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REMOVAL OF TETRACYCLINE FROM WATER WITH FLUORESCENT N-DOPED CARBON DOTS PRODUCED BY *Acacia tortilis* SEEDS.

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ABSTRACT

Tetracyclines are ranked as the second most used antibiotics worldwide and pose significant risks to human health and the environment when present in aquatic locations. The current study investigated the application of nitrogen-doped carbon dots (N-CDs) to remove tetracyclines (Doxycycline and Oxytetracycline) from aqueous solution. The N-CDs were derived from *Acacia tortilis* seed extract and applied at different concentrations (10, 20, 30 mg/ mL) to water samples containing 10 mg/mL of antibiotic. The effectiveness of this treatment was evaluated over periods of 16 and 24 hours using a UV-visible spectrophotometer. Characterization of the N-CDs was conducted through UV, Fourier-transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The results revealed that N-CDs produced from *A. tortilis* seed extract were of high quality, where the UV-Vis spectral profile showed peaks ranging from 251–293 nm and an average ζ-potential of -31.6 mV. FTIR indicated functional groups at peaks of 3300 cm^{-1} and 1631 cm^{-1} that corresponded to O-H and C=C. Such N-CDs revealed removal efficiencies for doxycycline and oxytetracycline, which reached 8.98% and 19.5%, respectively, with the highest efficiency observed at 30 mg/ mL concentration after 24 hours. N-CDs' ability to remove antibiotics from water is time- and concentration-dependent. This research demonstrates a promising, eco-friendly approach for mitigating antibiotic pollution in an aqueous solution, contributing to developing effective water treatment technologies.

KEYWORDS: Carbon dots; Nanofabrication; Green one-pot synthesis; *Acacia tortilis*;

INTRODUCTION

The contamination of aquatic systems with antibiotics leads to potential hazards that affect both human health and the ecosystem (Wang et al., 2023). Antibiotics are mainly used in human medical therapy and agriculture livestock as growth promoters and disease controllers (Kovalakova et al., 2020). Antibiotic residuals have frequently been detected in the surface groundwater and drinking water (Liu et al., 2017).

Antibiotic residuals reach aquatic systems by discharging wastewater treatment plant effluent, which can flow into surface water bodies or infiltrate groundwater containing significant concentrations of non-metabolized residuals (Carvalho and Santos 2016; Martínez 2008). Antibiotics have the potential to endure in aquatic environments for extended durations (Guo et al., 2020). For instance, tetracyclines (TCs) are not easily metabolized by humans and animals, leading to more than 70% of the original substance being excreted and consequently entering the environment (Xu et al., 2021). TCs cannot be easily degraded naturally because of their chemical stability. However, the byproducts of their degradation can sometimes be more toxic than the original substance (Xiao et al., 2023).

Furthermore, the presence of antibiotics in the surface water leads to the development of bacterial resistance and mutation (Wang et al., 2017). Antibiotic resistance is designated a significant global health threat by the World Health Organization, endangering humans and ecosystems (Leonard et al., 2015). Additionally, antibiotic residuals may trigger endocrine disruption, and there's a risk of harmful effects arising from unidentified byproducts (Zeng et al., 2018). Doxycycline (DO) and Oxytetracycline (OTC) are members of the tetracycline group that are used in treating various bacterial infections, including veterinary uses (Zaidi et al., 2019). Li et al. (2008) stated that many OTC and related substances remain in the water even after wastewater plant treatment. However, groundwater showed tetracyclines residual at low concentrations (MacKie et al., 2006). Since removing antibiotic residues by conventional wastewater treatment methods is inefficient (Langbehn et al., 2021), the emergence of antibiotic residues interfering with the development of aquatic species is also an expected disaster, and these antibiotic residues may build up in the food chain, significantly impacting human health leading to conditions such as nephropathy, joint disease, central nervous system defect, mutagenicity, and changes in photosensitivity (Kovalakova et al., 2020).

