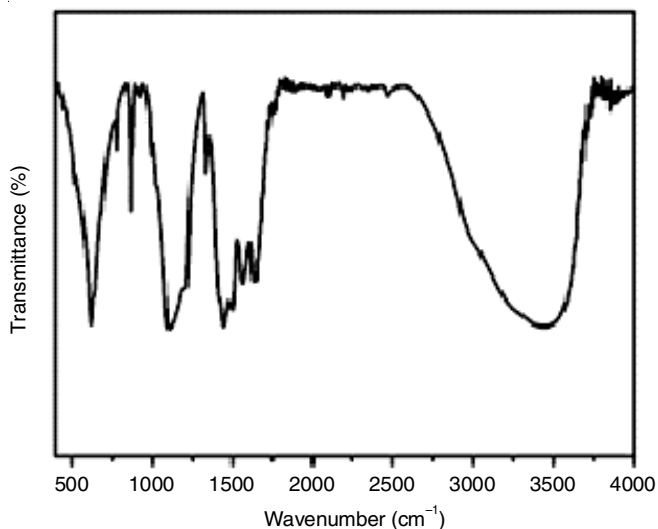


Fig. 4. FT-IR spectra of N-doped carbon dots

indicating the presence of  $sp^2$  hybridization. Further, the peaks at 1211 and 1100  $\text{cm}^{-1}$  can be ascribed to the stretching and bending vibrations of C-O bonds in carboxyl groups. These results manifest that the NCDs comprise multiple functional groups like -OH, -COOH and NH on their surface which makes them highly soluble in water. Further, these functional groups can act as linkers for the attachment of biomolecules to serve NCDs as nano-carriers [17].

**Optical properties:** UV-visible and fluorescence spectroscopic techniques were employed to study the optical properties of NCDs. Under day light, aqueous solution of NCDs appeared transparent and pale yellow coloured whereas the same solution exhibited bright blue emission under 360 nm UV lamp (Fig. 5). The absorption spectra and emission spectra of NCDs aqueous solution at ambient conditions is presented in Fig. 5. In the absorption spectra, two poorly resolved bands can be observed at around 290 and 370 nm. These bands might be aroused from the  $\pi-\pi^*$  transition of carbogenic core and  $n-\pi^*$  transition of heteroatomic surface functionalities, respectively [10]. The emission spectra of NCDs presented a strong peak

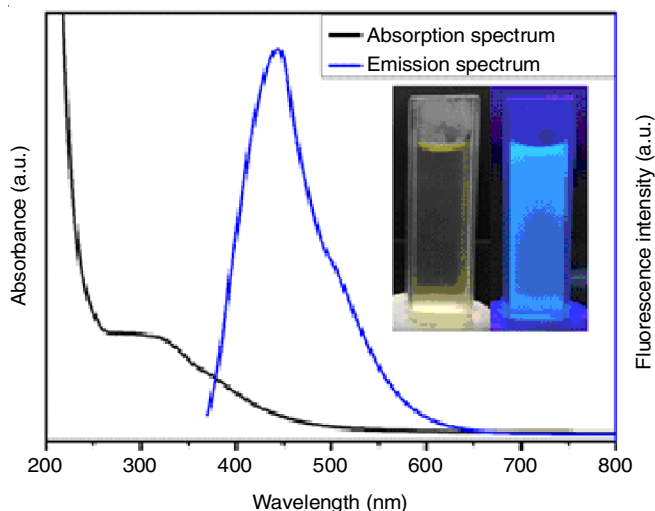


Fig. 5. Absorption and fluorescence emission spectra of NCDs, inset: photographs of NCDs aqueous solution exposed to day light (left) and 360 nm UV light (right)

centred at 445 nm ( $\lambda_{\text{ex}} = 360$  nm) with a stoke shift of 85 nm and full width at half maximum (FWHM) of 90 nm. These observations are well in accordance with the previous reports.

