



# Rapid Analysis of Trace Sulphite Ion Using Fluorescent Carbon Dots Produced from Single Use Plastic Cups

Manisha Kumari,<sup>1</sup> Ganga Ram Chaudhary,<sup>1</sup> Savita Chaudhary<sup>1,\*</sup> and Ahmad Umar<sup>2,3,\*</sup>

## Abstract

The recycling of waste plastic into useful advanced nanomaterials has played a lucrative impact on our ecosystem. The present work represents the reliable means to transmute plastic waste into highly luminescent carbon dots (CDs) having a quantum yield of 59%. The formed particles have possessed a strong fluorescence emission peak at 660 nm and an absorption peak at 270 nm. The developed particles were found to be highly stable towards variability in the reaction medium. Furthermore, various characterization techniques were accomplished to scrutinize the physical and chemical properties of obtained CDs. The strong optical and emission characteristics with a high surface-to-volume ratio of CDs have been explored in developing a highly efficient “turn-off” fluorescence sensor for sulphite anion in aqueous media with a limit of detection of 0.34  $\mu\text{M}$  under optimal conditions. The practical utilities of developed CDs have been explored over different ranges of water sources. The outcomes of the current work endowed a simple, rapid, benign, and remunerative sensory probe for the detection of sulphite ions from wasted plastics for environmental remediation.

**Keywords:** Carbon dots; Single-use plastic; Photoluminescent; Quantum yield; Fluorescence.

Received: 05 October 2021; Revised: 25 October 2021; Accepted: 26 October 2021.

Article type: Research article.

## 1. Introduction

Anions are recognized as essential components in the development of life.<sup>[1]</sup> For instance, the existence of phosphate in the genetic blueprint of life and its significant importance in the fabrication of high-energy compounds like adenosine triphosphate (ATP) is well established in the literature.<sup>[2]</sup> Anions such as chlorides played critical roles in the extracellular environment, involving regulation of acid-base fluid balance, acting as a counter ion for sodium and potassium ions.<sup>[3,4]</sup> The use of chlorides in ion channeling for pH equilibrium in gastric secretions has also been extensively researched in the literature.<sup>[5,6]</sup>

Beyond human psychological limits, the large number of anions prevailed on the earth's crust and in aquatic environments and possessed a vital role in the nourishment and perseverance of various life forms.<sup>[7,8]</sup> The imbalance in

the composition of anions either inside the human body or in environmental ambiance has produced an alarming impact on living flora and fauna.<sup>[6,9]</sup> Therefore the sensing of anions has been one of the most studied subject matter in recent times.<sup>[10,11]</sup> Out of the diverse range of anions, sulphite anions hold a particular interest among researchers.<sup>[12,13]</sup> Sulphite anions have been involved in various industrial, environmental, and biological processes.<sup>[14-16]</sup>

Sulphite ions are extensively utilized as a preservative, bleaching agent, and reducing agent in various food industrial processes.<sup>[17,18]</sup> Sulphite functions as an inhibitor and antioxidant in food and microbial activities.<sup>[19]</sup> Water, dried vegetables, fruits, vinegar, wine, and coconut water has also contained a certain amount of sulphite ions.<sup>[12]</sup> According to the US Food and Drug Administration (FDA) agency, the safe level of sulphite content in food is 10 mg/kg. Whereas, in liquid food, the sulphite content should not be more than 10 mg L<sup>-1</sup>.<sup>[20]</sup> The National Health Surveillance Agency (ANVISA) in Brazil reported that the safety level of sulphite in distinct foods such as coconut water, vinegar, and shredded coconut should be less than 200 mg L<sup>-1</sup> and the safer limit in pickles is found to be 100 mg L<sup>-1</sup>.<sup>[12]</sup> The existence of higher concentrations of sulphite ions would have detrimental effects on human health.<sup>[21]</sup> Therefore, the detection of sulphite is crucial for the safety of living flora and fauna. So

<sup>1</sup> Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh 160014, India.

<sup>2</sup> Department of Chemistry, Faculty of Science and Arts, Najran University, Najran-11001, Kingdom of Saudi Arabia.

<sup>3</sup> Promising Centre for Sensors and Electronic Devices (PCSED), Najran University, Najran-11001, Kingdom of Saudi Arabia.

\*Email: [schaudhary@pu.ac.in](mailto:schaudhary@pu.ac.in) (Dr. S. Chaudhary);

[ahmadumar786@gmail.com](mailto:ahmadumar786@gmail.com) (A. Umar)

far, various kinds of methodologies such as ion chromatography, chemiluminescence, UV-visible, electrochemical and spectrophotometric methods have been utilized for detecting sulphite ions.<sup>[22-25]</sup>

However, the expensive nature, time-consuming applications, and costly instrumentation have restricted their widespread applications.<sup>[26]</sup> Compared to various available methods, fluorescence-based sensing is one of the attractive means to detect the trace amount of sulphite in aqueous media. The ease of operation with low-cost, rapid, and quantitative characteristics of fluorescence-based methodologies has further supported their application in sulphite ion sensing.<sup>[27,28]</sup>

Up to now, a diverse range of fluorophores has been explored for developing fluorescence-based sensors.<sup>[29-31]</sup> However, the potential applications of carbon-based nanomaterials in fluorescence-based sensors are well documented in the literature.<sup>[32-35]</sup> CDs have been produced through a number of natural and synthetic resources and hold significant applications in environmental remediation.<sup>[36-39]</sup> However, the use of plastic for producing CDs was not much explored.<sup>[40-43]</sup> Plastic is one of the most broadly used non-biodegradable materials and the main contributor to landfill waste.<sup>[44]</sup> Over recent years, plastics have become an inextricable part of our society due to their thermo-stability, low production cost, minimal permeability to CO<sub>2</sub>, lightweight, transparency, and high strength with malleability.<sup>[45]</sup> As a result, a large quantity of solid plastic waste is produced every year.<sup>[46,47]</sup> The excessive consumption of non-biodegradable plastic products causes severe environmental problems in living beings. As a result, if somehow this single-used plastic waste is converted into advanced carbon-based nanoparticles then it will produce a major breakthrough in environmental remediation. Various scientific groups such as Huang *et al.* have utilized plastic waste materials for the generation of luminescent CDs.<sup>[46]</sup> Hu *et al.* have used waste polyethylene terephthalate (PET) as a carbon source for the synthesis of fluorescent CDs.<sup>[35]</sup> Nevertheless, toxic chemical treatment with tedious multistep processing has restricted the widespread utilization of these currently employed methodologies.<sup>[34]</sup> Consequently, there is an urgent requirement to explore an alternative means for economical and eco-friendly conversion of single-used waste plastic into highly fluorescent CDs.

In this perspective, the current work provides an efficient way of the complete transformation of single-use plastic cups into highly fluorescent CDs via a simple fast process. Here, in this study synthesis of CDs from single-used plastic cups has been accomplished by utilizing a one-step approach. The main objective of the chosen methodology is to diminish the cost of production, preserve natural resources, and boost the native environment. Considering the financial and ecological point of view, waste plastic has been provided as a budding precursor for the development of highly advanced CDs. The cost-effective synthetic process with the efficiency of scale-up has additionally aroused our interest in their sensing

applications. The advanced optical and fluorescence properties of CDs with great photostability further favored their usage in the field of detecting harmful toxins. The synthesized CDs were analyzed using several analytical techniques such as Fourier transform infrared resonance (FTIR) spectrophotometer FTIR, Ultraviolet (UV) absorbance spectrophotometer, Dynamic Light Scattering (DLS) instrument, X-ray powder diffraction (XRD), Fluorescence, High-Resolution Transmission Electron Microscopic (HRTEM) and Differential scanning calorimeter (DSC). Further, adjustable fluorescence properties of CDs prepared via upcycling of waste plastic cups have been explored in the analytical field for the detection of harmful sulphite anions in aqueous media. The outcomes of the current work endowed a simple, rapid, benign, and remunerative sensory probe for environmental remediation application.

## 2. Materials and Methods

### 2.1 Materials

Waste plastic cups were obtained from the trash bin of the Department of Chemistry, Panjab University, Chandigarh, India. Quinine Sulphate dye was purchased from Sigma-Aldrich with 98% purity. All the sodium anions (sulphite, acetate, bromide, carbonate, chloride, persulfate, nitrite, hydride carbonate, phosphate, hydroxide, and thiosulphate) have been purchased from Sigma-Aldrich having 99% purity. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and ethanol were taken from Fisher Scientific with 99% purity. Deionized water has been used for all experimentation purposes. All the chemicals were utilized as such without any further purification process.

