

Enhanced absorption and fluorescence quenching methods for the quantitative analysis of Cr(VI) ions using avocado seed-derived carbon quantum dots as pseudo-derivatising reagents.

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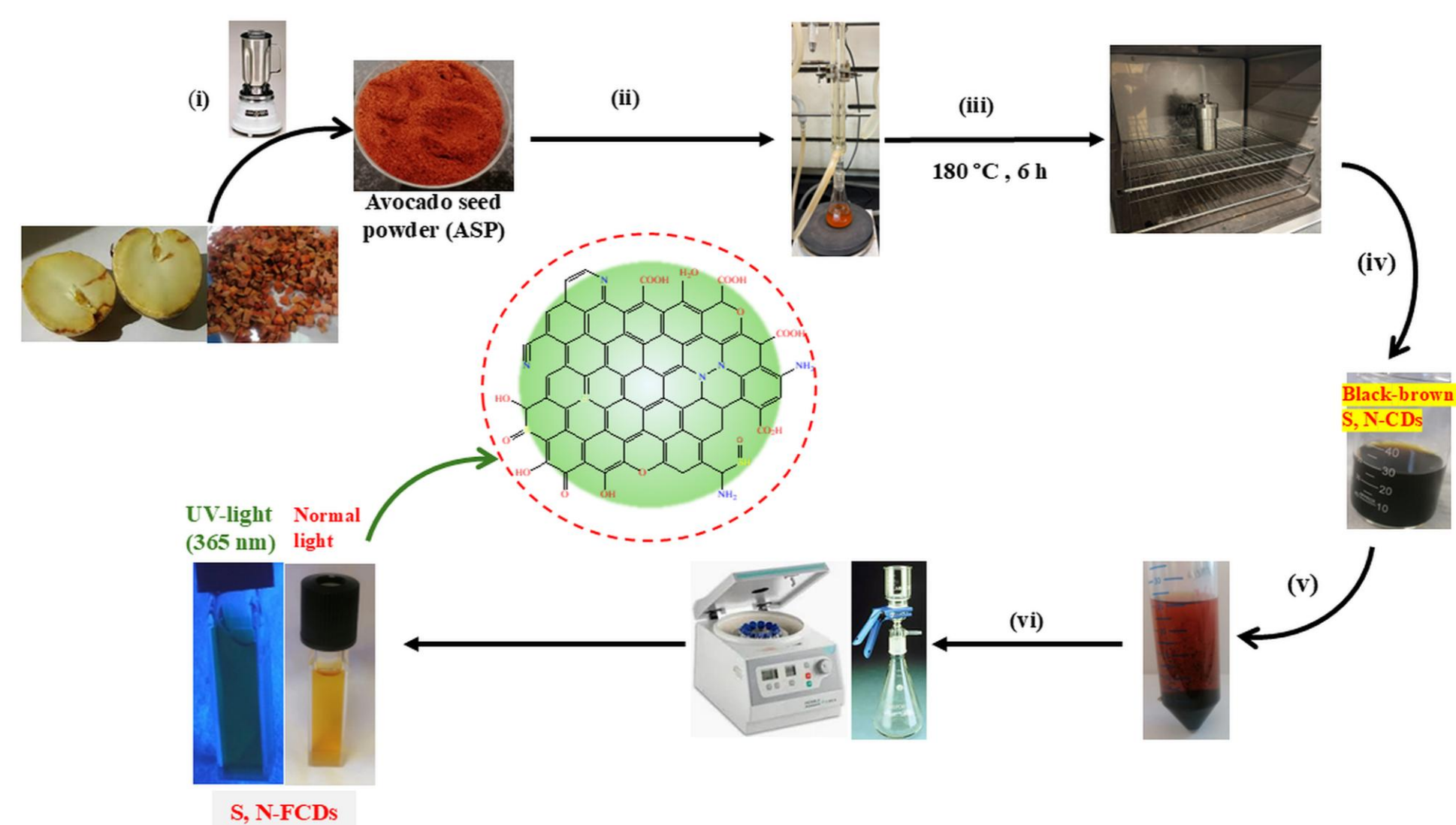
1. Introduction

