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Solar-driven photocatalytic ceramic membrane reactors from Tunisian clay for efficient paracetamol degradation

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Abstract

Pharmaceutical residues such as paracetamol are increasingly detected in aquatic environments, raising concerns about their persistence and potential ecological impact. In this study, a solar-driven photocatalytic membrane reactor (PMR) was developed using low-cost ceramic membranes fabricated from Matmata-Gabes clay (southern Tunisia) and functionalized with TiO₂ P25. The membranes were prepared by uniaxial pressing followed by sintering at 1000 °C, while TiO₂ was immobilized via dip-coating and calcined at 450 °C. The influence of catalyst loading and operating conditions was systematically investigated under both UV irradiation and natural sunlight. The results indicate that increasing TiO₂ loading improves surface hydrophilicity with the water contact angle decreasing to 17.5°, but excessive deposition reduces membrane porosity and permeability. Optimal performance was achieved at 0.6 g/L 1.0 and g/L of TiO₂ loading solution concentration under UV and solar conditions, respectively leading to degradation efficiencies of 74.9% and 55.5% after 5.5 h of treatment. In

addition, horizontal membrane configuration (0° inclination) enhanced photon utilization resulting in improved reaction kinetics. Although permeate flux declined over time due to fouling, the photocatalytic layer contributed to partial self-cleaning under irradiation. Over five consecutive cycles, the membranes retained more than 35% of their initial activity, indicating moderate stability. These findings demonstrate the potential of combining locally available materials with solar photocatalysis as a sustainable approach for decentralized water treatment, particularly in regions with high solar irradiance.

Keywords: Photocatalytic membrane reactor, Ceramic membrane, Matmata-Gabes clay, Titanium dioxide (TiO_2), Paracetamol degradation, Solar photocatalysis, Wastewater treatment

1. Introduction

The rapid growth in global water demand, driven by both population growth and industrial expansion, has placed considerable stress on freshwater resources [1]. At the same time, these water consumption triggers have significantly increased wastewater production, introducing a wide range of complex contaminants into aquatic environments. Among these, pharmaceutical residues have emerged as a major concern due to their persistence, potential for bioaccumulation, and biological activity even at very low concentrations (ng/L - $\mu\text{g/L}$) [2,3].

Paracetamol (acetaminophen), one of the most widely used analgesic and antipyretic drug, is frequently detected in municipal wastewater and surface waters. Reported concentrations can reach up to hundreds of $\mu\text{g/L}$ in untreated effluents, and its incomplete removal during conventional treatment raises concerns about its continuous release into the environment [4,5]. Such persistence may pose risks to aquatic organisms and, indirectly to human health through drinking water sources [6,7]. These challenges highlight the need for effective treatment strategies capable of degrading, rather than simply transferring such contaminants to a secondary pollution stream.

Conventional wastewater treatment plants (WWTPs) are not specifically designed to remove micropollutants such as pharmaceuticals [8]. Advanced oxidation processes (AOPs), including photocatalysis and ozonation, have demonstrated strong degradation potential through the generation of highly reactive species such as hydroxyl radicals ($\cdot\text{OH}$) [9,10]. However, their practical implementation is often limited by operational costs and, in the case of photocatalysis, by the need to recover suspended catalysts. Membrane processes, on the other hand, offer efficient physical separation but are affected by fouling and produce problematic concentrate stream that require further treatment [11].

To overcome these limitations, the integration of membrane filtration with heterogeneous photocatalysis has gained increasing attention. This hybrid configuration, known as a photocatalytic membrane reactor (PMR), combines separation and degradation within a single system, while also offering the possibility of in situ membrane self-cleaning [12,13]. In this context, ceramic membranes represent a promising alternative to polymeric materials due to their superior mechanical strength, chemical resistance, and thermal stability [14]. Nevertheless, their high production cost remains a key limitation. Recent efforts have therefore focused on developing low-cost ceramic supports from naturally abundant materials. In the case

of this study, red clay from the Matmata-Gabes region in Tunisia was selected due to its suitable composition and processing properties [15,16]. When coupled with titanium dioxide (TiO₂), a well-established photocatalyst known for its stability and non-toxicity can be transformed into reactive membranes suitable for water treatment applications [17,18]. Immobilizing TiO₂ on ceramic supports also avoids the need for post-treatment catalyst recovery, which is a major drawback of slurry-based systems [19].

Most studies still rely on artificial UV sources, which is a well-established technology. However, in high-irradiance regions such as North Africa (where this study was conducted), the use of natural sunlight should be explored [20]. In addition, the influence of reactor configuration, particularly membrane inclination, light distribution, hydrodynamics, and fouling behavior is not yet fully understood [21,22]. Improving catalyst adhesion using environmentally friendly additives such as natural binders also requires further investigation [23,24]. Considering these gaps, the present study focuses on the development of low-cost photocatalytic ceramic membranes based on Matmata-Gabes clay for the degradation of paracetamol. TiO₂ P25 nanoparticles were immobilized using a simple dip-coating approach involving natural additives to enhance coating stability. Attention was given to the combined effects of catalyst loading, irradiation source (UV vs. natural sunlight), and membrane inclination angle (0°, 20°, 40°, and 60°). By systematically analyzing these parameters, this work aims to better understand the interplay between reactor design and performance, and to propose a more sustainable and efficient approach for the treatment of pharmaceutical contaminants in water.

2. Materials and Methods

2.1. Raw Materials and Precursors

The ceramic membrane was prepared using natural red clay collected from the Matmata–Gabes region in southern Tunisia. This clay, rich in aluminosilicates, was chosen mainly because it is abundance, inexpensive, and easy to process traits making it suitable for sustainable water treatment applications [25,26]. Before use, the raw material was air- and sun-dried until the moisture content dropped below 5%. It was then ground with a disc grinder (Schneider) and passed through an 80 µm sieve (MATEST vibrator) to obtain a more uniform particle size. To create the porous structure required for microfiltration, cornstarch was added as a pore-forming agent. Arabic gum was also incorporated to improve the plasticity of the mixture and ensure sufficient mechanical strength of the green bodies. For the photocatalytic layer, commercial titanium dioxide (TiO₂ P25, Evonik Industries) was used. This material, composed of approximately 80% anatase and 20% rutile, is widely recognized for its photocatalytic activity. The coating suspension was prepared using nitric acid (2 M) as a peptizing agent, along with a starch solution (12%) to improve adhesion during deposition. Paracetamol, PCT (acetaminophen, C₈H₉NO₂, MW = 151.16 g/mol) was selected as the model pollutant [27].

2.2. Fabrication of Ceramic Membrane

The ceramic membrane was shaped via uniaxial pressing and subsequently sintered under optimized conditions. We used a blend of 96 wt.% sieved clay and 4 wt.% cornstarch to generate

the necessary porosity. Once the dry powders were homogenized in an automatic mixer (Proetisa), deionized water was introduced gradually to form a cohesive paste. To prevent cracking caused by trapped air bubbles during firing, the mixture underwent degassing in an ultrasonic bath (J.P. SELECTA) for 30 minutes [28], followed by a 48-hour rest period in a humid chamber to maximize workability.

The resulting paste was pressed into 7 cm × 10 cm × 3 mm blocks at 10 bars (Edibon EEU/20 KN) and air-dried for 24 hours. Sintering took place in a Nabertherm S30 muffle furnace. A heating rate of 4°C/min up to 1000°C was applied with a one-hour dwell time. This specific temperature profile was chosen after several trial runs. It successfully removed all organic additives and strengthened the ceramic matrix without triggering excessive vitrification that typically compromises flux in clay-based membranes [29,30].

2.3. Photocatalytic Functionalization via Dip-Coating

The TiO₂ coating was carried out employing a dip-coating method established for low-cost ceramics [31]. To prepare the photocatalytic suspensions, we dispersed TiO₂ P25 in ultrapure water at concentrations between 0.2 and 15 g/L. Crucially, we added small amounts of Arabic gum (0.01 g) and nitric acid (0.02 g) to act as a surfactant and peptizing agent, respectively, ensuring better dispersion. We also introduced 6.6 g of a 12% starch solution as a binder. The mixture underwent magnetic stirring for 2 hours, followed by 30 minutes of sonication to break up any particle agglomerates.

For the coating step, the ceramic membrane was immersed in the suspension at room temperature for 12 hours, allowing the TiO₂ to penetrate the surface pores. Afterward, the membranes were dried at 80°C for 24 hours and calcined at 450°C for 3 hours. This heat treatment served two purposes: it burned off the organic binders and stabilized the anatase phase, which secured strong adhesion of the TiO₂ to the clay surface [32,33]. Finally, we calculated the deposited TiO₂ mass by simply weighing the membranes before and after the coating process.

2.4. Characterization Techniques

2.4.1. Physicochemical Analysis of Raw Clay

The chemical composition of the Matmata–Gabes clay was analyzed by X-ray fluorescence (XRF) using an S4-Pioneer spectrometer equipped with a 4 kW generator and a rhodium anticathode. The surface functional groups were examined by Fourier transform infrared spectroscopy (FTIR, PerkinElmer) with an attenuated total reflectance (ATR) accessory. Measurements were carried out over the range of 450–4000 cm⁻¹, with a resolution of 4 cm⁻¹ [34].

2.4.2. Membrane Morphology and Properties

The raw and TiO₂-coated membranes were analyzed using several complementary methods to examine their morphology and physical characteristics. Surface wettability was assessed by measuring the static water contact angle with a KRÜSS goniometer. A 2 µL droplet of deionized water was disposed onto the membrane surface, and high-resolution images were taken and

processed with ADVANCE software to determine the contact angle. Total open porosity was measured gravimetrically using Archimedes' principle. Membrane samples were vacuum-saturated for 30 minutes, then weighed in three conditions, wet, dry, and suspended in water, to calculate porosity according to standard formulas [35]. Mechanical integrity and dimensions were evaluated by measuring the length, width, and at five points with a Metrica digital micrometer and visually inspecting the sintered membranes for cracks or abnormal shrinkage.

2.5. *Experimental Setup and Photocatalytic Reactor Configuration*

The photocatalytic degradation experiments were carried out using a custom-built laboratory-scale recirculation system. The setup featured a 2 L feed reservoir and a Masterflex L/S peristaltic pump adjusted to maintain a steady flow of 0.5 L/min. The flat-sheet ceramic membrane module (effective area: 40 cm²) was installed inside the designed reactor. A key feature of the system design was an adjustable inclination mechanism. It allows setting the membrane angle (θ) anywhere from 0° (horizontal) to 60°, which facilitates studying gravity effect on both hydrodynamics and light distribution across the surface.

