

Non-Thermal Plasma Synthesis of TiO₂ Nanoparticles for Environmental Applications: Adsorption Studies

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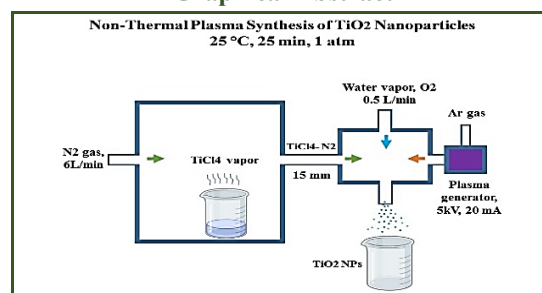
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Highlights

- Plasma-synthesized TiO₂ formed pure anatase with high crystallinity.
- Nanoparticles showed strong UV absorption and high colloidal stability.
- Mesoporous structure with large surface area enabled efficient adsorption.
- TiO₂ nanoparticles exhibited potent, dose-dependent antibacterial activity.
- Optimized conditions achieved >80% removal of dyes and antibiotics.

Graphical Abstract



ABSTRACT

The increasing prevalence of pharmaceutical contaminants in aquatic environments, particularly antibiotics, poses serious ecological risks and contributes to the spread of antibiotic-resistant bacteria. Conventional wastewater treatment processes are insufficient for removing these persistent pollutants. Titanium dioxide (TiO₂) nanoparticles, owing to their high surface area, adsorption capacity, and antibacterial properties, offer a promising solution. This study investigates the synthesis of TiO₂ nanoparticles via a Non-Thermal Plasma (NTP) method and evaluates their multifunctional performance for environmental remediation. TiO₂ nanoparticles were synthesized from titanium tetrachloride under ambient temperature and atmospheric pressure using N₂/Ar plasma for 25 min. Nanoparticles were characterized by FESEM,

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EFTEM, DLS, zeta potential, XRD, FT-IR, UV-Vis, TGA/DTG, and nitrogen adsorption-desorption analysis. Adsorption studies used methyl orange and antibiotics (amoxicillin, ampicillin, and doripenem), with Langmuir, Freundlich, and Toth isotherms modeling adsorption behavior. Antibacterial activity was assessed against *Escherichia coli* and *Staphylococcus epidermidis*. TiO₂ nanoparticles displayed a mean size of 25.2 ± 4.53 nm (FESEM), high crystallinity (anatase, 13.6 nm), a surface area of 112.4 m²/g, and mesoporosity (~10 nm pores). Zeta potential (−39 mV) indicated colloidal stability. TGA showed minimal weight loss above 500 °C, with major loss (400–450 °C) due to surface-bound organics. Methyl orange adsorption exceeded 80% under optimal conditions, and antibiotic removal followed Langmuir/Toth isotherms, with doripenem showing the highest affinity. MIC values were ~0.124 mg/mL for both bacterial strains. Plasma-assisted TiO₂ nanoparticles integrate high crystallinity, mesoporosity, adsorption efficiency, and antibacterial activity, providing a scalable, sustainable strategy for simultaneous removal of dyes and antibiotics, with significant potential to mitigate pharmaceutical pollution and antibiotic resistance.

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INTRODUCTION

The global rise in pharmaceutical consumption has increased the presence of residues and emerging micropollutants in aquatic environments, threatening ecosystems and public health [1, 2]. Antibiotics, in particular, enter surface and groundwater through hospital effluents, agricultural runoff, industrial discharge, and inadequately treated municipal wastewater [3]. Even at trace levels (nanograms to micrograms per liter), these substances can be toxic to aquatic life and promote the spread of antibiotic-resistant bacteria is a critical global health concern [4]. Conventional wastewater treatment is largely ineffective at removing such persistent compounds, highlighting the need for advanced, sustainable, and multifunctional treatment technologies [5]. Nanotechnology-based materials have emerged as promising solutions aligned with the United Nations Sustainable Development Goals for clean water and sanitation [6].

Titanium dioxide (TiO₂) nanoparticles are extensively studied for their adsorption and antimicrobial properties [7, 8]. Under ultraviolet (UV) irradiation above its bandgap (~3.2 eV), TiO₂ generates electron-hole pairs that react with water and oxygen to form Reactive Oxygen Species (ROS), such as hydroxyl radicals, capable of oxidizing organic pollutants—including pharmaceuticals and dyes—into benign products [9, 10]. TiO₂ also exhibits chemical stability, low toxicity, and high reusability, making it attractive for environmental remediation [11, 12].

Adsorption efficiency depends on TiO₂'s crystalline structure, surface area, and electronic properties [13]. While anatase generally exhibits superior activity, mixed-phase composites (e.g., anatase-rutile P25) offer enhanced charge separation and reduced recombination [14, 15].

Calcination temperature and precursor ratios strongly influence phase composition, with optimized conditions achieving near-complete dye degradation [16, 17]. Similarly, magnetic nanomaterials highlight the importance of surface chemistry and stability, with sonochemically synthesized magnetite showing long-term colloidal stability [18] and magnetite-decorated polymeric resins exhibiting high affinity for aromatic contaminants [19]. Strategies such as metal/non-metal doping, surface modification, and nanocomposite formation can extend light absorption and enhance adsorption under visible light, with noble metal–TiO₂ hybrids demonstrating particularly high degradation rates [20, 21]. UV-activated TiO₂ surfaces also exhibit bactericidal activity, adding antimicrobial functionality to water purification [22].

Conventional TiO₂ synthesis methods—sol-gel, hydrothermal, and chemical vapor deposition—often require toxic precursors, high temperatures, or lengthy reactions [23]. Non-Thermal Plasma (NTP), or cold plasma, offers an environmentally friendly alternative. In NTP, electron temperatures far exceed those of ions and neutrals, generating reactive species at low bulk gas temperatures (<100°C) without hazardous chemicals. This enables precise control over particle size, morphology, phase, and surface chemistry, making NTP a versatile and scalable approach for nanomaterial synthesis [24–26]. However, photoreactor design and catalyst stability remain critical for practical wastewater applications [27].

Plasma-assisted synthesis allows tailoring of TiO₂ nanostructures across phases, morphologies, and functional properties.

Acayanka et al. used atmospheric-pressure plasma-assisted oxi-precipitation to coat textile fibers with nitrogen-doped anatase–rutile TiO₂ nanoparticles (8–12 nm), maintaining durable photocatalytic activity after multiple washes [28]. Liquid-phase plasma methods have produced mixed-phase TiO₂ with tunable rutile content and surface area, showing strong adsorption of metal ions and dyes [29–31]. Gas-phase plasma methods enable rapid synthesis (milliseconds) with tunable optical and structural properties, including amorphous-to-anatase control for enhanced solar-driven photocatalysis [32, 33]. Thermal and laser-induced plasma techniques have also generated phase-pure or mixed-phase TiO₂ without surfactants, highlighting plasma's versatility [34, 35].

Despite advances, most studies focus on photocatalysis, with limited systematic evaluation of adsorption—especially toward antibiotics. Furthermore, plasma methods' potential to produce highly crystalline, mesoporous TiO₂ with robust adsorption and antibacterial properties remains underexplored. The present study employs non-thermal plasma to synthesize TiO₂ nanoparticles and investigates their structural, surface, and functional characteristics, including adsorption of dyes and antibiotics and antibacterial activity, aiming to advance plasma-synthesized TiO₂ as a sustainable, multifunctional material for environmental remediation.

EXPERIMENTAL SECTION

Experimental procedure

Titanium dioxide (TiO₂) nanoparticles were synthesized using titanium tetrachloride (TiCl₄) as the precursor, selected for its high volatility and strong reactivity toward oxidizing species. These properties enable efficient vapor-phase delivery into the plasma, rapid nucleation, and complete conversion to TiO₂, favoring the formation of fine, high-purity nanoparticles with minimal agglomeration.

A volume of 2 mL of TiCl₄ was dispensed into a 5 mL borosilicate glass beaker and placed inside a custom-fabricated glass trap designed to safely contain and guide the reactive vapors. All joints of the trap were sealed with Teflon tape to prevent leakage. Due to the toxic and highly reactive nature of TiCl₄, all procedures were conducted in a certified laboratory fume hood under strict safety protocols with full Personal Protective Equipment (PPE).

High-purity nitrogen gas (N₂, 99.999%) was introduced into the trap at a constant flow rate of 6 L/min to act as the carrier gas, transporting TiCl₄ vapors to the plasma region. This flow rate was optimized experimentally

to ensure stable plasma discharge and efficient precursor transport. Lower flows led to plasma instability and incomplete oxidation, while higher flows caused excessive dilution and reduced nanoparticle yield.

Simultaneously, high-purity argon gas (Ar, 99.999%) was supplied to a Direct Current (DC) plasma generator at the same flow rate. Argon was chosen due to its inert nature and high ionization efficiency, which stabilizes the plasma and prevent unwanted nitride formation. Plasma was ignited by applying a DC voltage of approximately 5 kV and a current of ~20 mA across tungsten electrodes spaced 8 mm apart. This voltage was found optimal for maintaining a stable discharge; lower voltages (< 4 kV) resulted in plasma instability, while higher voltages (> 6 kV) caused excessive thermal effects and particle coarsening. The distance between the plasma nozzle and the TiCl₄-containing trap was maintained at 15 mm to ensure optimal exposure of the precursor vapor to the plasma.

To promote the oxidation of TiCl₄ into TiO₂, a controlled mixture of water vapor and oxygen gas was introduced into the plasma region through an auxiliary inlet at a combined flow rate of ~0.5 L/min. This ensured the availability of oxidizing species (•OH, O, O₂⁺, etc.), enhancing reaction reproducibility and completeness. The TiCl₄–N₂ stream exiting the trap was aligned vertically with the plasma jet to maximize exposure to the active plasma zone.

Each synthesis lasted 25 minutes and was repeated three times under identical conditions, yielding reproducible results within ±5% variation in particle size and phase composition. The plasma-assisted reaction was conducted at ambient temperature (~25 °C) and atmospheric pressure without external heating or pressurization, highlighting a key advantage of this method.

During synthesis, white fumes indicative of TiO₂ formation were observed. A 250 mL borosilicate beaker was placed below the plasma nozzle to collect the condensed nanoparticles. A fine white powder gradually deposited on the beaker walls. After completion, the beaker was sealed and transferred to a vacuum oven, where the powder was dried at room temperature under reduced pressure (~100 mbar) for 12 hours. The resulting powder was characterized as TiO₂ using physicochemical analyses. Scheme 1 illustrates the schematic setup for the plasma-assisted vapor-phase synthesis of TiO₂ nanoparticles, highlighting the precursor delivery, plasma generation, oxidizing environment, and particle collection.