Various methods have been employed to remediate water, such as ozonation (Sánchez-Polo et al., 2008) and chemical reduction (Chen et al., 2012). These methods have many disadvantages; chemical methods are expensive and could produce toxic residuals (Mehrjouei, Müller, and Möller 2014). Recently, the adsorption method offered several benefits above other methods due to its lower power consumption, easy handling, and environmental friendliness (Ahmad et al., 2014). Nanoparticles (NPs) have attractive properties due to their tiny sizes, huge surface area, and high sensitivity to their bulk material counterpart (Bhilkar et al., 2023). Carbon dots (CDs) are a new class of spherical, crystalline carbon nanomaterials, ranging in size from 1 nm to 10 nm (Jing et al., 2023). CDs attract research attention due to their unique characteristics, such as biocompatibility, dispersibility, high chemical stability, and low environmental hazard, rendering them promising light-emitting materials (Hong et al., 2022; Liu et al., 2020). Green resources are preferred for CD production due to their affordability, ready availability, stability, straightforward process, safety, eco-friendliness, and abundant carbon sources (Jing et al., 2023). Limited studies have tested the ability of CDs to mitigate tetracyclines from aqueous solution; however, combinations of CDs with other materials have been employed for this purpose. Guo et al. (2017) prepared CDs/g-C3N4/ZnO nanocomposite through a thermal impregnation process, which showed efficient TC degradation (100%) in 30 minutes. Green synthetic protocols have been established for synthesizing N-CDs from various natural sources as green precursors by utilizing different plant parts. For instance, Atchudan et al. (2016) have prepared N-CDs from *Prunus persica* fruit extract. Furthermore, Korah et al. (2022) successfully synthesized N-CDs using Curcuma amada extract. For the current study, the seeds of *A. tortilis* were selected as a carbon source for synthesizing nitrogen-doped carbon dots (N-CDs). *A. tortilis* is a tree known as Umbrella thorn, is a halophyte, drought resistant, and

grown in Ethiopia, Yemen, Sudan, Somalia, part of Kenya, Tanzania, and Saudi Arabia (Meresa et al., 2016; Noumi and Chaieb 2012). *A. tortilis* seeds extract consists of 5.30% moisture, 3.99% ash, 9.19% fat, 14.31% fiber, 27.21% protein and 45.30% carbohydrates (Embaby and Rayan 2016). Hence, this study seeks to synthesize N-CDs using *A. tortilis* seed extract as a carbon source for the first time and assess their characteristics. While applied at varied concentrations, the N-CDs were investigated to remove DO and OTC from aqueous solutions. The study also examined how the treatment duration influences the effectiveness of mitigation.

MATERIALS AND METHODS

Chemical reagents

Doxycycline hyclats and oxytetracycline hydrochloride were provided by Saudi Pharmaceutical Industries (SPI). Acetone, methanol, and urea were obtained from the laboratory at Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia. Acacia tortilis ssp. Spirocarpa seeds are provided by RCRC Seed Bank in Riyadh, Saudi Arabia.

Biosynthesis of green, fluorescent N-CDs

To prepare N-CDs, 5 grams of plant seed powder were mixed with 50 mL of distilled water and stirred for 60 min. The mixture was then filtered using Whatman filter paper to eliminate undissolved particles, resulting in the collection of 20.0 mL of filtrate. Subsequently, 2.0 g of urea was introduced to the filtrate, and the resulting solution was heated in a crucible at 180°C for 2 hours. Once the crucible had cooled, the solid product was scraped and transferred into a centrifuge tube with 15 mL of acetone to separate N-CDs from any remaining unreacted materials. The successful formation of N-CDs was confirmed using a UV lamp, which typically causes N-CDs to fluoresce under its light, as demonstrated in Figure 1. The mixture was then centrifuged at 5500 rpm for 15 minutes, after which the supernatant was carefully removed, ensuring the pellet remained intact at the bottom. This pellet underwent multiple washing cycles with acetone and methanol (90:10) followed by centrifugation at 5500 rpm for 15 minutes in each cycle. Finally, the obtained N-CD pellet was stored in a well-sealed container for future use.

