



## NITROGEN DOPED CARBON DOTS A NOVEL NANOMATERIAL FOR SENSING TOXIC HEAVY METAL $Hg^{2+}$

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**ABSTRACT** This paper provides a general overview of green synthesis of self heteroatom doped N-carbon dots (N-CDs) from biomass derived pumpkin seeds with an energy gap of 2.35 eV and a quantum efficiency of 65.5%. Besides that, they possess graphitic carbon structure with spontaneous heteroatom doping of various metal ions and a size distribution of 5-8 nm and an interplanar distance of 0.334 nm, with an excellent electrochemical property. This work focused on the usage of these N-CDs in the detection of the heavy metal ions such as  $Hg^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ , and  $Mg^{2+}$  and the results have demonstrated a better detection limit of the heavy metal  $Hg^{2+}$  ions among other tested metal ions, owing to its excellent selective and sensitive property of fluorescence quenching analysis, resulted in the creation of non-fluorescent centres, effective charge transfer and overall energy transfer, within a minimum detection threshold limit of 20 nM.

**KEYWORDS** : Nitrogen Doped Carbon Dots, Pumpkin seeds, urea, mercury ion.

### 1 INTRODUCTION

Carbon dots, also known as CDs, are a significant component of carbon-based nanomaterial that ranges its size from 1 to 10 nm. They were initially identified in 2004 as quantum dots, and they were recently awarded the Noble Prize 2023 for their discovery and fabrication. The preparation mainly involves the process of pyrolysis, of carbon based biotic and abiotic components, resulted in the breakdown, dehydrolysis and carbonisation of the precursor content thereby, undergo significant changes in their physical and chemical properties, with a high quantum yield and a regulated emission wavelength [1–10]. These carbon dots have exposed the novel areas of usage due to their effective stability towards light, lower cytotoxicity risk, superior host compatibility, ease of surface modification, and inert chemical behaviour in the creation of fluorescent sensors, energy reservoirs, active cell imaging, in vivo research, photocatalytic degradation, and colored (LEDs) [11–21].

The Current work is regarding the green synthesised blue emitting doped with primarily nitrogen, and spontaneous trace elements such as phosphorus, sulfur, zinc, potassium, and magnesium doped CDs (N-CDs) in the size distribution of 5-8 nm with a broad absorption band lying between 250 and 550 nm and a significant fluorescence region appeared between 400-600 nm was observed. The fluorescence emission spectra showed a typical excitation-dependent behavior with an overall quantum yield of (65.50%) [22]; they have displayed the effective quenched fluorescence based sensing of  $Hg^{2+}$  metal ions. The results have demonstrated that the reaction of  $Hg^{2+}$  metal ions with the N-CDs dispersed in the phosphate buffer sol at PH-7 showed 50% fluorescence quenching within only 10 minutes of solution mixing, with a detection limit of 20 nM Therefore, self heteroatoms doped N-CQDs have been effectively utilised for examining of  $Hg^{2+}$  ions in actual water samples.

### 2 Experimental Sections:

#### 2.1 Materials and Chemicals

Pure ethanol,  $Zn(OAc)_2$ ,  $Pb(NO_3)_2$ ,  $NiCl_2$ ,  $Hg(NO_3)_2$ ,  $CaCl_2$ ,  $CuCl_2$ ,  $Mg(OAc)_2$ , phosphate buffer (PH 7.0) iodide solution purchased from local market.

#### 2.2 Methodology and Synthesis

The synthesis of spontaneous heteroatom doped N-carbon dots was recently reported by our team Abdullah et al. [22], utilising urea as a nitrogen source for surface passivation and pumpkin seeds as the carbon source at a weight percent ratio of 1:1. A dark, solid residue was seen when the slurry was subjected to 900 watts of microwave radiation for eight minutes. Larger, untreated particles were then eliminated from the solution by passing it through a 0.21 micron syringe filter. In the end, removing the ions and small molecules for six hours using a 10000 MWCO dialysis membrane and the pH was finally adjusted to around 5 by adding NaOH to the solution, thereafter, dried at 60 degrees for 2 days to obtain a fine powder of N-CDTs.