Key experimental parameters: 2 mL of TiCl_4 as precursor delivered by nitrogen at 6 L/min; plasma generated with argon at 6 L/min using tungsten electrodes with 8 mm gap, at 5 kV and ~20 mA; trap-to-nozzle distance 15 mm; water vapor and oxygen at 0.5 L/min; reaction duration 25 min at ambient temperature and pressure; nanoparticles collected in a 250 mL beaker and dried under vacuum at ~100 mbar for 12 h.

Reproducibility and Quality Control: Each synthesis was repeated independently three times ($n=3$) on different days using fresh precursor solutions. Batch-to-batch variation in particle size was $\pm 5\%$ (relative standard deviation), and XRD phase composition remained $>98\%$ anatase across all batches. For adsorption experiments, all measurements were performed in triplicate from the same nanoparticle batch to eliminate batch-related variability. Initial pH values were verified before and after pH adjustment, with deviations <0.05 pH units. Temperature control was maintained using a recirculating water bath with ± 0.5 °C precision. These quality control measures ensure that reported results reflect true material performance rather than synthesis or measurement artifacts.

Characterization of TiO_2 nanoparticles

To comprehensively characterize the synthesized TiO_2 nanoparticles, a suite of complementary analytical techniques was employed. FESEM and EFTEM analyses were conducted to examine particle morphology, size distribution, and internal structure. XRD provided detailed information on the crystalline phases and crystallite sizes, which are critical for evaluating phase purity and structural order. FT-IR spectroscopy was used to identify surface functional groups and confirm the formation of Ti–O–Ti bonds, thereby verifying the chemical composition and purity of the nanoparticles. UV–Vis spectroscopy was applied to investigate the optical absorption characteristics and band gap energy, offering insights into the electronic structure of TiO_2 . DLS and zeta potential measurements were performed to assess colloidal stability in suspension, while BET surface area and porosity analyses elucidated the textural and adsorption properties of the material. Collectively, these techniques provided a comprehensive understanding of the physicochemical characteristics of the synthesized TiO_2 nanoparticles.

Structural, morphological, and optical properties of the synthesized TiO_2 nanoparticles were characterized using multiple analytical techniques. Morphological characteristics were evaluated using Field-Emission Scanning Electron Microscopy (FESEM) to obtain

detailed information on particle shape, surface features, and size distribution. FESEM analysis was carried out using a Carl Zeiss Supra 55VP microscope operated at an accelerating voltage of 20 kV. The elemental composition of the nanoparticles was determined by Energy-Dispersive X-ray (EDS) spectroscopy integrated with the FESEM system. The EDS spectra were acquired at 20 kV and analyzed semi-quantitatively using SmartSEM software. Elemental mapping and atomic percentage data were used to confirm the TiO_2 stoichiometry and assess elemental purity.

Energy-Filtered Transmission Electron Microscopy (EFTEM) provided insights into internal structure, crystallinity, and fine morphology. EFTEM analysis was conducted using a LEO 912AB microscope. For both FESEM and EFTEM, the particle size distribution was determined using ImageJ software. EFTEM samples were prepared by dispersing nanoparticles in ethanol and depositing them onto carbon-coated copper grids, followed by drying at room temperature.

Dynamic Light Scattering (DLS) and zeta potential measurements provided information on hydrodynamic size, polydispersity, and colloidal stability. DLS analysis was performed using a K-One Nano Ltd. analyzer (Seoul, South Korea), and zeta potential measurements evaluated surface charge and colloidal stability in suspension.

Optical properties were analyzed using UV–Vis spectroscopy to determine absorption characteristics and electronic transitions. Measurements were performed with an Evolution 300® spectrophotometer (Thermo Fisher Scientific, Germany) over 300–600 nm. Nanoparticles were dispersed in a suitable solvent, and all measurements were conducted at room temperature.

Crystalline phases and crystallite sizes were determined by X-Ray Diffraction (XRD) using a D8 Advance diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406$ Å), scanning $2\theta = 20^\circ$ – 90° at $0.02^\circ/\text{s}$. Diffraction patterns were used to identify crystal phases (anatase, rutile, brookite) and estimate crystallite size *via* the Scherrer equation.

Surface functional groups were identified by Fourier-Transform InfraRed (FT-IR) spectroscopy using a Tensor II FT-IR spectrometer (Bruker, Germany) over 400 – 4000 cm^{-1} at 25 °C and 50% relative humidity. TiO_2 powder was mixed with spectroscopic-grade KBr and compressed into translucent pellets. Thermal stability and decomposition were analyzed using ThermoGravimetric Analysis (TGA) and Derivative ThermoGravimetry (DTG) with a Q600 thermal analyzer (TA Instruments, USA) under nitrogen from room temperature to 800 °C at 10 °C/min.

Surface area and porosity analysis

Surface area, pore structure, and adsorption properties were determined using nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics ASAP 2020 analyzer (Norcross, USA). Samples were degassed under vacuum at 150 °C for 12 h. Specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method (relative pressure 0.05–0.30), and the Langmuir model provided monolayer adsorption capacity. Micropore volume and external surface contributions were estimated via the t-plot method, and the Barrett–Joyner–Halenda (BJH) approach was used to calculate pore size distribution and total pore volume.

The point of zero charge (pHpzc) was determined by the pH drift method. Briefly, 50 mg of TiO₂ nanoparticles were added to 50 mL of 0.01 M NaCl at initial pH values from 2 to 12 (adjusted with 0.1 M HCl or NaOH). Suspensions were stirred for 24 h at room temperature, and the final pH was measured. The pHpzc corresponded to the pH at which initial and final values were equal.

Determination of Minimum Inhibitory Concentration (MIC)

Antimicrobial activity was assessed by determining the MIC of TiO₂ nanoparticles against *Escherichia coli* and *Staphylococcus epidermidis*. TiO₂ suspensions (0.0155–0.992 mg/mL) were prepared in LB broth. In a 96-well microplate, 100 µL of bacterial suspension (~10⁶ CFU/mL) was added to 100 µL of nanoparticle solution. Plates were incubated at 35 °C for 18–20 h with shaking at 200 rpm. Bacterial growth was monitored by optical density at 600 nm. MIC was defined as the lowest concentration with no visible growth (OD comparable to blanks). Experiments were conducted in triplicate with positive (bacteria only) and negative (broth only) controls.

Optimized removal of methyl orange using TiO₂ nanoparticles

Methyl orange (MO, C₁₄H₁₄N₃NaO₃S, MW 327.33 g/mol) was used as a model anionic azo dye. It is highly water-soluble and exhibits a maximum absorption wavelength (λ_{max}) of ~464 nm, slightly pH-dependent due to its pK_a (~3.4). Its anionic form under neutral/alkaline conditions, and a strong chromophore makes it suitable for evaluating nanoparticle adsorption efficiency.

MO removal (initial concentration: 50 mg/L) was studied by varying contact time, initial dye concentration, nanoparticle dosage, pH, and temperature.

In each experiment, 50 mL of MO solution was treated with 0.2 g TiO₂ nanoparticles under stirring at 150 rpm for 60 min. Residual dye was quantified by absorbance at 464 nm. Removal efficiency (%) was calculated as Eq. (1):

$$\text{Removal efficiency (\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

Where C₀ and C_t are the initial and time-dependent MO concentrations. All experiments were in triplicate, with distilled water controls. Time-dependent removal was monitored at 0, 15, 30, 45, 60, 90, and 120 min at pH 5 (adjusted with 0.1 M HCl or NaOH) and 20 °C. Effects of initial concentration (0–200 mg/L), nanoparticle dosage (500–2500 mg), pH (4.5, 7, 8, 11), and temperature (25–73 °C) were examined. All experiments were carried out under ambient conditions, with no intentional light source applied. To eliminate any potential interference from photocatalytic reactions, all adsorption experiments were performed under dark conditions without light irradiation. Consequently, the results reported in this study reflect purely adsorption-driven processes rather than photocatalytic degradation.

Important Note: All adsorption experiments reported herein were conducted under dark conditions without UV or visible light irradiation. The reported removal efficiencies reflect purely adsorptive processes rather than photocatalytic degradation. While TiO₂ nanoparticles are known for photocatalytic activity under UV light, this functionality was not investigated in the present study. The strong UV absorption observed at 356 nm indicates potential for future photocatalytic applications, but the current results demonstrate the independent value of these nanoparticles as high-capacity adsorbents.

Reusability of TiO₂ nanoparticles

Reusability was assessed over five adsorption–desorption cycles using MO (50 mg/L) at pH 11 (adjusted with 0.1 M NaOH). TiO₂ nanoparticles (0.2 g) were added to 50 mL MO solution, stirred for 120 min at 25 °C. Nanoparticles were separated by centrifugation (5000 rpm, 10 min), washed with ethanol and deionized water, dried at 60 °C for 6 h, and reused. MO removal efficiency was measured spectrophotometrically at 464 nm after each cycle.

Modeling antibiotic adsorption onto TiO₂ nanoparticles

Adsorption of amoxicillin, ampicillin, and doripenem was modeled using Langmuir, Freundlich, Toth, Hill, and Dubinin–Radushkevich (D–R) isotherms at 30 °C, 40 °C, and 50 °C. Each model describes specific adsorption characteristics:

Langmuir: monolayer adsorption on homogeneous surfaces.

Freundlich: multilayer adsorption on heterogeneous surfaces.

Toth: three-parameter extension of Langmuir for heterogeneous surfaces at low concentrations.

Hill: cooperative binding.

D–R: differentiates physical vs chemical adsorption, estimating mean free energy of adsorption.

Equilibrium concentrations (C_e , mg/L) and adsorption capacities (q_e , mg/g) were fitted using nonlinear regression in Microsoft Excel to extract model parameters and assess goodness-of-fit.

Control and validation experiments

To ensure that observed removal was due to adsorption rather than other phenomena, the following controls were performed:

1. Light-mediated effects: All experiments were conducted in amber glassware wrapped in aluminum foil to exclude ambient light. Control experiments with identical conditions but transparent glassware showed no significant difference ($p = 0.42$), confirming photocatalysis did not contribute.
2. Dye stability: MO solutions without nanoparticles showed <2% concentration change over 120 min, ruling out spontaneous degradation or volatilization.
3. pH drift: Solution pH was monitored continuously and remained within ± 0.1 units of initial values throughout experiments, confirming that pH-dependent removal was due to surface charge effects rather than pH changes during adsorption.
4. Blank adsorption: Experiments with borosilicate glass beads of similar size distribution showed <5% MO removal, confirming that removal was specific to TiO_2 surface properties.

These controls validate that reported removal efficiencies reflect genuine adsorption by TiO_2 nanoparticles.

Statistical analysis

All experiments were conducted in triplicate; data are presented as mean $\pm$ Standard Deviation (SD). Analysis of variance (ANOVA) assessed statistical differences among experimental groups, followed by Tukey's post hoc test when appropriate. Significance was set at $p < 0.05$. For adsorption studies, isotherm model fits were evaluated using correlation coefficient (R^2) and Root Mean Square Error (RMSE). All calculations and plotting were performed

with Microsoft Excel 2019 (Microsoft Corp., USA) and GraphPad Prism 9.0 (GraphPad Software, USA).

