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Method Optimization for the Removal of Tetracycline from Water Using Bio-Waste Derived Nanomaterials

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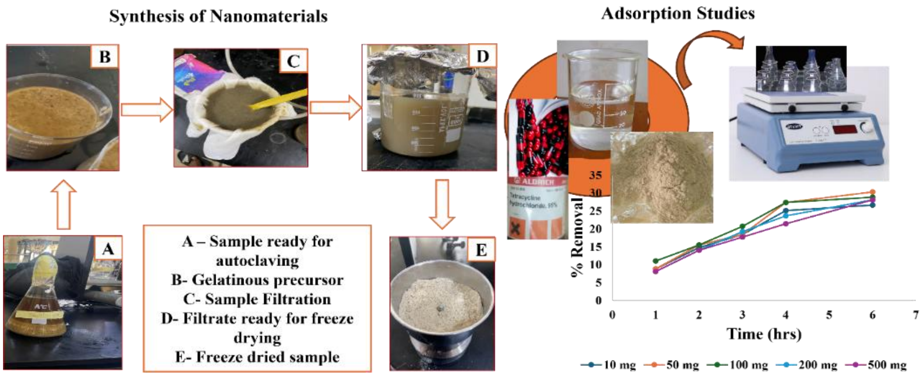
ABSTRACT

Pharmaceutically active compounds (PhACs) are essential chemical substances utilized for health maintenance and disease prevention. As a result of the widespread release, unregulated discharge and environmental effects of PhACs, there is a compelling need for efficient and sustainable removal strategies. This study focuses on the optimization of Tetracycline (TCN) removal from water using nanomaterials synthesized from potato peels. The adsorptive material used was prepared through chemical-hydrothermal processes and characterized using ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscopy). FTIR analysis showed prominent peaks at 3272, 1643 and 1416 cm^{-1} which were associated with O-H, C=C isolated and C=C conjugated vibrations respectively in the nanomaterial while SEM analysis showed an irregular amorphous flat sheet with porous structures. Three wavelengths at 270 nm, 357 nm and 370 nm were tested in optimization studies for determination of TCN in standard solutions using UV-Visible spectrophotometer. Wavelength at 357 nm was observed as the optimal wavelength, which gave a linear calibration curve with a regression coefficient of 0.99 and absorbance values that ranged from 0.071 ± 0.001 to 0.185 ± 0.001 for the studied concentrations of 0.5 to 50 mg/L. There was no significant difference in the level of TCN adsorbed by the different doses of nanomaterials (10, 50, 100, 200, and 500 mg). However, removal efficiency was observed to be significantly time dependent. Overall, results indicate the potential of these biowaste-derived nanomaterials for tetracycline removal, offering a sustainable, eco-friendly, and cost-effective solution for water purification.



KEYWORDS: Antibiotics; Adsorption studies; Nanomaterial; Potato peel; Water purification.

1. INTRODUCTION

The increase in human pharmaceutical intake results in the daily release of pharmaceutically active compounds (PhACs) into the environment [1]. Since conventional wastewater treatment methods are unable to entirely remove pharmaceuticals from contaminated water, the discharge of wasterwater remains the main source of these organic micro-pollutants [2,3]. The presence of pharmaceuticals and the dangers associated with their metabolites or conjugates in the environment are issues that have become a growing source of global concern, even though PhACs normally occur at trace amounts in a range of environmental matrices [4].

In Nigeria where portable water is sourced from underground systems, there is the likelihood that these untreated wastewater will percolate into the soil and contaminate underground water [5]. The presence of PhACs in portable water have been linked to carcinogenicity and genotoxicity [6,7]. Furthermore, a number of PhACs, including hormones, anxiolytics, antibiotics, psychoactive compounds, and antiepileptic medications, are recognized to present serious threats to aquatic lives [8–10].