Figure 1. Fluorescence properties of the greenly prepared N-CDs mediated by seed extract of *A.tortilis* under UV light at 365 nm

Characterization Methods

In this study, the microstructure and morphology of the N-CDs were investigated using advanced techniques. Transmission electron microscopy (TEM) analysis was conducted using the JEM-1400-Flash instrument to provide detailed insights into the microstructural characteristics of the N-CDs.
The products' shape, size, and morphology were analyzed using scanning electron microscopy (SEM, JSM-IT500HR). The EDX analysis with 15 kV accelerated voltage was applied (STD-PC80). Furthermore, ultraviolet-visible (UV-Vis) spectroscopy, carried out with a Thermo (Scientific Evolution 201 instrument, Serial Number: 5A4T346003, China), allowed the monitoring of the absorbance spectra and detection of the maximum surface plasmon resonance (SPR) of the N-CDs, which fell within the 250-450 nm range. To gain an understanding of the size and distribution of the N-CDs, Dynamic Light Scattering (DLS) measurements were performed using the NANO ZSP instrument (Malvern Instruments Ltd, Serial Number: MAL1118778, ver 7.11, UK) and three measurements per sample were performed. Moreover, Fourier-Transform Infrared Spectroscopy (FT-IR) was carried out using the SPECTRUM100 instrument (Perkin-Elmer, USA). This technique effectively analyzed the functional groups of biomolecules in the sample by measuring their infrared absorption and emission spectra. 64 scans per sample were done in the range between 400 and 4000 wavenumber cm^{-1}

Adsorption Experiments Effect of N-CDs Dose on Antibiotic Adsorption

A 10 mL solution containing individual OTC and DC at a 1.25 mg/mL concentration was tested using different N-CD concentrations (10, 20, and 30 mg). After that, the mixture was sealed using plastic wrap and agitated on a constant-temperature shaker at 180 rpm at room temperature. Finally, the sample was collected for measurement. An antibiotic solution was used as a control.

Effect of N-CDs treatment duration on antibiotic adsorption

The measurement process was conducted at two distinct time intervals: first, after 16 hours and then again after 24 hours. This approach was employed to thoroughly investigate the impact of contacting time on the adsorption process over specified durations.

Detection of antibiotic

The residual antibiotics concentration in the solution was determined by UV spectrophotometry. 1 mL of each concentration, including control, was centrifuged for 10 min, and the residual concentration of OTC and DC in the liquid was detected by UV spectrophotometer, where OTC was detected at 303 nm and DC at 358 nm. These wavelengths were selected based on the previously identified OTC and DC adsorption wavelengths. For the measurements, a standard curve has been created from the stock solution prepared by dissolving 0.025 g of individual DC and OTC in 25 mL of distilled water. For DC, precise volumes of 20, 40, 50, 60, and 80 µL were carefully transfered from stock solution into 1mL Eppendorf tube, and the volumes were adjusted to 1.0 mL using distilled water. The linear standard curve range was constructed at 0.5-2 mg/mL ($R^2 = 0.999$). For OTC, 10, 20, 30, 60, and 70 µL were carefully trannbsfered from stock solution into 1mL

Eppendorf tube, and the volumes were adjusted to 1.0 mL using distilled water. The linear standard curve range was constructed as 0.25- 1.75 mg/mL (R2 = 0.999). The removal efficacy (RE%) was determined using the following formula:

$$Removal\ Efficacy\ (\%) = \left(\frac{Initial\ Concentration - Final\ Concentration}{Initial\ Concentration}\right) \times 100 \quad (1)$$

Statistical analysis

The statistical analysis, including the mean, standard deviation, and relative standard deviation, were computed using Microsoft Excel 2019. Spectra for FTIR and UV-Vis were generated using OriginPro® 2023b.