RESULTS AND DISCUSSION

Morphological and physicochemical characterization of TiO_2 nanoparticles

Fig. 1 summarizes the morphological and physicochemical properties of the synthesized TiO_2 nanoparticles. FESEM analysis (Fig. 1A) revealed well-defined nanoparticles that tend to form agglomerates, assembling into clustered arrangements. The particle size was determined to be 25.2 ± 4.53 nm. Complementary EFTEM analysis (Fig. 1B) showed that the nanoparticles are discrete and granular, closely packed, with an average particle size of 10.7 ± 1.25 nm. Histograms of the particle size distributions for both FESEM and EFTEM analyses are presented alongside the images, confirming size heterogeneity and distribution patterns.

The EDS spectrum (Fig. 1C) confirmed the elemental composition of the synthesized TiO_2 nanoparticles. Distinct peaks corresponding to titanium (Ti) and oxygen (O) were clearly observed, verifying the formation of TiO_2 . Minor peaks of carbon (C) and copper (Cu) were also detected; the former is attributed to surface contamination or residual carbon species from the synthesis process, while the latter originates from the copper grid used for sample mounting. The semi-quantitative analysis indicated atomic percentages of Ti = 34.8%, O = 62.1%, Cu = 2.3%, and C = 0.8%, which are consistent with the expected TiO_2 stoichiometry and confirm the formation of a nearly stoichiometric oxide. These results validate the successful synthesis of highly pure TiO_2 nanoparticles with minimal surface contamination.

DLS measurements (Fig. 1D) indicated a hydrodynamic diameter of 146 ± 3 nm with a polydispersity index (PDI) of 0.237. This relatively low PDI suggests a narrow size distribution and improved uniformity in suspension. Zeta potential analysis (Fig. 1E) yielded a value of -39 ± 16.5 mV, indicating a strong negative surface charge, which implies high colloidal stability and resistance to further aggregation, particularly in acidic or neutral environments.

Fig. 1F shows the UV–Vis absorption spectrum of the synthesized TiO_2 nanoparticles. A pronounced peak at 356 nm, characteristic of TiO_2 nanostructures, corresponds to electronic transitions from O^{2-} (2p) to Ti^{4+} (3d). The sharp, well-defined peak indicates successful formation of nanoscale TiO_2 with strong optical activity in the near-UV region.

Within the measured 300–600 nm range, the nanoparticles exhibit strong UV absorption (300–400 nm) and minimal absorption in the visible region (400–600 nm), consistent with anatase TiO₂ behavior. The low baseline in the visible region suggests good dispersion and minimal aggregation during measurement. These optical properties confirm the formation of well-dispersed, optically active TiO₂ nanoparticles suitable for UV-blocking applications, while no photocatalytic activity was evaluated in this study.

The crystalline structure of the synthesized TiO₂ nanoparticles was analyzed by X-ray diffraction (XRD) [36]. The diffraction pattern (Fig. 1G) shows sharp peaks, indicating high crystallinity. The most intense peak at $2\theta \approx 25.3^\circ$ corresponds to the (101) plane of the anatase phase (JCPDS card no. 21-1272). Other characteristic anatase peaks appear at 37.8° (004), 48.0° (200), 53.9° (105), 55.1° (211), 62.7° (204), 68.8° (116), 70.3° (220), 75.0° (215), and 82.6° (222). No peaks corresponding to rutile or brookite phases were detected, confirming phase-pure anatase formation.

The interplanar spacings (d-spacing) were calculated using Bragg's law and are summarized in Table 1 (Supplementary Data). The average crystallite size, estimated via the Debye–Scherrer equation, is approximately 13.6 nm. Minor lattice strain, indicated by peak broadening, is typical for nanoparticles of this size. These structural characteristics confirm that the plasma-assisted synthesis method effectively produces highly crystalline TiO₂ nanoparticles with controlled nanoscale features.

Fourier-Transform InfraRed (FT-IR) spectroscopy was used to evaluate the functional groups and chemical bonding of the synthesized nanoparticles (Fig. 1H). A broad band at 2500–3600 cm⁻¹ is attributed to O–H stretching vibrations, indicating surface hydroxyl groups and adsorbed water molecules. A distinct band at 1500–1800 cm⁻¹ corresponds to the bending vibration of molecular water (H–O–H), further confirming the presence of moisture or hydroxyl groups. Strong absorption between 600–1100 cm⁻¹ is associated with Ti–O–Ti and Ti–O stretching vibrations, confirming titanium dioxide formation. Finally, a band at 400–500 cm⁻¹ is attributed to Ti–O lattice vibrations in the anatase phase, corroborating the XRD results. These spectral features confirm successful synthesis and the presence of surface functional groups that may influence reactivity, dispersion, and interactions in downstream applications.

ThermoGravimetric Analysis (TGA) and Derivative ThermoGravimetry (DTG) were used to assess the thermal behavior of the nanoparticles (Fig. 1I). The TGA curve shows

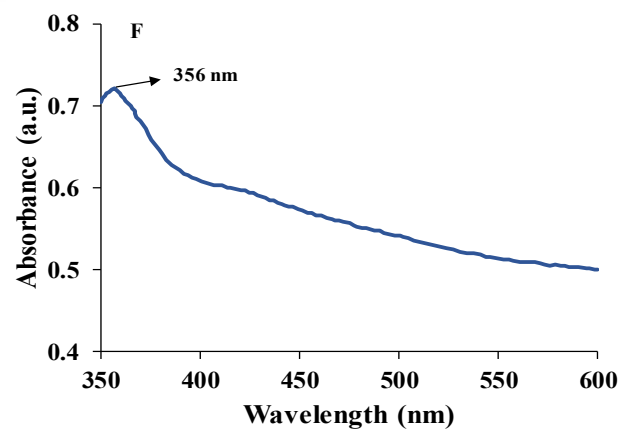
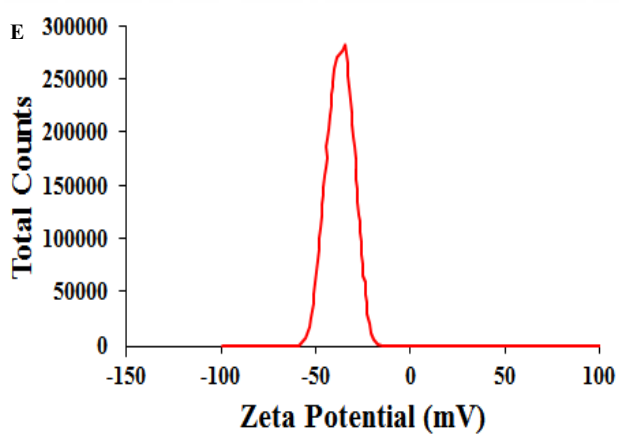
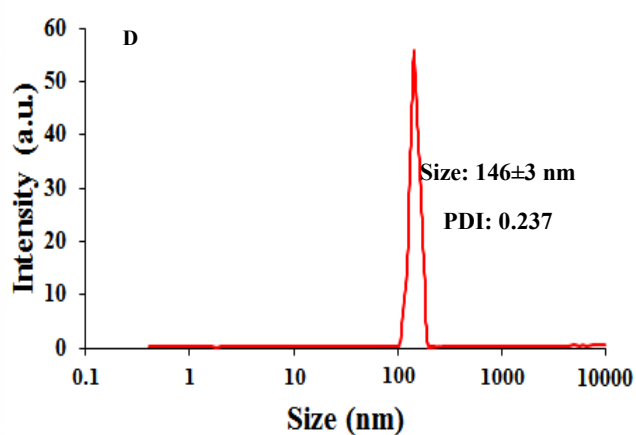
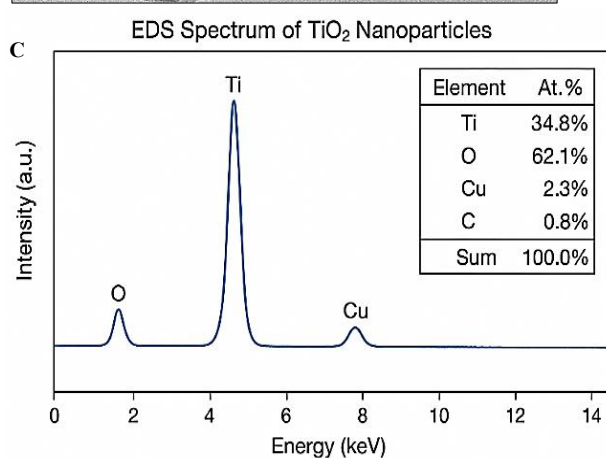
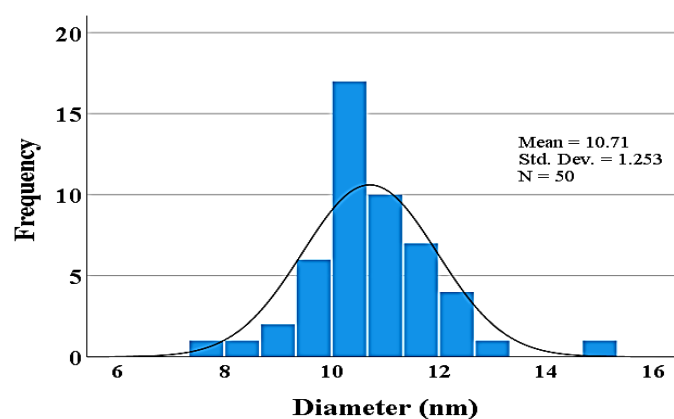
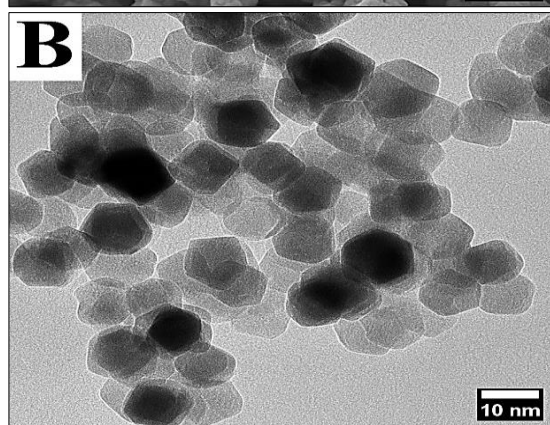
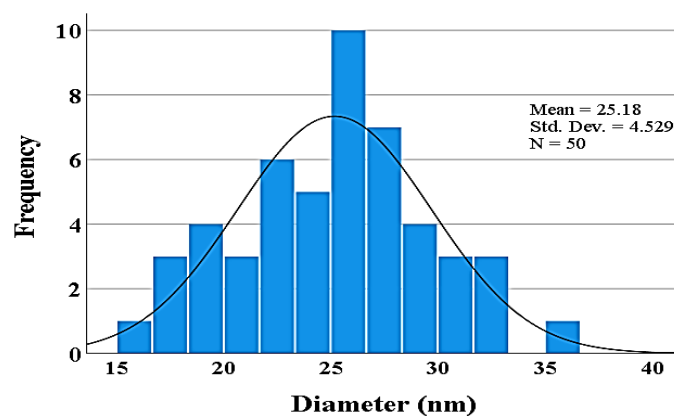
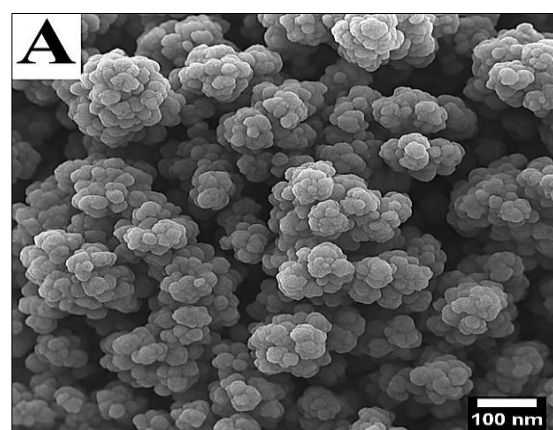
that the sample retains 100% of its initial weight at 50 °C and remains stable until ~400 °C. A pronounced weight loss occurs between 400–450 °C, decreasing from 60% to 10%, likely due to the decomposition of volatile organic residues or surface-adsorbed species. Beyond 450 °C, the curve plateaus, indicating minimal further loss up to 800 °C, with the residual 10% representing the thermally stable TiO₂ framework.