Antibiotics are being used extensively [11,12], which is causing their presence in a wider range of matrices and their environmental fate to become a global issue [13]. Multiple mechanisms such as electrostatic interaction, hydrophobic contact, hydrogen bonding, π-π interactions, and cation exchange, are involved in the adsorption of antibiotics from polluted water [14]. Carbon nanomaterials are an important class of adsorbent that excel in the electrostatic adsorption of antibiotics [15]. Previous studies have performed adsorptive removal of pollutants using chemically synthesized nanomaterials [16,17] while some studies synthesized nanomaterials for other purposes [18–20]. Here, we evaluated the adsorptive properties of nanomaterials derived from sweet potato peels for the removal of tetracycline (TCN) in spiked water by synthesising benign nanomaterials from potato peels, performing functional group and morphological characterization of the synthesized materials and testing the efficacy of the synthesised materials.

2. MATERIALS AND METHODS

2.1. Sample collection and synthesis

Sweet potato peels, used as carbon source, obtained from one of the kitchens within Chrisland University, were wrapped in aluminum foil, and kept in Zip lock® bags. The samples were washed several times with distilled water, then dried in a thermostated oven at 100 ℃ till constant weight, to ensure total elimination of moisture. After 29 hours, the hard and brittle sample was pulverized. 50 g of sample was then weighed and immersed in 2 L, 2% NaOH for 24 hours. Soaked potato peels were washed with distilled water, until completely neutral, autoclaved for 2 hours at 120℃, homogenized for 2 hours and filtered using a Buchner filtration set up. The filtrate was kept at 4°C prior to freeze-drying performed on a LYOTRAP lyophilizer.

2.2. Characterization of Freeze-dried materials

ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) was used to identify the presence of functional groups. The freeze-dried samples were evenly combined with KBr powder at a ratio of 1:100, ground down, and then compressed under 10 tons to create pellets. The disc containing the prepared pellet was then put inside the FT-IR spectrometer (MY19322004 Agilent Technologies Cary 630) disc holder. 32 scans were performed on the samples to get a transmission spectrum at 4 cm^{-1} resolution and a scanning range of 4000 cm^{-1} - 400 cm^{-1}.

The surface morphology and elemental analysis of freeze-dried samples were determined using field emission scanning electron microscopy with energy dispersive X-ray (SEM-EDX) (FEI Inspect F50 American Nancorporation).

2.3. Optimization and instrumental analysis of TCN

Stock standard solution containing 100 mg/L tetracycline (TCN) was prepared from a tetracycline hydrochloride (95%) standard (Sigma Aldrich). Calibration standards of 0.5, 1, 5, 10, 25 and 50 mg/L were prepared from the stock standard. Three different wavelengths (270 nm, 357 nm, 370 nm) were used to test the optimal wavelength for analysis of TCN in the standard solutions using a Biobase 752N UV-VIS spectrometer.

2.4. Adsorption studies

Batch adsorption study was performed employing different adsorbent dosage of nanomaterial against the same concentration of TCN. Here, 10, 50, 100, 200, and 500 mg of nanomaterial were introduced into separate conical flasks containing the same concentration of TCN (100 mL, 50 mg/L TCN). The sample material was then placed on an orbital shaker (ZD-9556) operated at an angular velocity of 130 rpm. After the first, second, third, fourth, fifth and sixth hour of shaking, 5 mL of aqueous sample was taken and centrifuged at 3000 rpm for 5 minutes. After which the supernatant was carefully separated from the solid residue and absorbance measurements were taken on the UV-VIS spectrophotometer. Procedural blanks were also analyzed.

3. RESULTS AND DISCUSSION

3.1. Functional groups and morphology of synthesised nanomaterials

Synthesized nanomaterials were composed of irregular flakelike sheets with porous structures (Fig. 1A, B & C). The FTIR spectra of synthesized nanomaterial in Fig. 1D revealed prominent bands at 3272 cm^{-1}, indicating the presence of O-H. Other important peaks present are 1643 cm^{-1}, 1416 cm^{-1} and 1080 cm^{-1}, which were associated with C-O, C=C isolated and C=C conjugated vibrations respectively in the nanomaterial.