**Fluorescence spectra:** The emission spectra of NCDs was recorded at various excitation wavelengths. As shown in Fig. 6, the emission intensity increased with increase in the excitation wavelength from 300 to 360 nm. However, further increase in the excitation wavelength resulted in a clear decrease in the emission intensity. Furthermore, with increase in the excitation wavelength from 300 to 480 nm a clear red shift in the emission peak position from 437 nm to 535 nm was observed. These results suggest that the CDs do not obey Kasha's rule which suggest that the emission peak position of a fluorophore will not depend on the excitation wavelength. This kind of excitation dependent emission nature is considered as the characteristic feature of CDs and makes them as fluorescent probe for multi-colour imaging [18]. The origin of this excitation dependent nature is either due to the optical selection of differently sized nanoparticles (quantum effect) and/or different emissive traps on their surface or some other mechanism altogether, is presently unresolved and a matter of debate among the scientific community [1]. Quantum yield of NCDs determined by using quinine sulphate as reference compound is found to be 11 %, which is higher than several previous reports [19-21]. The reason for this higher quantum yield can be attributed to the doping with nitrogen element [22].

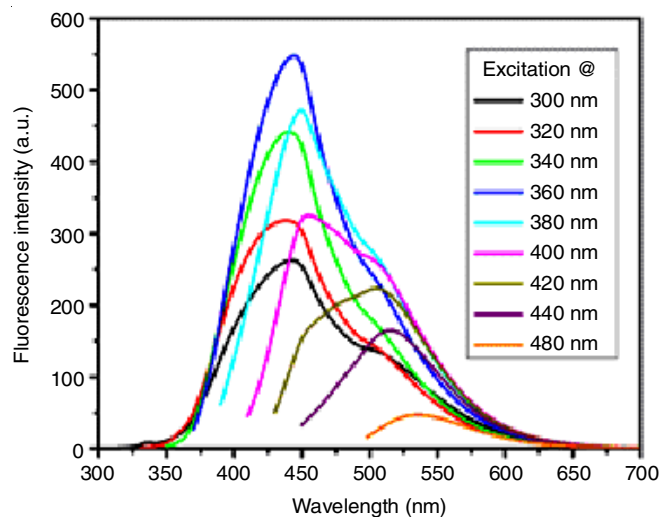


Fig. 6. Emission spectra of NCDs at different excitation wavelengths

**Fluorescence stability:** It is well known that the emission intensity of many fluorescent probes will be disrupted by complex environmental conditions. Hence to test the ability of NCDs to be used as a fluorescent probe for various practical applications, their fluorescence stability was tested under diverse conditions. Firstly, we have examined the effect of ionic strength by recording the emission spectra of NCDs at various KCl concentrations. As shown in Fig. 7a, only a slight decrease in the emission intensity appeared even at a high KCl concentration of 2M. This verifies the tolerance of NCDs to high ionic conditions and further extends their applicability to similar ion rich biological environments [23]. As shown in Fig. 7, solution pH has some significant effect on the emission intensity

