https://doi.org/10.48048/tis.2025.9562

Understanding Tetracycline-Nanoceramic Interactions: A Study Using UV-Vis, Fluorescence Spectroscopy and HPLC

Hillary N. Jufer[1], Kim Wilmer M. Balagot[2,3], Alfredo S. Dumalsen[4], Hunter N. Tonn[4] and Elmer-Rico E. Mojica[3,4,*]

[1]*Department of Environmental Studies and Science, Pace University, New York 10038, United States*
[2]*Chemistry and Biotechnology Section, Material Science Division, Department of Science and Technology, Forest Products Research and Development Institute (DOST-FPRDI), College Laguna 4031, Philippines*
[3]*Institute of Chemistry, University of the Philippines Los Banos, College Laguna 4031, Philippines*
[4]*Department of Chemistry and Physical Sciences, Pace University, New York 10038, United States*

([*]Corresponding author's e-mail: emojica@pace.edu)

Received: 19 December 2024, Revised: 3 February 2025, Accepted: 13 February 2025, Published: 20 March 2025

Abstract

Tetracyclines (TCs) are among the most widely used antibiotics for disease control and livestock feed due to their broad-spectrum therapeutic properties. However, their extensive use, particularly oxytetracycline (OTC) and doxycycline (DC), has led to their widespread presence in water and soil environments, raising ecological and public health concerns. The electron-rich functional groups of TCs, including ketone, carboxyl, amino, and hydroxyl moieties, enable strong complexation with metal oxides, making nanoceramic materials promising adsorbents for their removal. In this study, the adsorption behavior of OTC and DC onto commercial nanoceramics (SiO_2, Al_2O_3, TiO_2, and ZnO) was investigated using UV-Vis absorption, fluorescence spectroscopy, and high-performance liquid chromatography (HPLC). Spectroscopic analyses revealed significant reductions in absorbance and fluorescence intensity upon nanoceramic addition, indicating strong antibiotic adsorption and fluorescence quenching, particularly for ZnO and Al_2O_3. TiO_2 also demonstrated moderate adsorption capacity, while SiO_2 exhibited a distinct behavior, enhancing fluorescence intensity and increasing HPLC peak areas, suggesting weaker adsorption interactions possibly influenced by solvation effects or surface passivation. HPLC results confirmed that DC exhibited a higher adsorption rate than OTC, with TiO_2 and Al_2O_3 achieving over 80 % removal efficiency. The unique behavior of SiO_2 suggests that it does not strongly adsorb tetracyclines but may influence their solubility or molecular stability. These findings provide mechanistic insights into tetracycline-nanoceramic interactions and underscore the importance of material-specific adsorption behaviors for wastewater treatment applications.

Keywords: Absorbance**,** Antibiotics**,** Fluorescence, HPLC, Nanoceramics, Tetracycline

Introduction

Tetracyclines are the most widely used antibiotics in the United States, particularly for veterinary medicine. Animal wastes, commonly used as fertilizers on croplands, contribute to the accumulation of antibiotics near areas with large confined animal feeding operations or CAFO [1]. Between 2005 to 2007, tetracyclines accounted for 38 % of the 27.85 million pounds of total antibiotics used [2]. Globally, the widespread use of tetracyclines has raised concerns about their present in the environment, as they are often detected as concentrations as high as 1,000 ug/kg [3]. For example, chlortetracycline (CTC) has been identified at levels of 20 mg/kg in agricultural soils, highlighting its persistence and potential ecological impacts [4]. Tetracyclines excreted by livestock, primarily through feces and urine, range from 70 % to

90 % of the administered dose. For instance, studies show that pigs excreted 72 % of administered TCs, which subsequently degrade into antibiotic residues depending on environmental pH. These residues can exhibit altered biological activity compared to the parent compound, further complicating their environmental impact [5,6].

Current methods of removing antibiotics from water include chemical, biological and physical methods. Chemical methods primarily involve transformation or degradation of antibiotics and include several oxidation processes, such as Fenton oxidation, ozonation, electrochemical oxidation (EO), and photocatalytic oxidation, among others [7]. This approach is highly successful for antibiotic degradation; however, its application is limited on a small scale due to elevated energy consumption, expenses, and complex operational requirements [8]. Biological methods, on the other hand, utilize microorganisms to degrade antibiotics and include conventional activated sludge (CAS) procedures, membrane bioreactors (MBRs), and anaerobic reactor systems, among others. This method is regarded as the most cost-effective and environmentally sustainable for the removal of antibiotics from wastewater; nonetheless, it presents uncertainties, such as the potential impact of antibiotic-resistant bacteria on the overall treatment efficacy [8]. Lastly, physical methods primarily rely on separation techniques and include membrane filtration and adsorption. Adsorption has various advantages over the other removal methods dues to its simplicity, affordability, reliability, minimal use of energy, rapid performance and quick adsorbent recovery to its low cost and rapid performance [9]. These methods are widely used, and activated carbons, clay materials, zeolites and biochars are effective adsorbent materials in removing antibiotics. With the advancement of nanomaterials and novel composite materials, their efficacy in wastewater treatment has significantly improved [8].

Nanomaterials can be classified to carbon-based nanomaterials, semiconductor-based nanomaterials, metal nanoparticles, polymer-based nanomaterials, and lipid-based nanomaterials [10]. Recently, metal-based nanomaterials particularly metal oxide nanoparticles such as silicon oxide (SiO_2), aluminum oxide (Al_2O_3), titanium oxide (TiO_2) and zinc oxide (ZnO), have been identified as promising materials for removing antibiotics from aqueous systems due to their strong adsorption reactivity and capacity and high specific areas [11]. These materials offer advantages such as fast kinetics, selective sorption of pollutants and high adsorption capacities [2,12]. Additionally, they also strong photocatalytic reaction to destroy organic contaminants which includes antibiotics. It is made possible through the presence of oxygen which can break down the organic contaminant on the surface of the metal oxide nanoparticle through photocatalysis. The production and enhancement of oxygen vaccines is made possible through the absorption of semiconducting nanomaterials by photons. The organic contaminants are then converted to low-to-intermediate toxic products and it finally results in the formation of chemicals such as carbon dioxide, water, and inorganic ions [13,14].