### 2.2 Synthesis of CDs

The formulation of CDs was planned via transforming waste plastic into luminescent CDs through a single-step process (Scheme 1). In current work, waste plastic cups were used as a precursor constituent for the development of CDs. For the synthesis, plastic cups were placed in closed lid silica crucible and allowed to undergo thermal calcination in a muffle furnace at 350 °C for 2 h. After the completion of the reaction, the crucible was set aside to cool down at room temperature. The obtained blackish-brown-colored powder was sieved using a mesh size of 0.21 mm and further ground in electrical pestle mortar to remove the bigger-sized particles. The obtained ground powder was allowed to disperse in 300 ml of distilled water under stirring at room temperature for 24 h under optimal conditions. Afterwards, the formed solution was allowed to centrifuge at 6500 rpm for 10 minutes to separate aggregated form of particles. The obtained supernatant was collected and purified by filtering the respective solution through a 0.22 µm filter membrane. The formed suspension was heated and further, lyophilized to produce powder form at 110 °C for 1 h. A black powder was obtained from CDs-C (CDs obtained from waste plastic cups) and preserved under room temperature for further analytical techniques. The quinine sulphate dye was used as a reference material for



**Scheme 1.** Schematic illustrations showing the synthetic route of CDs from waste plastic cups.

calculating the quantum yield ( $\phi$ ) of prepared CDs-C. The standard solution of the respective dye was synthesized in 0.1M H<sub>2</sub>SO<sub>4</sub> solution. The following equation was employed for the calculation of quantum yield:

$$\phi_X = \phi_R \left( \frac{I_X}{I_R} \right) \left( \frac{\eta_X^2}{\eta_R^2} \right) \left( \frac{A_R}{A_X} \right) \quad (1)$$

where  $\phi$  refers to the quantum yield, R denotes the reference Quinine sulphate dye, X refers to the sample, I refers to the integrated emission intensity,  $\eta$  corresponds to the refraction index and A represents the obtained absorption values of the system.

### 2.3 Characterization Techniques

High-Resolution Transmission Electron Microscopic (Hitachi H7500) studies were performed to measure the morphological characteristics of CDs-C at 100 kV. LAB INDIA UV-visible

spectrophotometer was used to measure the optical of CDs-C. The fluorescence emission spectrum was obtained from a Perkin Elmer LS 55 instrument. REMI R-24 centrifuge was employed for the synthesis and ultra-centrifugation of CDs-C. The hydrodynamic radii of CDs-C were estimated using Malvern ZEN 1690 Dynamic Light Scattering instrument.

Mettler Toledo Q20 Differential Scanning Calorimetry instrument was used to optimize the temperature effect on the decomposition of CDs-C in a nitrogen gas atmosphere. Fourier transforms infrared (FTIR) spectra were determined on Perkin Elmer (RX1) FTIR spectrometer instrument. In order to investigate the crystalline size and diffraction pattern of the developed CDs-C, the respective X-ray powder diffraction (Panalytical X'Pert) method was utilized with Cu-K $\alpha$  radiation. The thermal calcination of precursor sources was performed in the AICIL muffle furnace. IKA C-MAG HS 7

stirrer was operated for the complete solubilization and magnetic stirring of the solutions of synthesized CDs-C.

### 3. Results and Discussion

#### 3.1 Surface and structural analysis

FTIR analysis has been used to determine the nature of functional groups formed over the surface of formed CDs-C (Fig. 1a). From the obtained data, the main characteristic transmission peak was observed at  $3540\text{ cm}^{-1}$ . This peak has represented the existence of -OH functional groups in CDs-C.<sup>[47]</sup> The strong peak at  $1420\text{ cm}^{-1}$  has been assigned to the stretching vibration of C-O functionalities present on the exterior surface of CDs-C. The typical peaks around  $1050\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$  existed due to C-O and C-O-C bonding in CDs-C.<sup>[48]</sup> The small peak between  $800\text{--}700\text{ cm}^{-1}$  was assigned to the C=C bending vibration. The occurrence of these functional groups over the exterior surface has further enhanced the fluorescence sensing aptitude of formed CDs-C towards harmful toxins.<sup>[49]</sup> XRD profiles (Fig. 1b) displayed the crystalline nature of synthesized CDs-C. The presence of peaks at  $2\theta = 22.1^\circ$ ,  $24.8^\circ$ ,  $29.9^\circ$ ,  $36.6^\circ$  and  $39.4^\circ$  with diffracting planes of (002), (101), (105), (006), and (111) are existed in CDs-C. Furthermore, the occurrence of small peaks

has shown that the development of synthesized CDs has prevailed in each direction. Additionally, the crystalline size was calculated using the Debye-Scherrer equation as follows and found to be 29.4 nm:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

The surface morphology of prepared CDs-C was evaluated through HRTEM analysis at different magnifications (Fig. 1c). HRTEM image has exhibited the existence of monodispersed and spherical nature of synthesized particles having a size less than 10 nm. The corresponding value of hydrodynamic diameter for CDs-C was 27.4 nm with a poly-dispersity index (PDI) value of 0.5, as represented in Fig. 1d.

#### 3.2 Optical properties of synthesized CDs-C

To optimize the absorption and emission characteristics of developed CDs-C, their UV-visible and fluorescence spectra were recorded in aqueous media. The absorption is scrutinized as the promptest phenomenon which can be accomplished within a few minutes. Consequently, it is efficiently utilized to investigate the electronic energy levels of synthesized CDs-C. The results of absorption spectra of CDs-C have displayed a shoulder peak in the wavelength range of 250-360 nm which