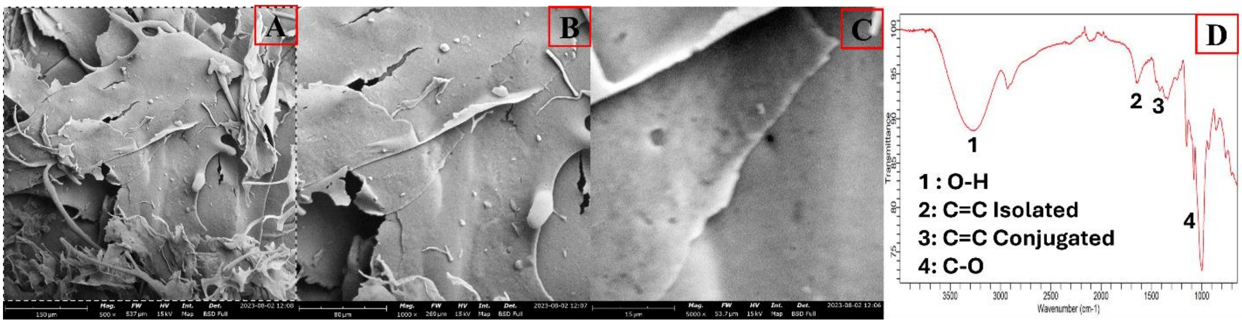


Fig. 1: Morphology of synthesized nanomaterials (A, B & C). FTIR wave bands showing prominent functional groups in synthesized nanomaterials (D)

3.2. Optimal wavelength for determination of TCN in spiked water

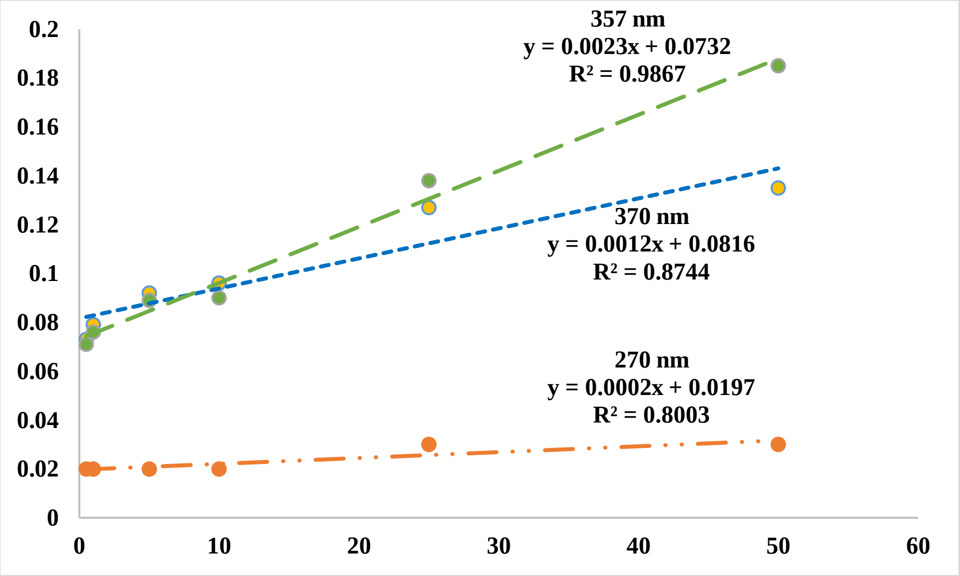


Fig. 2: Calibration plot at 270 nm, 357 nm, and 370 nm for TCN standard solutions

Triplicate analysis of tetracycline standard solutions gave linear calibration plot, for mean values, over the studied concentration (0.5 – 50 mg/L) range, with regression coefficients of 0.80, 0.87, and 0.99 at 270, 370, and 357 nm respectively. The wavelength at 357 nm was considered the optimal wavelength, having the highest r^2 value of 0.9867 (Fig. 2) with absorbance values that ranged from 0.071 ± 0.001 to 0.185 ± 0.001 for 0.5 to 50 mg/L TCN standard solutions.