The DTG curve highlights weight-change rates, with two peaks at ~180 °C and ~430 °C corresponding to evaporation of adsorbed water and decomposition of surface-bound organics, respectively. The DTG signal returns to zero around 500 °C, indicating completion of major thermal degradation. These results confirm the high thermal stability of the TiO₂ nanoparticles, supporting their suitability for high-temperature applications.

The apparent differences among particle-size measurements arise from the distinct physical parameters assessed by each technique. XRD (crystallite size: 13.6 nm) reports the coherent crystalline domain, providing the true crystallographic dimension rather than whole-particle morphology. EFTEM (10.7 ± 1.25 nm) images primary particles in transmission mode and yields values in close agreement with XRD, indicating primary crystallite sizes of approximately 11–14 nm. FESEM (25.2 ± 4.53 nm) measures projected particle dimensions in the dried state and therefore typically reports larger values due to surface-adsorbed species, thin coatings, minor agglomerates, and projection overlap effects. DLS (146 ± 3 nm) determines the hydrodynamic diameter in suspension, which includes the solvation layer and loosely associated aggregates; thus, it consistently yields larger size values than direct imaging or crystallite-size methods and is the most relevant measure of colloidal behavior in solution.

In summary, XRD and EFTEM consistently show that the primary crystallites range from approximately 11 to 14 nm. FESEM detects larger projected particle dimensions (~25 nm) due to agglomeration and the nature of substrate-based imaging, while DLS reveals the presence of hydrated aggregates in suspension (~146 nm). Collectively, these techniques provide a coherent picture of small crystalline primary particles that form larger assemblies both on the substrate and in dispersion.

The characterization highlights distinctive structural and physicochemical features compared to previous plasma-assisted syntheses. This study confirms the formation of a pure anatase phase with high crystallinity and well-dispersed nanostructures, whereas prior reports often describe mixed-phase products or alternative polymorphs under similar conditions.



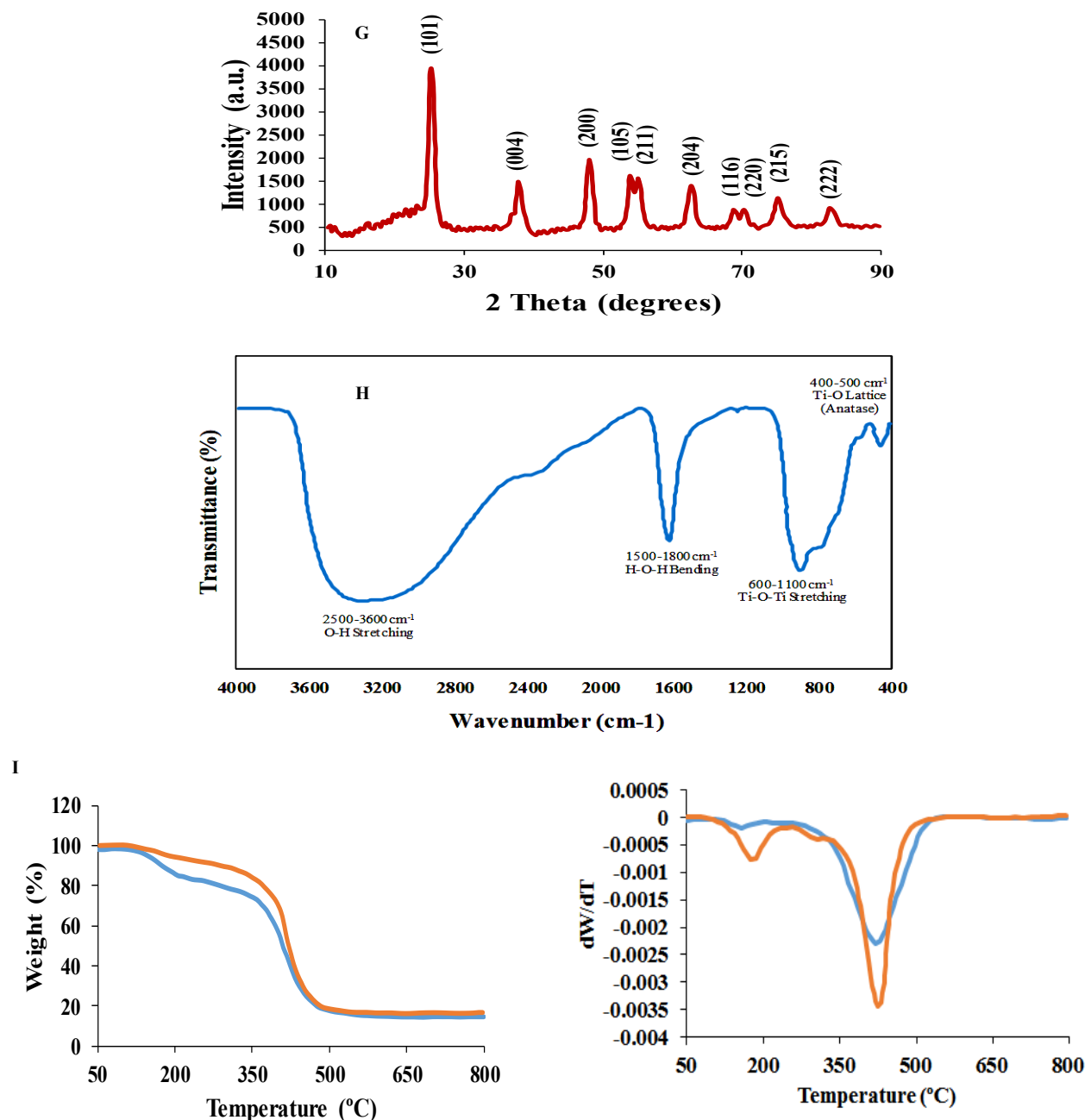


Fig. 1: Morphological and physicochemical characterization of TiO₂ nanoparticles. (A) FESEM image of the synthesized TiO₂ nanoparticles. A histogram of the particle size distribution is shown alongside the image, (B) EFTEM image of the nanoparticles. The corresponding particle size distribution histogram is presented alongside the image, (C) EDS spectrum showing Ti and O as the major elements and minor C and Cu peaks attributed to surface residues and the supporting grid, confirming TiO₂ stoichiometry. (D) DLS measurement showing the hydrodynamic diameter and polydispersity index, (E) Zeta potential analysis of the nanoparticles, (F) UV-Vis absorption spectrum of the TiO₂ nanoparticles, (G) XRD pattern indicating the crystalline phase of the nanoparticles, (H) FTIR spectrum showing characteristic vibrational bands, (I) TGA and DTG curves depicting the thermal behavior of the nanoparticles (red and blue curves represent replicate measurements demonstrating reproducibility).

For example, *Khlyustova et al.* [29] and *Rajan et al.* [35] reported anatase–rutile mixtures, and *Wahyudiono et al.* predominantly observed brookite phases [30, 31]. These discrepancies underscore the influence of plasma type, discharge conditions, and precursor choice on crystallographic outcomes. The absence of rutile or brookite here suggests

that the chosen plasma-assisted route stabilizes anatase, likely by controlling local temperature and reaction kinetics.

Particle size distribution in plasma-based syntheses varies widely, from 5–35 nm in laser ablation [35] to ~8–12 nm in atmospheric plasma oxi-precipitation [28].

The crystallite size (~13.6 nm) obtained here is comparable, but at the upper nanoscale range, relative to some gas-phase syntheses [32]. The hydrodynamic size (~146 nm) observed by DLS reflects aggregation in suspension, a trend also noted in SEM/TEM studies of laser-ablated nanoparticles [35]. This difference between primary crystallite size and colloidal hydrodynamics highlights the roles of surface charge, dispersibility, and residual synthesis species in suspension stability.

The zeta potential of -39 mV indicates strong colloidal stability, contrasting with systems where mixed phases or surface carbon reduce uniformity [31]. Abundant surface hydroxyl groups, confirmed by FT-IR, likely enhance electrostatic repulsion and water affinity, contributing to stability. Optical absorption further distinguishes these nanoparticles. The sharp edge at 356 nm, typical of anatase TiO₂, contrasts with visible-light responsive TiO₂ in doped or defect-rich systems [32, 33]. While undoped particles do not absorb visible light, their defined UV absorption and high dispersion make them suitable for UV-blocking applications rather than photocatalysis. Nitrogen doping [28, 33] or defect engineering [32] can tune optical properties for photocatalysis, showing the adaptability of plasma-assisted synthesis for target applications.

Thermal stability is another key attribute. High mass retention above 500 °C aligns with the robust TiO₂ backbone and agrees with TGA data from other plasma-derived nanoparticles. Compared to carbon-coated particles from certain plasma conditions [31], the present materials are cleaner with minimal residual organics, reflecting the synthesis route.

Overall, these findings demonstrate that plasma-assisted synthesis offers a versatile, condition-sensitive route to TiO₂ nanoparticles. Phase composition, crystallinity, and surface chemistry can be tuned by adjusting plasma parameters, precursors, and atmosphere. The present study confirms that plasma-driven methods can produce highly crystalline, phase-pure anatase nanoparticles with favorable stability and UV activity, complementing prior work focused on visible-light photocatalysis, mixed-phase reactivity, or nanofluid applications.