In the recent years, among the nanomaterials, ZnO, TiO_2, SiO_2 have the largest production in the world with an average annual peak production of 28,000, 40,000 and 55,000 tons, respectively [15]. Thus, in this study, the potential of SiO_2, Al_2O_3, TiO_2 and ZnO as nanomaterials for remediating TCs focusing on oxytetracycline (OTC) and doxycycline (DC) (**Figure 1**) was investigated. These commercially available nanoceramics were selected due to their unique properties that makes them particularly suited for antibiotic adsorption. Compared to biochar, graphene oxide and metal-organic frameworks, nanoceramics offer superior thermal and chemical stability, ease of commercial availability and relatively low production costs. While biochar and graphene oxide exhibit high adsorption capacities, their synthesis processes often rely on high-energy inputs or non-renewable precursors. Similarly, MOFs, though effective, present challenges such as complex fabrication methods, high costs, and limited scalability. Nanoceramics, on the other hand, provide a balance between performance and practicality, with proven efficiencies in pollutant adsorption and compatibility with existing wastewater treatment systems. Despite their potential, nanoceramics face several challenges that limit their practical applications. These challenges include high production costs, reliance on non-renewable resources, secondary pollution, limited regeneration efficiency, and variable performance across different pollutants [16]. Highlighting and addressing these challenges are crucial for advancing the utility of nanoceramics in environmental remediation.

The remediation of TCs with the nanomaterials was evaluated using UV-Vis absorption spectroscopy, fluorescence spectroscopy and high-performance liquid chromatography (HPLC). The antibiotic solutions prepared under controlled laboratory conditions, serve as models for ground water, wastewater, and environmental effluents. This study aims to determine the remediation effect of nanoceramics to TCs, with the broader goals of developing cost-effective strategies for mitigating antibiotics pollution. In addition, this study contributes by investigating the molecular-level interactions of tetracycline analogs with commercial nanoceramics to identify mechanisms that can enhance adsorption efficiency and reduce environmental risks. Specifically, this work builds on past studies by focusing on the interactions of tetracyclines with nanoceramics at the chromophore level, addressing gaps in the mechanistic understanding of adsorption processes. The findings aim to advance the optimization of nanoceramics for real-world wastewater treatment applications.

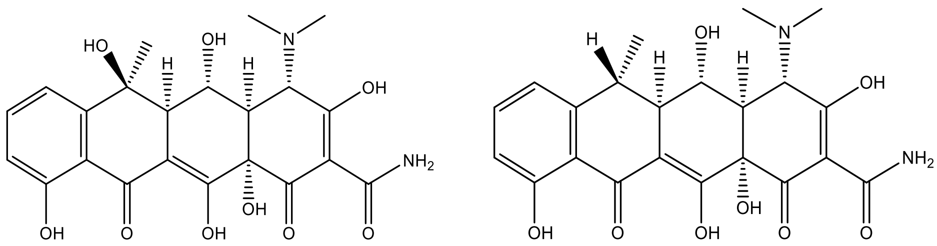

Figure 1 Structure of oxytetracycline (left) and doxycycline (right).

Materials and methods

Reagents

Commercially available nanomaterials: aluminum oxide (Al_2O_3), silicon oxide (SiO_2), titanium oxide (TiO_2) and zinc oxide (ZnO) were purchased from Sun Innovations, Inc. Oxytetracycline (OTC), doxycycline (DC) and methanol were all purchased from Sigma Aldrich (analytical grade, > 99 % purity).

Antibiotic-nanomaterial mixture preparation

Each nanomaterial (1.0 mg) was individually weighed into separate Eppendorf tubes. Stock solutions of the tetracycline antibiotics were prepared by dissolving solid standard initially in methanol. A 10-ppm solution of OTC and DC, as well as a mixed solution containing both TCs, was prepared. The nanomaterial was added to 2.0 mL of the antibiotic solution in the respective tube. The resulting mixture were incubated at room temperature for 1 h with periodic manual shaking. Following incubation, the samples were centrifuged at 10,000 rpm for 2 min using a mini-centrifuge to settle nanoparticles. The supernatant was filtered through a 0.22 um syringe filter to remove any suspended particles before analysis. These conditions, including antibiotic concentrations and pH values, were chosen to reflect common environmental contamination scenarios reported in wastewater and agricultural runoff studies.

Instrumentation

These instrumental methods (UV Vis and fluorescence spectroscopy and HPLC) were selected for their sensitivity and ability to detect both individual and binary mixtures of antibiotics in solution, providing quantitative insights into the adsorption efficiencies of different nanoceramics.

The ultraviolet-visible (UV-Vis) absorption spectra and fluorescence emission spectra were collected at room temperature using a quartz cuvette with cell pathlength of 1.0 cm. The absorbance spectra from 200 to 600 nm were obtained using Jasco V-570 spectrophotometer (Easton, MD). The emission spectra, on the other hand, were collected using a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon Inc., Edison, NJ) with excitation wavelength of 350 nm. Standard solutions of antibiotics were also analyzed for comparison to understand the relative impact of nanomaterial adsorption on the spectra.

The concentration of the antibiotics without and added with nanomaterials was determined using chromatographic analysis (HPLC). An Agilent 1,100 unit was used with a Zorbax Eclipse XDB-C8 column (4.6×150 mm (Agilent)). A mobile phase of 11 % methanol: 22 % acetonitrile: 67 % 0.01 M oxalic acid was used for TC analysis. Standard solutions of all antibiotics were also analyzed to compare with those solutions mixed nanomaterials.

High-performance liquid chromatography (HPLC) was performed using an Agilent 1100 HPLC system equipped with a Zorbax Eclipse XDB-C8 column (4.6×150 mm, Agilent). The mobile phase consisted of 11 % methanol, 22 % acetonitrile, and 67 % 0.01 M oxalic acid at a flow rate of 1.0 mL/min. The injection volume was 20 µL. OTC and DC were detected at 360 nm. Retention times were recorded for both tetracyclines, and peak areas were used to quantify the antibiotics in solution. These methods were selected for their sensitivity and ability to detect both individual and binary mixtures of antibiotics in solution, providing quantitative insights into the adsorption efficiencies of different nanoceramics.