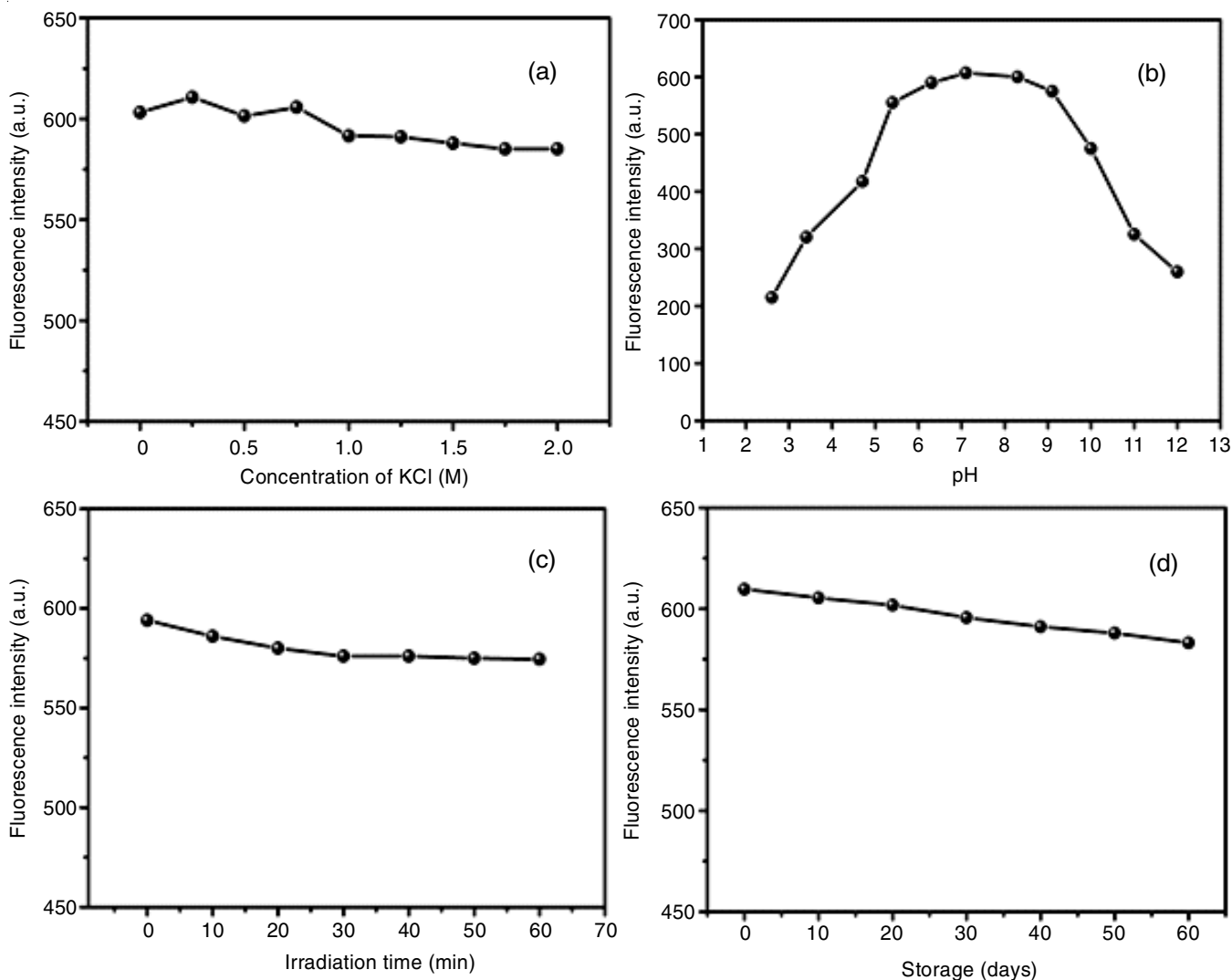


Fig. 7. Effect of (a) concentration of KCl (b) solution pH (c) UV light exposure time and (d) storage on the fluorescence intensity of NCDs ( $\lambda_{em} = 445$  nm and  $\lambda_{ex} = 360$  nm)

but fortunately the emission intensity was high and remained almost constant in the pH range of 5 to 9 which is the common pH range of many environmental and biological samples.

Strong acidic and basic conditions cause some severe protonation and deprotonations on the surface of NCDs which might lead to the aggregation of nanoparticles and result in decreased fluorescence emission [24]. Photostability or resistance to photo-bleaching is an important characteristic for a fluorophore to be used in various applications ranging from imaging to optoelectronics. Photostability studies were performed by continuously irradiating the aqueous solution of NCDs under 360 nm UV lamp for 1 h. No significant decrease in the emission intensity was observed even after 1 h of exposure (Fig. 7c), indicating the superior photo stability of NCDs. Furthermore, the shelf life of NCDs aqueous solution was evaluated by storing it under ambient conditions. Again, no substantial decrease in the emission intensity was observed even after storing for 60 days and the solution remained clear, implying the great stability and long shelf life of NCDs (Fig. 7d). All these results suggested that the produced NCDs are highly stable and can serve as excellent candidates for diverse applications.

## Conclusion

To summarize, we have successfully demonstrated a simple microwave assisted method for the production of N-doped carbon dots with quantum yield as high as 11 %. The synthesized NCDs contain various polar surface functionalities which impart favourable aqueous solubility. N-doped carbon dots (NCDs) displayed excitation dependent emission behaviour which is crucial in multicolour imaging. Further, NCDs exhibited strong fluorescence emission which is stable to various environmental conditions such as high ionic strength, solution pH and continuous irradiation. Furthermore, they showed long shelf life of 60 days. All these properties make NCDs an excellent fluorescent probe for wide variety of applications ranging from bioimaging and chemical sensing to optoelectronic devices.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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