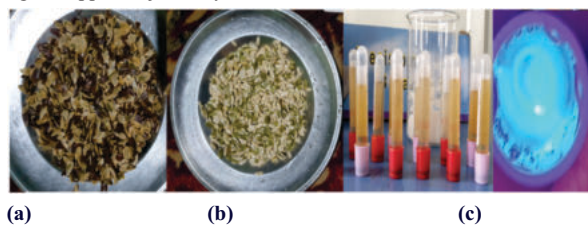
#### 2.3 Preparing different concentrations of N-CDs and metal ion solutions

1 mL of phosphate buffer (0.05M) was immersed in 10  $\mu$ L of diluted photoluminescent heteroatom doped N-CDs solution and 0.005, 0.010, 0.020, 0.030 and 0.050  $\mu$ Moles of  $Hg^{2+}$  were pipetted into a 2 mL vial simultaneously. The mixture was then diluted to 250  $\mu$ L with water and thoroughly mixed. In the same way, the other metal ion buffer solutions were produced with optimal concentration of (0.020  $\mu$ M) with these N-CDs. Similarly, prepare a dispersion of  $Hg^{2+}$  ionic solution in buffer with tap water, spring water and river water after centrifuging at 5000 rpm for 10 minutes and then filtering the water samples by 0.22  $\mu$ m syringe filters.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization and properties of self-hetero atom doped N-carbon dots

The results depicted in Fig. 1(a) demonstrate the first use of pumpkin seeds as a carbon source to produce self heteroatom doped N-carbon dots, and the use of "urea" as a nitrogen supply to modify their surface states or passivate their edges. Once the microwave irradiation process is completed, Fig. 1(b) and (c) provide a clear image of N-CDs. In the presence of sunlight, the solution appears light brown, and under UV light, it appeared just as cyan color.



**Figure 1: (a) Pumpkin seed precursor (b) Carbon dots under visible light (c) Carbon dots under UV light.**

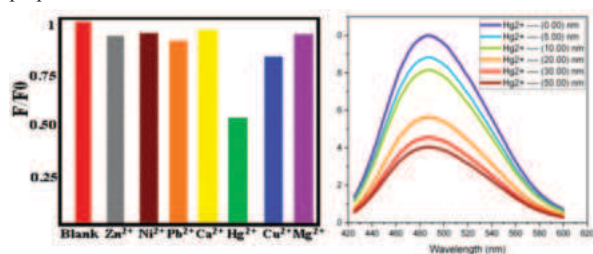
The as-prepared N-CDs' morphology, size distribution, elemental analysis, and optical characteristics were previously reported by our team Abdullah et al. via Springer Publishing Company [22]. The X-ray diffraction pattern clearly displayed a large peak at  $20^{\circ}$ – $40^{\circ}$ , which also suggested the creation of microscopic nanoparticles. These findings also demonstrated that the N-CDs have a consistent size distribution, with an average size of 5-8 nm. The largest peak at  $24^{\circ}$  validated the (002) lattice planning and showed a graphitic-like core structure with an interplanar spacing of 0.334 nm. Moreover, the FTIR spectroscopy revealed the different surface functional entities, such as O-H, N-H, and COO-/amide II, which has activated the surface of these N-CDs with oxygen-reactive species and were highly useful from an application standpoint.

Furthermore, broad absorption and emission zone with wavelength range of 254-550 nm and 400-600 nm was seen in the optical characteristics, with absorption peaks at 324 nm and emission peak at 462 nm associated with the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition in the N-doped CDs. These synthetic N-CDs have low direct bandgap energy of about 2.35 eV, or 527 nm. The overall quantum efficiency of the created N-

CDs was around 65.50%, in accordance with the reference standard quinine sulphate dispersed in 0.1 mole of  $H_2SO_4$ .