Two distinct irradiation conditions were tested. For artificial UV light, a 9 W SYLVANIA lamp ($\lambda = 365$ nm, 170 mA) was positioned 8 cm above the membrane, delivering an intensity of approximately 1.2 mW/cm². For natural light, the experiments were conducted outdoors between 9:00 and 17:00 to ensure capturing peak sunlight. During these runs, solar irradiance, ambient temperature, and wind speed were recorded every minute using a Davis Vantage Pro2 weather station. In both scenarios, the system operated in recirculation mode to ensure constant contact between the pollutant and the catalytic membrane under the light source throughout the experiment.

2.6. *Operational Protocol and Analytical Methods*

Degradation trials were conducted using a synthetic paracetamol solution prepared at an initial concentration of 10 mg/L. Initially, the system was operated under complete darkness for 30 minutes. This dark phase was essential to establish adsorption-desorption equilibrium between the pollutant molecules and the membrane surface, ensuring that subsequent removal was driven purely by photocatalysis rather than physical adsorption.

Throughout the experiments, which ran for up to 7 hours depending on the specific conditions, aliquots were collected every 30 minutes, and the residual paracetamol concentration was measured via UV-Vis spectrophotometry (LABOMED, INC) at its characteristic maximum absorption wavelength ($\lambda_{\text{max}} = 243$ nm). The degradation efficiency (R , %) was determined using the standard formula below. Due to the use of UV-Vis measurements, a paracetamol concentration several orders of magnitude higher than those typically found in natural environments were employed to ensure measurement reliability. Simultaneously, membrane permeate flux (J) was continuously monitored to track fouling dynamics and evaluate the potential self-cleaning capability induced by the photocatalytic effects.

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_0 and C_t represent the initial and time-dependent concentrations, respectively.

2.7. *Experimental Design*

To systematically decouple the interactive effects of reactor geometry and catalyst loading, a comprehensive full factorial experimental design was implemented. This approach allowed us to rigorously evaluate three critical operational variables: (i) TiO_2 loading, which was varied from 0 to 15 g/L (with a focused kinetic study on the 0–1 g/L range); (ii) membrane inclination angle, tested at four distinct positions (0° , 20° , 40° , and 60°) to assess gravitational impacts on hydrodynamics and photon flux; and (iii) irradiation source, comparing controlled artificial UV against natural solar conditions. The resulting matrix consisted of 33 unique experimental runs, ensuring that every combination of factors was explored to identify the optimal synergy between filtration transport and photocatalytic degradation. Beyond initial optimization, long-term viability was assessed by subjecting the best-performing configuration to five consecutive 5-hour cycles, interspersed with hydraulic cleaning to simulate realistic operational interruptions. Rather than relying solely on statistical modeling, the significance of each parameter was determined through direct comparative analysis of degradation kinetics, permeate flux evolution, and mass transfer rates. This data-driven approach allows us to isolate the dominant mechanisms governing process efficiency such as light shielding at high loadings or photon capture losses at steep angles, and to propose an optimized operating window based on observed performance trends rather than theoretical predictions alone.

3. Results and Discussion

3.1. *Characterization of Raw Clay Material*

The fabrication of high-performance ceramic membranes relies strongly on the properties of the starting material. In this work, natural red clay collected from the Matmata–Gabes region in southern Tunisia was chosen as the main precursor due to its abundance, affordability, and suitability for ceramic processing. The FTIR spectrum of the raw clay powder (Fig. 1) provides clear insight into its structural composition and confirms its aluminosilicate nature, which is a key requirement for the fabrication of stable ceramic membranes. The dominant absorption band located at around 1029 cm^{-1} is associated with the asymmetric stretching of Si–O–Si bonds, reflecting the presence of a well-developed silicate network. This assignment is further supported by the band observed at 466 cm^{-1} , which corresponds to the bending vibrations of the same Si–O–Si linkages, indicating structural continuity within the silica framework. Additional features in the spectrum reveal the contribution of aluminum-containing phases. In particular, the peaks at 524 cm^{-1} and 919 cm^{-1} can be attributed to Si–O–Al bonds and Al–OH deformation modes, respectively. These signals are commonly linked to clay minerals such as kaolinite and illite, which are frequently encountered in Tunisian deposits and are known for their thermal resistance and suitability for ceramic processing [34]. A weaker band near 798 cm^{-1} is associated with hydroxyl group deformation influenced by Mg^{2+} and Al^{3+} cations, while the absorption at 693 cm^{-1} reflects mixed Si–O–Al vibrational modes.

The presence of hydroxyl groups and metal–oxygen bonds is particularly important, as they play a direct role during thermal treatment. Upon heating, dehydroxylation reactions are expected to occur, leading to structural rearrangements and the progressive formation of more stable crystalline phases. Depending on the sintering temperature, this transformation may

result in the development of mullite-like or spinel-type structures, both of which contribute to improved mechanical strength and long-term stability of the final ceramic membrane.

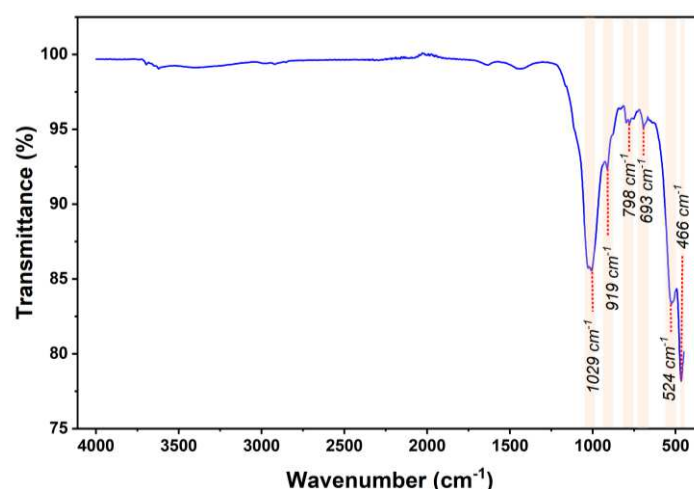


Fig. 1. FTIR spectrum of clay powder

The XRF analysis was performed to obtain a quantitative description of the clay composition, reported as oxide weight percentages (Table 1). The data show that the Matmata–Gabes clay is largely dominated by silica (SiO_2 , 59.38 wt%) and alumina (Al_2O_3 , 28.81 wt%). These two components play a central role in the development of the ceramic structure, as they act as network formers and are directly responsible for the mechanical rigidity and chemical resistance required in membrane-based water treatment. Their relatively high proportions suggest that the material is well suited for producing stable and durable ceramic support after sintering.

A notable fraction of iron oxide (Fe_2O_3 , 14.16 wt%) was also identified. This component not only explains the typical reddish-brown appearance of the raw clay but also contributes positively during thermal treatment. Fe_2O_3 behaves as a fluxing agent, encouraging the formation of a transient liquid phase at temperatures close to 1000 °C. This liquid phase enhances particle rearrangement and bonding, leading to improved densification while limiting the need for very high sintering temperatures, which is advantageous from an energy consumption standpoint [36]. In addition to these major constituents, smaller amounts of MgO (1.74%), K_2O (2.47%), CaO (0.91%), and Na_2O (0.39%) were detected. Although present in minor quantities, these oxides play an important role in modifying the thermal behavior of the system. As alkali and alkaline earth elements, they contribute to lowering the eutectic temperature and promote vitrification, thereby strengthening intergranular bonding within the ceramic matrix.

Overall, the chemical composition obtained here is consistent with values reported for similar North African clays. Such agreement reinforces the suitability of this raw material as a low-cost and sustainable alternative to conventional ceramic precursors like high-purity alumina or zirconia, which are often associated with higher production costs [26,37].

Table 1: Chemical composition of Matmata-Gabes red clay powder determined by X-ray Fluorescence (XRF) analysis.

Oxide Component	MgO	K ₂ O	SO ₃	Fe ₂ O ₃	CaO	Na ₂ O	Al ₂ O ₃	SiO ₂
Concentration (wt%)	1.74	2.47	0.65	14.16	0.91	0.39	28.81	59.38

3.2. Physicochemical Properties of Sintered Ceramic Supports

The green bodies were converted into functional ceramic supports via a controlled sintering process at 1000 °C. This thermal treatment critically defines the membrane's final microstructure, porosity distribution, and mechanical strength. During heating, the samples underwent several key transformations: evaporation of adsorbed water, decomposition of the starch pore-former, and densification of the clay matrix through solid-state diffusion and partial liquid-phase sintering. These changes were tracked using two macroscopic indicators: mass loss and volumetric shrinkage. As illustrated in Fig. 2a and 2b, both parameters followed a nearly linear trend relative to the initial sample volume. Volumetric shrinkage ranged from 12.45% to 18.68%, with larger samples shrinking more significantly. This is likely attributed to the combined effects of starch removal and particle rearrangement during densification. Similarly, mass loss measurements confirmed the efficient elimination of organic additives, showing a direct proportionality to the initial sample mass.

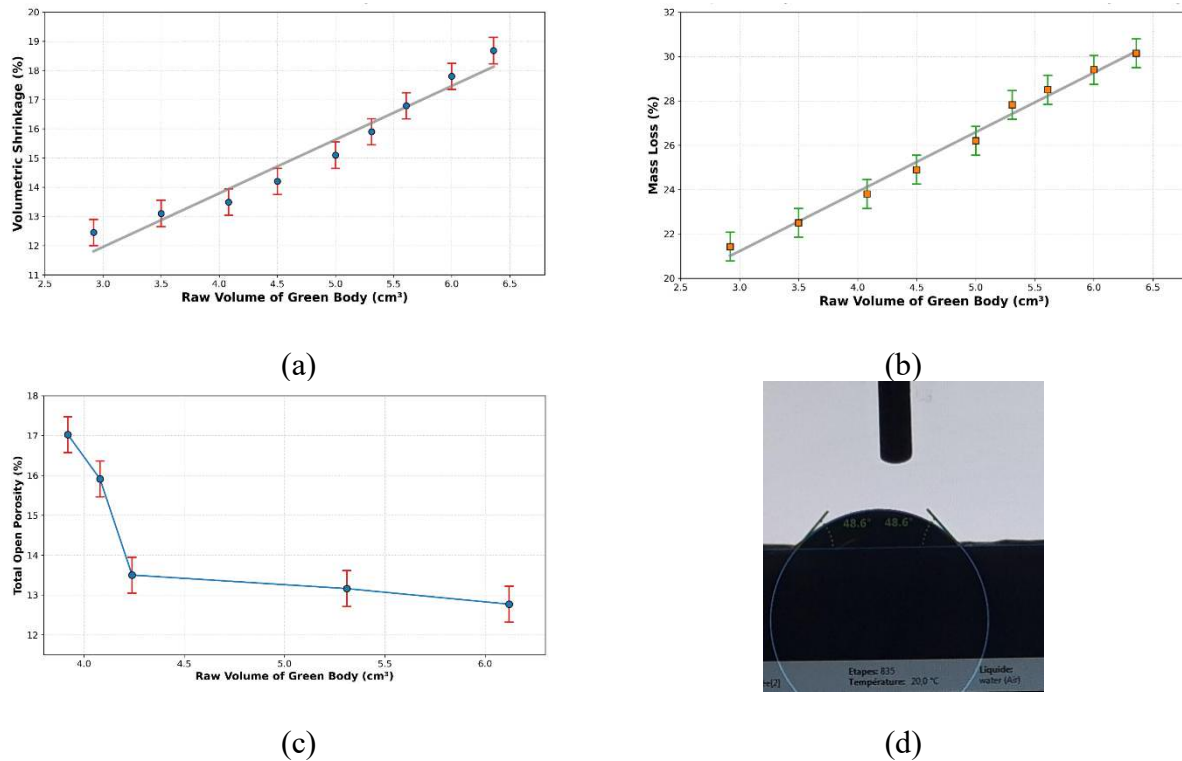


Fig. 2. Physiochemical properties of ceramic membrane: Volumetric Shrinkage vs. Raw Volume (a), Mass Loss vs. Raw Volume (b), open porosity evolution as a function of the raw volume of the green bodies (c), and Water contact angle (d)