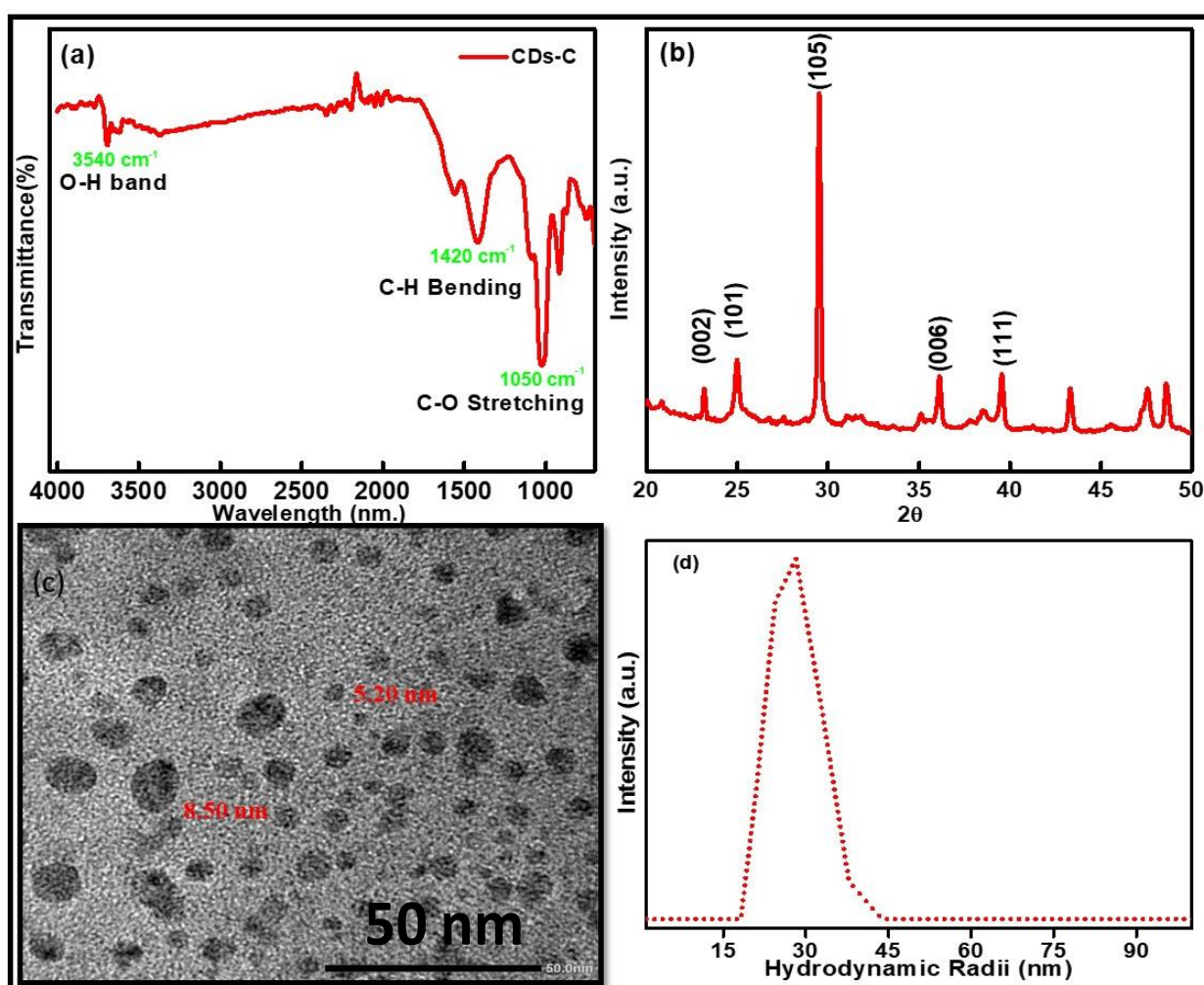
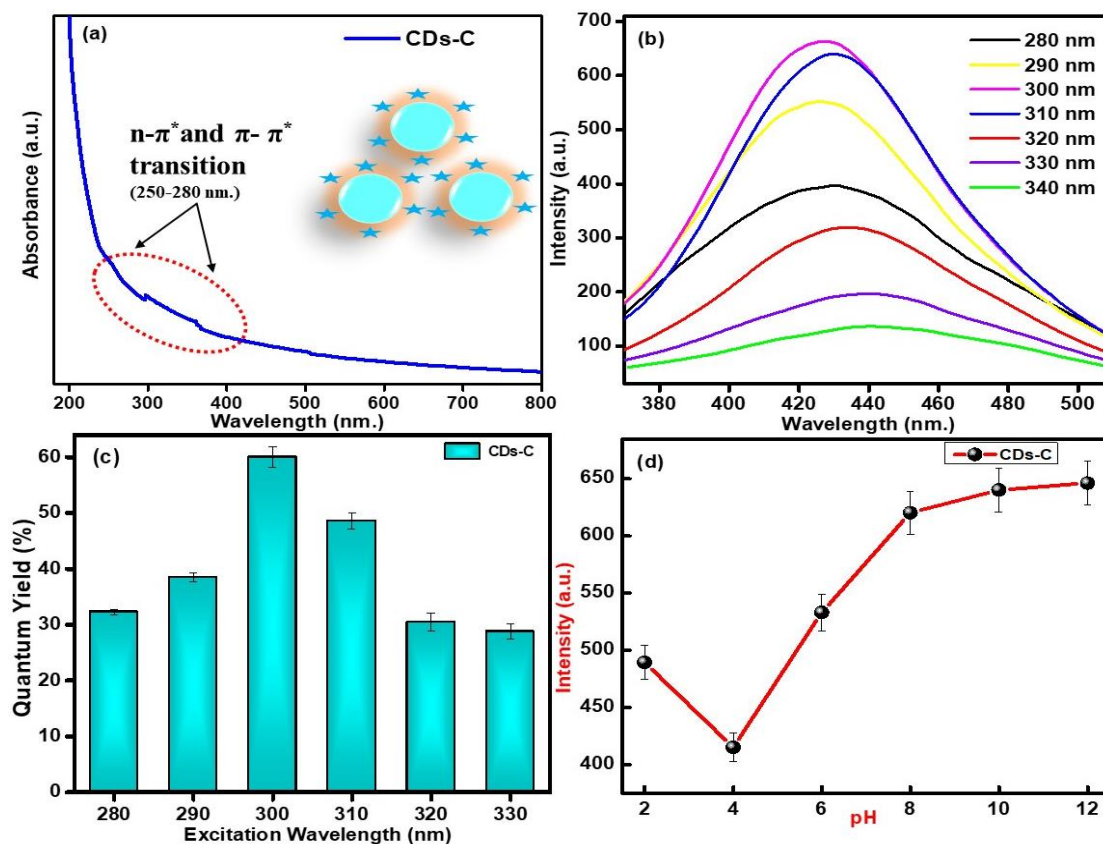


Fig. 1 (a) FTIR spectra, (b) XRD profile, (c) HRTEM image, and (d) DLS analysis spectrum of CDs-C.

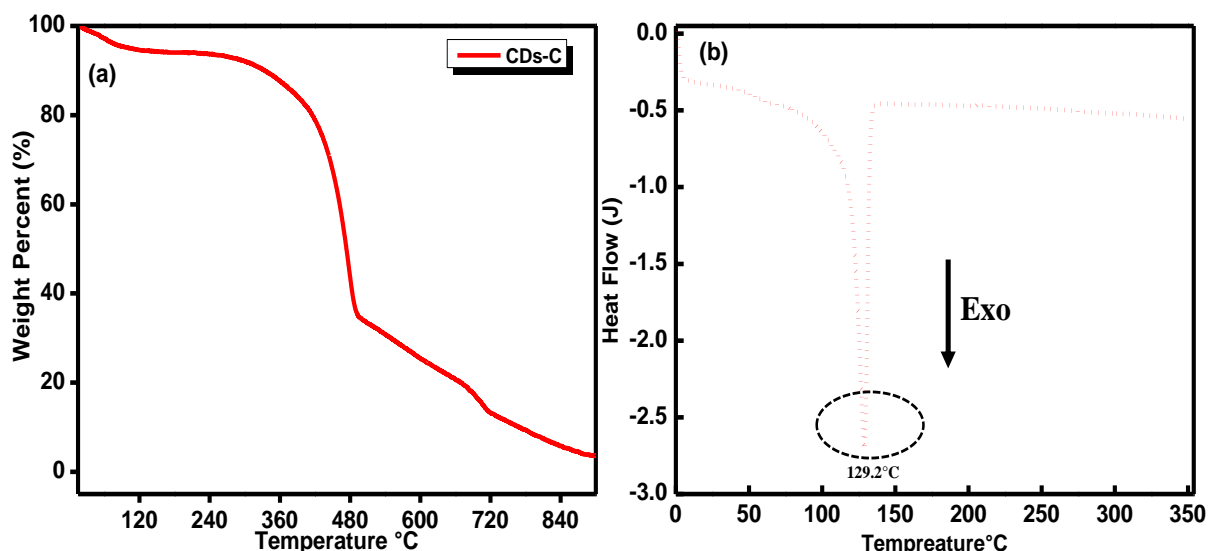
further verified the development of CDs-C (Fig. 2).<sup>[50]</sup> The respective peak represents the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition of  $-C=O$ ,  $-C-OH$ ,  $C-C$ , and  $-C=C$  bonds that exist in the  $sp^2$  hybridization of synthesized CDs-C.<sup>[51-53]</sup> These kinds of bonds appeared due to the existence of hydroxyl ( $-OH$ ) and carboxylic ( $-COOH$ ) groups on the exterior surface of CDs-C. Due to the existence of the  $n$ - $\pi^*$  transition, a significant amount of fluorescence emission characteristic was also noticed in these formed particles. Additionally, the aqueous samples of synthesized particles have reflected brownish coloration under natural visible light. However, oceanic blue color was displayed by the formed CDs-C when irradiating the particles with UV illumination at 350 nm.