RESULTS AND DISCUSSION

Characterization of N-CDs

Results from the current study indicated that *A. tortilis* seed extract was a viable material to fabricate N-CDs that were further tested for their catalytic activity to eliminate DC and OTC from an aqueous solution. The absorption behavior of N-CDs was observed by UV-vis spectroscopy. Figure 2 showed the absorption as a broad peak around the range of 251–293 nm, which is attributed to n→ π* transition of the carbonyl group in the CDs (D'Souza et al., 2016) or it could be due to typical absorption of an aromatic π system (Lu et al., 2019). A similar absorption range of CDs prepared from gelatin was observed between 250–290 nm (Liang et al., 2013). In addition, to determine the electrical charges on the surface of N-CDs and their colloidal stability, a zeta potential test has been applied. Figure 3 illustrates -31.64 mV as the average of ζ-potential. The negative zeta potential guaranteed excellent colloidal stability for N-CDs (Zulfajri et al., 2019). Negative zeta potential values might indicate the presence of negatively charged carboxyl and hydroxyl functional groups (Abd Rani et al., 2021) on the N-CDs surface.

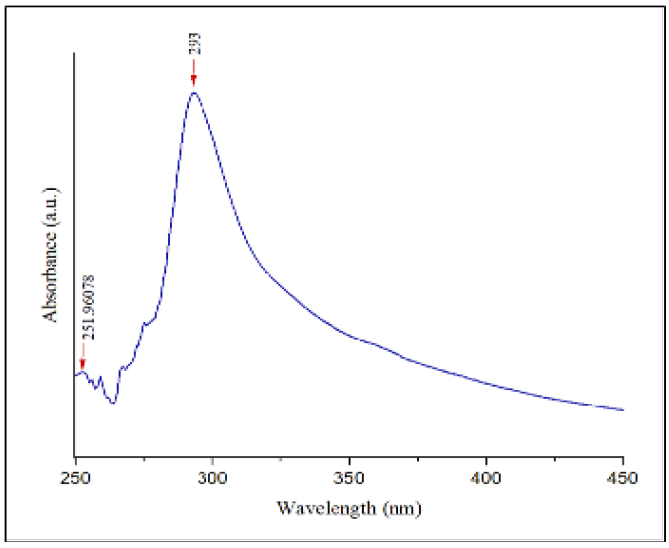

Figure 2. The analysis of UV-Vis absorption spectra for the N-CDs prepared using *A. tortilis* seed extract.

Moreover, the FTIR spectrum was acquired to determine the surface functional groups of the obtained N-CDs. Figure 4 represents the FT-IR spectrum of N-CDs, highlighting absorption bands in the range of 3300 and 1631 cm^{-1}. Bands at 3300 cm^{-1}. correspond to the stretching vibrations of OH (hydroxyl) and NH (amine) groups, which might be responsible for the hydrophilic characteristics of the N-CDs. Liu et al. (2021) suggested that peak at 1631 cm^{-1}. could be attributed to the amide bonding from C=C stretching. Similar peaks were observed in Kalanidhi and Nagaraaj's (2021) study when N-CDs were prepared with betel leaves. Thus, the author suggested the presence of functional groups rich in oxygen and carbon that indicate the formation of N-CDs rich in alcohol and amines. Such functional groups might have a role in N-CDs' ability to adsorb antibiotics (Ahuja et al., 2022; Sadegh et al., 2017). Further characterization of N-CD distribution was evaluated by transmission electron microscopy (TEM). Figure 5 a show well-dispersed N-CDs at 500 nanoscales. Figure 5 B represents the aggregation of semi-circular shapes at a 50 nm scale. The tiny circular structures within these aggregations at a 20 nm scale are the N-CDs with an average diameter of 7nm, as shown in Figure 5 c. Similar observations have also been found when N-CDs were prepared with Jackfruit seed extract (Raji et al., 2019). Figure 6 a-c represents an SEM image for N-CDs fabricated by *A.tortilis* seed extract. Figure 6 a identifies a smooth surface with a folded structure. Sabet & Mahdavi (2019) reported N-CDs quantum dots using grass extract, revealing tiny particles clustered together, forming larger, chunkier structures. This aggregation happens because the tiny carbon particles may have high surface energy.