The controlled decomposition of starch was particularly critical, as it generated the interconnected macropore network required for microfiltration. Achieving this without defects demanded a precise heating profile. A rapid temperature ramp would have released gases too abruptly causing internal stress and cracking. Instead, we selected a moderate heating rate of 4 °C/min. This allowed the organic phase to decompose gradually, ensuring uniform pore development and yielding defect-free membranes with robust structural integrity [28].

Following sintering, the transport and surface properties of the uncoated ceramic supports were evaluated. Using Archimedes' principle, the total open porosity (ϵ) was determined to quantify the interconnected pore volume accessible to fluids. As shown in Fig. 2c, porosity did not scale linearly with the initial green body volume. Instead, a distinct decrease was observed as sample size increased. Specifically, for raw volumes between 3.9 and 6.1 cm³, porosity dropped from approximately 17% to < 13%. This could be attributed to variations in the compaction stage. The compaction behavior prior to starch burnout significantly influences the final pore structure. Notably, the curve in Fig. 2c exhibits a distinct reduction point between 3.9 and 4.2 cm³ indicative of a shift in the leading densification mechanism. This shift suggests a change in the dominant densification mechanism. Particle rearrangement might govern the process at smaller volumes, whereas elastic deformation and frictional forces might become more influential as volume increases restricting particle mobility. Understanding this threshold is crucial for fine-tuning fabrication parameters to achieve target porosity levels for specific filtration applications [28].

To validate the practical viability of our sintered membrane for water treatment, we conducted detailed wettability assessments. As illustrated in Fig. 2d, the bare clay membrane exhibited a static water contact angle of 48.6°. This value confirms an intrinsic hydrophilic character, a critical trait that distinguishes our low-cost ceramic from many conventional polymeric alternatives. In practical filtration scenarios, this natural affinity for water significantly lowers the energy barrier required to wet the pore network, thereby facilitating immediate flux initiation without the need for pre-wetting. Furthermore, the hydrophilic surface acts as a defensive barrier as it minimizes the irreversible adsorption of hydrophobic organic foulants known for causing severe flux decline in standard polymeric membranes [38]. When considering these wetting properties alongside the previously observed moderate porosity (reaching up to 25%) and controlled volumetric shrinkage, the overall picture becomes clear. The specific thermal processing conditions applied to the Matmata-Gabes clay successfully yielded a robust membrane structure. These combined physical and surface characteristics confirm that the substrate is not only mechanically stable but also chemically primed for the subsequent dip-coating steps necessary to immobilize the TiO₂ photocatalytic layer effectively.

3.3. Effect of TiO₂ Loading on Membrane Properties

TiO₂ P25 nanoparticles were immobilized onto the sintered clay supports using a straightforward dip-coating technique. To ensure the coating was both stable and eco-friendly, we incorporated Arabic gum as a natural surfactant and starch as a binding agent. This specific combination was chosen to secure the photocatalytic layer firmly adhered to the ceramic membrane without compromising its mechanical integrity. The TiO₂ suspension concentration

was systematically varied from 0.2 to 15 g/L to evaluate how loading impacts catalyst mass, surface wettability, and overall porosity. As depicted in Fig. 3a, the specific mass of fixed TiO₂ increased linearly with the precursor concentration. Starting at a modest 0.75 mg/cm² for the 0.2 g/L suspension, then climbed steadily to a maximum of 5.73 mg/cm² at the highest concentration of 15 g/L. This consistent upward trend confirms that the deposition method effectively drives nanoparticle penetration into the superficial pores of the clay matrix. Arabic gum might have played an important role in ensuring homogeneous distribution. Simultaneously, the starch binder might have contributed to anchoring these particles to the surface, maintaining strong adhesion even through the rigorous drying and calcination stages required to crystallize the anatase phase [12].

We observed a dramatic shift in surface wettability as the TiO₂ loading increased, fundamentally altering the membrane's interaction with water. The static water contact angle decreased sharply from an initial 48.6° to a remarkably low 17.5° once the suspension concentration reached 15 g/L (Fig. 3b). This transition toward super-hydrophilicity stems from two synergistic mechanisms: the inherently high surface energy of the TiO₂ nanoparticles and the significant increase in surface roughness created by the deposited particulate layer. The surface roughness acts as an amplifier according to Wenzel's model, and the intrinsic hydrophilic nature of TiO₂ forces water to spread across the interface rather than beading up [39]. From an operational standpoint, this extreme hydrophilicity offers a critical defense against fouling. The modified surface promotes the formation of a tightly bound hydration layer that effectively repels hydrophobic organic molecules, consequently mitigating their direct adhesion to the membrane pores. While these surface modifications greatly enhance antifouling potential, they introduced a complex trade-off regarding the membrane's internal transport properties, which will be discussed next.

The total open porosity of the functionalized membranes underwent a sharp exponential decline as catalyst loading increased as shown in Fig. 3c. Starting from 21.7% for the bare membrane, the porosity dropped to a mere 1.1% at the maximum loading of 15 g/L. This is attributed to the physical accumulation of TiO₂ nanoparticles, which effectively clogged the surface pores and formed a dense, impermeable cake layer. This observation reveals a fundamental trade-off inherent to photocatalytic membrane design. While depositing more catalyst theoretically increases the number of available active sites for degradation, it simultaneously creates substantial hydraulic resistance. In practice, this blockage restricts permeate flux and prevents pollutant molecules from diffusing deep into the internal pore network where catalytic sites remain unused. Consequently, maximizing catalyst mass does not equate to maximizing performance; instead, it risks creating a diffusion-limited system. Recognizing this critical balance between catalytic activity and hydraulic permeability, the subsequent kinetic experiments were deliberately restricted to the intermediate loading range. In such range, sufficient catalyst is deposited to drive efficient reactions without significantly compromising the membrane's porous structure or permeate flow [33,40].

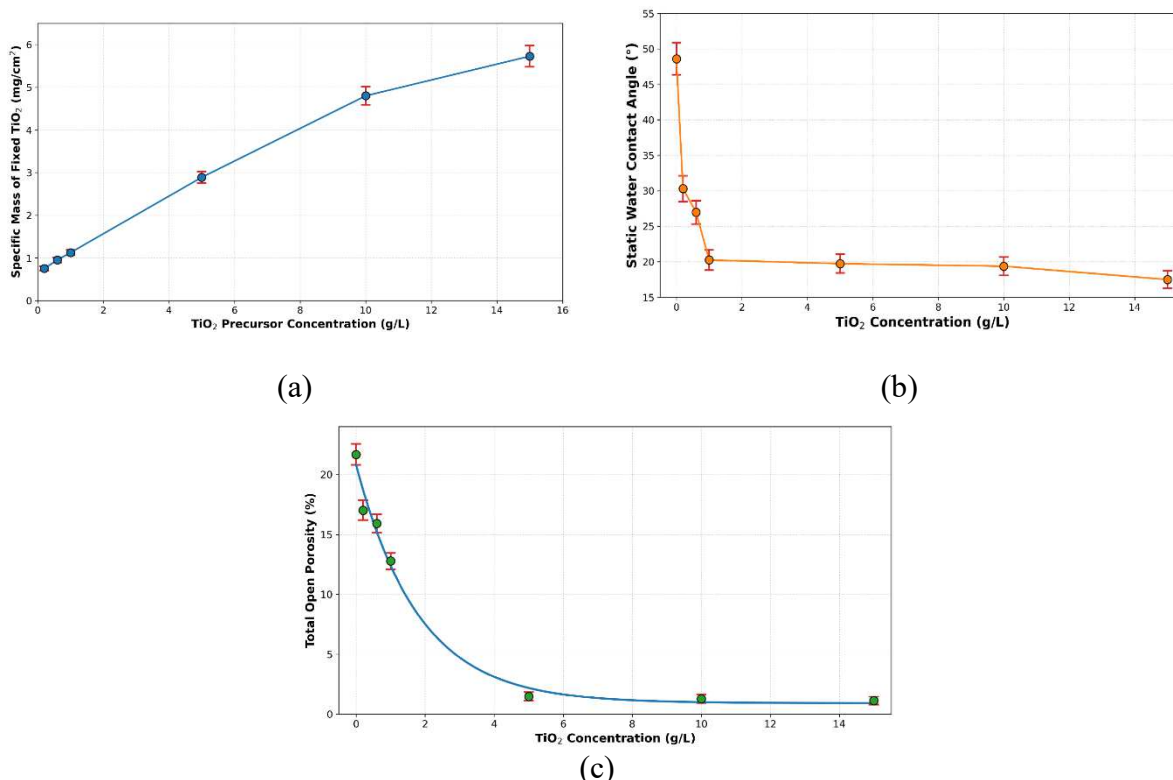


Fig. 3. Effect of TiO_2 on membrane composition and characteristics: Evolution of Specific Mass of Fixed TiO_2 as function of the precursor concentration (a), Static water contact angle (b), and Porosity (c).