Furthermore, the emission behavior of CDs-C synthesized by upcycling the waste plastic cup was investigated using fluorescence spectroscopy at different excitation wavelengths ranging from 280 nm to 340 nm (Fig. 2b). The outcomes have shown that the maximum emission was observed at 300 nm. In the emission spectrum, the fluorescence emission intensity was found to be 660 nm when excitation was given at 300 nm, which displays the well-defined photoluminescence characteristic of synthesized CDs-C. Due to this, further photoluminescence behavior was studied by using an excitation wavelength of 300 nm. The fluorescence emission properties of CDs-C have summed up to be controlled when a substantial number of particles becomes excited at a specific wavelength.<sup>[51]</sup> These types of fluorescence characteristic properties were further connected with the surface passivation

effect and quantum confinement effect in the as-synthesized CDs-C obtained from the upcycled waste plastic cup. The quantum yield ( $\phi$ ) of prepared CDs was detected to be 59% at 300 nm excitation. Moreover, the corresponding effect of excitation wavelength on the value of  $\phi$  has been explored to extend the scope of prepared CDs-C in fluorescence imaging applications (Fig. 2c). Furthermore, the stability of CDs-C was checked in different pH mediums in the range of 2 to 12. The results of the respective study showed that the emission intensity was decreasing on increasing the pH ranging from 2 to 4. However, further enhancement in the pH value has displayed a linear increment in fluorescence emission with pH ranging to 12 as shown in (Fig. 2d). From the data, it is quite clear that the formed carbon particles have high stability in a basic medium. Additionally, the stability of the developed CDs-C system was evaluated by probing their fluorescence behavior as well as by observing their visual aggregation tendency for a time of 30 days. The prepared aqueous solutions of CDs-C have not revealed any visual aggregation in the samples. Also, the photoluminescence behavior of respective solutions was found to be similar after 30 days. Hence, these outcomes confirmed that the synthesized CDs-C possessed a very high stability rate. From here, it can be inferred that formed CDs-C generated from the waste plastic has outstanding optical and emission characteristics. Furthermore, respective properties endorse their potential usage as a persistent chemo-sensor in the field of toxin sensing.



**Fig. 2** (a) UV-visible absorption spectra, (b) fluorescence emission spectrum, (c) variation in Quantum yield value as a function of excitation wavelength, and (d) pH-dependent variation in fluorescence emission intensity of CDs derived from plastic waste.



**Fig. 3** (a) TGA curves and (b) DSC graphs of C-dots prepared via upcycling of waste plastic.

### 3.3 Thermal stability

The thermal behavior of CDs-C fabricated from the recycling of plastic waste was further scrutinized by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. The TGA results demonstrated the two weight losses which occurred in the range of 150 °C to 660 °C during the thermal analysis of the sample. The first weight loss was due to the evaporation of water molecules from the surface of CDs-C.<sup>[54]</sup> Furthermore, the second weight loss was attributed to the pyrolysis and decomposition of various functional moieties present over the facade of developed CDs-C (Fig. 3a). These end results recommend the high thermal stability and purity of the CDs-C synthesized from upcycled plastic waste. Moreover, the heating behavior of CDs-C was checked using DSC analysis under a nitrogen atmosphere. The DSC spectrum has revealed the exothermic nature of synthesized CDs-C which means the heat release process occurred in the sample (Fig. 3b). The glass transition temperature value was determined to be 129.2 °C for formed

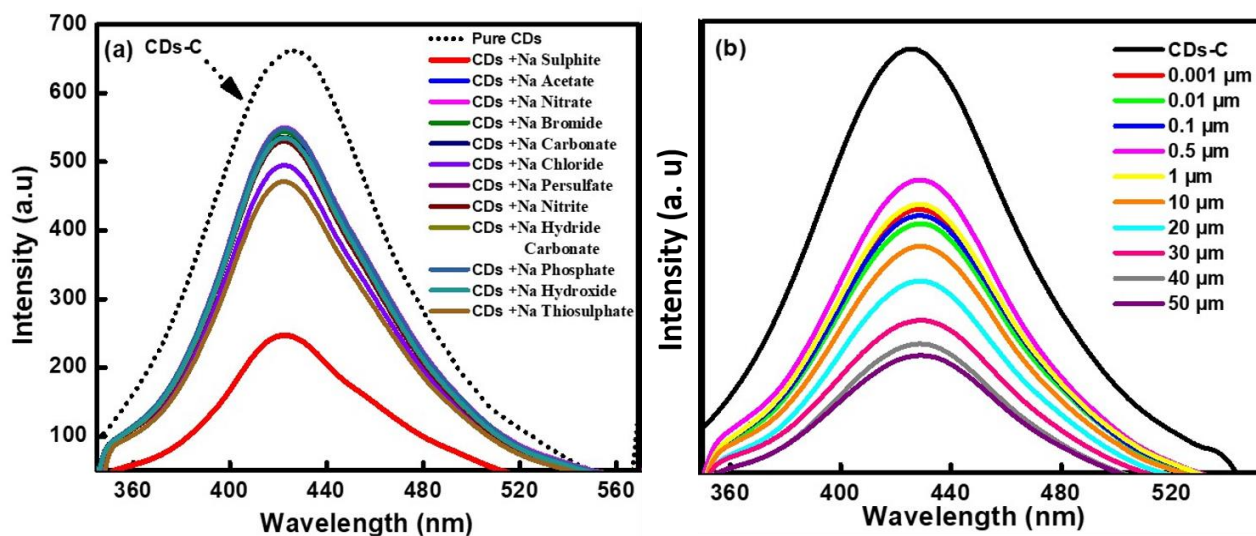
CDs-C. The outcomes of this experimental verification have further approved the high thermal stability of CDs-C.

### 3.4 Sensing activity of developed CDs-C

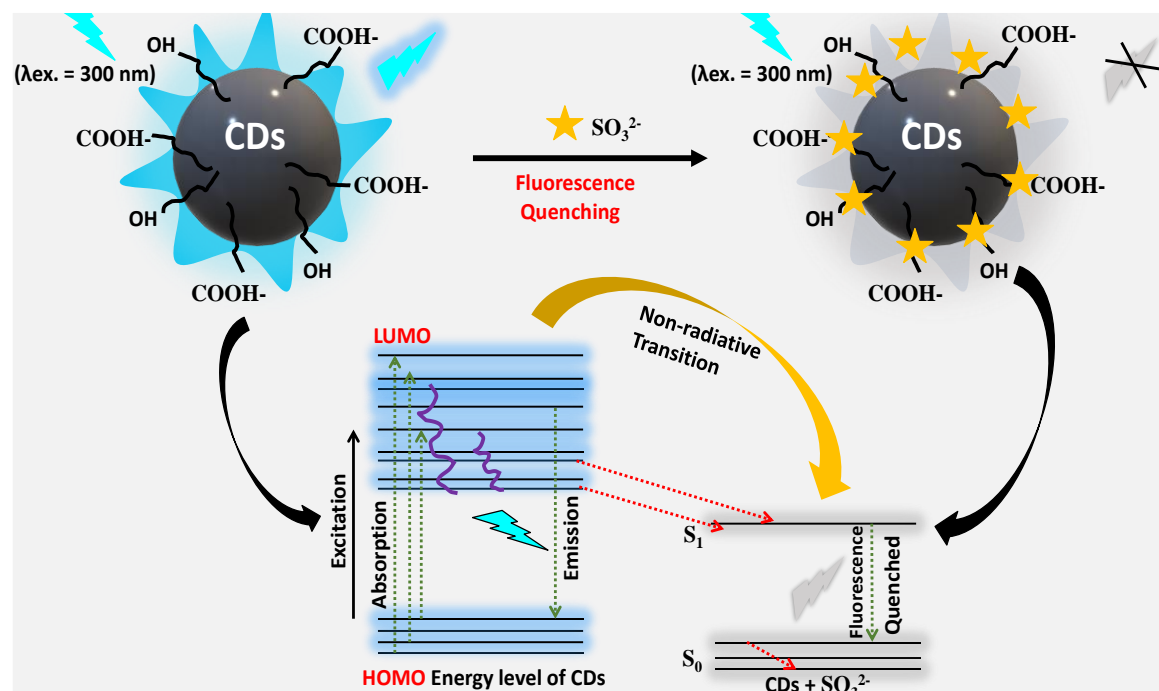
#### 3.4.1 Selectivity study of anion

The contamination of human health and the ecosystem is escalating rapidly due to the continuous release of noxious anions from industrial waste.<sup>[55]</sup> The well-defined fluorescence properties of CDs-C have suggested we accomplish the potential application of formed particles in fluorescence-based anion sensing.<sup>[56-60]</sup>

For the experimentation, the emission spectrum of CDs-C was investigated against 12 different anions which include sodium salts of various anions such as sulphite ( $\text{SO}_3^{2-}$ ), acetate ( $\text{AcO}^-$ ), bromide ( $\text{Br}^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), chloride ( $\text{Cl}^-$ ), persulfate ( $\text{S}_2\text{O}_8^{2-}$ ), nitrite ( $\text{NO}_2^-$ ), hydride carbonate ( $\text{HCO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), hydroxide ( $\text{OH}^-$ ) and thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ). The CDs-C has shown comparable variations to each kind of chosen anion. All the chosen sodium anions have exhibited



**Fig. 4** (a) Fluorescence of CDs in the presence of various sodium anions, (b) concentration variation plot of Sulphite ion in the presence of CDs.