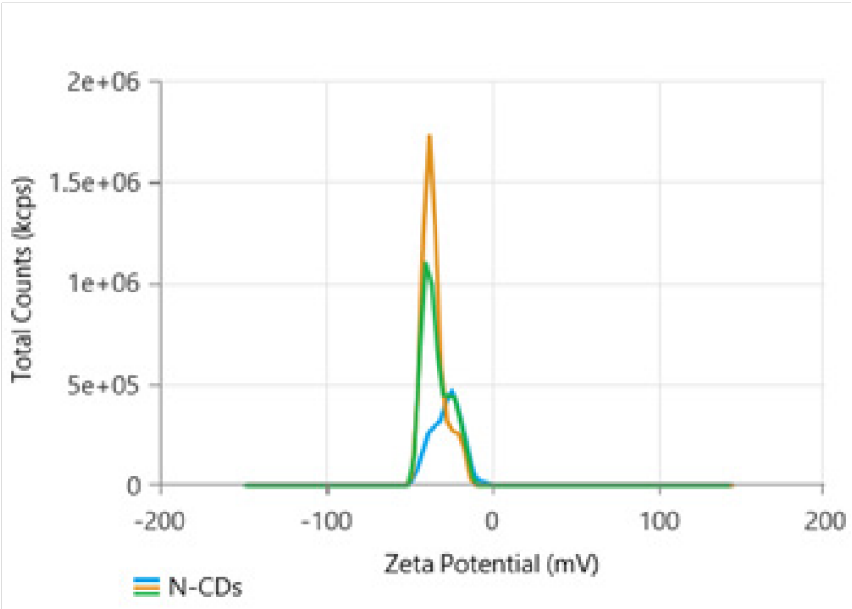

Figure 3. Average zeta potential of -31.64 mV for the N-CDs prepared using seed extract of *A. tortilis*. The figure presents the mean zeta potential of three readings.

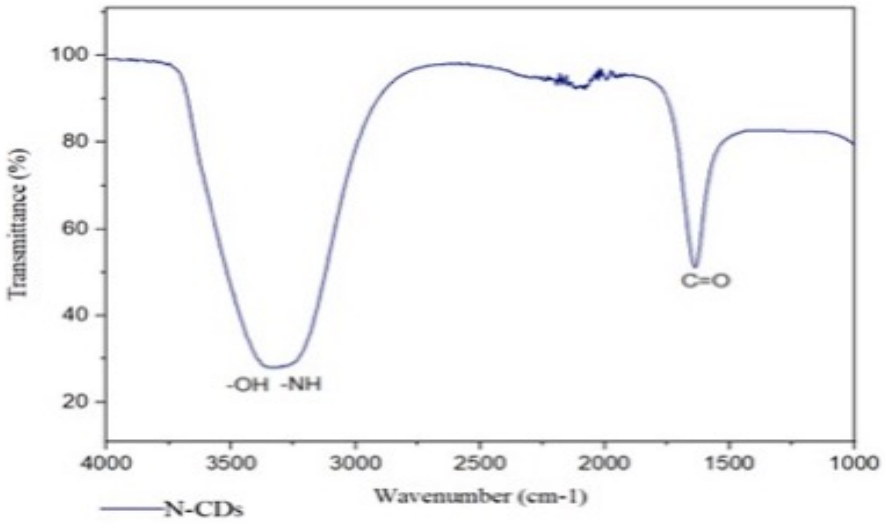

Figure 4. FTIR spectrum of N-CDs prepared by *A.tortilis* seed extract where two major peaks appeared (between 3300 to 3500 cm^{-1} and at 1631cm^{-1}).