3.4. Photocatalytic Performance: Effect of TiO_2 Loading on Degradation Efficiency

The photocatalytic performance of the functionalized membranes was evaluated by tracking PCT degradation under UV irradiation. The results revealed a distinct non-monotonic relationship between degradation efficiency and TiO_2 loading. As detailed in Fig. 4a, the removal rate climbed from a baseline of 26.6% for the bare membrane, driven primarily by physical adsorption, to a sharp maximum of 50.0% when using a 0.6 g/L TiO_2 suspension after 3 hours. This peak represents the optimal balance between active site availability and light penetration. However, pushing the loading beyond this point proved counterproductive. Increasing the concentration to 1 g/L caused a slight dip to ~47% and further increases up to 15 g/L triggered a severe drop in performance with efficiency plummeting to just 15.9%. This sharp decline confirms that excessive catalyst deposition creates mass transfer barriers and light shielding effects that outweigh the benefits of additional active sites.

This non-linear performance trend could be a result of a complex interplay of competing physical and chemical mechanisms that shift as catalyst loading increases. At the lower end of the spectrum, the reaction is fundamentally kinetically limited. The sparse distribution of TiO_2 nanoparticles provides an insufficient number of active sites to generate the critical concentration of $\bullet\text{OH}$ required for rapid pollutant degradation. In this regime, the scarcity of catalytic centers acts as the primary bottleneck, restricting the overall degradation rate regardless of how much time the pollutant spends in the reactor. However, as the loading increased beyond the optimal threshold of 0.6 g/L, the dynamics flip entirely. The severe pore blockage documented in Section 3.3 becomes the governing factor. Creating a dense,

impermeable cake layer that physically obstructs the transport of paracetamol molecules from the bulk fluid to the active sites buried within the membrane matrix. Compounding this mass transfer resistance is a significant optical limitation: excessively thick catalyst layers induce intense light scattering and shielding. This "screening effect" prevents photons from penetrating deep into the porous structure. Hence, only the superficial outer layer of the coating remains photo-active while the underlying material sits idle, effectively wasting the deposited catalyst [41]. These observations corroborate recent investigations into immobilized systems, which argue that simply maximizing catalyst mass often yields diminishing returns due to these unavoidable diffusion barriers and optical depth constraints [2,42]. Consequently, the identified optimum dopant concentration of 0.6 g/L represents a precise engineering compromise where the density of active sites, photon penetration depth, and molecular diffusion rates are perfectly balanced to achieve peak efficiency.

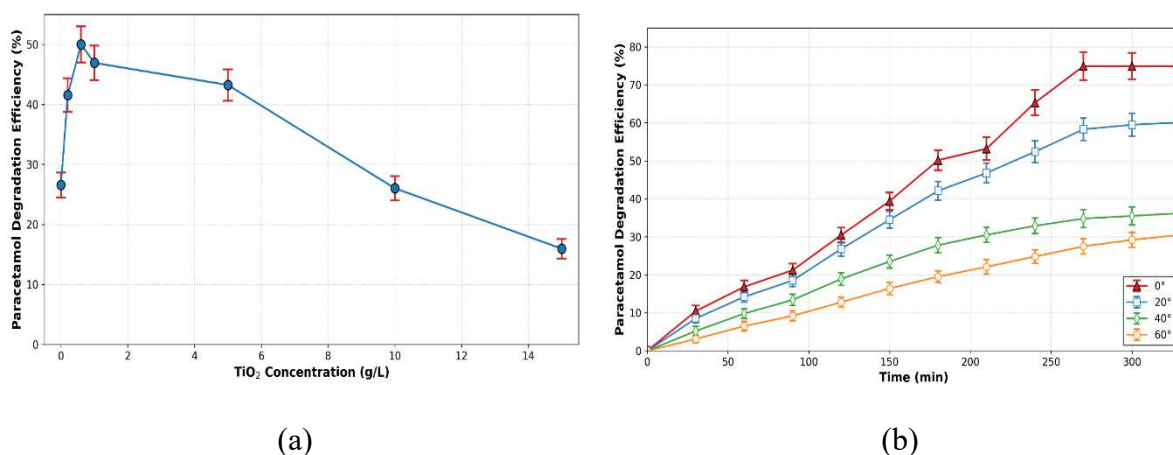


Fig. 4. PCT degradation: With different TiO₂ loading (a), and various inclination angle settings (b).

3.5. Role of Inclination Angle on Reactor Performance

This section discusses the impact of PMR geometry by systematically evaluating how the membrane module's inclination angle (θ) dictates overall process efficiency. By testing configurations at 0°, 20°, 40°, and 60°, we sought to identify the optimal reactor orientation for maximizing photocatalytic performance. The findings revealed that degradation efficiency is critically sensitive to this geometric parameter. Specifically, under UV irradiation with an optimized catalyst doping concentration of 0.6 g/L, the horizontal configuration ($\theta = 0^\circ$) yielded a peak degradation of 74.9%. In stark contrast, tilting the module to 60° caused performance to plummet to just 30.5% (Fig. 4b), underscoring the vital role of photon capture geometry in reactor design.

The high performance of the horizontal orientation ($\theta = 0^\circ$) stems from a synergistic optimization of both optical and hydrodynamic factors that are often treated in isolation. Primarily, this configuration maximizes photon capture efficiency by aligning the membrane surface under the perpendicular light incidence. Since our UV lamp was positioned directly above the reactor, the horizontal setup ensured that the entire active area received the maximum

possible photon flux density with minimal reflection losses. As we tilted the module, the effective projected area exposed to the light diminished strictly according to Lambert's cosine law ($I_{eff} = I_0 \cos \theta$). This geometric reduction directly throttled the generation rate of electron-hole pairs within the TiO₂ lattice, causing a cascade effect that lowered the production of reactive oxygen species and ultimately suppressed degradation kinetics [43].

Apart from optics, the angle of inclination was shown to affect hydrodynamics of the boundary layer dynamics close to the surface of the catalyst. While classic knowledge indicates that steeper angles would improve shear stress and suppress fouling in crossflow structures as gravity would increase cake sliding, our recirculation arrangement was limited in practice. Due to the horizontal point, the recirculatory flow had a different interaction effect on the illuminated surface in our experiments. Hydrodynamic analysis suggests a trade-off between mass transfer efficiency and residence time as a function of inclination. While steeper inclinations likely promote higher flow velocities and turbulence, thereby thinning the boundary layer and enhancing the mass transfer coefficient, they simultaneously reduce the contact time between the pollutant and the catalytic surface. Conversely, at lower inclinations, although the residence time is longer, the flow regime becomes more laminar with a thicker diffusion boundary layer, limiting the exposure of paracetamol to the active sites. The optimal inclination angle identified, in this study, represents a balance where mass transfer is sufficiently enhanced without compromising the necessary residence time for photocatalytic reaction. Additionally, at very steep angles, partial detachment of the liquid film may reduce the effective catalytic area available for degradation. These findings highlight a pivotal insight for reactor engineering: optimizing geometric configuration is just as critical as material selection when scaling solar-driven PCM. The module inclination, often an afterthought in design, can effectively dictate the success or failure of the system, especially when relying on directional light sources like the sun or fixed-position lamps where angle of incidence is paramount [44].

3.6. Comparative Analysis: UV vs. Solar Irradiation

To rigorously evaluate the sustainability and real-world viability of our system for decentralized applications, we conducted a direct comparative study between controlled artificial UV irradiation and natural sunlight. Kinetic modeling confirmed that paracetamol degradation adhered to pseudo-first-order behavior ($\ln(C_0/C) = k_{obs} \cdot t$) under both conditions, providing a robust framework for comparing reaction rates. Under artificial UV illumination (9 W, $\lambda = 365$ nm), the system achieved a rate constant (k_{obs}) of 0.245 min⁻¹, driving approximately 75% degradation within just 5.5 hours. In contrast, natural sunlight yielded a more modest rate constant (k_{obs}) of 0.138 min⁻¹, resulting in 55.5% removal over the identical timeframe (Fig. 5).

This performance gap could be attributed to two fundamental constraints. First, the wide bandgap of TiO₂ P25 (~3.2 eV) restricts activation primarily to the UV-A region, which comprises a mere 5% of the terrestrial solar spectrum. Most of the solar energy resides in the visible and infrared ranges, which remain untapped by undoped P25. Second, unlike the stable, continuous output of our laboratory lamp, natural sunlight is inherently intermittent, fluctuating with cloud cover and atmospheric turbulence. Despite these limitations, achieving >55% degradation using only passive solar energy validates the system's potential for off-grid

deployment in sun-rich regions. Our extended trials, running up to seven hours, revealed a crucial compensatory mechanism: cumulative degradation increased by 39% relative to shorter durations. This indicates that prolonged solar exposure can effectively offset slower kinetics, allowing the system to reach meaningful removal efficiency simply by extending operation time. These results strongly support the feasibility of coupling low-cost, locally sourced ceramic membranes with passive solar energy. Such an approach offers a technically robust and economically sustainable solution for pharmaceutical remediation, directly aligning with global shifts toward green engineering and the integration of renewable resources in wastewater management [17,45].

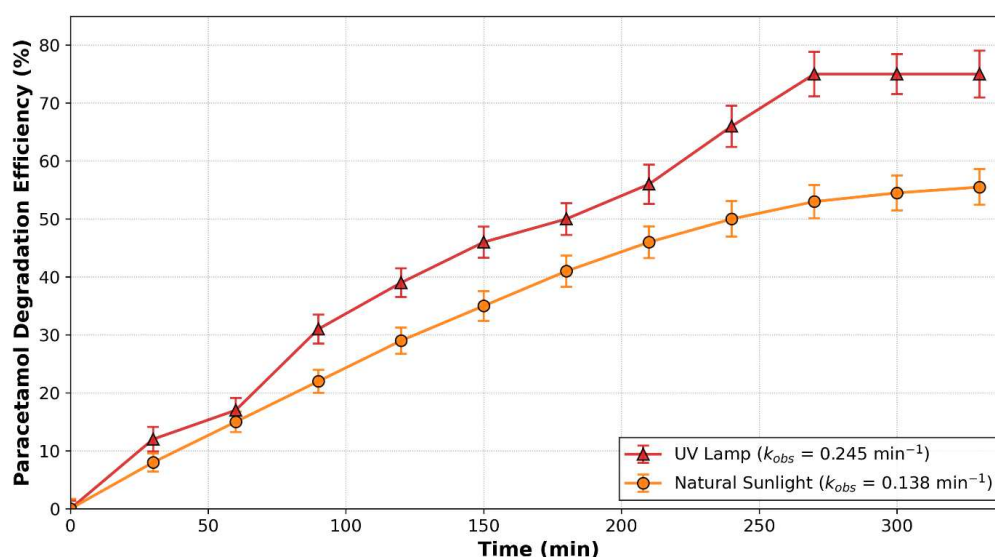


Fig. 5. Comparative kinetics: UV lamp vs. natural sunlight irradiation.