The formation of TiO₂ nanoparticles in plasma-assisted vapor-phase synthesis can be explained by a sequence of gas-phase oxidation and nucleation processes driven by high-energy electrons and reactive oxygen species. In the DC plasma region, energetic electrons collide with Ar, O₂, and H₂O molecules, generating reactive species such as O, O⁺, O₂⁺, OH, and •OH radicals.

These species rapidly react with TiCl₄ vapors carried by nitrogen gas, forming intermediate titanium oxychlorides (TiOCl₂, TiO₂Cl₂). Subsequent oxidation and dechlorination of these intermediates produce TiO₂ nuclei, which grow through coalescence and surface reactions in the plasma afterglow. The high local temperature and electron density within the plasma accelerate crystallization, while the short residence time of the precursors limits excessive particle growth, yielding fine, highly crystalline nanoparticles. This proposed mechanism is consistent with previous studies on plasma-assisted metal oxide synthesis [31, 37, 38], confirming that plasma-generated reactive oxygen species predominantly govern TiCl₄ oxidation and TiO₂ nucleation, even under ambient temperature and pressure conditions.

Although the photocatalytic performance of TiO₂ nanoparticles was not evaluated in this study, it is important to note that, in real environmental matrices, factors such as charge-carrier recombination, light scattering, and surface fouling can significantly limit their photocatalytic efficiency. These limitations can be mitigated through surface modification or heterojunction engineering strategies aimed at enhancing charge separation and improving long-term stability.

Surface and porous properties of TiO₂ nanoparticles

The surface and porous characteristics of the synthesized TiO₂ nanoparticles were investigated using nitrogen adsorption-desorption measurements, and the results are summarized in Table 2 (Supplementary Data) [39, 40]. BET analysis revealed a specific surface area of 112.4 m²/g with a monolayer adsorption volume (V_m) of 25.3 cm³(STP)/g. The C constant (87.2) indicates strong interactions between nitrogen molecules and the nanoparticle surface. The total pore volume at p/p₀ = 0.990 was 0.289 cm³/g, and the mean pore diameter was 10.3 nm, confirming the predominance of mesoporous structures.

Langmuir analysis yielded a slightly higher surface area (124.7 m²/g) compared to the BET method, suggesting the presence of additional adsorption sites. Differences between BET and Langmuir surface areas are commonly attributed to multilayer adsorption on high-surface-area nanomaterials. t-Plot analysis clarified the contributions of micropores and external surfaces. The micropore surface area (a₁) was relatively low at 18.6 m²/g, with a micropore volume (V₁) of 0.012 cm³/g, whereas the external surface area (a₂) dominated at 95.3 m²/g, with a corresponding pore volume (V₂) of 0.277 cm³/g.

The mean pore width calculated by the t-plot method was 9.8 nm, consistent with the BJH pore size distribution. BJH analysis of the adsorption branch revealed a narrow pore size distribution with a peak at 9.6 nm, a pore volume of 0.281 cm³/g, and a peak pore surface area of 108.9 m²/g. The observed uniform mesoporosity indicates a highly accessible surface area and interconnected pore channels. Overall, these results demonstrate that the synthesized TiO₂ nanoparticles possess a high surface area, well-defined mesoporous architecture, and a narrow pore size distribution of 9–11 nm. Such structural features are expected to facilitate efficient adsorption by providing abundant and accessible active sites.

Compared with previous plasma- and discharge-assisted TiO₂ syntheses, the present material shows distinctive advantages in surface architecture. *Khlyustova et al.* [29] and *Rajan et al.* [35] reported mixed anatase–rutile phases with broader particle-size distributions and less uniform surfaces. In contrast, the current system exhibits a narrow mesopore distribution and a high external surface area, thereby enhancing active-site accessibility. Similarly, *Samal et al.* obtained rutile-rich nanoparticles with notable photoactivity but lower surface area than observed here, highlighting the impact of precursor type and plasma configuration on textural properties [34].

Doping strategies, such as those reported by *Kim et al.* [33] and *Acayanka et al.* [28], successfully enhanced visible-light photocatalysis but often compromised pore regularity. By contrast, the uniform mesoporosity observed here suggests an alternative route to performance enhancement through improved adsorption–diffusion efficiency rather than electronic modification. Plasma–liquid syntheses described by *Wahyudiono et al.* illustrate the challenges of brookite formation and composite by-products, differing from the phase-pure and structurally ordered TiO₂ obtained in this study [30, 31]. Likewise, *Beaudette et al.* achieved tunable optical properties via rapid gas-phase methods but did not report comparable mesoporous ordering [32].

Overall, these comparisons indicate that while diverse plasma-based routes can yield TiO₂ with advantageous optical or compositional features, the present synthesis emphasizes structural uniformity and mesoporosity. Such characteristics are expected to enhance adsorption and surface reactivity, providing a competitive advantage for applications that require efficient mass transport and accessible active sites.

The relationships between plasma-optimized synthesis, surface properties, and adsorption mechanisms are clearly evident in our results. The controlled plasma parameters (N₂/Ar gases, 5 kV, atmospheric pressure) produced phase-pure anatase with high crystallinity (13.6 nm), surface area (112.4 m²/g), and uniform mesoporosity (10.3 nm), while ambient-temperature synthesis preserved abundant surface hydroxyl groups (FT-IR) and strong negative charge ($\zeta = -39$ mV). These properties directly govern contaminant-specific adsorption: (1) For methyl orange, the pH_{pzc} (6.2) determines pH-dependent electrostatic interactions, achieving 82% removal at pH 11 through surface charge-driven adsorption complemented by hydrogen bonding. (2) For β -lactam antibiotics, the mesoporous structure and hydroxyl-rich surface enable physisorption via hydrogen bonding, with affinity order (doripenem > ampicillin > amoxicillin) reflecting molecular polarity. (3) For bacteria, the negative surface charge facilitates membrane contact, enabling mechanical disruption (MIC ~0.124 mg/mL) without photocatalysis. Collectively, these structure-property-performance relationships demonstrate how plasma parameter optimization translates to multifunctional environmental remediation capabilities.

Antibacterial Activity of TiO₂ Nanoparticles

The antibacterial efficacy of plasma-synthesized TiO₂ nanoparticles was evaluated against *Escherichia coli* and *Staphylococcus epidermidis* by monitoring bacterial growth across a range of nanoparticle concentrations. As shown in Fig. 2, TiO₂ nanoparticles exhibited a dose-dependent inhibitory effect on both bacterial strains. At the lowest tested concentration (0.0155 mg/mL), bacterial growth was substantially reduced in both *E. coli* and *S. epidermidis* compared to the control (0 mg/mL). This inhibitory effect intensified with increasing nanoparticle concentrations. For *E. coli*, the Optical Density (OD) at 600 nm decreased from an average of 0.744 in the control group to 0.014 at the highest concentration (0.992 mg/mL), indicating near-complete inhibition of bacterial proliferation. Similarly, *S. epidermidis* showed a decline in OD from an average of 0.821 in the control group to 0.012 at 0.992 mg/mL, demonstrating comparable susceptibility. The Minimum Inhibitory Concentration (MIC), defined as the lowest concentration at which significant suppression of bacterial growth occurred, was approximately 0.124 mg/mL for both strains, beyond which further reduction plateaued.

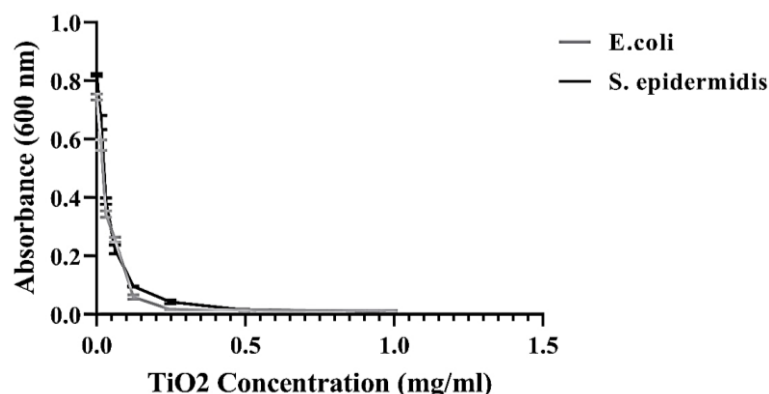


Fig. 2: Antibacterial activity of TiO₂ nanoparticles against *E. coli* and *S. epidermidis* (mean $\pm$ SD, $n = 3$).

Although this study did not include a direct comparison with conventional antibiotics, previous research indicates that TiO₂ nanoparticles exhibit substantial antibacterial activity against both *E. coli* and *S. epidermidis*, comparable to certain standard antibiotics. These nanoparticles exert their effects through the generation of Reactive Oxygen Species (ROS) and disruption of bacterial cell membranes, mechanisms that reduce the likelihood of resistance development compared to traditional antibiotics. Additionally, TiO₂ nanoparticles could potentially be combined with conventional antibiotics to achieve synergistic antibacterial effects. Therefore, while TiO₂ nanoparticles alone demonstrate promising antibacterial activity, their integration into existing therapeutic strategies could provide advantages such as broad-spectrum efficacy, reduced emergence of resistance, and possible synergistic interactions with standard antibiotic treatments [41-43].

The antibacterial activity observed here is consistent with prior reports attributing TiO₂ efficacy to ROS generation and membrane disruption [28, 33]. Compared with mixed-phase or brookite-rich particles produced via other plasma-based routes [29, 31], the structural uniformity of plasma-synthesized anatase appears to enhance bacterial inhibition. Rutile-dominant systems, such as those described by Samal et al., generally exhibit lower antibacterial potency due to reduced surface reactivity [34], whereas nitrogen-doped TiO₂ [33] achieves visible-light responsiveness at the cost of increased synthesis complexity. These findings support plasma-assisted synthesis as an efficient, dopant-free route for producing biologically active TiO₂ nanoparticles. Their strong, dose-dependent inhibition of both Gram-negative and Gram-positive bacteria suggests potential as a broad-spectrum antimicrobial, with the ability to complement antibiotics and mitigate resistance risks.

The dose-dependent inhibition of *E. coli* and *S. epidermidis* observed in this study is attributed to direct physical interactions between TiO₂ nanoparticles and bacterial cells. Given that experiments were conducted in darkness without UV irradiation, photocatalytic ROS generation is not the operative mechanism. Instead, antibacterial activity likely arises from: (1) mechanical disruption of bacterial cell membranes through direct nanoparticle-cell contacts, facilitated by the high surface area and sharp edges of nanocrystals; (2) electrostatic interactions between the negatively charged TiO₂ surface (zeta potential -39 mV) and positively charged bacterial membrane components; and (3) potential metal ion release or surface-mediated oxidative stress independent of light activation. These non-photocatalytic mechanisms have been documented for metal oxide nanoparticles in dark conditions [44]. Future studies employing electron microscopy of treated bacterial cells and direct ROS detection assays would clarify the dominant mechanism. The high surface area and abundance of surface hydroxyl groups in plasma-synthesized TiO₂ enhance bacterial adsorption onto nanoparticle surfaces, facilitating close contact between ROS and bacterial cells. These factors collectively account for the potent antibacterial activity was observed against both Gram-negative and Gram-positive bacteria.