**Scheme 2.** Schematic illustrations of the quenching mechanism of CDs in the presence of  $\text{SO}_3^{2-}$  ion.

minor changes in emission intensity in comparison to CDs-C. On the other hand, the developed CDs-C was assessed to be greatly selective towards  $\text{SO}_3^{2-}$  through a fluorescence quenching mechanism (Fig. 4a). Since, the obtained strongest quencher ( $\text{SO}_3^{2-}$ ) is studied as a prominent environmental pollutant in environmental water resources, hence utmost attention paid to the detection of  $\text{SO}_3^{2-}$  anion by utilizing CDs-C (Scheme 2).

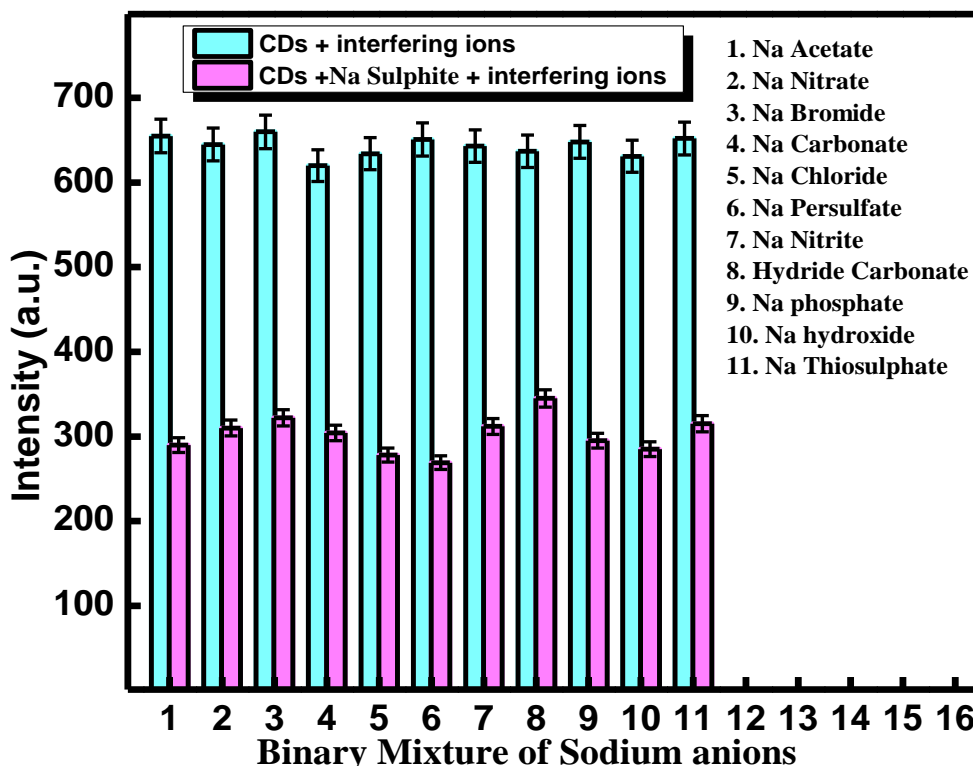
The “turn-off” emission intensity in the fluorescence spectra of CDs was chiefly ascribed to the robust and stable complex formation of  $\text{SO}_3^{2-}$  ion with different functional groups such as hydroxyl, carboxyl, and aldehyde on the surface of CDs-C. Due to the existence of various functional moieties over the facade of CDs-C, they bring out a better platform for the detection of  $\text{SO}_3^{2-}$  owing to the remarkable complex formation of formed particles. The development of the steady state chelates complex of CDs-C and  $\text{SO}_3^{2-}$  has activated the variabilities in the environment of CDs-C and has further combined the elementary charges in the bonded atoms. The substantial combination of CDs-C and  $\text{SO}_3^{2-}$  serves to enhance the non-radiative recombination of elementary charges in the CDs-C and developed quenching in intensity.<sup>[24]</sup> Moreover, the physical interaction of CDs-C and  $\text{SO}_3^{2-}$  leads to the hindrance of plasmon coupling and electric field distribution of the emission intensity. The selectivity of the proposed sensor was also investigated using the titration-metric method. The concentration of  $\text{SO}_3^{2-}$  was varied in the range of 0.001  $\mu\text{M}$  to 50  $\mu\text{M}$  (Fig. 4b). From the obtained fluorescence spectrum, the luminescence intensity has shown a linear decrement as the concentration of  $\text{SO}_3^{2-}$  ion increases in the presence of CDs-C. On comparing with the available literature (Table 1), it was clear that the formed sensory probe in this work has provided high selectivity and sensitivity

towards  $\text{SO}_3^{2-}$  ion. These results have suggested that developed CDs have high potency and sensitivity for the detection of  $\text{SO}_3^{2-}$  ion.

The outcomes have evidently revealed that the developed CDs-C can provide an effective sensing system for the sensitive and selective detection of  $\text{SO}_3^{2-}$  anion up to a very low detection limit in aqueous media using fluorescence quenching methodology. To evaluate the reproducibility of the designed chemo-sensor, all the experimentation was conducted in a set of triplicates. Out of various sodium anions, fabricated CDs-C were ascertained to be robustly discriminating towards  $\text{SO}_3^{2-}$  anion, and no recognizable alternation was scrutinized for any other inspected sodium anions. The potential selectivity of developed CDs-C towards  $\text{SO}_3^{2-}$  was also evaluated, as illustrated in Fig. 5. The different 12 sodium anions including sodium sulphite, acetate, bromide, carbonate, chloride, persulfate, nitrite, hydride carbonate, phosphate, hydroxide, and thiosulphate were probed for the same experimental conditions having 50  $\mu\text{M}$  concentration of  $\text{SO}_3^{2-}$  anion. After the comparison of fluorescence emission intensities of  $\text{SO}_3^{2-}$  with other chosen sodium anions, it was observed that only  $\text{SO}_3^{2-}$  anion provoked the quenching tendency for CDs-C. On the other hand, the presence of other targeted anions has not altered much fluorescence intensity of CDs-C. These results have convincingly promoted that the as-synthesized CDs-C were found to be highly selective and sensitive for  $\text{SO}_3^{2-}$  ion over any other related anions. The phenomenon of formed vigorous association of  $\text{SO}_3^{2-}$  ion with carboxyl and hydroxyl groups on the surface of CDs has induced the establishment of non-radiative recombination of available charges which makes it high selective for  $\text{SO}_3^{2-}$  ion. These favorable results verified that the developed chemo-sensors are authentically selective and showed an

**Table 1.** Comparison between the forecasting outcomes with the reported papers and recently developed sensor.

S. No	Material	Detection limit of SO <sub>3</sub> <sup>2-</sup> ion (µm)	Linear range (µm)	Technique used	Ref.
1	Au NPs	1 µm	5 µm - 0.41 mM	Electrochemical Sensor	[61]
2	Pyrazoline based sensor	7.56 µm	No linear range found	Fluorescence and colorimetric sensor	[62]
3	Electrogenerated Iodine	0.1 mM	0.4-1.2 mM	Coulometric titration	[24]
4	On-line membrane separation method	5.0 µm	No linear range found	Flow injection analysis	[25]
5	CDs	0.34 µm	0.001µm-50µm	Fluorescence	This work



**Fig. 5** Emission profile showing the effect of interference study of Sulphite ion with different chosen anions in the presence of CDs-C.

exceptionally high sensitivity for toxic SO<sub>3</sub><sup>2-</sup> ion sensing.

Furthermore, the fluorescence quenching mechanism of SO<sub>3</sub><sup>2-</sup> in the presence of developed CDs-C has been established by the stern-Volmer relationship.<sup>[46]</sup>

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \tag{3}$$

where F<sub>0</sub> and F represent the emission intensity of CDs-C in the absence and presence of SO<sub>3</sub><sup>2-</sup> ion, Q is the concentration of SO<sub>3</sub><sup>2-</sup> in the solution and K<sub>SV</sub> corresponds to the stern-Volmer association constant. Also, the value of the limit of detection (LOD) was determined by employing the standard formula given below:

$$LOD = \frac{3SD}{P} \tag{4}$$

herein, S.D. corresponds to the standard deviation and P represents the slope of the stern-Volmer plot (Fig. 6a). The

binding efficiency of synthesized CDs-C with SO<sub>3</sub><sup>2-</sup> was determined using Benesi-Hildebrand (B-H) plot (Fig. 6b). The values of the limit of detection, quantization limit, binding constant and fluorescence quenching factor have been specified in Table 2. The limit of detection of the produced sensor was determined to be 0.34 µm.