3.7. Permeate Flux Evolution and Fouling Behavior

Monitoring the evolution of permeate flux (J) throughout the filtration cycles offered a window into the complex interplay between hydraulic resistance and photocatalytic activity within our reactor. As depicted in Fig. 6, the system exhibited the classic signature of membrane fouling: a sharp, time-dependent decline in flux from an initial peak of 2411 L/m²·h down to approximately 50 L/m²·h over the 5.5-hour operational window. Although acetaminophen molecules are significantly smaller than the membrane pores, the observed severe fouling could at least partially be attributed to the formation of photocatalytic degradation intermediates. During oxidation, reactive intermediates recombine forming bigger molecules that could accumulate on the pore entrance or in the hydraulic channels leading to their partial or complete blockage.

The most compelling finding of this study lies in the striking inverse correlation between this flux decline and the rising degradation efficiency. Even as water permeability plummeted, the rate of paracetamol removal continued to climb steadily. This paradox suggests that the fouling layer itself is not a static inert barrier; rather, it acts as a secondary reactive zone. The immobilized TiO₂ nanoparticles generate a continuous stream of reactive oxygen species (ROS), specifically •OH and superoxide anions (•O₂⁻), which aggressively attack the organic

foulants adsorbed on the surface. Instead of forming a dense, impermeable crust, these contaminants are oxidatively fragmented into smaller, soluble compounds. This dynamic process, widely recognized as the "self-cleaning effect," effectively mitigates the formation of an irreversible cake layer that would otherwise permanently choke the membrane [46]

In contrast to conventional non-photocatalytic controls, where flux loss is typically permanent and demands harsh chemical intervention for recovery, the TiO₂-functionalized membranes established a unique dynamic equilibrium. Here, the rate of foulant deposition was partially offset by the rate of oxidative decomposition. Although the flux did not stabilize at a constant value, the persistence of high degradation rates amidst severe hydraulic resistance confirms that the catalytic sites remained accessible and active. This intrinsic antifouling capability represents a transformative advantage for photocatalytic membranes, promising significantly extended operational lifespans and reduced maintenance burdens. Looking ahead, future optimization strategies could integrate periodic hydraulic backwashing synchronized with illumination cycles to further amplify flux recovery and sustain long-term performance.

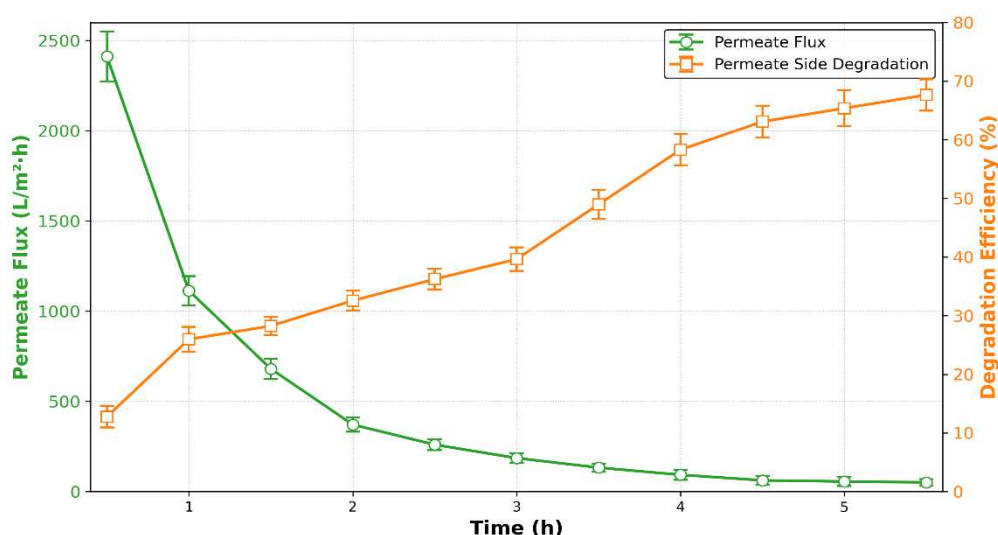


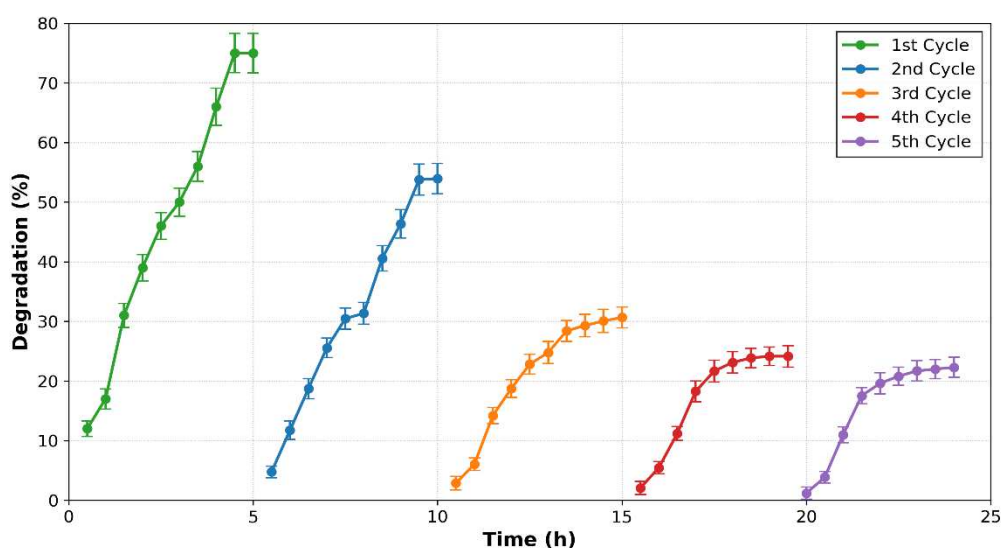
Fig. 6. Evolution of permeate flux vs. permeate degradation efficiency.

3.8. Long-term Stability and Reusability

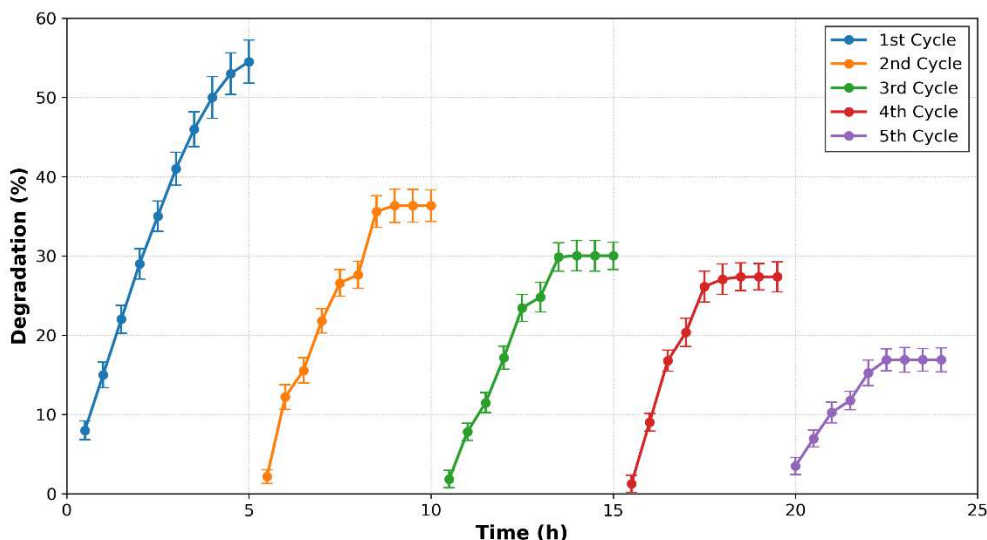
Assessing the long-term stability and reusability of photocatalytic membranes is not merely an academic exercise; it is a fundamental prerequisite for determining their commercial viability in real-world water treatment scenarios. To evaluate this durability, the optimized membranes were tested for five consecutive operational cycles under both artificial UV and natural solar irradiation for 5 hours. The data presented in Fig. 7 reveals a clear erosion of degradation efficiency as the cycle number increases. Under the intense stress of UV irradiation (Fig. 7a), performance declined from an initial peak of 74.9% in the first cycle to just ~22.3% by the fifth, representing a substantial 70% loss in activity. Similarly, under solar radiation (Fig. 7b), the decline was severe, dropping from an initial ~55.5% to approximately 17.0%, which corresponds to a ~69% reduction in efficiency.

This progressive decay is likely due to a convergence of three distinct deactivation mechanisms. Primarily, the active sites likely suffered from partial exhaustion due to the accumulation of recalcitrant intermediate byproducts. These species, which may resist complete mineralization within the limited five-hour window, adsorb strongly onto the catalyst surface, effectively blocking access for fresh pollutant molecules. Secondly, despite our rigorous calcination protocol and the use of robust natural binders, we cannot rule out TiO_2 nanoparticles leaching. The continuous shear forces generated by the recirculating flow over 25 hours may have gradually eroded the coating integrity. Finally, irreversible pore blocking by non-degraded organic residues likely increased hydraulic resistance, severely limiting the diffusion of paracetamol to the internal catalytic zones where reaction rates are highest.

Interestingly, while the total percentage loss was comparable between the two sources ($\sim 70\%$ for UV vs. $\sim 69\%$ for Solar), the membrane exhibited a slightly different degradation profile under solar conditions. This suggests that the milder reaction environment afforded by sunlight may play a subtle protective role. The lower photon flux and consequently reduced rate of radical generation under solar irradiation likely result in less aggressive oxidative attack on the organic binder matrix and the clay support itself, potentially preserving the structural cohesion of the catalyst layer better than the harsh high-energy UV source during the early cycles. Furthermore, the extended exposure times inherent to solar experiments might facilitate a more gradual degradation of intermediates, slightly delaying the rapid site-blocking observed under intense UV. Despite the observed decline, the system maintained measurable catalytic activity ($>17\%$) even after 25 hours of cumulative operation. While this level of durability is promising for a low-cost, clay-based material, the substantial loss of efficiency underscores the absolute necessity of implementing periodic regeneration protocols, such as mild thermal treatment or chemical washing, to fully restore performance and extend operational lifespan in practical applications [7].



(a)



(b)

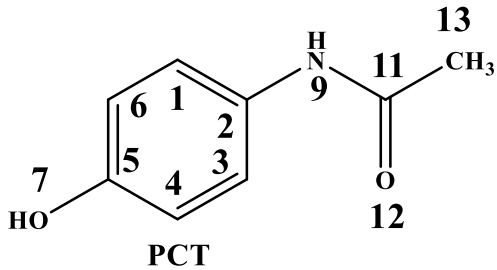
Fig. 7. Reusability study: PCT degradation over 5 cycles (a) UV radiation (b) solar radiation.