3.3. Effect of adsorbent dose on the removal efficiency of TCN

Batch absorption studies revealed a continuous increase in the adsorption concentration of TCN in spiked water with increase in time for all quantities (10, 50, 100, 200, and 500 mg) of nanomaterials employed (Fig. 3). Although the adsorption efficiency was statistically indistinguishable among tested doses of nanomaterials ($p > 0.05$), 50 mg adsorptive material gave the best removal efficiency, having the highest increase at the sixth hour. Aside the first and third hour, where 100 mg adsorptive material gave slightly higher removal value than 50 mg, at every other time no adsorptive material had higher removal efficiency than 50 mg.

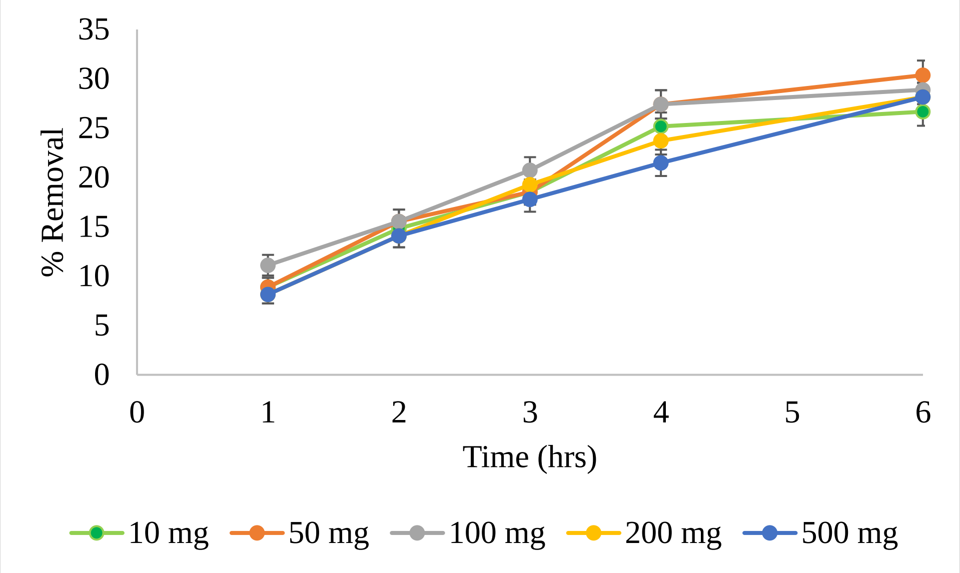


Fig 3: Percentage (%) removal of TCN from (50 mg/L) spiked water over six hours using different doses of nanomaterials. Error bars showing the mean values ± SD from triplicate determinations.

In addition, the other higher doses of adsorptive nanomaterials, viz., 200 mg and 500 mg, resulted in a decrease in removal efficiency across the studied time. The presence of O-H and C=C functional groups in our adsorptive nanomaterials is an indication of strong intermolecular attraction via hydrogen bonding and π-π interaction with TCN, which contains NH_2 functional group in addition to several OH and pi bond.

3. 4. Effects of adsorption time on the removal efficiency of TCN

Comparing the effect of time and adsorbent dosage on the adsorptive removal of TCN, it is obvious that that time had a more profound effect on the adsorptive removal of TCN from aqueous solutions than the adsorbent dosage. This suggests that the diffusion of tetracycline to the adsorptive site is crucial in the adsorption process [21]. In addition, the fact that percentage adsorption did not increase significantly with increase in adsorbent loadings shows that the mass transfer of TCN from the bulk solution to the surface of the adsorbent is slow and hence increasing the amount of adsorbent does not significantly increase the adsorptive removal of TCN [22] while adsorption time was found to significantly affect TCN removal efficiency. Our results revealed that TCN has a maximum adsorption capacity of 0.135 mg of TCN/mg.

4. CONCLUSION

This pilot study determined the efficiency of using nanomaterials synthesized from potato peels for the removal of tetracycline from spiked water. Overall, results indicate the potential of biowaste-derived nanomaterials for tetracycline removal, offering a sustainable, eco-friendly, and cost-effective solution for water purification. Further research employing more robust synthesis and characterization techniques as well as detailed removal studies using real wastewater samples, rather than spiked samples, are recommended.

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