Water pollution from chromate waste is pervasive and requires affordable, user-friendly analytical methods are needed for the sensitive and selective identification of Cr(VI) in ambient water samples. Atomic spectroscopic methods (AAS, XRF, ICP-OES, ICP-MS) are sensitive but expensive and restrict data collection to the laboratory. Avocado seed-derived carbon quantum dots doped with sulfur and nitrogen (S, N-CDs) were synthesised through a hydrothermal method (**Scheme 1**) and used as a two-probe optical sensing nanomaterial for the sensitive detection and quantitative analysis of Cr(VI) ions in water samples. The sensing of the analyte, the CD reagent, was based on changes in its surface using host-guest surface interaction absorption (HGSIA) and fluorescence/photoluminescence (PL) quenching. The CDs were characterised using surface characterisation techniques (SEM, TEM, FT-IR, XPS) (**Fig 1.**), and the optical properties were evaluated using UV-vis absorption and Fluorescence spectroscopy (**Fig. 2 - 6**). The HGSIA interactions and PL quenching of the S, N-CDs by Cr(VI) were studied; the quantitative aspects of the two methods were evaluated and fully validated in spiked river and Cr(VI) contaminated samples.

1.2. Problem statement

Cr(VI) is a toxic heavy metal that requires constant monitoring in water bodies due to adverse effects on humans and the environment. Current analytical methods used for detection and quantification are expensive to acquire and available only in certain laboratories. Carbon dots offer easy-to-use, green, selective, and sensing reagents for the detection and quantification of Cr(VI).

3. Synthesis of S, N-CDs



Scheme 1. Synthesis of the S,N-CDs from the avocado seed extract.

3. Connection to UN SDGs



- Enables monitoring of toxic Cr(VI) contamination
- Utilizes sustainable biomass waste (avocado seeds).
- Supports low-cost environmental water quality assessment.
- Contributes to safer water resources.