3.9. Proposed Reaction Pathways and Conceptual Process Scheme

Drawing upon our experimental findings and established principles of heterogeneous photocatalysis, the degradation of paracetamol within this reactor system is driven by a complex, radical-mediated oxidation cascade. Upon exposure to irradiation, the immobilized TiO_2 semiconductor absorbs photons with energy exceeding its bandgap, triggering the generation of electron-hole (h^+) pairs. These charge carriers migrate to the catalyst surface, where holes oxidize adsorbed water molecules or surface hydroxyl groups to yield highly potent $\cdot\text{OH}$. Simultaneously, conduction band electrons (e^-) reduce dissolved molecular oxygen, generating $\cdot\text{O}_2^-$. These reactive oxygen species act as the primary oxidants, aggressively attacking the paracetamol structure, specifically targeting the electron-rich aromatic ring and the vulnerable amide linkage.

The proposed degradation pathway initiates with the hydroxylation of the benzene ring, producing transient intermediates such as catechol and hydroquinone. The commonly detected degradation products (DPs) of paracetamol during its degradation are shown in scheme 1. The formation of these commonly detected products during the degradation of paracetamol is explained using DFT analysis. Gaussian 09 software was used to compute the FED_{HOMO} , FED_{LUMO} and point charges of each atom in paracetamol. The atom/sites with highest $\text{FED}_{\text{HOMO}} + \text{FED}_{\text{LUMO}}$ are susceptible to be attacked by $\cdot\text{OH}$ via addition reaction while those with highest point charge values are expected to target by $\cdot\text{OH}$ via H-abstraction [47]. Moreover, sites whose $2\text{FED}_{\text{HOMO}}$ is higher tend to be directly oxidized by holes or targeted via electron abstraction [48]. The values of $\text{FED}_{\text{HOMO}} + \text{FED}_{\text{LUMO}}$, $2\text{FED}_{\text{HOMO}}$ and point charges of each atom are given in Table 2.

Table 2: Values of FEDs and point charges of paracetamol.

 PCT			
Atom	$FED^2_{HOMO} + FED^2_{LUMO}$	$2FED^2_{HOMO}$	Point charge
1C	0.437518	0.167463996	-0.18278
2C	0.166255	0.164890695	0.32948
3C	0.435224	0.116431281	-0.19567
4C	0.368981	0.076978335	-0.21167
5C	0.16109	0.160903232	0.288034
6C	0.397548	0.092520275	-0.18343
7O	0.252204	0.2522015	-0.61665
9N	0.344068	0.344002199	-0.86872
11C	0.004487	0.004092086	0.645188
12O	0.153483	0.15341122	-0.48636
13C	0.011247	3.02242E-05	-0.65804

As shown in the scheme (Fig.8), DP1 resulted from the attack of $\cdot OH$ at C3 owing to its high $FED^2_{HOMO} + FED^2_{LUMO}$ (0.377009). Moreover, further hydroxylation of DP1 led to the production of DP2. Additionally, DP3 was produced via direct oxidation of C3 owing to its high $2FED^2_{HOMO}$ followed by deacetylation, which would then convert into DP4. Subsequent oxidative attacks lead to ring cleavage, breaking the stable aromatic structure into aliphatic short-chain carboxylic acids, including oxalic, formic, and acetic acid. Through continued oxidation, these organic fragments are ultimately mineralized into harmless end products. Crucially, the Matmata-Gabes clay support serves a dual function in this process; beyond providing a robust mechanical scaffold for the TiO_2 layer, its inherent adsorptive capacity likely concentrates pollutant molecules near the active catalytic sites, thereby enhancing local reaction kinetics prior to oxidation.

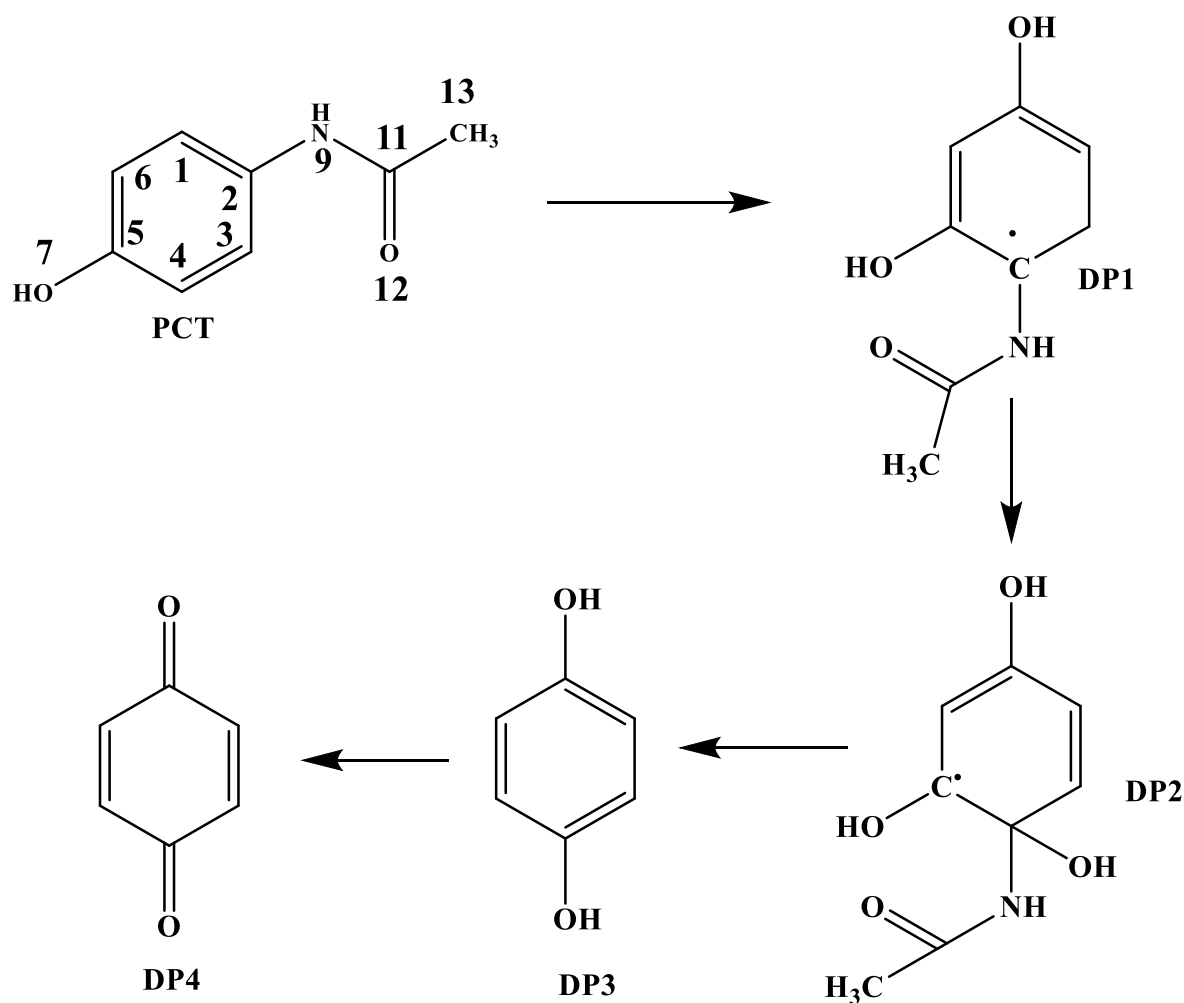


Fig.8. Proposed degradation pathway of paracetamol.

Fig. 9 illustrates the conceptual framework of our optimized PMR. The system operates in a continuous recirculation mode, pumping the paracetamol feed from a reservoir through a reactor housing the horizontally oriented (0° inclination) TiO₂-coated membrane. This specific geometric configuration was selected to maximize photon capture efficiency from natural sunlight penetrating the reactor window. As the solution flows across the retentate side, pollutants are degraded upon contact with the illuminated catalyst surface, while purified water permeates through the porous matrix. By synergistically integrating low-cost locally sourced clay, eco-friendly dip-coating functionalization, optimized reactor geometry, and passive solar energy, this study proposes a sustainable, scalable solution for mitigating pharmaceutical contamination. This approach holds particular promise for decentralized water treatment applications in sun-rich, developing regions where conventional infrastructure is limited.

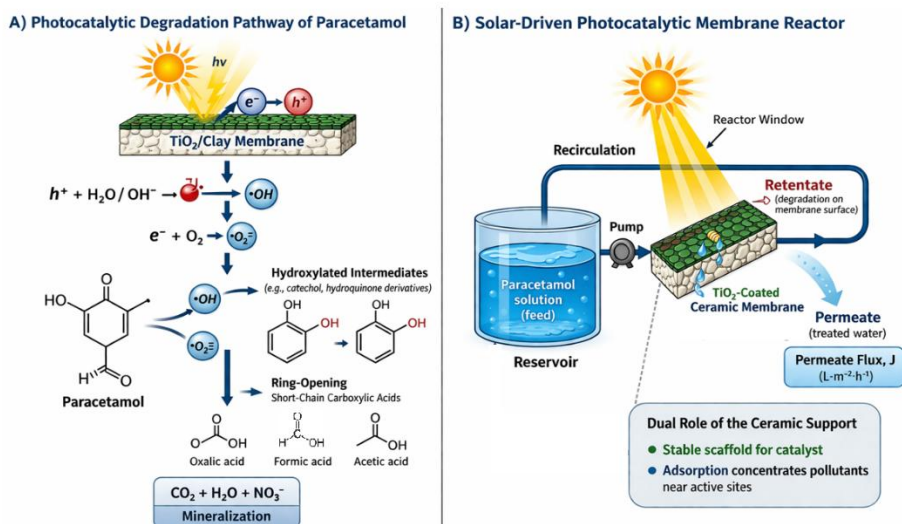


Fig. 8. Proposed radical-mediated photocatalytic degradation solar-driven TiO_2 -coated ceramic membrane reactor (PMR) system concept.

3.10. Toxicity-ECOSAR Tool Evaluation

ECOSAR software was used to predict the ecotoxicological profiles of the parent compound PCT and four degradation products (DP1-DP4). Three representative aquatic organisms, i.e. fish, daphnia and green algae, were assessed concerning both acute and chronic toxicity endpoints in compliance with the hazard classification criteria set by the European Union (EU) and the Chinese chemical safety standards. According to the EU standards, substances with acute $\text{LC}_{50}/\text{EC}_{50}$ values higher than 100 mg/L are non-hazardous, those within the range of 10-100 mg/L are harmful, those in the 1-10 mg/L range are toxic, and those lower than 1 mg/L have very high acute toxicity [49]. In the case of chronic exposure, compounds with chronic value (ChV) greater than 10 mg/L are considered to be environmentally safe, compounds of 1 and 10 mg/L are moderately toxic, and those below 0.1 mg/L are highly toxic [50,51].