Moreover, elemental mapping in Figure 6 b represented the even distribution of C and O elements on the N-CDs surface. Furthermore, EDX spectra in Figure 6 c showed the presence of C and O elements. Perumal et al. (2022) obtained closely related SEM analysis results when preparing N-CDs from Red Malus floribunda fruits.

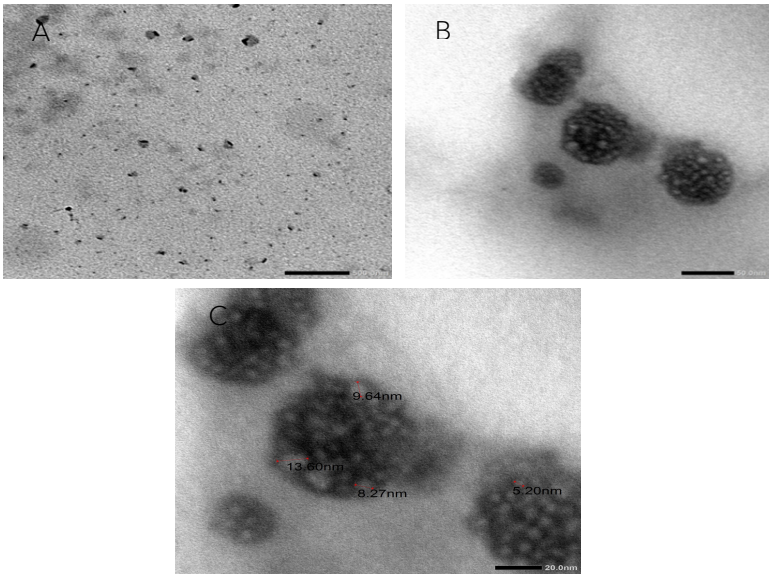

Figure 5. TEM images of N-CDs prepared by *A. tortilis* seed extract showed welldispersed N-CDs (a), three main clusters of N-CDs (b), and the same clusters at higher magnification (c).