4. Characterization

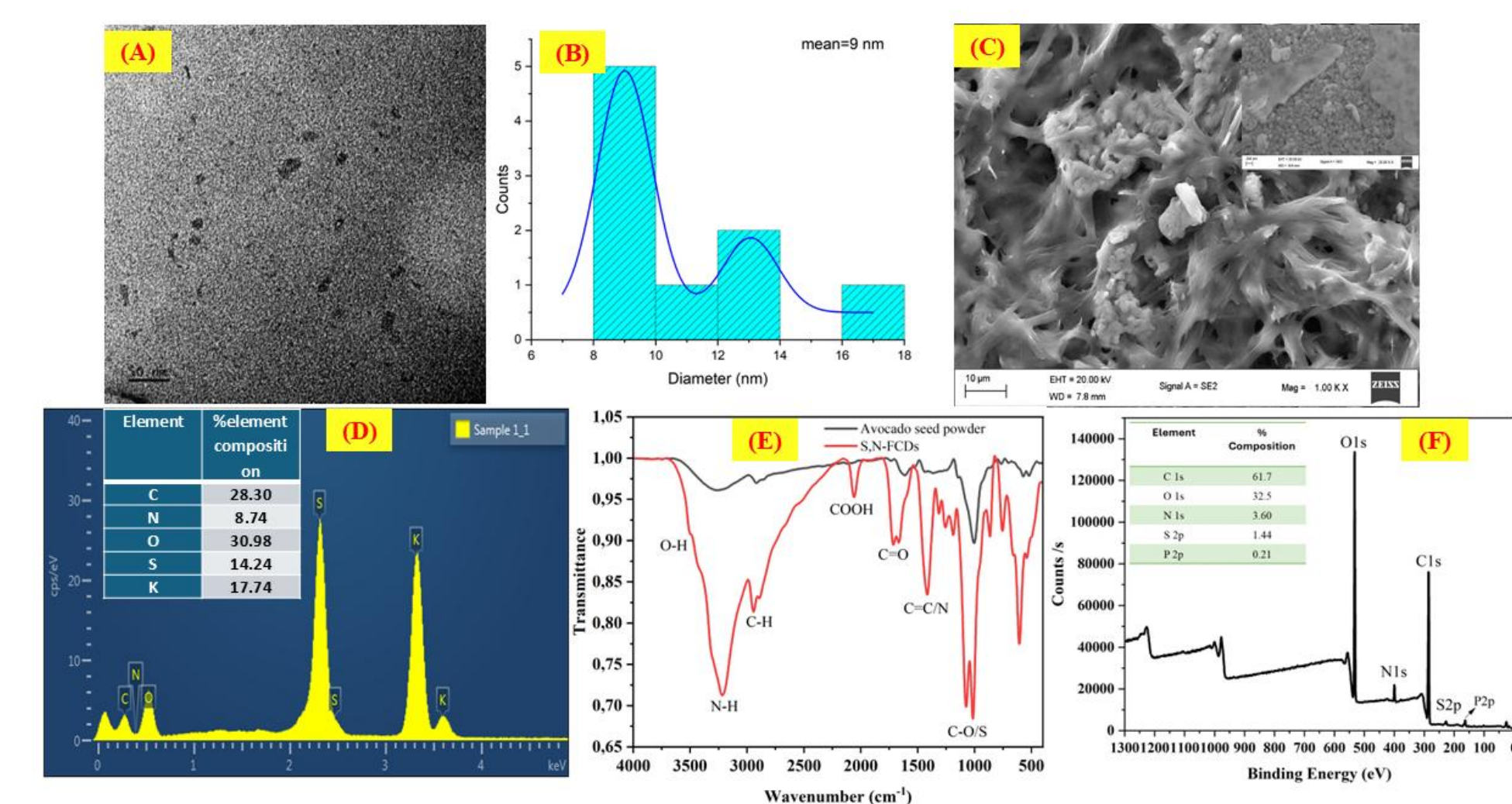


Figure 1. (A) TEM micrographs of S, N-CDs (B) TEM micrographs of S,N-CDs (size range: 9.2 – 15.6 nm) (C) SEM image (D) EDX spectrum (E) Overlaid FTIR spectra. (F) XPS analysis of the S,N-CDs

5. Results

❖ Evaluation of the S, N-CDs PL, and UV-Vis Absorption (HGSIA)