**Table 2.** The values of the limit of detection, quantization limit, binding constant, and fluorescence quenching factor of developed CDs-C from plastic waste.

S. No.	Parameter	CDs -C
1.	Limit of Detection (LOD)	0.34 µm
2.	Quantitation limit	1.25 µm
3.	Binding constant	0.25 µm
4.	Fluorescence quenching factor	0.67 µm
5.	Fluorescence recovery	92-96%

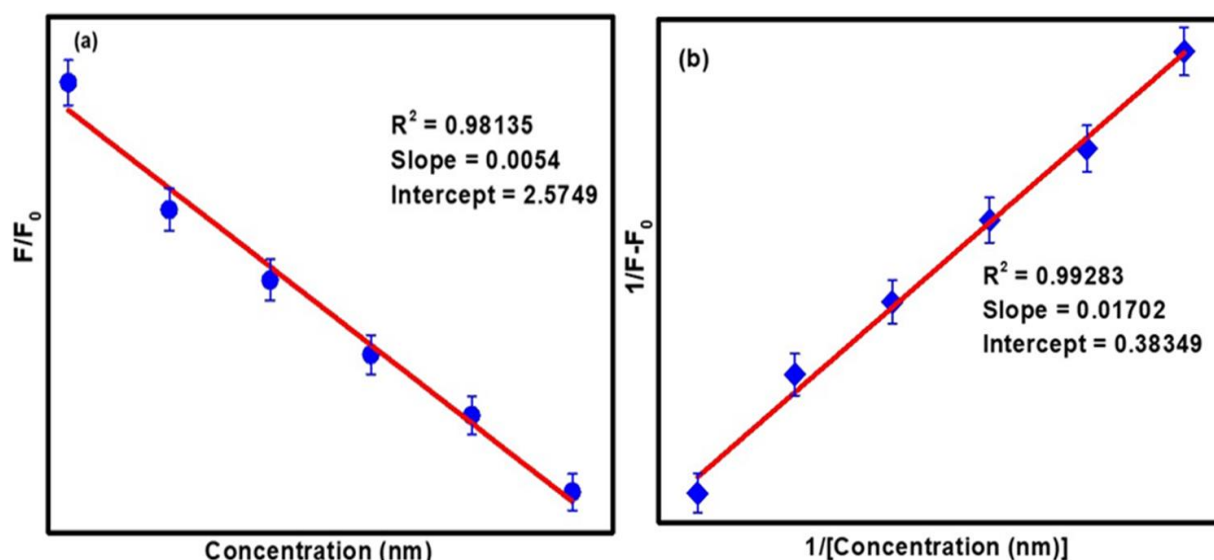


Fig. 6 (a) Stern-Volmer and (b) B-H plot of developed CDs-C from plastic waste.

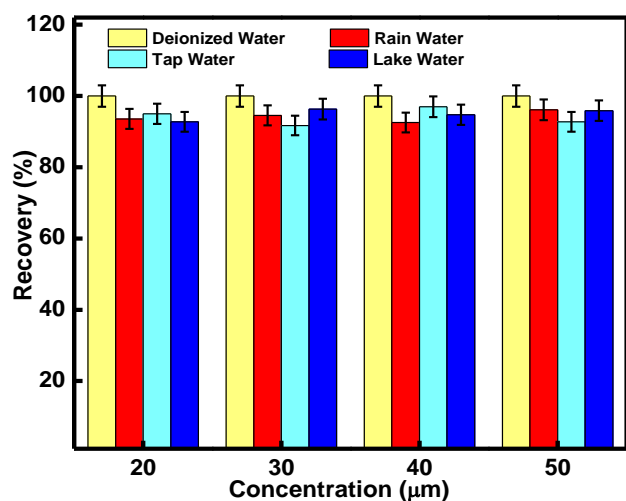


Fig. 7 Recovery study of CDs-C in presence of a different concentration of  $\text{SO}_3^{2-}$  anion in different real water samples.

### 3.5 Practical application of designed CDs-C sensor in real water samples

The practical applicability of the developed CDs-C probe system for sulphite ion ( $\text{SO}_3^{2-}$  ion) has been investigated using four different sources of water mediums including deionized water, tap water, rainwater, and lake water (Fig. 7). Sulfur dioxide is considered to be a pivotal contributor to acid rain which is quite detrimental to plants, infrastructure and specifically to animals and human health. Also, when sulfur dioxide breaks down in water under neutral pH conditions, it becomes viable in the form of sulphite ( $\text{SO}_3^{2-}$ ) ions.<sup>[63]</sup> Hence, the produced sensor has been utilized herein for the detection of sulphite ( $\text{SO}_3^{2-}$ ) ions in rainwater as well as other environmental water sources. All three real water samples (deionized water, tap water, rainwater, and lake water) were acquired from the local regions of Chandigarh and spiked with various concentrations of sulphite ( $\text{SO}_3^{2-}$ ) ions. Afterward, luminescence emission profiles of the respective samples have

been observed at the excitation wavelength of 300 nm. The obtained results have exhibited excellent agreement in utilizing water sources with our established sensor system. The recovery value was determined to be in the range of 92 to 96% which has confirmed the potential adequacy of the synthesized CDs-C for practical purposes. The outcomes have also implied that the proposed sensing methodology has high selectivity for sulphite ( $\text{SO}_3^{2-}$ ) in the presence of environmental water mediums. Moreover, the fabrication of the developed sensor system was relatively economical with a facile working principle. The utilization of waste plastic cups has also proliferated the scope of the proposed sensor. In addition, the suggested sensing system has sustained the green approach for the  $\text{SO}_3^{2-}$  anion detection by using CDs based sensor.

### 4. Conclusion

To summarize, an effort has been put forth for the facile fabrication of CDs-C by simple thermal calcination of upcycled waste plastic cups. This methodology has offered an environmentally reliable way for converting waste to wealth by dipping the expenditure of vitally important raw materials. The recycling of waste plastic into useful advanced nanomaterials is a major captivating matter of concern in the recent scientific world attributable to its lucrative impact on our ecosystem. The current synthetic route was successfully optimized for expansible mass-formation of CDs-C accompanied by better control of the optical properties as well as the size of the particles. Furthermore, various characterization techniques have been evaluated for the detailed physicochemical and structural verification of CDs-C. The fabricated CDs-C possessed a very high quantum yield of 59% and displayed admirable aqueous solubility. The main outcome of the current work is that the developed system is selective towards toxic pollutant sulphite ( $\text{SO}_3^{2-}$ ) ions. The particles are a turn-off sensor due to fluorescence quenching

in the emission intensity of CDs-C. The value of the limit of detection was found to be 0.34  $\mu\text{m}$  with a regression coefficient of 0.98. Furthermore, the practical application of CDs-C fabricated from waste plastic has been utilized for the sulphite ( $\text{SO}_3^{2-}$ ) ions sensing in different water resources. The outcomes of the current work have provided a potential accomplishment for the recycling of waste plastic irrespective of further modifications or technical work with the objective of conserving environmental fate and eradicating blossoming glitches of waste plastic. In a large framework, the developed CDs-C endowed a simple, rapid, benign, and remunerative sensory probe for environmental remediation.

### Acknowledgment

Manisha Kumari is thankful to Haryana State Council for Science and Technology, Panchkula for financial support under HSCSIT/R&D/2020/476. Savita Chaudhary is thankful to the DST Inspire Faculty award [IFACH- 17], Haryana State Council for Science and Technology [HSCSIT/R&D/2020/476], DST Chandigarh and DST Purse grants II for financial assistance. Ganga Ram Chaudhary would like to acknowledge the support of UGC, India under the INDO-US 21st Century knowledge Initiative project [F.No. 194-2/2016 (IC)]. The authors are thankful to the Sophisticated Analytical Instrumentation Facility (SAIF, CIL), Panjab University, Chandigarh. The authors are thankful to Panjab University SAIF CIL for technical support. Ahmad Umar would like to acknowledge Najran University, the Ministry of Education, Kingdom of Saudi Arabia for their support.

### Conflict of interest

There are no conflicts to declare.

### Supporting information

Not applicable.