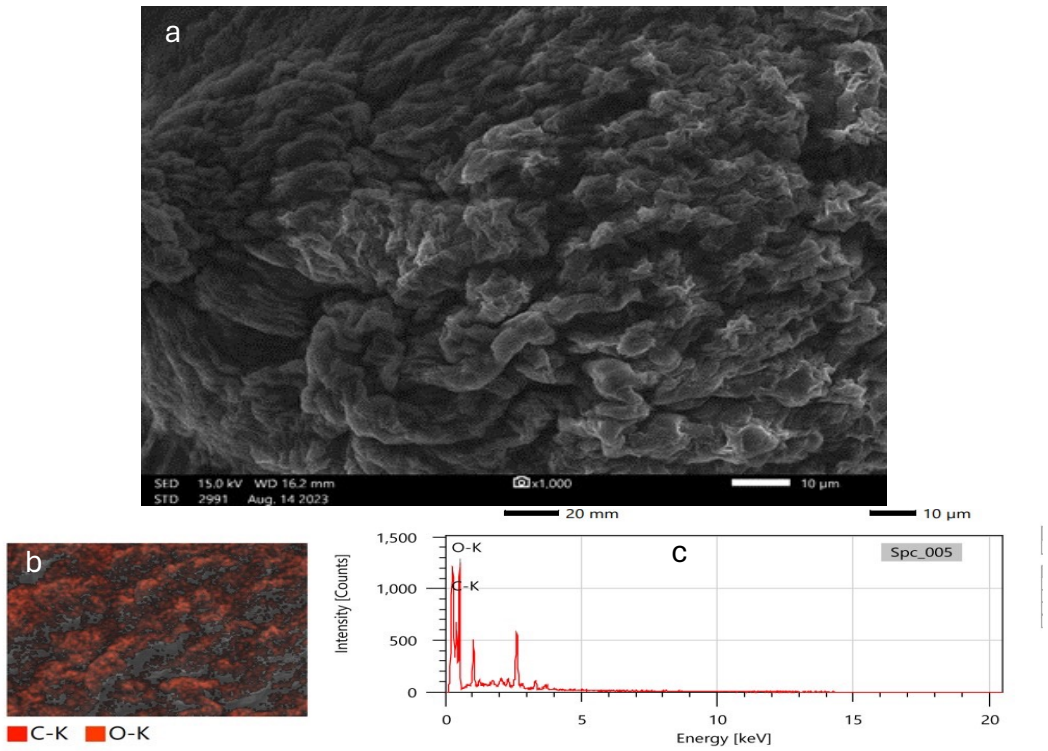

Figure 6. SEM image for N-CDs prepared by *A. tortilis* seed extract (a), EDX elemental mapping (b), and EDX spectrum (c).

Effect of Dose and time on the efficacy of N-CDs on antibiotics adsorption

The current study aimed to assess the efficacy of prepared N-CDs in mitigating antibiotic contamination in water. The concentrations of DC in water before and after treatment with three different concentrations of N-CDs (10 mg, 20 mg, and 30 mg) at two separate time intervals, 16 and 24 hours, were presented in Table 1. The results obtained after 16 hours indicated a noteworthy trend as the dosage of N-CDs increases, the removal efficacy also increases where the removal efficacy percentages were 5.19%, 6.33%, and 7.40% for N-CD concentrations of 10 mg, 20 mg, and 30 mg, respectively. Such findings highlighted the dose-dependent effectiveness of N-CDs in mitigating DC from contaminated water. The results obtained after 24 hours showed removal efficacy percentages of 6.09%, 6.35%and 8.98% for N-CD concentrations of 10 mg, 20 mg, and 30 mg, respectively. A similar pattern of dose-dependent effectiveness was observed at both exposure durations. Notably, the removal efficacy percentages increased after 24 hours compared to 16 hours for all tested concentrations, where the highest removal efficiency was observed in N-CD concentrations at a concentration of 30 mg.

The concentrations of OTC in water before and after treatment with varied concentrations of N-CDs at two distinct time intervals, 16 and 24 hours, are displayed in Table 2. After 16 hours of treatment, it was observed that the removal efficacy percentages for OTC increased as the dosage of N-CDs escalated. Removal percentages were 1.5%, 2.5%, and 4.1% for N-CD concentrations of 10 mg, 20 mg, and 30 mg, respectively. This initial data indicated that higher doses of N-CDs led to more efficient removal of OTC from the water. The results obtained after 24 hours also demonstrated a dosedependent pattern. The removal efficacy

percentages after 24 hours were 6.1%, 5.1%, and a notable 19.5% for N-CD concentrations of 10 mg, 20 mg, and 30 mg, respectively. Reduction percentages were increased compared to the 16-hour treatment for all N-CD concentrations, with the highest removal efficacy observed in N-CD concentrations at 30 mg.

A study conducted by Karaca et al. (2023) indicated the usage of N-CQDs/TiO2 for the removal of their study despite using a relatively high dose (0.2 g/L) of Tetracycline; the adsorption of TC molecules on the N-CQDs/TiO2 surface was only 1.52% over a 120-minute duration. Variations compared to the current findings could be related to the different N-CDs used. However, the initial concentration of TC in the solution can also impact adsorption efficiency. Ekande & Kumar, (2023) explored the effectiveness of N-CDs prepared at high carbonization temperatures ranging from 700°C to 1000°C. He indicated their capacity to adsorb approximately 95% to 98% for Ciprofloxacin (CIP) and TC within 5 minutes. Such a high adsorption rate compared to our materials' efficiency could be attributed to the differences in the carbonization temperature and source since they utilized Polyaniline polymer as the starting material. Variations in carbonization may lead to differences in the composition of active sites and functional groups on the surface of the N-CDs, which ultimately influences the adsorption rates.