The ECOSAR results are summarized in Table 3. With respect to acute toxicity, the parent compound (PCT) exhibited $\text{LC}_{50}/\text{EC}_{50}$ values far exceeding 100 mg/L for all three tested organisms, specifically 4457.7 mg/L for fish, 2157.2 mg/L for daphnia, and 829.7 mg/L for green algae, thereby classifying it as non-hazardous under EU acute toxicity criteria.

Luckily, all commonly detected products, i.e., DP1, DP2, DP3 and DP4 are non-hazardous, as evident by their $\text{LC}_{50}/\text{EC}_{50}$ and ChV values (Table 3). Among all DPs, DP1 showed very high $\text{LC}_{50}/\text{EC}_{50}$ values (fish (52,977.7 mg/L), daphnia (23,069.9 mg/L), green algae (5,736.4 mg/L), confirming its non-hazardous nature. DP4 also demonstrated non-hazardous acute toxicity (fish (3333.3 mg/L), daphnia (1609.8 mg/L), green algae (614.1 mg/L)).

Regarding chronic toxicity, the results further reinforce the favorable environmental profile of the studied compounds. The parent compound (PCT) recorded ChV values of 360.8 mg/L (fish), 134.8 mg/L (daphnia), and 152.2 mg/L (green algae), all substantially exceeding the 10 mg/L threshold, classifying it as environmentally safe under prolonged exposure conditions. All four

degradation products similarly fell within the environmentally safe category. DP2 displayed the highest chronic values across all organisms (fish (19,777.8 mg/L), daphnia (4635.0 mg/L), green algae (2755.9 mg/L)), followed by DP1 (fish (3786.6 mg/L), daphnia (1075.0 mg/L), green algae (831.9 mg/L)) and DP4 (fish (269.2 mg/L), daphnia (100.1 mg/L), green algae (112.1 mg/L)). While DP3 exhibited the lowest chronic values in the dataset (fish (58.8 mg/L), daphnia: (26.4 mg/L), green algae (38.4 mg/L)), still comfortably exceeded the 10 mg/L safety threshold and therefore also classified as environmentally safe.

Overall, the ecotoxicological assessment based on the ECOSAR approach under the tested conditions shows that the parent compound and all the degradation products identified are not associated with the risk of acute or chronic toxicity to aquatic organisms. These findings suggest that the photocatalytic degradation process studied herein is environmentally benign, effectively converting the parent compound into less harmful intermediates, and underscores the potential suitability of this approach for practical environmental remediation applications.

Table 3: ECOSAR Toxicities of PCT and its degradation products.

Toxicity	Organisms	PCT	DP1	DP2	DP3	DP4
Acute (mg/L)	Fish (LC ₅₀) 96h	4457.747	52977.668	301821.78	668.7476	3333.3003
	Daphnia (LC ₅₀) 48h	2157.1592	23069.88	122099.86	347.27173	1609.8115
	Green algae (LC ₅₀) 96h	829.6586	5736.358	22389.662	178.80289	614.06036
Chronic (mg/L)	Fish (ChV)	360.84058	3786.6284	19777.848	58.830727	269.18616
	Daphnia (ChV)	134.81766	1074.9963	4635.04	26.412386	100.052765
	Green algae (ChV)	152.18661	831.9325	2755.9077	38.37829	112.13966

4. Conclusion

This study evaluated the viability of a solar-driven PMR that synergistically couples low-cost ceramic supports derived from Tunisian Matmata-Gabes clay with TiO₂ P25 functionalization for the effective degradation of paracetamol. Our investigation uncovered a fundamental trade-off governing catalyst loading. While higher TiO₂ concentrations significantly enhanced surface hydrophilicity, driving the water contact angle down to 17.5°, excessive deposition triggered severe pore blockage, drastically reducing permeability. We identified an optimal operational window at 0.6 g/L for UV irradiation and 1.0 g/L for natural sunlight, achieving peak degradation efficiencies of 74.9% and 55.5%, respectively after 5.5 hours. Crucially, reactor geometry emerged as a decisive factor; a horizontal configuration (0° inclination) maximized photon capture efficiency and pollutant-catalyst contact time, outperforming steeper angles by a significant margin. While inclined configurations may promote higher mass transfer coefficients due to increased turbulence, the reduced residence time and lower effective photon

flux (due to light incidence angle) at steeper inclinations limited the overall degradation efficiency. Thus, the horizontal setup provided the optimal balance for this photocatalytic system. Although permeate flux naturally declined due to fouling, the system demonstrated a robust "self-cleaning" mechanism where photocatalytic oxidation actively degraded adsorbed organic layers, preventing irreversible clogging. Nevertheless, reusability assessments over five consecutive cycles revealed a gradual loss of activity, underscoring the necessity for periodic regeneration strategies to sustain long-term performance.

The primary scientific contribution of this work lies in validating a sustainable, circular economy approach, transforming abundant local clay into high-performance reactive membranes, thereby offering a cost-effective alternative to expensive commercial ceramics. By proving the system's efficacy under natural sunlight, the specific potential was highlighted for decentralized, off-grid water treatment in sun-rich regions like North Africa. While challenges regarding environmental variability and catalyst leaching remain at the laboratory scale, these findings provide a critical foundation for industrial scaling. Future research must now pivot toward optimizing continuous-flow reactor designs, evaluating performance against complex real-world wastewater matrices, and exploring hybrid advanced oxidation processes to further boost mineralization rates and ensure operational longevity in practical applications.

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Clinical Trial Number: not applicable.

Ethics, Consent to Participate, and Consent to Publish declarations: not applicable.

Data availability statement: The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

- [1] V.K. Khilchevskyi, Ya.B. Oliinyk, V.I. Zatserkovnyi, Global problems of water resources scarcity, in: XIV International Scientific Conference "Monitoring of Geological Processes and Ecological Condition of the Environment," European Association of Geoscientists & Engineers, Kyiv, Ukraine, 2020: pp. 1–5. <https://doi.org/10.3997/2214-4609.202056001>.
- [2] Y. Shi, J. Huang, G. Zeng, W. Cheng, J. Hu, Photocatalytic membrane in water purification: is it stepping closer to be driven by visible light?, 584 (2019) 364–392.
- [3] S. Anjanapriya, M. SulaimanMumtaz, M.H.A.K. Mohideen, A. Radha, N. Sasirekha, B. Sawicka, V. Tamizhazhagan, Pharmaceutical pollution crisis in the world: A menace to ecosystem, *Entomology and Applied Science Letters* 8 (2021) 77–89.
- [4] T. Aus der Beek, F.-A. Weber, A. Bergmann, S. Hickmann, I. Ebert, A. Hein, A. Küster, Pharmaceuticals in the environment—Global occurrences and perspectives, 35 (2016) 823–835.

- [5] Y. Guo, P.S. Qi, Y.Z. Liu, A review on advanced treatment of pharmaceutical wastewater, in: IOP Conference Series: Earth and Environmental Science, IOP Publishing, 2017: p. 012025. <https://iopscience.iop.org/article/10.1088/1755-1315/63/1/012025/meta> (accessed May 14, 2026).
- [6] W.J. Lee, P.S. Goh, W.J. Lau, A.F. Ismail, Removal of Pharmaceutical Contaminants from Aqueous Medium: A State-of-the-Art Review Based on Paracetamol, *Arab J Sci Eng* 45 (2020) 7109–7135. <https://doi.org/10.1007/s13369-020-04446-1>.
- [7] E. Brillas, J.M. Peralta-Hernández, Removal of paracetamol (acetaminophen) by photocatalysis and photoelectrocatalysis. A critical review, 309 (2023) 122982.
- [8] D. Daniel, R. Dionísio, G.D. De Alkimin, B. Nunes, Acute and chronic effects of paracetamol exposure on *Daphnia magna*: how oxidative effects may modulate responses at distinct levels of organization in a model species, *Environ Sci Pollut Res* 26 (2019) 3320–3329. <https://doi.org/10.1007/s11356-018-3788-y>.
- [9] P.K. Pandis, C. Kalogirou, E. Kanellou, C. Vaitsis, M.G. Savvidou, G. Sourkouni, A.A. Zorpas, C. Argirusis, Key points of advanced oxidation processes (AOPs) for wastewater, organic pollutants and pharmaceutical waste treatment: A mini review, 6 (2022) 8.
- [10] L. Sawunyama, O.A. Oyewo, N. Seheri, S.A. Onjefu, D.C. Onwudiwe, Metal oxide functionalized ceramic membranes for the removal of pharmaceuticals in wastewater, 38 (2023) 102787.
- [11] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, 1 (2000) 1–21.
- [12] A. Bouazizi, M. Breida, B. Achiou, M. Ouammou, J.I. Calvo, A. Aaddane, S.A. Younssi, Removal of dyes by a new nano-TiO₂ ultrafiltration membrane deposited on low-cost support prepared from natural Moroccan bentonite, 149 (2017) 127–135.
- [13] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R. Zhang, Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review, 268 (2020) 121725.
- [14] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, Elsevier, 2009. <https://www.sciencedirect.com/science/article/pii/S0920586109003344> (accessed May 14, 2026).
- [15] C. Dezani, Photocatalyse hétérogène en réacteurs ouverts pour la gestion de la ressource solaire: expérimentations sur différents médias et modélisation, PhD Thesis, Université de Perpignan, 2020. <https://theses.hal.science/tel-03105379/> (accessed May 14, 2026).
- [16] D. Faust, M. Pachtmann, G. Mettig, P. Seidel, M. Bouaziz, J.M.R. Espejo, F.D.D. Olmo, C.-B. Roettig, S. Kreutzer, U. Hambach, Sandy soils in silty loess: the loess system of Matmata (Tunisia), *Quaternaire. Revue de l'Association Française Pour l'étude Du Quaternaire* (2020) 175–186.
- [17] A. Zrelli, W. Elfalleh, A. Ghorbal, B. Chaouachi, Valorization of date palm wastes by lignin extraction to be used for the improvement of polymeric membrane characteristics, 66 (2022) 70–81.
- [18] A. Boushila, R. Elbeji, A. Zrelli, S. Najar, Valorizing Waste Bricks in Geopolymer Membrane Preparation for Treating Oily Wastewater: Effects of Curing Temperature