### References

- [1] J. D. Toner, D. C. Catling, *Proceedings of the National Academy of Sciences*, 2020, **117**, 883–888, doi:10.1073/pnas.1916109117.
- [2] Z. Liu, C. Deng, C. Yu, X. Wang, J. Ding, H. Zhu, *Journal of Alloys and Compounds*, 2019, **777**, 26–33, doi: 10.1016/j.jallcom.2018.09.107.
- [3] T. J. Jentsch, V. Stein, F. Weinreich, A. A. Zdebik, *Physiological Reviews*, 2002, **82**, 503–568, doi: 10.1152/physrev.00029.2001.
- [4] S. Verma, V. Ravichandiran, N. Ranjan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2021, **255**, 119624, doi: 10.1016/j.saa.2021.119624.
- [5] C. Demigné, H. Sabboh, C. Puel, C. Rémésy, V. Coxam, *Nutrition Research Reviews*, 2004, **17**, 249–258, doi: 10.1079/nrr200485.
- [6] A. D. G. Gunn, *Differential Diagnosis*, 1981, 215–240, doi: 10.1007/978-94-009-8060-0\_12.
- [7] X. Wu, A. M. Gilchrist, P. A. Gale, *Chem*, 2020, **6**, 1296–1309, doi: 10.1016/j.chempr.2020.05.001.
- [8] B.P. Morgan, S. He, R.C. Smith, *Inorganic chemistry*, 2007, **46**, 9262–9266, doi:10.1021/ic701374h.
- [9] P. A. Gale, *Chemical Communication*, 2011, **47**, 82–86, doi: 10.1039/c0cc00656d.
- [10] P. D. Beer, P. A. Gale, *Angewandte Chemie International Edition*, 2001, **40**, 486–516, doi: 10.1002/1521-3773(20010202)40:3486:aid-anie486>3.0.co;2-p.
- [11] R. Martinez-Mez, F. Sancenon, *Chemical reviews*, 2003, **103**, 4419–4476, doi: 10.1021/cr010421e.
- [12] V. Sudha, S.M. Senthil Kumar, R. Thangamuthu, *Journal of Alloys and Compounds*, 2018, **749**, 990–999, doi: 10.1016/j.jallcom.2018.03.287.
- [13] J. Zhang, X. Xu, X. Yang, *The Analyst*, 2012, **137**, 3437, doi: 10.1039/c2an35609k.
- [14] Z. Abedinzadeh, *Canadian Journal of Physiology and Pharmacology*, 2001, **79**, 166–79170, doi: 10.1139/y00-085.
- [15] T. Fazio, C. R. Warner, *Food Additives and Contaminants*, 1990, **7**, 433–454, doi: 10.1080/02652039009373907.
- [16] I.T.T. Higgins, *Environmental Health: An International Journal*, 1971, **22**, 584–590, doi: 10.1080/00039896.1971.10665906.
- [17] X. Wang, H. Li, M. Wu, S.-L. Ge, Y. Zhu, Q.-J. Wang, P.-G. He, Y.-Z. Fang, *Chinese Journal of Analytical Chemistry*, 2013, **41**, 1232–1237, doi: 10.1016/s1872-2040(13)60673-8.
- [18] I. H. A. Badr, A. Plata, P. Molina, M. Alajarin, A. Vidal, L. G. Bachas, *Analytica Chimica Acta*, 1999, **388**, 63–69, doi: 10.1016/s0003-2670(99)00023-9.
- [19] B. Sinduja, S. A. John, *Analytical and Bioanalytical Chemistry*, 2019, **411**, 2597–2605, doi: 10.1007/s00216-019-01697-2.
- [20] R. Rawal, S. Chawla, T. Dahiya, C. S. Pundir, *Analytical and Bioanalytical Chemistry*, 2011, **401**, 2599–2608, doi: 10.1007/s00216-011-5325-4.
- [21] T. Uchacz, G. Jajko, A. Danel, P. Szlachcic, S. Zapotoczny, *New Journal of Chemistry*, 2019, **43**, 874–883, doi: 10.1039/c8nj05017a.
- [22] C. Zheng, X. An, J. Gong, *RSC Advances*, 2015, **5**, 32319–32322, doi: 10.1039/c5ra01986a.
- [23] I. V. Pulyayeva, N. L. Yegorova, L. P. Experiandova, A. B. Blank, *Analytica Chimica Acta*, 1997, **357**, 239–245, doi: 10.1016/s0003-2670(97)00585-0.
- [24] D. Lowinson, M. Bertotti, *Food Additives and Contaminants*, 2001, **18**, 773–777, doi: 10.1080/02652030117536.
- [25] X. Su, W. Wei, *The Analyst*, 1998, **123**, 221–224, doi: 10.1039/a706727e.
- [26] R. Rawal, S. Chawla, C. S. Pundir, *Biosensors and Bioelectronics*, 2012, **31**, 144–150, doi: 10.1016/j.bios.2011.10.007.
- [27] M. Y. Wu, K. Li, C. Y. Li, J. T. Hou, X. Q. Yu, *Chem Commun*, 2014, **50**, 183–185, doi: 10.1039/c3cc46468g.
- [28] X. Jiang, J. Xu, Y. Zhang, H. Wang, L. Zeng, Y. Zhang, *Analytical Methods*, 2016, **8**, 1572–1576, doi: 10.1039/c5ay02983j.