### 3.2 Detection of $Hg^{2+}$ ions

Testing the fluorescence quenching effectiveness in the presence of various ambient toxic metal ions, such as  $Hg^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ , and  $Mg^{2+}$  allowed us to examine the N-CDs' selectivity towards  $Hg^{2+}$ . Fig. 2(a) demonstrated that under the identical circumstances, these representatives (metal ions) caused variations in their relative PL intensity (F/F<sub>0</sub>) of these CNDs and the maximum photoluminescent quenching was caused by  $Hg^{2+}$  metal ion. After that, the addition of more  $Hg^{2+}$  concentration to the buffer solution showed a much reduced PL quenching. These findings suggested that the N-CDs have a strong affinity for  $Hg^{2+}$  detection. This is because,  $Hg^{2+}$  has a greater affinity for the carboxylic and amide groups on the surface of N-CDs, and caused the exceptional selectivity and specificity towards  $Hg^{2+}$  metal ion specimen rather than any other metal ion demonstrated above. As a result, the interaction between N-CDs and  $Hg^{2+}$  ions induced by these functional groups, resulted in the fluorescence quenching of the as prepared N-CDs nanomaterial.



(a) Figure showing max selectivity of  $Hg^{2+}$  by N-CDs among various metal ions (b) PL spectra of N-CDs showing sensitivity of  $Hg^{2+}$  at different concentrations (from top to bottom: 0.00, 0.005, 0.01, 0.020, 0.030 and 0.050  $\mu M$ ).

The photoluminescence spectra at various  $Hg^{2+}$  concentrations allowed us to further investigate the system's sensitivity and the findings demonstrated that concentration of  $Hg^{2+}$  affected the PL spectra's intensity as illustrated in Fig. 2(b). The detection limit comes out to be 20-30 nM, which is less than the highest amount of mercury in drinking water allowed by the International World Health Organisation (6 ppb, 30 nM). Furthermore the quenching rate with concentration of  $Hg^{2+}$  and N-CDs demonstrated that at higher concentrations of  $Hg^{2+}$  the sensing performance is more reliable and accurate and can be seen in Fig. (3). However, 98% PL was recovered by adding the iodide to the buffer solution resulting in the formation of mercurous iodide, which then removed the  $Hg^{2+}$  from the N-CDs surface and hence PL intensity was recovered back.

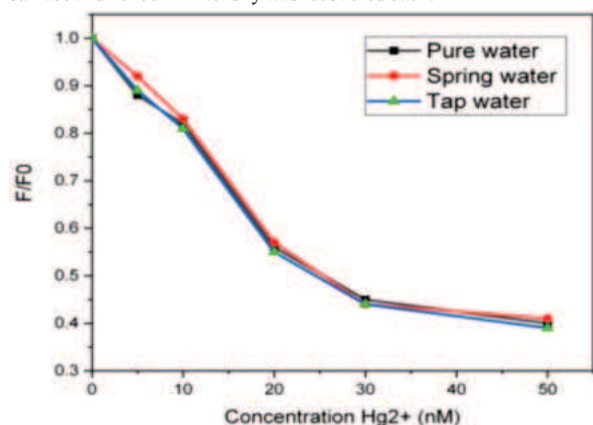


Figure 3: Photoluminescent quenching rate of N-CDs in DI, spring and tap water against concentration of  $Hg^{2+}$ .

Spring water and tap water from the nearby city of Kulgam in India were tested to see how well this FL sensing system worked with actual water samples. Here 5, 10, 20, 30 and 50 nM's of  $Hg^{2+}$  were added to these two water samples, and the findings showed almost 98% identical results to that of the buffered pure water dispersion samples illustrated in Fig. (3). Thus, N-CDs offer enormous potential for environmental pollution monitoring.

## 4 CONCLUSIONS

Here we have explored Heteroatom doped N-carbon dots derived from pumpkin seeds with a high fluorescence quantum yield of 65.50% and an energy gap of 2.35 eV. Furthermore, we have utilized these N-CDs for the sensitive and selective detection of the  $Hg^{2+}$  metal ions among various tested metal ions and the LOD comes out to be 20-30 nM's which is a limit of standard water purity and can be efficiently used in day today water quality checks.

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## Declaration of interests

There are no conflicts of interest to declare by the authors.

## Data availability:

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

## Supplementary information:

Not applicable.

## Ethical approval:

Not applicable.

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