Results and discussion

There are 3 peaks that can be observed in both DC and OTC solution. These are at 250, 270 and 360 nm. These peaks can be due to the presence of 2 chromophores in the TC group structure [17,18]. The A chromophore consists of the β-tricarbonyl system of ring A, responsible for the strong absorption at around 270 nm, while the BCD chromophore comprises the π-electron system present in rings B, C and D, which produces a major visible peak at 360 nm (**Figure 2**) [18]. The BCD peak is also responsible for the pale to dark bright yellow color observed in all TC samples. Reduction in the absorbance of both DC and OTC solutions were observed when nanomaterials are added as presented in **Figures 3** and **4**. Furthermore, the following changes were observed when nanomaterials are mixed with TC solutions: Broadening and shifting (red shift) of the peak at around 370 nm and the disappearance of peak at around 250 nm.

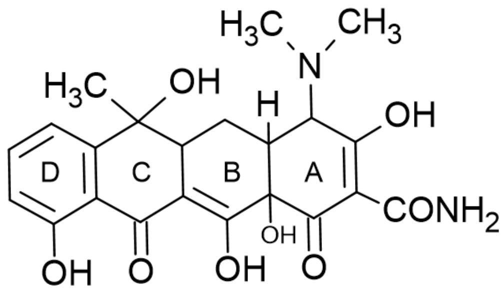

Figure 2 Structure of tetracycline (TC).

As presented in **Figure 3**, the addition of nanomaterials in the DC solution leads to a reduction in absorbance. ZnO exhibited the lowest absorbance, succeeded by Al_2O_3, TiO_2, and SiO_2 when compared to the DC solution only. The absorbance reduction for ZnO at the peak of 270 nm is 80 %. The absorbance reductions were 75 % for Al_2O_3, 63 % for TiO_2, and 30 % for SiO_2. For the peak at 360 nm, reduction of the absorbance ranges from 83 % for ZnO to 35 % of SiO_2. It has also been observed that there is a red shift in the peak at this region with DC solution containing ZnO and Al_2O_3 showing significant shift of 5 nm. The same can be observed for DC added with SiO_2 and TiO_2 although not as significant as the other 2 nanomaterials. The DC solution added with ZnO and Al_2O_3 also showed broadening of the peak at this region. Lastly, the peak at 270 nm disappeared upon addition of the different nanomaterials with the exception of SiO_2.

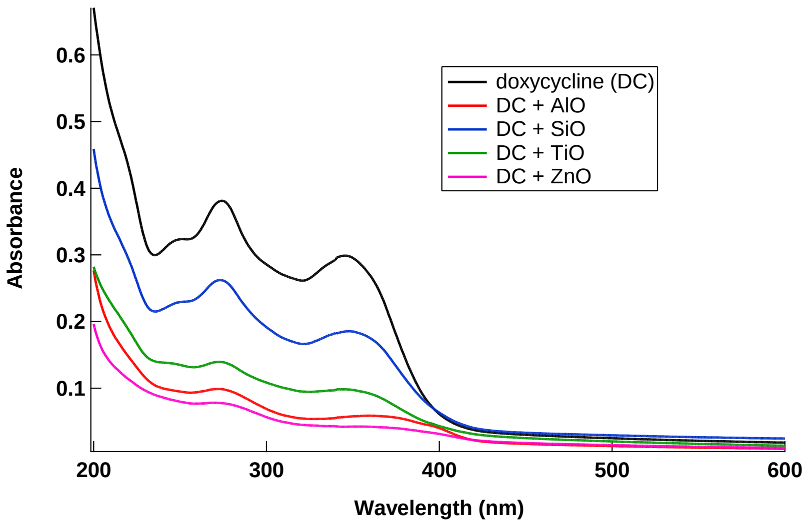

Figure 3 Average absorbance spectra of DC solutions without and with nanomaterials.

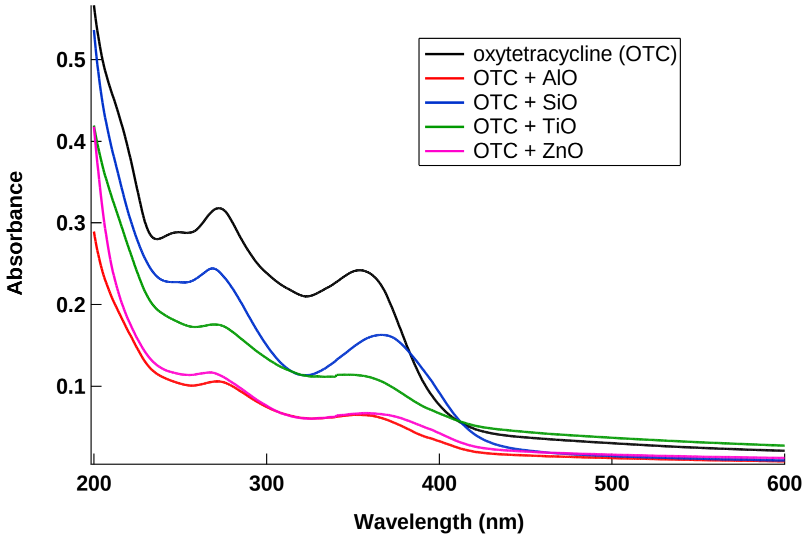

Figure 4 Average absorbance spectra of OTC solutions without and with nanomaterials.

For OTC, on the other hand, as presented in **Figure 4**, the same trend can be observed as that in DC in the reduction of absorbance. Both Al_2O_3 and ZnO had the lowest absorbance among the 4 nanomaterials and SiO_2 had the highest absorbance although lower than the OTC solution. The reduction in absorbance at 280 nm was 19 % for SiO_2, 44 % for TiO_2, 66 % for ZnO and 63 % for Al_2O_3. The reduction, on the other hand, at peak of 360 nm was 28 % for SiO_2, 44 % for TiO_2, and 76 % for both ZnO and Al_2O_3.

Shifting of peaks varies from one nanomaterial to the other. At 270 nm, both SiO_2 and ZnO showed a slight blue shift while both Al_2O_3 and TiO_2 showed a slight red shift. On the other hand, at 360 nm, all OTC solutions added with nanomaterials red shifted by as much as 10 nm with ZnO. It was also observed that the peak at 260 nm disappeared upon addition of any nanomaterials similar to that of DC solution.

Addition of nanomaterials to solution containing both TCs were also performed. Similar to results of individual TC solutions (DC and OTC), reduction in absorbance was observed.