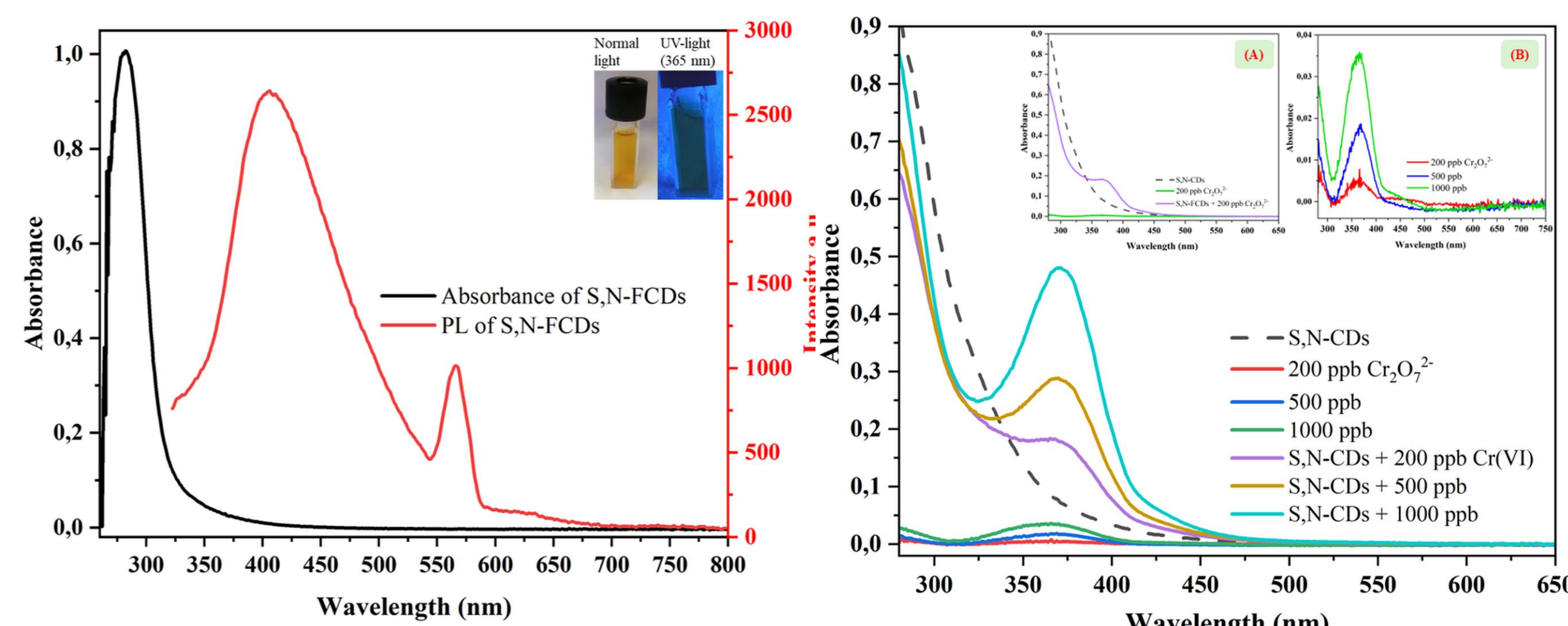


Figure 2. (a) Overlaid Spectra of absorption and photoluminescence of the 8.3 mg/L of S,N-CDs (b) Overlaid spectra of S,N-CDs (8.3 mg/L) using HGSIA with 200, 500, 1000 ppb of Cr(VI) in S,N-CDs and pure Cr(VI) standards in ultrapure water using the HGSIA method