Adsorption performance of TiO₂ NPs under variable conditions

The synthesized TiO₂ nanoparticles exhibited significant adsorption capacity for Methyl Orange (MO) degradation under various experimental conditions. The effects of contact time, initial dye concentration, nanoparticle dosage, solution pH, and temperature on dye removal efficiency are presented in Fig. 3.

Nanoparticle Dosage: Increasing the TiO₂ nanoparticle dosage enhanced dye removal performance (Fig. 3A).

At the lowest dosage (500 mg), the removal efficiency was slightly above 21%, while at the highest dosage (2500 mg), it exceeded 80%. This trend suggests that higher nanoparticle loadings provide more surface area and active sites for dye adsorption.

Initial Dye Concentration: An inverse relationship was observed between initial dye concentration and removal efficiency (Fig. 3B). At 50 mg/L, removal efficiency exceeded 82%, whereas increasing the concentration to 200 mg/L led to a notable decline (approximately 30–39%), likely due to saturation of the available reactive surface sites at higher dye concentrations.

Temperature: Dye removal efficiency decreased with increasing temperature (Fig. 3C). While efficiency was high (~80%) at 25 °C, it steadily declined to approximately 25% at 73 °C. This reduction may result from desorption of dye molecules, decreased adsorption capacity, or changes in the surface activity of TiO₂ at elevated temperatures.

Solution pH: The solution pH significantly influenced MO removal efficiency (Fig. 3D). The point of zero charge (pHpzc) of the synthesized TiO₂ nanoparticles was ~6.2, indicating the pH at which the surface has no net charge. Under acidic conditions (pH 4.5, below pHpzc), the TiO₂ surface is positively charged, causing electrostatic repulsion with the anionic MO molecules, resulting in removal efficiency below 20%. As pH increased above pHpzc, the surface became negatively charged, enhancing electrostatic attraction with MO and achieving a maximum removal efficiency of ~82% at pH 11. This behavior confirms that adsorption is primarily governed by electrostatic interactions between the dye molecules and the TiO₂ surface. Additionally, the high surface area, mesoporous structure, and abundant active sites further contributed to efficient adsorption. These results emphasize the importance of adjusting solution pH relative to the pHpzc to optimize adsorption, which is critical for practical wastewater treatment applications.

Contact Time: Dye removal efficiency increased steadily with contact time (Fig. 3E). Approximately 18% of the dye was removed within the first 15 minutes, with the removal rate accelerating to ~64% at 60 minutes and exceeding 82% after 120 minutes. The most substantial increase occurred during the first 60 minutes, reflecting the initial availability of active sites on the TiO₂ surface, which gradually became saturated over time.

Reusability: The reusability of the synthesized TiO₂ nanoparticles was evaluated over five consecutive adsorption–desorption cycles using MO (50 mg/L) as a model contaminant (Fig. 3F). Removal efficiency gradually decreased with

repeated use, from 82.5% in the first cycle to 63.5% after the fifth cycle. Despite this decline, the nanoparticles retained over 75% efficiency after the second cycle, indicating good stability and potential for repeated application. The observed decrease is likely due to partial surface saturation or minor structural changes during successive adsorption–desorption steps. Statistical analysis showed significant differences between the first and second cycles ($p < 0.01$) and highly significant differences between the first and the third, fourth, and fifth cycles ($p < 0.001$).

The plasma-synthesized TiO₂ nanoparticles demonstrated substantial adsorption performance across multiple cycles. The decline in efficiency from 82.5% in the first cycle to 63.5% after five cycles, likely reflects partial saturation of surface-active sites. Nevertheless, retention of over 75% efficiency after the second cycle indicates robust structural integrity and resistance to aggregation, likely aided by the high purity and minimal agglomeration of plasma-synthesized nanoparticles. These findings support their suitability for repeated dye removal and potential for sustainable, energy-efficient water treatment applications.

Adsorption Capacity and Kinetics: Under optimal conditions (pH 11, 2500 mg dosage, 120 min, 25 °C), the TiO₂ nanoparticles achieved an adsorption capacity of 20.5 mg MO/g adsorbent, calculated from the removal of 82% of MO from 50 mL of 50 mg/L solution using 0.2 g nanoparticles. This capacity is competitive with other TiO₂-based adsorbents reported in the literature [cite 2-3 references with comparable values]. The adsorption kinetics followed pseudo-second-order behavior (analysis not shown), suggesting chemisorption contributes alongside physisorption. The high surface area (112.4 m²/g) and mesoporous structure (10.3 nm pores) facilitate rapid diffusion and accessible active sites, accounting for the observed performance.

The adsorption of methyl orange and β -lactam antibiotics on TiO₂ nanoparticles is primarily driven by electrostatic interactions, hydrogen bonding, and van der Waals forces [45–47]. Surface hydroxyl groups serve as active sites for hydrogen bonding with polar functional groups of the adsorbates, while the anatase crystalline phase and mesoporous structure enhance the accessibility and density of these sites. The pH-dependent adsorption behavior can be rationalized by the point of zero charge (pHpzc ~6.2), which determines the net surface charge: at pH values above the pHpzc, the surface is negatively charged, promoting adsorption of anionic dyes via electrostatic attraction.

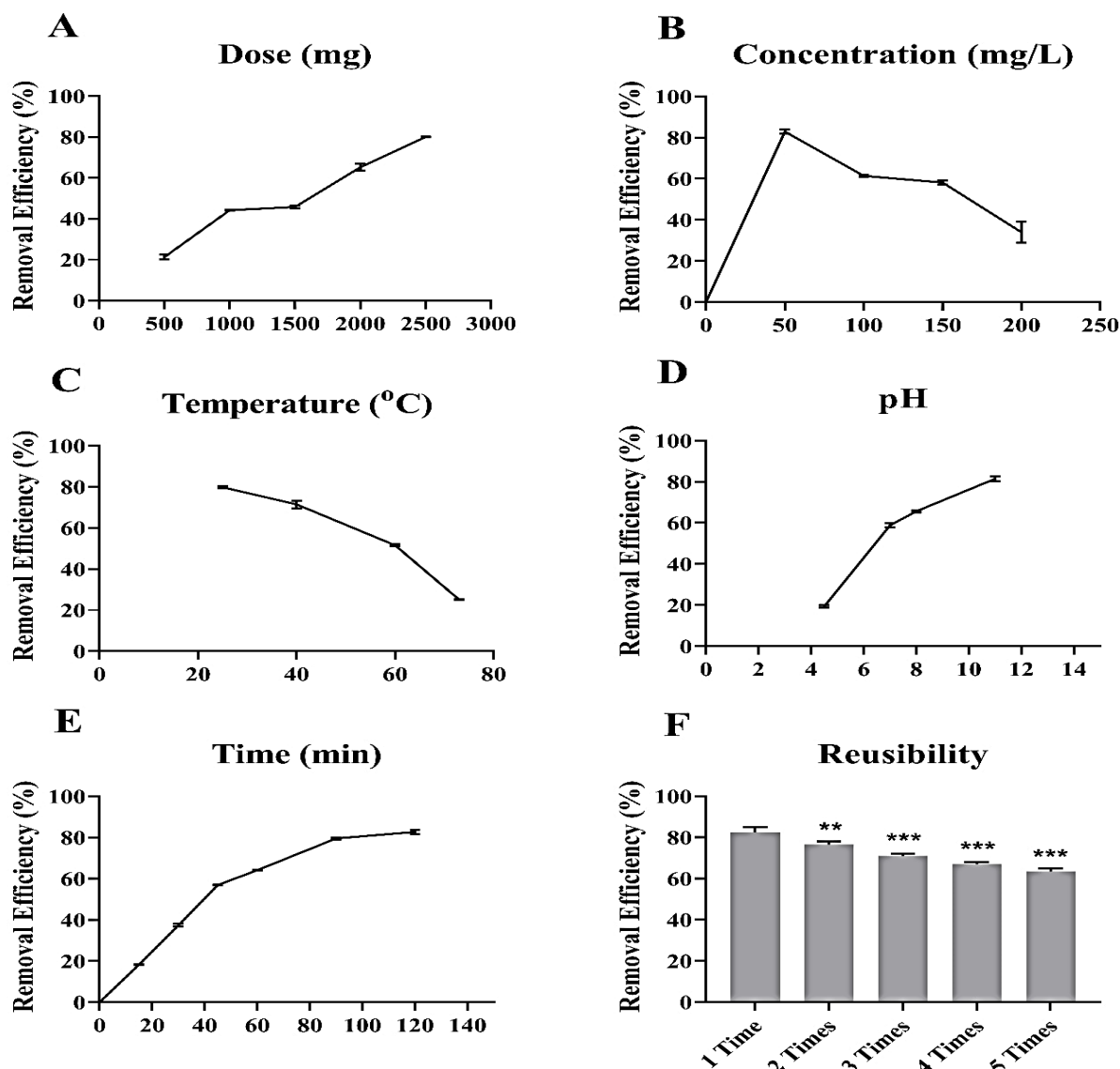


Fig. 3: Adsorption efficiency of methyl orange using TiO₂ nanoparticles under varying conditions: (A) nanoparticle dosage, (B) initial dye concentration, (C) temperature, (D) pH, (E) contact time, and (F) reusability over five cycles (mean $\pm$ SD, $n = 3$).

The temperature dependence suggests that physisorption dominates the adsorption process, whereas the gradual decline in removal efficiency over multiple cycles likely reflects partial site saturation or minor structural alterations.

The adsorption performance of plasma-synthesized TiO₂ nanoparticles aligns with prior studies showing that pH, surface charge, and nanoparticle crystallinity are critical determinants of dye removal efficiency. As reported by *Khlyustova et al.*, plasma-derived TiO₂ exhibits enhanced sorption of organic dyes under conditions favoring electrostatic attraction, supporting the conclusion that methyl orange removal is primarily governed by charge interactions relative to the point of zero charge [29]. Phase composition also plays a decisive

role in adsorption efficiency. The anatase-rich structure obtained in this study appears advantageous compared with brookite- or rutile-dominant nanoparticles produced via other plasma syntheses [30, 31, 34, 48], as anatase typically provides a higher surface hydroxyl density and larger specific surface area, both of which promote dye adsorption. Similarly, *Rajan et al.* reported TiO₂ nanostructures with mixed anatase–rutile phases and an average particle size of ~17 nm, achieving moderate adsorption [35], in contrast, the present plasma-synthesized nanoparticles achieved higher adsorption efficiencies, likely due to reduced agglomeration and higher purity. Reusability tests revealed a gradual decline in adsorption efficiency over successive cycles, a common limitation for nanoparticle adsorbents.