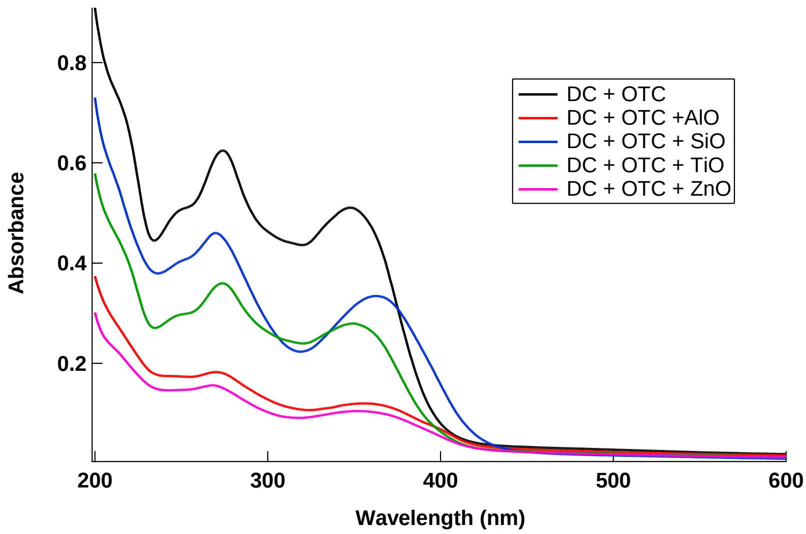

Figure 5 Average absorbance of DC and OTC mixture without and with nanomaterials.

As presented in **Figure 5**, 3 peaks at 250, 270 and 360 nm were also observed when DC and OTC are both mixed in a prepared solution. The peak at 250 nm disappeared when ZnO and Al_2O_3 nanomaterials were added. ZnO had the highest percentage reduction at 71 %, followed by Al_2O_3 at 67 %, TiO_2 at 39 % and SiO_2 at 22 %. A blue shift of 5 nm was observed at 270 nm upon the addition of each nanomaterial, with SiO_2 exhibiting the most significant shift. ZnO exhibited the highest percentage reduction at 77 %, followed by Al_2O_3 at 73 %, TiO_2 at 42 %, and SiO_2 at the lowest with 22 %. Significant red shifts are observed at 360 nm upon the addition of SiO_2 and TiO_2. A red shift was also observed upon the addition of ZnO and Al_2O_3, and there was a significant reduction in peak intensity in the solutions containing these nanomaterials. SiO_2 exhibited the most significant redshift, having shifted by 10 nm. ZnO exhibited the highest percentage reduction at 77 %, followed by Al_2O_3 at 73 %, TiO at 44 % and SiO_2 at 24 %. One study shows a removal rate of 92.0 % of within 40 using minhydroxyapatite nanowires (HApNWs) [19] while another study showed the removal of 90 % of TC in only 20 min using a novel porous nanocomposite composed of hydroxyapatite nanorods (HAP), a MIL-101(Fe) metal-organic framework, and Fe_3O_4 nanoparticles [20]. Unlike the present study which readily utilized the commercial nanoceramics, these reported studies, however, involved fabrication or synthesis of materials.

The observed reduction in absorbance of tetracycline solutions upon the addition of nanoceramics indicates strong adsorption interactions between the antibiotics and the nanoceramic surfaces. This reduction can be primarily attributed to the interactions of the electron-rich chromophores present in tetracyclines with the surfaces of metal oxide nanoceramics. Specifically, the β-tricarbonyl group in ring A and the conjugated π-systems in rings B, C, and D of tetracycline molecules are susceptible to interactions such as hydrogen bonding, electrostatic attractions, and π-π stacking with nanoceramics like ZnO and Al_2O_3. These interactions disrupt the electronic transitions within the chromophores, leading to a measurable decrease in absorbance Mojica *et al.* [18]. Furthermore, the adsorption of tetracycline molecules may induce structural or conformational changes that alter their optical properties, as suggested by the red shifts and peak broadening observed in UV-Vis spectra. These findings align with previous studies that demonstrated how adsorption onto active surfaces affects the electronic environment of antibiotics [17]. It is also possible that the adsorption of the TC antibiotics on the nanoceramics was a combination effect of both electrostatic interaction and complexation as reported in one study involving TC interaction with Fe_3O_4 incorporated polyacrylonitrile nanofiber mat (Fe-NFM) [21].

Among the nanoceramics tested, ZnO and Al_2O_3 exhibited the most significant reductions in absorbance, reflecting their higher adsorption efficiencies. Their strong interactions with tetracycline molecules can be attributed to their high surface energy and chemical reactivity, which enhance their ability to bind with functional groups such as hydroxyl and amino groups. These findings are consistent with earlier work on adsorption efficiencies of nanomaterials for removing antibiotics [21].

In addition, the changes observed in the absorbance profile would only mean that the chromophore system is affected with the addition of nanomaterials. It is possible that the shifts can be attributed to the non-electrostatic-dispersion interaction between the added nanomaterial and the TC molecular by hydrophobic, π-π interactions. The results obtained are similar to one study that reported the addition of reduced graphene oxide with a TC solution. The peaks observed in TC solution at 356 and 275 nm shifted to 348 and 262 nm, respectively, upon addition of the reduced graphene oxide [22]. Furthermore, the changes in absorbance profile could also due to the photodegradation of TC during the UV irradiation which was enhanced by the addition of nanoceramics. This could be mostly due to the active oxygen species generated during the photocatalytic process involving nanoceramic, such as OH. radical, hole and superoxide ion [23]. The disappearance of peak at 270 and 360 nm during UV irradiation which was enhanced by nanoceramics is due to the production of acylamino and hydroxyl groups [24] and 4a,12a-anhydro-4-oxo-4-dedimethylaminote-tracycline [25], respectively.