❖ Evaluation of selectivity and sensitivity of S,N-CDs using HGSIA and FL

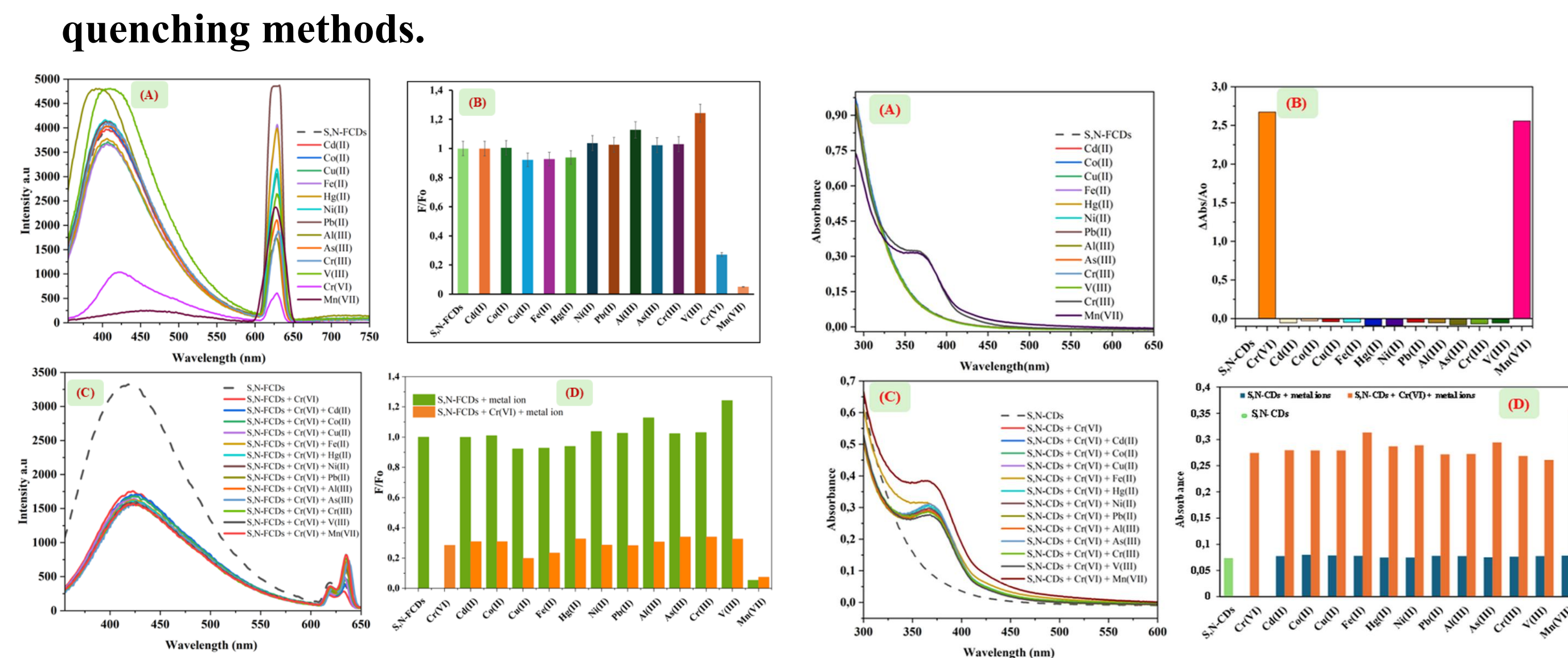
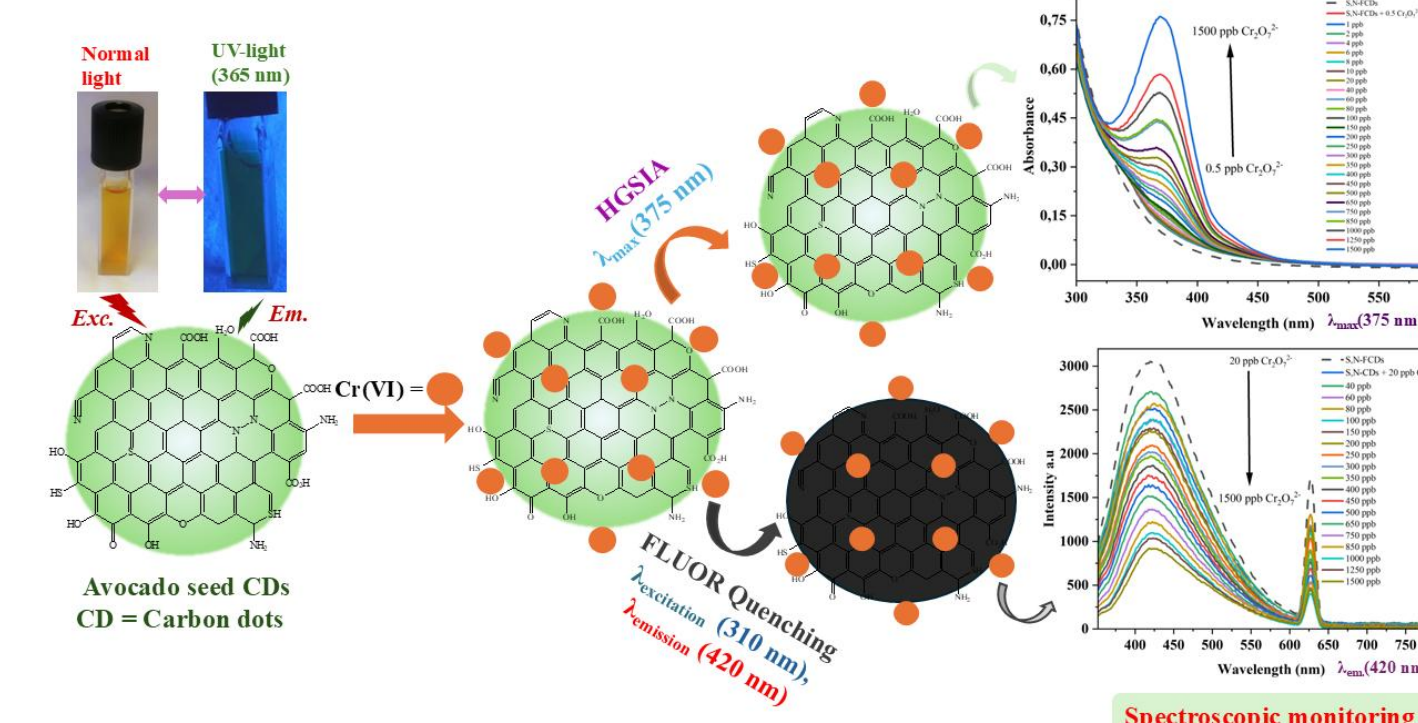


Figure 3. Sensitivity and selectivity of S,N-CDs towards Cr(VI) at 375 nm, pH 9, by the HGSIA method.

Figure 4. Sensitivity and selectivity of S,N-CDs towards Cr(VI) at 375 nm, pH 9, by the FL quenching method.

❖ Possible sensing mechanism for S, N-CDs using HGSIA and PL-quenching method.



5. Results

❖ HGSIA linear calibration of Cr(VI) in S,N-CD solution.