- and Liquid-to-Solid Ratio, Arab J Sci Eng 50 (2025) 3855–3867.
<https://doi.org/10.1007/s13369-024-09214-z>.
- [19] A. Kwarciak-Kozłowska, Removal of pharmaceuticals and personal care products by ozonation, advance oxidation processes, and membrane separation, in: *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, Elsevier, 2019: pp. 151–171.
<https://www.sciencedirect.com/science/article/pii/B978012816189000007X> (accessed May 14, 2026).
- [20] M. Ulbricht, Advanced functional polymer membranes, 47 (2006) 2217–2262.
- [21] M.O. Mavukkandy, S.A. McBride, D.M. Warsinger, N. Dizge, S.W. Hasan, H.A. Arafat, Thin film deposition techniques for polymeric membranes—A review, *Journal of Membrane Science* 610 (2020) 118258.
- [22] G. Carre, Compréhension des mécanismes lors de la photocatalyse appliquée à la dégradation des microorganismes: application au traitement de l'air et aux textiles auto-décontaminants, PhD Thesis, Université de Strasbourg, 2013.
<https://theses.hal.science/tel-00998196/> (accessed May 14, 2026).
- [23] I. Onal, S. Soyer, S. Senkan, Adsorption of water and ammonia on TiO₂-anatase cluster models, 600 (2006) 2457–2469.
- [24] S. Yamazaki, D. Takaki, N. Nishiyama, Y. Yamazaki, Factors affecting photocatalytic activity of TiO₂, in: *Current Developments in Photocatalysis and Photocatalytic Materials*, Elsevier, 2020: pp. 23–38.
<https://www.sciencedirect.com/science/article/pii/B9780128190005000035> (accessed May 14, 2026).
- [25] S. Khemakhem, Elaboration de membranes de microfiltration et d'ultrafiltration en céramique à base d'argile tunisienne, PhD Thesis, PhD thesis, Université de Sfax, Tunisia, 2005. https://www.researchgate.net/profile/Sabeur-Khemakhem/publication/281798991_These_de_Doctorat_Preparation_de_membranes_a_base_d'argile_tunisienne/links/57e3020b08aec0198dd8398/These-de-Doctorat-Preparation-de-membranes-a-base-d'argile-tunisienne.pdf (accessed May 14, 2026).
- [26] adel zrelli, A. Bessadok, Q. Alsahy, Important Parameters of Ceramic Membranes Derived from Oasis Waste and Its Application for Car Wash Wastewater Treatment, *JMSR* (2021). <https://doi.org/10.22079/jmsr.2021.529855.1488>.
- [27] W.J. Lee, P.S. Goh, W.J. Lau, A.F. Ismail, Removal of Pharmaceutical Contaminants from Aqueous Medium: A State-of-the-Art Review Based on Paracetamol, Arab J Sci Eng 45 (2020) 7109–7135. <https://doi.org/10.1007/s13369-020-04446-1>.
- [28] O. Samhari, Membranes céramiques et polymères modifiées par de l'oxyde de graphène pour la rétention de molécules organiques et le dessalement d'eaux saumâtres et d'eau de mer, PhD Thesis, Université Rennes 1; Université Hassan II (Casablanca, Maroc), 2021. <https://theses.hal.science/tel-03421544/> (accessed May 15, 2026).
- [29] S. Saja, A. Bouazizi, B. Achiou, M. Ouammou, A. Albizane, J. Bennazha, S.A. Younssi, Elaboration and characterization of low-cost ceramic membrane made from natural Moroccan perlite for treatment of industrial wastewater, *Journal of Environmental Chemical Engineering* 6 (2018) 451–458.
- [30] Y. Abed, A. Zrelli, B. Chaouachi, Investigation of TiO₂ concentration and calcination temperature effects on hybrid membrane properties for wastewater treatment,

- Iran. J. Chem. Chem. Eng. (IJCCE) Research Article Vol 43 (2024).
https://www.ijcce.ac.ir/article_708255_5ae0dd6a4e0ee546ff1bbf50e58c0809.pdf
 (accessed May 15, 2026).
- [31] A. Bouazizi, M. Breida, B. Achiou, M. Ouammou, J.I. Calvo, A. Aaddane, S.A. Younssi, Removal of dyes by a new nano-TiO₂ ultrafiltration membrane deposited on low-cost support prepared from natural Moroccan bentonite, Elsevier, 2017.
<https://www.sciencedirect.com/science/article/pii/S0169131717303708>
 (accessed May 15, 2026).
- [32] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R. Zhang, Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review, Elsevier, 2020.
<https://www.sciencedirect.com/science/article/pii/S0959652620317728>
 (accessed May 15, 2026).
- [33] J.M. Juoi, M.A. Musa, N. Zaharuddin, T.J.S. Anand, INFLUENCE OF TiO₂ SOL-GEL FORMULATION ON MICROSTRUCTURE AND PHOTOCATALYTIC EFFICIENCY OF CERAMIC TILE COATINGS, Journal of Advanced Manufacturing Technology (JAMT) 19 (2025) 67–84.
- [34] B.H. Stuart, Infrared spectroscopy: fundamentals and applications, John Wiley & Sons, 2004.
<https://books.google.com/books?hl=fr&lr=&id=xQVog8RrJKcC&oi=fnd&pg=PR5&dq=Infrared+Spectroscopy:+Fundamentals+and+Applications&ots=LlBkpeElg&sig=idYtv0nfVJzRVp1q6PfdEXx1D6M> (accessed May 15, 2026).
- [35] C. Astm, R23 Standard Test Methods for Determination of Water Absorption and Associated Properties by Vacuum Method for Pressed Ceramic Tiles and Glass Tiles and Boil Method for Extruded Ceramic Tiles and Non-tile Fired Ceramic Whiteware, Appl. Phys 21 (2018) 23–34.
- [36] S. Saja, A. Bouazizi, B. Achiou, M. Ouammou, A. Albizane, J. Bennazha, S.A. Younssi, Elaboration and characterization of low-cost ceramic membrane made from natural Moroccan perlite for treatment of industrial wastewater, Elsevier, 2018. <https://www.sciencedirect.com/science/article/pii/S2213343717306437>
 (accessed May 15, 2026).
- [37] R.B. Amar, W. Aloulou, H. Aloulou, A. Attia, Development and Application of Low-Cost Ceramic Membranes Based on Apatite for Wastewater Treatment, in: S. Bandyopadhyay (Ed.), Low Cost Ceramic Membranes, Springer Nature Singapore, Singapore, 2026: pp. 77–98. https://doi.org/10.1007/978-981-96-1602-2_3.
- [38] L. Sawunyama, O.A. Oyewo, N. Seheri, S.A. Onjefu, D.C. Onwudiwe, Metal oxide functionalized ceramic membranes for the removal of pharmaceuticals in wastewater, Elsevier, 2023.
<https://www.sciencedirect.com/science/article/pii/S2468023023001578>
 (accessed May 15, 2026).
- [39] A. Malijevský, Does surface roughness amplify wetting?, 141 (2014).
<https://pubs.aip.org/aip/jcp/article/141/18/184703/675478> (accessed May 15, 2026).
- [40] M. Esfandiaribayat, M. Binazadeh, S. Sabbaghi, M. Mohammadi, S. Ghaedi, H. Rajabi, Tetracycline removal from wastewater via g-C₃N₄ loaded RSM-CCD-optimised hybrid photocatalytic membrane reactor, Sci Rep 14 (2024) 1163.
<https://doi.org/10.1038/s41598-024-51847-5>.

- [41] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R. Zhang, Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review, Elsevier, 2020.
<https://www.sciencedirect.com/science/article/pii/S0959652620317728> (accessed May 15, 2026).
- [42] Y. Shi, J. Huang, G. Zeng, W. Cheng, J. Hu, Photocatalytic membrane in water purification: is it stepping closer to be driven by visible light?, Elsevier, 2019.
<https://www.sciencedirect.com/science/article/pii/S0376738819302534> (accessed May 15, 2026).
- [43] J. Gomes, J. Lincho, E. Domingues, M. Gmurek, P. Mazierski, A. Zaleska-Medynska, T. Klimczuk, R.M. Quinta-Ferreira, R.C. Martins, TiO₂ nanotube arrays-based reactor for photocatalytic oxidation of parabens mixtures in ultrapure water: Effects of photocatalyst properties, operational parameters and light source, 689 (2019) 79–89.
- [44] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catalysis Today* 147 (2009) 1–59.
- [45] L. Prieto-Rodriguez, S. Miralles-Cuevas, I. Oller, A. Agüera, G.L. Puma, S. Malato, Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO₂ concentrations, 211 (2012) 131–137.
- [46] M. Sökmen, İ. Tatlıdil, C. Breen, F. Clegg, C.K. Buruk, T. Sivlim, Ş. Akkan, A new nano-TiO₂ immobilized biodegradable polymer with self-cleaning properties, 187 (2011) 199–205.
- [47] W. Ahmad, R. Shah, H.U. Haq, D. Khan, S. Khan, A. Al-Anazi, J.A. Khan, N.R. Binte Razzak, C. Han, UV-activated and Fe²⁺-catalyzed H₂O₂ for the treatment of dye-contaminated water: kinetics, mechanism and toxicity investigations, *MDPI*, 2024.
<https://www.mdpi.com/2073-4344/14/12/906> (accessed May 16, 2026).
- [48] W. Ahmad, N. Akhtar, A. Choi, M. Ateeq, N.S. Shah, J.A. Khan, A. Al-Anazi, C. Han, Hydrothermally engineered TiO₂/CdS nanocomposite for efficient photocatalytic degradation of carbamazepine, hydrogen evolution and antibacterial applications, Elsevier, 2025.
<https://www.sciencedirect.com/science/article/pii/S1383586625047288> (accessed May 16, 2026).
- [49] W. Ahmad, R. Shah, D. Khan, J.A. Khan, N.S. Shah, A. Al-Anazi, C. Han, Enhanced visible-light driven degradation of carbamazepine and hydrogen evolution using nitrogen-doped TiO₂ nanoparticles, Elsevier, 2025.
<https://www.sciencedirect.com/science/article/pii/S0272884225060675> (accessed May 16, 2026).
- [50] N.S. Shah, J.A. Khan, M. Sayed, Z.U.H. Khan, H.S. Ali, B. Murtaza, H.M. Khan, M. Imran, N. Muhammad, Hydroxyl and sulfate radical mediated degradation of ciprofloxacin using nano zerovalent manganese catalyzed S₂O₈²⁻, Elsevier, 2019.
<https://www.sciencedirect.com/science/article/pii/S1385894718317170> (accessed May 16, 2026)
- [51] Reham R. Abdullah, Kadhum M. Shabeeba, Aseel B. Alzubaydi, Alberto Figoli, Alessandra Criscuoli, Enrico Drioli, Qusay F. Alsalhy, Characterization of the Efficiency of Photo-Catalytic Ultrafiltration PES Membrane Modified with Tungsten Oxide in the

Removal of Tinzaparin Sodium, Engineering and Technology Journal, 40 (12) (2022) 1633-1641.