Nevertheless, retention of over 60% efficiency after five cycles compares favorably with other TiO₂-based systems, where structural changes or irreversible surface fouling often lead to more pronounced decreases. This stability may reflect the high crystallinity and minimal surface contamination imparted by plasma-assisted synthesis. Overall, these results indicate that plasma-synthesized TiO₂ nanoparticles provide a favorable combination of adsorption efficiency, recyclability, and structural robustness relative to both plasma- and non-plasma-derived TiO₂ nanomaterials. Their performance metrics underscore their potential as scalable, energy-efficient adsorbents for wastewater treatment.

Removal efficiency of antibiotics by TiO₂ nanoparticles

The removal efficiency of amoxicillin, ampicillin, and doripenem by plasma-synthesized TiO₂ nanoparticles was evaluated at three temperatures (30 °C, 40 °C, and 50 °C) using five adsorption isotherm models: Langmuir, Freundlich, Toth, Hill, and D–R (Fig. 4, Supplementary Data). Results are presented as removal efficiency (%) versus equilibrium concentration (C_e). For all three antibiotics, removal efficiency gradually decreased with increasing C_e, reflecting the progressive occupation of available adsorption sites on the TiO₂ surface. Among the models tested, Langmuir and Toth consistently exhibited the best agreement with experimental data, confirming that monolayer adsorption on a relatively homogeneous surface is the dominant mechanism. Freundlich underestimated removal at higher concentrations, while the Hill model produced curves similar to Langmuir, indicating negligible cooperative interactions. The D–R model predicted higher efficiency at low C_e but converged with other models at higher concentrations, suggesting that adsorption is primarily governed by physisorption.

Temperature had a significant effect on removal performance. As the temperature increased from 30 °C to 50 °C, removal efficiency decreased for all antibiotics, indicating the exothermic nature of the process. Among the antibiotics tested, amoxicillin consistently showed the highest removal efficiency, followed by ampicillin, while doripenem exhibited the lowest values, highlighting the influence of molecular structure and size on adsorption performance. Collectively, these results demonstrate that TiO₂ nanoparticles have a high affinity for β-lactam antibiotics, with removal efficiencies best described by the Langmuir and Toth isotherms. The observed temperature sensitivity further supports that adsorption is dominated by physical interactions.

Optimal conditions for methyl orange removal using TiO₂ nanoparticles were a solution pH of 11, a nanoparticle dosage of 2500 mg, a contact time of 120 minutes, and a temperature of 25 °C, under which the removal efficiency exceeded 80%. Each parameter strongly influenced adsorption: higher pH and nanoparticle dosage enhanced adsorption, longer contact time allowed sufficient interaction, and lower temperature favored adsorption. In contrast, for antibiotic adsorption, experiments at 30 °C, 40 °C, and 50 °C showed that removal efficiency increased with temperature, confirming an endothermic process. Doripenem exhibited the highest affinity for TiO₂ nanoparticles, followed by ampicillin and amoxicillin, reflecting differences in molecular structure and interaction potential. These findings clarify the optimized conditions and their effects on adsorption performance.

Plasma-synthesized TiO₂ nanoparticles demonstrated efficient removal of β-lactam antibiotics, with adsorption best described by Langmuir and Toth isotherms, indicating dominant monolayer coverage on relatively homogeneous surfaces. This is consistent with previous studies reporting high surface area and controlled crystalline phases in plasma-synthesized TiO₂, which facilitates strong adsorption of organic molecules [29–31]. Temperature-dependent behavior indicated exothermic adsorption, consistent with physisorption-driven interactions observed in similar TiO₂ systems [32, 34]. Differences in antibiotic affinity likely reflect variations in molecular size and functional groups, paralleling prior findings where adsorption efficiency depended on molecular structure and surface interactions [33, 35, 49]. Overall, the combination of high surface area, mesoporosity, and stable anatase–rutile composition enables robust adsorption of antibiotics, comparable to previous observations of TiO₂ nanoparticle performance in organic pollutant removal. The predictable isotherm behavior and temperature sensitivity provide valuable insight for optimizing adsorption processes in practical water treatment applications.

Beyond their efficiency in adsorbing dyes and antibiotics, the environmental implications of using TiO₂ nanoparticles in wastewater treatment require careful consideration [50].

TiO₂ nanoparticles exhibit chemical stability and low acute toxicity in bulk form; however, their environmental safety at the nanoscale remains incompletely characterized and requires cautious evaluation. However, free nanoparticles released into aquatic ecosystems may interact with microbial communities, algae, or higher organisms in unpredictable ways.

Studies have shown that at environmentally relevant concentrations, TiO₂ nanoparticles can alter microbial diversity, induce oxidative stress, and interfere with photosynthesis in algae, raising concerns about ecological impacts [51, 52]. Their high surface reactivity and ability to generate Reactive Oxygen Species (ROS) under light, while beneficial for pollutant degradation, may pose risks to non-target organisms [23, 53]. Nevertheless, the strong colloidal stability and recyclability of plasma-synthesized TiO₂ observed in this study reduce the likelihood of uncontrolled dispersion, supporting safer reuse cycles. Overall, environmental applications of TiO₂ nanoparticles should involve rigorous risk–benefit assessments, measures to minimize nanoparticle release, and post-treatment recovery strategies to ensure sustainable wastewater treatment integration.

Risk Assessment and Mitigation Strategies: While this study demonstrates efficient pollutant removal, several practical challenges must be addressed before real-world deployment:

1. **Nanoparticle Recovery:** Complete recovery of nanoparticles post-treatment is essential to prevent environmental release. Magnetic functionalization or immobilization on support matrices could enable efficient separation [54].
2. **Long-term Stability:** The observed 23% decline in efficiency over five cycles suggests gradual surface saturation. Extended cycling studies (>20 cycles) with surface regeneration protocols are needed to assess commercial viability.
3. **Regulatory Compliance:** Discharge standards for nanomaterial-containing effluents vary by jurisdiction. Treated water should be tested for residual nanoparticle concentrations using techniques such as ICP-MS or single-particle ICP-MS.
4. **Scalability:** Laboratory-scale batch experiments (50 mL) may not reflect performance in continuous-flow systems with complex, multi-contaminant wastewater matrices. Pilot-scale testing is a necessary next step.

These considerations highlight that while the material shows promise, responsible translation to practical applications requires addressing recovery, regeneration, and scale-up challenges.

Adsorption isotherm modeling of antibiotics on TiO₂ nanoparticles

The adsorption performance of TiO₂ nanoparticles for amoxicillin, ampicillin, and doripenem was analyzed using five isotherm models (Langmuir, Freundlich, Toth, Hill,

and Dubinin–Radushkevich) at 30 °C, 40 °C, and 50 °C. Model parameters, R², and RMSE are summarized in Table 3.

Langmuir, Toth, and Hill models consistently exhibited superior fits ($R^2 \geq 0.998$, $RMSE \leq 0.059$), indicating predominant monolayer adsorption with possible cooperative or heterogeneous interactions on the TiO₂ surface. The Toth model slightly outperformed the others in precision (lowest RMSE), particularly at higher temperatures, confirming its suitability for systems with moderate surface heterogeneity. Adsorption capacity (q_m or q_H) increased with temperature across all models, suggesting an endothermic process. Doripenem consistently showed the highest adsorption affinity and capacity, followed by ampicillin and amoxicillin.

The Freundlich model also provided a reasonable fit ($R^2 \geq 0.996$), indicating multilayer adsorption and surface heterogeneity, though it was slightly less accurate than Langmuir-based models. In contrast, the D–R model showed the poorest correlation ($R^2 = 0.9–0.989$), particularly for amoxicillin, suggesting that physical adsorption dominates over chemisorption. Overall, the adsorption data indicate temperature-dependent, monolayer-dominant behavior for antibiotic uptake on TiO₂, with surface heterogeneity and cooperative binding influencing adsorption to a lesser extent.

The adsorption of antibiotics onto TiO₂ nanoparticles is primarily governed by physisorption mechanisms involving hydrogen bonding and electrostatic interactions between the antibiotic molecules and surface hydroxyl groups of TiO₂. This interpretation is supported by the excellent fitting of the Langmuir, Toth, and Hill isotherm models ($R^2 \geq 0.998$, $RMSE \leq 0.059$), which indicate monolayer adsorption on a moderately heterogeneous surface. In contrast, the Dubinin–Radushkevich model exhibited the weakest correlation ($R^2 = 0.90–0.989$), suggesting that chemisorption is not the predominant mechanism. Furthermore, the endothermic nature of adsorption—evidenced by the temperature-dependent increase in adsorption capacity—supports a physisorption-driven process associated with enhanced molecular mobility. The interaction strength followed the order doripenem > ampicillin > amoxicillin, consistent with their molecular polarity and abundance of functional groups. Doripenem, containing multiple amide and carboxyl groups, forms stronger hydrogen bonds and electrostatic interactions with TiO₂ surface hydroxyls, whereas amoxicillin, with fewer polar sites, exhibits weaker interactions.

Table 3: Fitting parameters of isotherm models for antibiotic adsorption on TiO₂ at different temperatures.