The adsorption system employed by N-CDs as an adsorbent for removing both DC and OTC antibiotics might be achieved through π–π electron acceptor–donor interactions, as described by Ekande & Kumar, (2023). The interaction of the OH− group with the benzene rings in the antibiotic (DC and OTC) structure may lead to more electrons, resulting in π–π electron acceptor–donor interaction between the antibiotics and N-CDs (Sun et al., 2020). This agrees with FTIR results that indicated the presence of hydroxyl and amide groups on the surface of N-CDs that actively contribute to removing DC and OTC from contaminated water. Different mechanisms have been widely employed to mitigate antibiotics from aqueous solution. For example, Qu et al. (2020) used ZnO/N and S-CQDs under simulated sunlight for 20 min and natural sunlight for 50 min, respectively, where 92.9% and 85.8% of ciprofloxacin (CIP) were removed. Herein, this variation in the removal efficacy and the reduction in the adsorption as time increases could be attributed to the mechanism itself. During the photocatalytic process, the surface of the N-CDs captures photons originating from the light source, and these absorbed photons then provide the energy needed to create electron-hole pairs (Liu et al., 2019). A hole emerges when an electron undergoes excitation from the valence band to the conduction band. Subsequently, this hole engages in reactions with either water or hydroxyl ions, ultimately resulting in the creation of hydroxyl radicals (Alkian et al., 2020). These hydroxyl radicals readily react with organic molecules, converting them into more friendly substances such as CO_2 and H_2O (Syafei et al., 2017).

Table 1. The concentration of doxycycline (mg/mL) and the removal efficacy of N-CDs prepared by *A.tortilis* seeds extract at different concentrations (10, 20, and 30 mg) after 16 and 24 hours. Data presented are mean ± SD.

	Control	N-CDs (10 mg/mL)		N-CDs (20 mg/mL)		N-CDs (30 mg/mL)	
		16h	24 h	16h	24 h	16h	24 h
Mean	354.1±2.8	335.7±0.4	332.5±0.2	331.7±2.4	331.6±0.5	327.9±0.4	322.3±0.6
RSD	0.8	0.1	0.06	0.7	0.1	0.1	0.1
Reduction (%)		5.19%	6.09%	6.33%	6.35%	7.40%	8.98%

Table 2. The concentration of oxytetracycline (mg/mL) and the removal efficacy of N-CDs prepared by *A.tortilis* seeds extract at different concentrations (10, 20, and 30 mg) after 16 and 24 hours. The data presented mean ± SD.

	Control	N-CDs (10 mg/mL)		N-CDs (20 mg/mL)		N-CDs (30 mg/mL)	
		16h	24 h	16h	24 h	16h	24 h
Mean	319.5±3.4	314.5±1.7	300.0±2.8	311.4±3.7	303.2±3.03	306.4±2.4	257.1± 0.6
RSD	1.0	0.5	0.9	1.2	0.9	0.7	0.2
Reduction (%)		1.5%	6.1%	2.5%	5.1%	4.1%	19.5%

CONCLUSIONS

This study demonstrated the feasibility of producing cost-effective, environmentally friendly fluorescent N-CDs by the principles of sustainable green development using *A.tortilis* seed extract. Through TEM analysis, the synthesized sample showed a small size where the ζ-potential average was -31.6 mV. The findings also unveiled the presence of essential phytochemical compounds in the seed extracts of *A.tortilis*; as evidenced by FTIR analysis, such compounds may play a crucial role in the mitigation process. The prepared N-CDs exhibited a removal efficiency of 8.98% for DC and 19.5% for OTC. Higher efficiency could be obtained when a higher concentration is applied. This research underscores the promise of employing green methods for synthesizing N-CDs, offering an environmentally friendly approach to address the removal efficiency of antibiotics from water resources.

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Declaration of interests

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

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