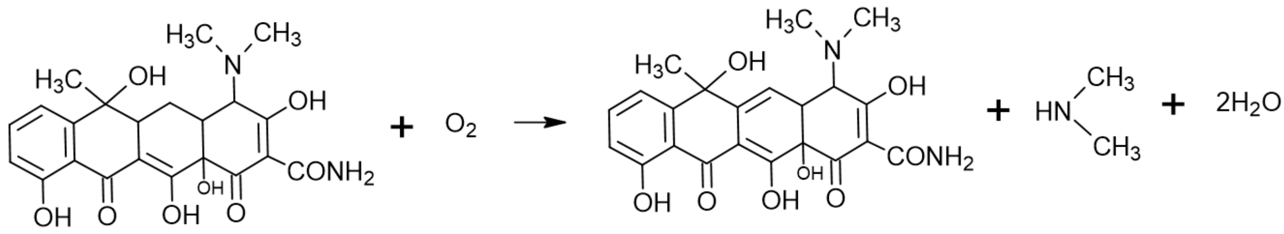

Figure 6 Photodegradation of TC into 4a, 12a-anhydro-4-oxo-4-dedimethylaminotetracycline (AT).

To look further on their interaction, the emission intensity of the same resulting solution was obtained. Results from the fluorescence studies showed conflicting trends when the antibiotics are mixed with nanomaterials. Doxycycline (DC) exhibited less fluorescence in comparison to OTC as shown by the higher Rayleigh scattering in DC solutions compared to OTC solutions. The removal of the hydroxyl group from the general structure of OTC could have contributed to the weak fluorescent nature of DC.

As presented in **Figure 7**, 2 peaks around 410 and 460 nm were observed in the DC solution emission spectra. Upon addition of nanomaterials, SiO_2 and Al_2O_3 enhanced the emission signal with SiO_2 having the highest signal (4× than the DC solution) followed by Al_2O_3 (2× than the DC solution). The peak was also broader for SiO_2 (which have 2 peaks at 445 and 500 nm) and Al_2O_3 (maximum peak at 465 nm). The other 2 nanomaterials solution (TiO and ZnO) has almost the same emission signal as the DC solution with ZnO maximum peak red shifting to 505 nm while TiO_2 maximum peak blue shifting to 450 nm.

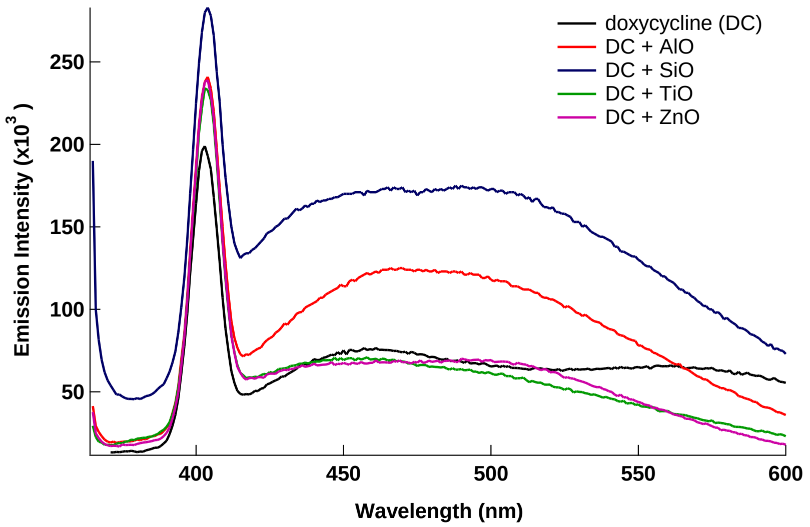

Figure 7 Average emission spectra of DC solutions without and with nanomaterials at an excitation wavelength of 350 nm.

As presented in **Figure 8**, SiO_2 enhanced the emission spectra of OTC solution which was also observed to DC solution spectra. In addition to the enhanced signal, there was a redshift of 15 nm in the maximum peak. The red shift was apparent upon the addition of ZnO to the OTC solution, despite a reduction in emission intensity. The other nanomaterials (TiO_2 and Al_2O_3) also exhibited a reduction in emission intensity that was slightly lesser than that observed with ZnO. Furthermore, a blue shift is observed in the fluorescence emission profile of OTC when combined with TiO_2 and AlO.

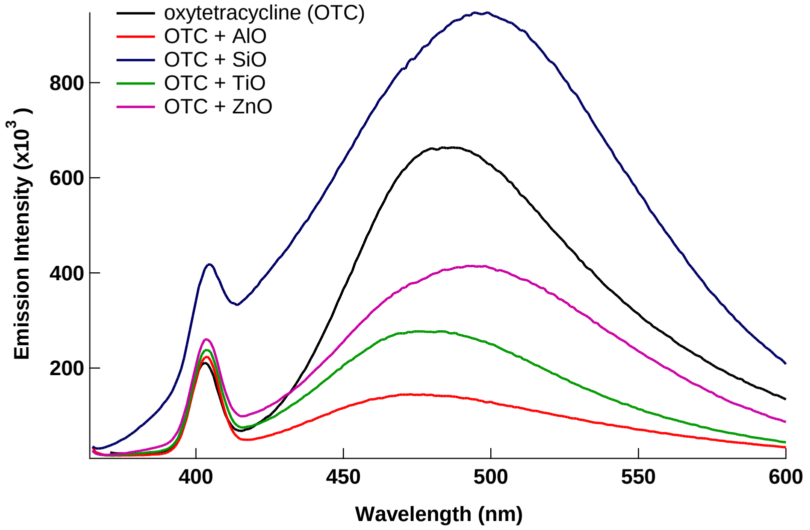

Figure 8 Average emission spectra of OTC solutions without and with nanomaterials at an excitation wavelength of 350 nm.

Furthermore, the addition of nanomaterials to the mixture of DC and OTC resulted in an increase of the emission signal as presented in **Figure 9**. Generally, the fluorescent properties of the solutions can be attributed to OTC, however the addition of DC enhanced the signal of the mixed solution, as only SiO_2 exhibited a stronger signal when combined with the OTC solution. The addition of DC in the mixture resulted in a blue shift of the peaks observed in the solution containing only OTC. For instance, the peak of OTC solution blue shifted from 484 to 497 nm upon mixing with DC. This can also observe in solutions added with nanomaterials. By comparing the solution containing the 2 TCs, a red shift can be seen from both SiO_2 and ZnO by 4 nm while a blue shift can be observed when Al_2O_3 and TiO were added with Al_2O_3 shifting to as high as 20 nm.