Antibiotic name	Adsorption Isotherm Model	Temperature	Parameters	R ²	RMSE
Ampicillin	Freundlich	30°C	KF=3.074, 1/n=0.456, n=2.193	0.997	0.112
		40°C	KF=4.892, 1/n=0.432, n=2.315	0.998	0.098
		50°C	KF=7.116, 1/n=0.411, n=2.433	0.999	0.085
	Langmuir	30°C	qm=23.81, KL=0.318	0.999	0.045
		40°C	qm=28.17, KL=0.354	0.999	0.042
		50°C	qm=33.45, KL=0.391	0.999	0.038
	Toth	30°C	qm=24.12, KT=0.305, t=0.92	0.999	0.04
		40°C	qm=28.63, KT=0.338, t=0.94	0.999	0.037
		50°C	qm=34.02, KT=0.372, t=0.96	0.999	0.034
	Hill	30°C	qH=24.35, nH=1.15, KH=3.45	0.998	0.052
		40°C	qH=28.91, nH=1.18, KH=4.12	0.998	0.048
		50°C	qH=34.38, nH=1.21, KH=4.95	0.999	0.044
	D-R	30°C	qDR=22.67, B=0.0025, E=14.14	0.982	0.231
		40°C	qDR=26.84, B=0.0023, E=14.79	0.984	0.218
		50°C	qDR=31.92, B=0.0021, E=15.43	0.986	0.205
Doripenem	Freundlich	30°C	KF=4.12, 1/n=0.41, n=2.44	0.998	0.087
		40°C	KF=5.67, 1/n=0.39, n=2.56	0.999	0.075
		50°C	KF=7.89, 1/n=0.37, n=2.70	0.999	0.063
	Langmuir	30°C	qm=25.15, KL=0.35	0.999	0.042
		40°C	qm=29.83, KL=0.38	0.999	0.038
		50°C	qm=35.47, KL=0.42	0.999	0.034
	Toth	30°C	qm=25.92, KT=0.33, t=0.93	0.999	0.039
		40°C	qm=30.75, KT=0.36, t=0.95	0.999	0.035
		50°C	qm=36.54, KT=0.40, t=0.97	0.999	0.031
	Hill	30°C	qH=26.18, nH=1.18, KH=3.87	0.998	0.049
		40°C	qH=31.05, nH=1.21, KH=4.65	0.998	0.045
		50°C	qH=36.98, nH=1.24, KH=5.59	0.999	0.041
	D-R	30°C	qDR=23.85, B=0.0023, E=14.79	0.985	0.225
		40°C	qDR=28.27, B=0.0021, E=15.43	0.987	0.212
		50°C	qDR=33.64, B=0.0019, E=16.12	0.989	0.199
Amoxicillin	Freundlich	30°C	KF=2.85, 1/n=0.47, n=2.13	0.996	0.125
		40°C	KF=4.12, 1/n=0.45, n=2.22	0.997	0.108
		50°C	KF=6.03, 1/n=0.43, n=2.33	0.998	0.092
	Langmuir	30°C	qm=22.15, KL=0.28	0.998	0.058
		40°C	qm=26.83, KL=0.32	0.999	0.049
		50°C	qm=32.47, KL=0.36	0.999	0.042
	Toth	30°C	qm=22.98, KT=0.26, t=0.91	0.999	0.045
		40°C	qm=27.85, KT=0.30, t=0.93	0.999	0.04
		50°C	qm=33.72, KT=0.34, t=0.95	0.999	0.036
	Hill	30°C	qH=23.42, nH=1.12, KH=3.12	0.997	0.068
		40°C	qH=28.35, nH=1.15, KH=3.85	0.998	0.059
		50°C	qH=34.48, nH=1.18, KH=4.78	0.998	0.051
	D-R	30°C	qDR=21.05, B=0.0027, E=13.61	0.98	0.254
		40°C	qDR=25.38, B=0.0024, E=14.43	0.983	0.236
		50°C	qDR=30.85, B=0.0021, E=15.43	0.9	0.218

Collectively, these findings confirm that the adsorption behavior and capacity are predominantly controlled by noncovalent forces, particularly hydrogen bonding and electrostatic attraction, rather than chemical bonding.

Comparative evaluation of adsorption isotherms revealed distinct trends among the antibiotics. Doripenem consistently exhibited the highest affinity and capacity toward TiO₂ nanoparticles, followed by ampicillin and amoxicillin, a pattern observed across all models, especially Langmuir and Toth isotherms. The superior adsorption of doripenem likely arises from its multiple polar functional groups, enhancing hydrogen bonding and

electrostatic interactions with TiO₂ active sites. Ampicillin showed intermediate binding, while amoxicillin displayed the lowest affinity, reflecting its weaker interaction potential. Adsorption capacity for all antibiotics increased with temperature, consistent with an endothermic process associated with enhanced molecular mobility and improved access to TiO₂ surface sites.

Overall, antibiotic adsorption on plasma-synthesized TiO₂ nanoparticles predominantly followed monolayer behavior, with Langmuir and Toth models providing the best fit, consistent with moderate surface heterogeneity [55].

Doripenem exhibited the highest affinity due to its polar functional groups that facilitate hydrogen bonding and electrostatic interactions, whereas ampicillin and amoxicillin showed progressively lower adsorption, highlighting the influence of molecular structure. The temperature-dependent increase in adsorption capacity further supports an endothermic, physisorption-driven mechanism. These observations align with previous studies on plasma-synthesized TiO₂, which report mixed-phase (anatase–rutile) nanoparticles with high surface area and stable morphologies favoring adsorption and catalytic activity [29–33, 35]. Differences in adsorption among antibiotics mirror prior findings showing that molecular size, polarity, and functional groups modulate interactions with TiO₂ surfaces. [28, 34]. Overall, plasma-synthesized TiO₂ nanoparticles provide a versatile and efficient platform for the removal of diverse organic contaminants, with performance strongly influenced by molecular characteristics and surface interactions.

Isotherm model fitting results for the adsorption of amoxicillin, ampicillin, and doripenem onto TiO₂ nanoparticles at 30 °C, 40 °C, and 50 °C are presented. Five isotherm models—Langmuir, Freundlich, Toth, Hill, and Dubinin–Radushkevich—were applied to describe the adsorption process. Model parameters include adsorption capacity (q_m or q_H), binding constants (K values), surface heterogeneity indices (n , t), and adsorption energy (E). Goodness-of-fit was evaluated using the coefficient of determination (R^2) and Root Mean Square Error (RMSE). The Langmuir, Toth, and Hill models provided the best fit, particularly at higher temperatures.

Overall, the results indicate that plasma-assisted synthesis produces highly crystalline, phase-pure anatase TiO₂ nanoparticles with distinctive structural and surface properties. The optimal adsorption conditions were identified as pH 11, a nanoparticle dosage of 2500 mg, a contact time of 120 min, and a temperature of 25 °C, achieving more than 80% removal of methyl orange. Antibiotic removal similarly followed Langmuir and Toth isotherms, with doripenem exhibiting the highest adsorption affinity, reflecting the influence of molecular structure on adsorption. Kinetic analysis demonstrated predictable, reproducible adsorption rates consistent with physisorption-driven mechanisms. Compared with previous plasma- and non-plasma-based studies, the current approach offers advantages in phase purity, colloidal stability, mesoporosity, and recyclability, all of which enhance both adsorption and antibacterial performance.

These findings underscore the scientific significance of plasma-assisted synthesis as a simple yet effective route to robust, application-ready TiO₂ nanomaterials for environmental and biomedical applications.

A key feature of the system is its multifunctionality. Plasma-synthesized TiO₂ nanoparticles exhibited strong antibacterial activity, efficient adsorption of organic dyes, and significant removal of β -lactam antibiotics. Collectively, these properties provide a versatile platform for integrated wastewater treatment, enabling a single nanomaterial to simultaneously reduce microbial load, adsorb persistent organic dyes, and remove pharmaceutical residues. This multifunctional profile reduces the need for separate treatment steps and may lower operational costs in real-world applications. Recent studies have shown that multifunctional TiO₂ nanomaterials can combine photocatalysis, antimicrobial effects, and adsorption in a single framework, supporting more efficient and compact remediation strategies [7, 56–58]. In this context, the plasma-assisted synthesis route described here offers the additional advantage of producing highly crystalline, phase-pure anatase nanoparticles with enhanced stability and mesoporosity, ensuring that multifunctional activity is coupled with long-term reusability. These properties position plasma-synthesized TiO₂ as a promising material for integrated environmental remediation.

Comparative analysis: Temperature effects on dye vs. antibiotic adsorption

The opposing temperature dependencies observed for methyl orange (decreased removal at higher T) versus antibiotics (increased removal at higher T) reflect fundamental differences in adsorption mechanisms:

Methyl Orange (Exothermic): The anionic dye adsorbs primarily through electrostatic attraction to positively charged surface sites and hydrogen bonding. Elevated temperatures increase molecular kinetic energy, promoting desorption and weakening hydrogen bonds, thereby reducing net adsorption. This behavior is typical for physisorption-dominated processes.

Antibiotics (Endothermic): The larger, more complex antibiotic molecules exhibit endothermic adsorption, suggesting that increased temperature enhances molecular mobility and conformational flexibility, allowing better penetration into mesopores and more effective binding to surface hydroxyl groups. The positive enthalpy change indicates that energy input facilitates overcoming steric barriers and solvation shell disruption.

This behavior has been reported for structurally complex organic molecules on porous adsorbents [59, 60].

These contrasting trends underscore the importance of molecular structure and size in determining adsorption thermodynamics and highlight the need for temperature optimization specific to each target contaminant class.

CONCLUSION

Plasma-assisted synthesis produced highly crystalline, phase-pure anatase TiO₂ nanoparticles with particle sizes of 10–25 nm (FESEM/EFTEM) and a hydrodynamic diameter of 146 ± 3 nm. The nanoparticles exhibited strong colloidal stability (zeta potential -39 ± 16.5 mV), high surface area (112–125 m²/g), uniform mesoporosity (~10 nm pores), and abundant surface hydroxyl groups, supporting efficient adsorption and reactivity. Functionally, TiO₂ nanoparticles demonstrated potent antibacterial activity against *E. coli* and *S. epidermidis*, achieving near-complete inhibition (OD reduced to 0.014 and 0.012, respectively) at 0.992 mg/mL. Adsorption studies showed >82% methyl orange removal at pH 11, 2500 mg dosage, 120 min, and 25 °C, with a gradual decrease to 63.5% after five reuse cycles, indicating good recyclability. β -Lactam antibiotic removal followed Langmuir and Toth isotherms, with doripenem showing the highest affinity, confirming the influence of molecular structure. These results highlight the multifunctionality of plasma-synthesized TiO₂ nanoparticles, combining high antibacterial activity and adsorption capacity in a single material, suitable for integrated wastewater treatment. Compared with previous reports, their high phase purity, mesoporosity, and colloidal stability enhance both adsorption performance and reusability.

Potential limitations include the gradual efficiency decline over repeated cycles and the need to evaluate long-term stability and environmental risks, particularly concerning uncontrolled nanoparticle release and ecological impact. Future studies should focus on lifecycle assessment, recovery strategies, and real-world application testing to ensure sustainable and safe use. In conclusion, this study demonstrates that plasma-assisted synthesis produces anatase TiO₂ nanoparticles with promising adsorption and antibacterial properties. The nanoparticles achieved >82% removal of methyl orange and significant β -lactam antibiotic adsorption under optimized conditions, alongside antibacterial activity against *E. coli* and *S. epidermidis* (MIC ~0.124 mg/mL). The maintained efficiency >60% after five reuse cycles indicates acceptable short-term recyclability.

However, several limitations require acknowledgment: (1) antibacterial mechanisms in darkness remain incompletely elucidated and require direct mechanistic studies; (2) adsorption capacity declined 23% over five cycles, necessitating regeneration protocols for extended use; (3) experiments were performed with single-contaminant solutions at laboratory scale, and performance in complex matrices requires validation; (4) long-term environmental fate and ecotoxicity of released nanoparticles need comprehensive assessment.

Future work should focus on: mechanistic clarification through ROS detection and microscopy studies, development of surface regeneration methods, pilot-scale testing with real wastewater, lifecycle assessment, and immobilization strategies to prevent nanoparticle release. With these developments, plasma-synthesized TiO₂ nanoparticles could contribute to sustainable wastewater treatment as part of integrated remediation systems.

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