- [29] C. Duan, J.-F. Zhang, Y. Hu, L. Zeng, D. Su, G. M. Bao, *Dyes and Pigments*, 2019, **162**, 459-465, doi: 10.1016/j.dyepig.2018.10.057.
- [30] M. H. Lee, J. S. Kim, J. L. Sessler, *Chemical Society Reviews*, 2015, **44**, 4185-4191, doi: 10.1039/c4cs00280f.
- [31] Y. Huang, Y. Luo, H. Liu, X. Lu, J. Zhao, Y. Lei, *Engineered Science*, 2021, **14**, 59-69, doi: 10.30919/es8d1161.
- [32] Z. Gao, X. Li, L. Shi, Y. Yang, *Spectrochimica Acta Part A*, 2019, **220**, 117080, doi: 10.1016/j.saa.2019.04.072.
- [33] S. Chaudhary, M. Kumari, P. Chauhan, G. Ram Chaudhary, *Waste Management*, 2021, **120**, 675-686, doi: 10.1016/j.wasman.2020.10.038.
- [34] S. Bhatt, M. Bhatt, A. Kumar, G. Vyas, T. Gajaria, P. Paul, *Colloids and Surfaces B: Biointerfaces*, 2018, **167**, 126-133, doi: 10.1016/j.colsurfb.2018.04.008.
- [35] Y. Hu, Z. Gao, J. Yang, H. Chen, L. Han, *Journal of Colloid and Interface Science*, 2019, **538**, 481-488, doi: 10.1016/j.jcis.2018.12.016.
- [36] D. Pan, F. Su, C. Liu, Z. Guo, *Advanced Composites and Hybrid Materials*, 2020, **3**, 443-461, doi: 10.1007/s42114-020-00190-0.
- [37] Y. Liu, X. Li, Y. Sun, J. Heo, Y. Lee, D. H. Lim, H. J. Ahn, K. K. Cho, R. Yang, J. H. Ahn, *Science of Advanced Materials*, 2020, **12**, 1627-1633, doi: 10.1166/sam.2020.3814.
- [38] Y. F. Tian, R.J. Liao, *Journal of Nanoelectronics and Optoelectronics*, 2020, **15**, 1089-1093, doi: 10.1166/jno.2020.2815.
- [39] J. Tang, J. Zhang, P. Shi, Y. Xiao, Y. Shi, L. Ding, W. Xu, *Science of Advanced Materials*, 2020, **12**, 966-972, doi: 10.1166/sam.2020.3731.
- [40] M. Li, K. Han, Y. Gao, Z. Teng, J. Li, M. Wang, *Journal of Nanoelectronics and Optoelectronics*, 2020, **15**, 284-290, doi: 10.1166/jno.2020.2700.
- [41] H. Choi, C. Choi, S. H. Kwon, Y. Park, W. Choi, *Science of Advanced Materials*, 2020, **12**, 1261-1264, doi: 10.1166/sam.2020.3790.
- [42] H. Cheng, Z. Zhou, D. Qin, W. Huang, J. Feng, T. Tang, G. Hu, L. Li, *Science of Advanced Materials*, 2020, **12**, 693-700, doi: 10.1166/sam.2020.3709.
- [43] G. Wang, NuerbiYayalikun, X. Mamat, Y. Li, X. Hu, P. Wang, X. Xin, G. Hu, *Science of Advanced Materials*, 2020, **12**, 376-382, doi: 10.1166/sam.2020.3567.
- [44] S. Chen, Z. Liu, S. Jiang, H. Hou, *Science of the Total Environment*, 2020, **710**, 136250, doi: 10.1016/j.scitotenv.2019.136250.
- [45] O. Alam, M. Billah, D. Yajie, Resources, *Conservation and Recycling*, 2018, **132**, 121-129, doi: 10.1016/j.resconrec.2018.01.037.
- [46] J. Huang, X.Y. Yin, J. Y. Yang, M. L. Guo, *Materials Letters*, 2014, **117**, 112-115, doi: 10.1016/j.matlet.2013.11.104.
- [47] L. A. Romero-Cano, A. I. Zárate-Guzmán, F. Carrasco-Marín, L. V. González-Gutiérrez, *Journal of Electroanalytical Chemistry*, 2019, **837**, 22-29, doi: 10.1016/j.jelechem.2019.02.005.
- [48] R. Gnanasambandam, *Food Chemistry*, 2000, **68**, 327-332, doi: 10.1016/s0308-8146(99)00191-0.
- [49] P. Chauhan, S. Chaudhary, R. Kumar, *Journal of Cleaner Production*, 2021, **279**, 123639, doi: 10.1016/j.jclepro.2020.123639.
- [50] S. Chaudhary, S. Kumar, B. Kaur, S. K. Mehta, *RSC Advances*, 2016, **6**, 90526-90536, doi: 10.1039/c6ra15691f.
- [51] P. Chauhan, J. Saini, S. Chaudhary, *Nano-Structures & Nano-Objects*, 2020, **24**, 100585, doi: 10.1016/j.nanoso.2020.100585.
- [52] M. I. S. Dela Cruz, N. Thongsai, M. Daniel G de Luna, I. In, P. Paoprasert, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2019, **568**, 184-194, doi: 10.1016/j.colsurfa.2019.02.022.
- [53] A. Vijeata, G. R. Chaudhary, A. Umar, S. Chaudhary, *Engineered Science*, 2021, **15**, 197-209, doi: 10.30919/es8e512.
- [54] O. Mkhari, T. D. Ntuli, N. J. Coville, E. N. Nxumalo, M. S. Maubane-Nkadimeng, *Diamond and Related Materials*, 2021, **118**, 108500, doi: 10.1016/j.diamond.2021.108500.
- [55] M. A. Masood, Y. Chen, S. Yao, S. Li, W. He, Z. Guo, *Journal of Photochemistry and Photobiology A: Chemistry*, 2021, **404**, 112885, doi: 10.1016/j.jphotochem.2020.112885.
- [56] X. Ma, W. Zhong, J. Zhao, S. L. Suib, Y. Lei, *Engineered Science*, 2020, **9**, 44-49, doi: 10.30919/es8d805.
- [57] J. Liu, C. Liu, Z. Zhou, *Microchimica Acta*, 2019, **186**, 1-7, doi: 10.1007/s00604-019-3413-x.
- [58] R. Vadivel, M. Nirmala, K. Raji, B. Siddaiah, P. Ramamurthy, *Journal of the Indian Chemical Society*, 2021, **98**, 100181, doi: 10.1016/j.jics.2021.100181.
- [59] X. Ma, W. Zhong, J. Zhao, S. L. Suib, Y. Lei, *Engineered Science*, 2020, **9**, 44-49, doi: 10.30919/es8d805.
- [60] X. Wu, W. Li, P. Wu, C. Ma, Y. Liu, M. Xu, S. Liu, *Engineered Science*, 2018, **4**, 111-118, doi: 10.30919/es8d785.
- [61] X. Wang, H. Li, M. Wu, S.-L. Ge, Y. Zhu, Q.-J. Wang, P.-G. He, Y.-Z. Fang, *Chinese Journal of Analytical Chemistry*, 2013, **41**, 1232-1237, doi: 10.1016/s1872-2040(13)60673-8.
- [62] T. Uchacz, G. Jajko, A. Danel, P. Szlachcic, S. Zapotoczny, *New Journal of Chemistry*, 2019, **43**, 874-883, doi: 10.1039/c8nj05017a.
- [63] C. Yu, M. Luo, F. Zeng, S. Wu, *Analytical Methods*, 2012, **4**, 2638, doi: 10.1039/c2ay25496d.

#### Author Information



**Manisha Kumari** has done his Ph.D. under the supervision of Dr. Savita Chaudhary and Prof. Ganga Ram Chaudhary from the Department of Chemistry Panjab University, Chandigarh, India. She received his master's degree in chemistry. Her research interests mainly focus on the fabrication of advanced carbon dots and their application in waste water management. The particles are mainly prepared from the waste biomass and used further for the development of fluorescence based sensor.



**Ganga Ram Chaudhary** Director SAIF/CIL/UCIM and Senior Professor in Department of Chemistry, Panjab University, Chandigarh. He has made significant contributions in the field of Thermodynamics, Catalysis and Nano chemistry. Prof. Chaudhary is credited with more than 150 publications in international journals of repute with h-index of 24 and is an author of about 10 books/chapters. He has been credited with various precious project including developed efficient Photo Voltaic (PV) Solar Power Plant and Concentrated Solar Power (CSP) Plants for integrated Electric Vehical charging station and Indo-US Partnership on Green Chemistry/Engineering and Technologies Education. Some of important research work of Prof. Chaudhary include: Synthesis and characterization of metal oxide nanoparticles and its utility for the removal of water contaminants. Recent work belongs to the design of novel Metallo-surfactants that can be engineered according to the requirement and act as a carrier and template for nanoparticle synthesis. Successful attempt was made to synthesize metallic nanoparticles and used them for the degradation of harmful toxins.



**Savita Chaudhary** received her B.Sc, M.Sc and Ph.D. degrees in Chemistry from the Panjab University in Chandigarh, India. Dr. Chaudhary has published over 125 research articles in peer-reviewed international journals and 8 book chapters. She was awarded the DST-DAAD PPP fellowships in 2008. She is the recipient of prestigious Haryana Yuva Vigyan Ratan Award. She is an editorial member of the International Journal of Chemistry and Chemical Engineering (IJCCE) and Advanced Science, Engineering, and Medicine. She is also specialized in the modern analytical and spectroscopic techniques used for the characterizations and applications of semiconductor nanomaterials. Dr. Chaudhary is specialized in the synthesis, growth, properties, and applications of engineered nanostructures in the areas of gas, luminescent and biosensors, environmental remediation, catalysis, and photocatalysis. She has made significant contributions in the fields of surfactant chemistry and nano chemistry. Her recent work focuses on the design of different types of nanoparticles possessing higher biocompatibility applicable as carrier for herbicides.



**Ahmad Umar** received his Ph.D. in semiconductor and chemical engineering from Chonbuk National University, South Korea. He worked as a research scientist in Brain Korea 21, Centre for Future Energy Materials and Devices, Chonbuk National University, South Korea, in 2007–2008. Afterwards, he joined the Department of Chemistry in Najran University, Najran, Saudi Arabia. He is a distinguished professor of chemistry and served as deputy director of the Promising Centre for Sensors and Electronic Devices (PCSED), Najran University, Najran, Saudi Arabia. Professor Ahmad Umar is specialized in 'semiconductor nanotechnology', which includes growth, properties and their various high technological applications, for instance, gas, chemicals and biosensors, optoelectronic and electronic devices, field effect transistors (FETs), nanostructure-based energy-harvesting devices, such as solar cells, Li-ion batteries, super-capacitors, semiconductor nanomaterial-based environmental remediation, and so on. He is also specialized in the modern analytical and spectroscopic techniques used for the characterizations and applications of semiconductor nanomaterials. He contributed to the world of science by editing world's first handbook series on Metal Oxide Nanostructures and Their Applications (5-volume set, 3500 printed pages, [www.aspbs.com/mona](http://www.aspbs.com/mona)) and handbook series on Encyclopedia of Semiconductor Nanotechnology (7-volume set; [www.aspbs.com/esn](http://www.aspbs.com/esn)), both published by American Scientific Publishers ([www.aspbs.com](http://www.aspbs.com)). He has published more than 600 research papers in reputed journal with h-index of 77 and i10-index of 381 with total citations over 21000 (According to Google scholar).

**Publisher's Note:** Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.