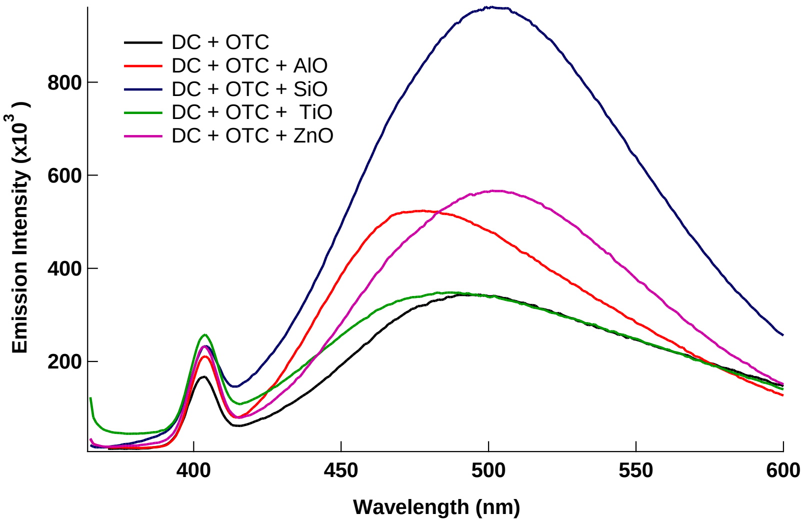

Figure 9 Average emission spectra of OTC and DC mixtures without and with nanomaterials at an excitation wavelength of 350 nm.

The interaction of oxytetracycline (OTC) and doxycycline (DC) with nanoceramics was characterized by distinct fluorescence quenching behaviors, driven by structural and electronic differences between the 2 antibiotics. OTC, which retains a hydroxyl group at the C5 position, exhibited stronger fluorescence intensity compared to DC. This structural feature facilitates intramolecular hydrogen bonding, stabilizing the excited-state energy levels and reducing non-radiative decay, as previously observed in pH-dependent spectroscopic studies of tetracyclines [18]. In contrast, DC lacks this hydroxyl group, resulting in weaker fluorescence and greater susceptibility to quenching by nanoceramics such as ZnO and Al_2O_3. These findings align with reports highlighting the critical role of functional groups in mediating interactions between tetracyclines and adsorbents [26].

The fluorescence quenching mechanism for ZnO and Al_2O_3 likely involves dynamic electron transfer from the excited-state tetracycline molecules to the nanoceramic surfaces, a process well-documented for materials with high electron affinity [11]. Static quenching, through the formation of non-fluorescent ground-state complexes, further contributed to reduced emission intensity. The hydroxyl and amino groups of tetracyclines served as primary interaction sites, engaging in hydrogen bonding or electrostatic interactions with the nanoceramic surfaces [17]. For instance, ZnO's high surface energy promoted strong adsorption, altering the electronic environment of the chromophores and inducing red shifts in fluorescence spectra (**Figure 4**). These shifts are consistent with studies on graphene oxide, where similar quenching mechanisms were reported [22].

Notably, SiO_2 exhibited anomalous behavior, enhancing fluorescence intensity in DC solutions by fourfold (**Figure 6**). This phenomenon may arise from weak hydrogen bonding between tetracycline molecules and silanol groups on the SiO_2 surface, stabilizing radiative transitions rather than quenching fluorescence. Unlike ZnO and Al_2O_3, SiO_2 lacks electron-accepting metal centers, which likely diminishes electron transfer efficiency. Such behavior mirrors observations with hydrophilic silica nanoparticles, where solvation effects enhance emission intensity [26]. Further investigation using advanced surface characterization techniques, such as FTIR or XPS, is warranted to confirm these interactions.

To further evaluate the adsorption of tetracyclines onto nanoceramic surfaces, HPLC analysis was conducted to quantify the reduction of OTC and DC concentrations in solution. The chromatograms revealed distinct peaks at ~2.0 min for OTC and ~6.0 min for DC (**Figure 10**). The peak area at these retention times was used to determine the antibiotic concentration before and after nanomaterial addition. A significant reduction in OTC and DC peak intensities was observed upon exposure to ZnO, Al_2O_3, and TiO_2, confirming effective adsorption by these materials.

Interestingly, DC exhibited a higher percent reduction than OTC, indicating that doxycycline has a stronger affinity for nanoceramic surfaces. This result aligns with fluorescence quenching data, where DC demonstrated greater susceptibility to adsorption-mediated interactions. The addition of TiO_2 and Al_2O_3 resulted in more than 80 % reduction in DC concentration, while ZnO showed slightly lower efficiency, with a reduction just under 80 %. This trend can be attributed to differences in surface chemistry, where TiO_2 and Al_2O_3 facilitate stronger electrostatic interactions and hydrogen bonding with the functional groups of DC [20].

Surprisingly, SiO_2 exhibited a negative trend, where the addition of SiO_2 to DC solutions led to an apparent increase in HPLC peak area rather than a reduction (**Figure 11**). This result is consistent with fluorescence data, suggesting that SiO_2 does not effectively adsorb DC but rather enhances its dispersibility in solution. Weak hydrogen bonding between SiO_2 and DC may lead to a more homogeneous distribution of the antibiotic, preventing aggregation and allowing for higher detection sensitivity in HPLC analysis [27]. Such behavior highlights the importance of selecting adsorbents based on their surface chemistry and interaction mechanisms with target contaminants.

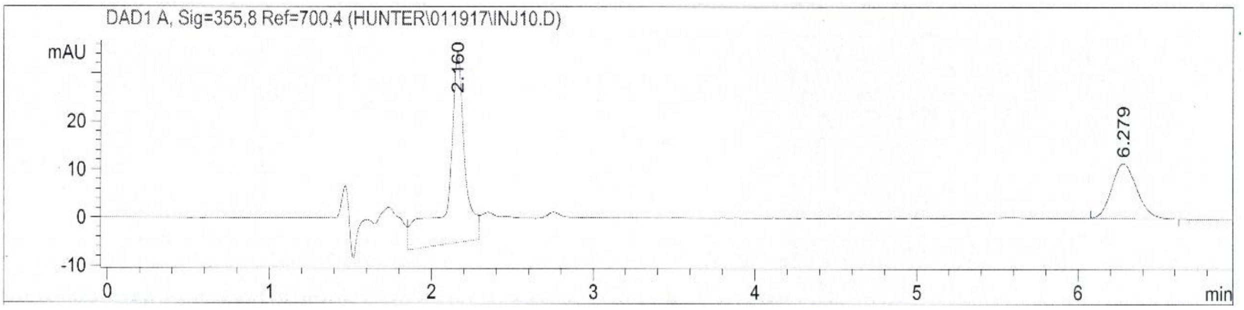

Figure 10 HPLC chromatogram of OTC and DC mixture.