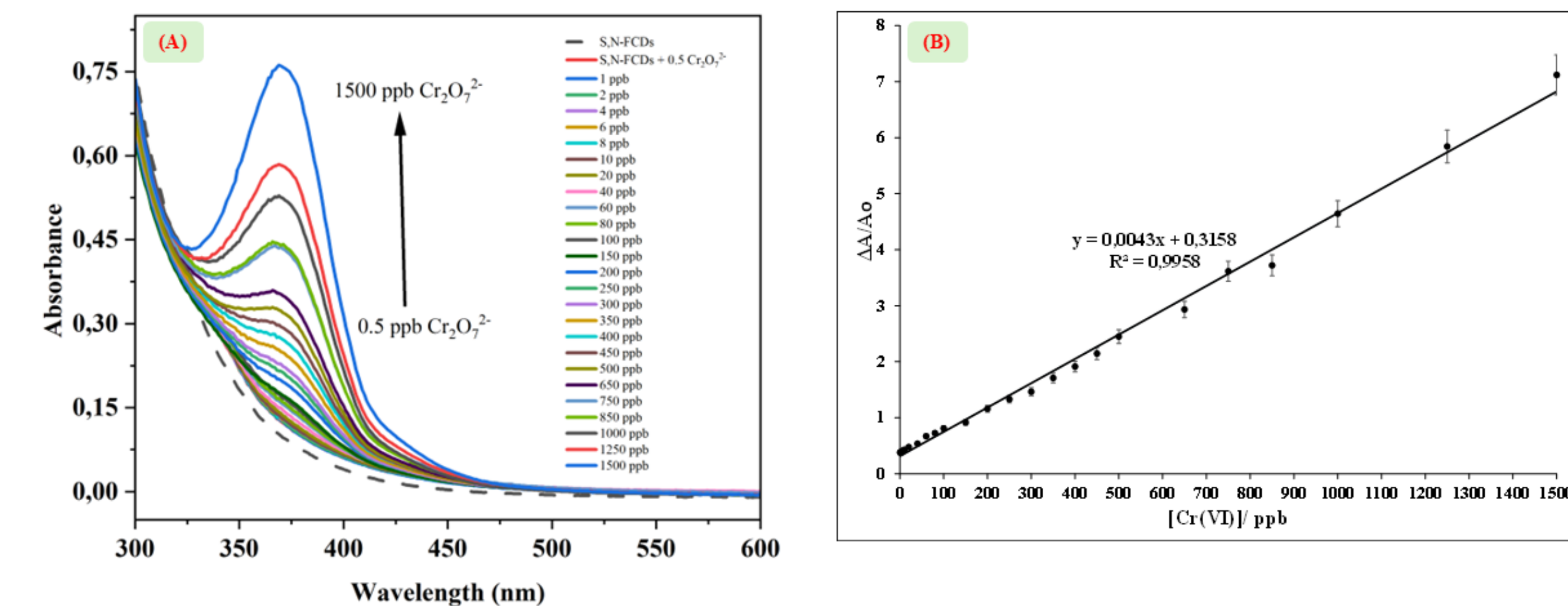


Figure 5. (a) Overlaid spectra of Cr(VI) titration with S,N-CDs using HGSIA at pH 9. (b) Calibration curve Cr(VI) at 375 nm using surface plasmon absorption interaction with the S,N-CDs.

❖ FL quenching linear calibration of Cr(VI) in S,N-CD solution.