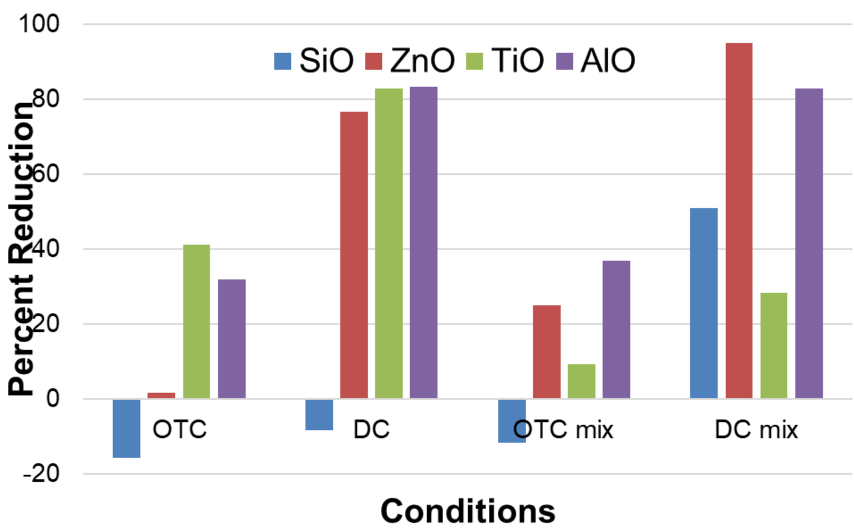

Figure 11 Percent reduction of peak area after addition of nanomaterials.

All fluorescence and HPLC measurements were performed in triplicate, with standard deviations below 5 %**,** ensuring statistical reliability. The adsorption efficiencies observed for ZnO and Al_2O_3 (~80 % for DC and OTC) are comparable to those of activated carbon (70 - 90 %) but exhibit significantly faster kinetics (< 1 h vs. 2 - 4 h) [21]. However, practical implementation of nanoceramics for wastewater treatment must consider factors such as nanoparticle leaching and regeneration costs. ZnO, despite its high adsorption capacity, poses potential ecotoxicity risks due to metal ion leaching. In contrast, SiO_2, while exhibiting lower adsorption efficiency (~30 % for DC), is inert and may be preferable in environmentally sensitive applications.

Although this study provides mechanistic insights into tetracycline-nanoceramic interactions, several limitations must be acknowledged. The lack of adsorption isotherm models (e.g., Langmuir/Freundlich) prevents a detailed quantitative analysis of binding capacities and surface heterogeneity. Future research should integrate isotherm modeling with spectroscopic data to refine mechanistic interpretations. Additionally, testing under real-world conditions, such as variations in pH, temperature, and competing contaminants, is critical for evaluating scalability. Recent advances in regenerable nanoceramics, such as magnetic Fe_3O_4 composites, offer promising pathways for cost-effective remediation [28]. Addressing these gaps will help translate laboratory findings into practical applications, advancing nanoceramics as sustainable tools for mitigating antibiotic pollution.

Conclusions

This study systematically investigated the adsorption behavior of tetracycline analogs, oxytetracycline (OTC) and doxycycline (DC), onto commercial nanoceramics (SiO_2, Al_2O_3, TiO_2, and ZnO) using UV-Vis absorption, fluorescence spectroscopy, and HPLC. The results demonstrated that ZnO and Al_2O_3 exhibited strong adsorption capacities, as evidenced by significant reductions in absorbance and fluorescence intensity, suggesting efficient binding through electron transfer, hydrogen bonding, and electrostatic interactions. TiO_2 also showed moderate adsorption efficiency, while SiO_2 exhibited anomalous behavior, enhancing fluorescence intensity and increasing HPLC peak areas instead of reducing them. This behavior suggests a weaker adsorption mechanism, potentially driven by solvation effects or surface passivation rather than strong molecular interactions.

HPLC results confirmed that DC exhibited a higher adsorption rate than OTC, with TiO_2 and Al_2O_3 achieving more than 80 % removal efficiency. The unique behavior of SiO_2, which showed increased peak areas in HPLC, suggests that it may not effectively adsorb tetracyclines but rather influence their solubility or stability in solution. These findings highlight the material-specific nature of tetracycline adsorption and the need for careful selection of nanoceramics for wastewater treatment applications.

Future studies should incorporate adsorption isotherm models (Langmuir, Freundlich) to quantify binding affinities and provide deeper mechanistic insights. Additionally, experiments in real wastewater matrices, including varying pH, competing ions, and temperature fluctuations, will be essential to validate the practical applicability of these nanoceramics. Advanced surface characterization techniques, such as Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Nuclear Magnetic Resonance (NMR), should be employed to further elucidate molecular-level interactions. Investigating the reusability and regeneration efficiency of these materials will also be critical for their sustainable application in environmental remediation.

Overall, this study contributes to the growing body of knowledge on nanoceramic-based antibiotic removal and underscores the importance of material-specific adsorption behaviors. Understanding these interactions will aid in the optimization of nanomaterials for large-scale applications in wastewater treatment and pharmaceutical contamination mitigation.

Acknowledgements

We would like to acknowledge Ruel Desamero of the Department of Chemistry, York College CUNY, New York, United States for the use of instruments.

References

[1] PP Amador, RM Fernandes, MC Prudêncio, MP Barreto and IM Duarte. Antibiotic resistance in wastewater: occurrence and fate of

Enterobacteriaceae producers of class A and class C β-lactamases. *Journal of Environmental Science and Health Part A Toxic/Hazardous Substances & Environmental Engineering* 2015; **50(1)**, 26-39.

[2] C Santhosh, V Velmurugan, G Jacob, SK Jeong, AN Grace and A Bhatnagar. Role of nanomaterials in water treatment applications: A review. *Chemical Engineering Journal* 2016; **306**, 1116-1137.

[3] L Liu, YH Liu, CX Liu and X Huang. Accumulation of antibiotics and tet resistance genes from swine wastewater in wetland soils. *Environmental Engineering and Management Journal* 2016; **15(10)**, 2137-2145.

[4] AK Sarmah, MT Meyer and ABA Boxall. A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. *Chemosphere* 2006; **65(5)**, 725-759.

[5] H Jufer, L Reilly and ERE Mojica. *Antibiotics pollution in soil and water: Potential ecological and human health issues. In:* J Nriagu (Ed.). Encyclopedia of environmental health. 2nd Eds. Elsevier, Amsterdam, Netherlands, 2019, p. 118-131.

[6] S Zheng, Y Wang, C Chen, X Zhou, Y Liu, J Yang, Q Geng, G Chen, Y Ding and F Yang. Current progress in natural degradation and enhanced removal techniques of antibiotics in the environment: A review. *International Journal of Environmental Research and Public Health* 2022; **19(17)**, 10919.

[7] A Huang, M Yan, J Lin, L Xu, H Gong and H Gong. A review of processes for removing antibiotics from breeding wastewater. *International Journal of Environmental Research and Public Health* 2021; **18(9)**, 4909.

[8] L Zhu, X Lin, Z Di, F Cheng and J Xu. Occurrence, risks, and removal methods of antibiotics in urban wastewater treatment systems: A review. *Water* 2024; **16(23)**, 3428.

[9] OA Ajala, SO Akinnawo, A Bamisaye, DT Adedipe, MO Adesina, OA Okon-Akan, TA Adebusuyi, AT Ojedokun, KAAdegoke and OS Bello. Adsorptive removal of antibiotic pollutants from wastewater using biomass/biochar-based adsorbents. *RSC Advances* 2023; **13(7)**, 4678-4712.

[10] LA Kolahalam, IK Viswanath, BS Diwakar, B Govindh, V Reddy and Y Murthy. Review on nanomaterials: Synthesis and applications. *Materials Today Proceedings* 2019; **18(4)**, 2182-2190.

[11] Y Zhang, B Chen, L Zhang, J Huang, F Chen, Z Yang, J Yao and Z Zhang. Controlled assembly of Fe_3O_4 magnetic nanoparticles on graphene oxide Nanoscale. *Nanoscale* 2011; **3(4)**, 1446-1450.

[12] MM Khin, AS Nair, VJ Babu, R Murugana and S Ramakrishna. A review on nanomaterials for environmental remediation. *Energy & Environmental Science* 2012; **5(8)**, 8075-8109.

[13] S Ahmed, MG Rasul, R Brown and MA Hashib. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. *Journal of Environmental Management* 2011; **92(3)**, 311-330.

[14] A Gupta, JR Saurav and S Bhattacharya. Solar light based degradation of organic pollutants using ZnO nanobrushes for water filtration. *RSC Advances* 2015; **5(87)**, 71472-71481.

[15] Z Alhalili. Metal oxides nanoparticles: General structural description, chemical, physical, and biological synthesis methods, role in pesticides and heavy metal removal through wastewater treatment. *Molecules* 2023; **28(7)**, 3086.

[16] AI Osman, EMA El-Monaem, AM Elgarahy, CO Aniagor, M Hosny, M Farghali, E Rashad, MI Ejimofor, EA López-Maldonado, I Ihara, PS Yap, DW Rooney and AS Eltaweil. Methods to prepare biosorbents and magnetic sorbents for water treatment: A review. *Environmental Chemistry Letters* 2023; **21(4)**, 2337-2398.

[17] MP Ravele, OA Oyewo and DC Onwudiwe. Controlled synthesis of CuS and Cu_9S_5 and their application in the photocatalytic mineralization of tetracycline. *Catalysts* 2021; **11(8)**, 899.

[18] ERE Mojica, E Nguyen, M Rozov and FV Bright. pH-dependent spectroscopy of tetracycline and its analogs. *Journal of Fluorescence* 2014; **24(4)**, 1183-1198.

[19] S Zhao, J Ren, F Zhang, Y He, X Han and R Wang. Fabrication of nano-hammer shaped

CuO@HApNWs for catalytic degradation of tetracycline. *Environmental Research* 2024; **249(1)**, 118410.

[20] M Beiranvand, S Farhadi and A Mohammadi-Gholami. Adsorptive removal of tetracycline and ciprofloxacin drugs from water by using a magnetic rod-like hydroxyapatite and MIL-101(Fe) metal-organic framework nanocomposite. *RSC Advances* 2022; **12(53)**, 34438-34453.

[21] Q Liu, Y Zheng, L Zhong and X Cheng. Removal of tetracycline from aqueous solution by a Fe_3O_4 incorporated PAN electrospun nanofiber mat. *Journal of Environmental Sciences* 2015; **28**, 29-36.

[22] DW Wang, YX Song, XF Ye, G Qian, SY Wang and Z Cheng. Study on adsorption of two sulfonamide antibiotics by graphene oxide. *Chinese Journal of Analytical Chemistry* 2018; **46(2)**, 211-216.

[23] G Safari, M Hoseini, M Seyedsalehi, H Kamani and A Mahvi. Photocatalytic degradation of tetracycline using nanosized titanium dioxide in aqueous solution. *International journal of Environmental Science and Technology* 2014; **12**, 603-616.

[24] XD Zhu, YJ Wang, RJ Sun and DM Zhou. Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO_2. *Chemosphere* 2013; **92(8)**, 925-932.

[25] M Addamo, V Augugliaro, A Di Paola, EIG Lopez, V Loddo, G Marci and L Palmisano. Removal of drugs in aqueous systems by photo assisted degradation. *Journal of Applied Electrochemistry* 2005; **35(7)**, 765-774.

[26] EE Ghadim, F Manouchehri, G Soleimani, H Hosseini, S Kimiagar and S Nafisi. Adsorption properties of tetracycline onto graphene oxide: equilibrium, kinetic and thermodynamic studies. *PLoS ONE* 2013; **8(11)**, e79254.

[27] C Santhosh, V Velmurugan, G Jacob, SK Jeong, AN Grace and A Bhatnagar. Role of nanomaterials in water treatment applications: A review. *Chemical Engineering Journal* 2016; **306**, 1116-1137.

[28] RM Kakhki and H Bolandhemmat. Synthesis of Ag/CuS doped mineral magnetite nanocomposite with improved photocatalytic activity against tetracycline and diclofenac pollutants. *Scientific Reports* 2024; **14(1)**, 19009.