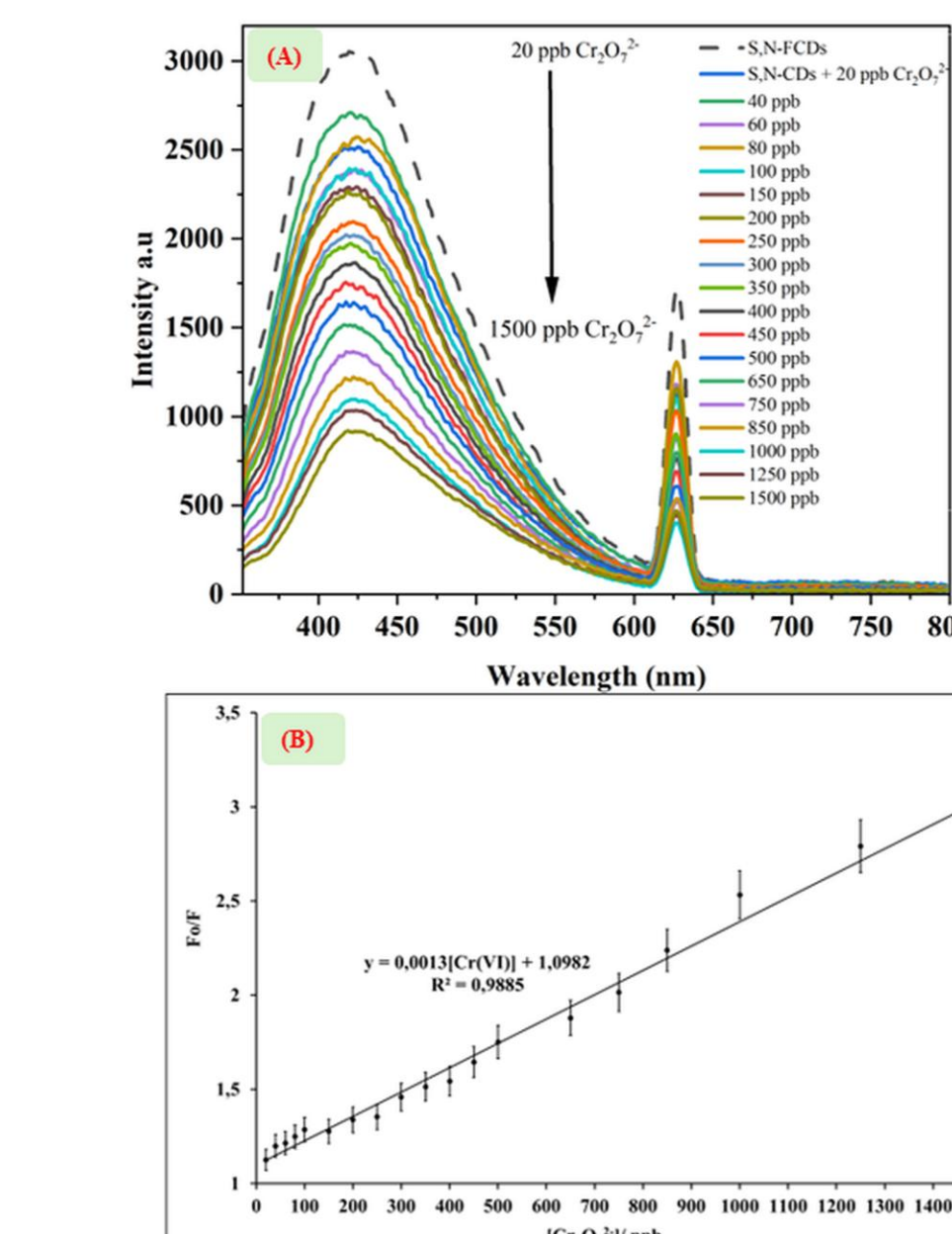


Figure 6. (A) Overlaid Cr(VI) titration spectra with S, N-CDs using PL emission quenching method. (B) The calibration curve of the Cr(VI) at 420 nm using PL/ Fluorescence quenching of the S, N-CDs (and the Stern-Volmer calibration equation)

Table 1: Comparative tabulated data of SPAS and PL of S,N-CDs used in spiked Msunduzi Municipality river water sample

Method	LOD 3s/10SD _{bla}	LOQ 3s/10SD _{bla}	Spiked/pp b	%recover y	%RSD N=3
HGSIA	0.14 nk	0.49 nk	20	96	2.4
PL	5.9	25	20	89	4.7

6. Conclusions

- Mono-dispersed S,N-CDs with a dull-green fluorescence (PL) emission were hydrothermally synthesised from avocado seed powder and the carbon nanomaterial showed a moderate quantum yield of 17.7%.
- Both the HGSIA and the PL-quenching analytical methods were calibrated for the quantitative analysis of trace levels of Cr(VI) ions, with the former method showing superior sensitive, with LOD/LOQ in the lower ppb range for Cr(VI) and a wider linear range spanning 3 orders of magnitude (0.5-1500 ppb).
- The two new quantitative analytical methods were further validated for accuracy using Cr(VI) spiked tap and river water samples, recording acceptable % recoveries in the range 89-105%
- The (green) analytical methods could positively detect Cr(VI) ions in a laboratory segregated waste water contaminated with Cr(VI) (a positive check sample), hence placing both as promising optical-sensing methods for the routine quantitative analyses of Cr(VI) ions in real environmental water samples.

References

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