

Engineered Micro/Nano Structures for Effective Water Remediation

This chapter explores the development of various multiscale-engineered platforms for water remediation. The first section focuses on the fabrication of carbon nanofiber membranes using electrospinning and pyrolysis techniques, followed by the incorporation of titanium disulfide (TiS_2) nanoparticles for oil/water separation applications. The second section highlights the decoration of a *Ficus religiosa* leaf mesh with a hybrid nanocomposite for simultaneous oil/water separation and wastewater degradation. Finally, the chapter explores the development of a polymeric optofluidic microreactor with microchannels coated with nanocatalysts for the degradation of methylene blue (MB) dye.

7.1 TiS_2 NANOPARTICLE ANCHORED CANDLE-SOOT DECORATED CARBON NANOFIBERS BASED MEMBRANE FOR OIL/WATER SEPARATION

In this study, we describe a simple and efficient way for fabricating a Titanium disulfide (TiS_2)-anchored candle-soot (CS)-decorated carbon nanofiber (CNF) membrane by a series of electrospinning, carbonization, and solvothermal growth techniques. The NFs membrane had an exceptional hydrophobic and oleophilic characteristics, with a water contact angle (WCA) of $\sim 133^\circ$ and an oil contact angle (OCA) of $\sim 3^\circ$, respectively. Because of its superior multi-cycle efficiency as well as its stability, the $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane plays a significant role in the implementation of oil/water separation in real-world conditions.

7.1.1 Introduction

Recent years have seen a rise in the number of accidents involving oil spills and the discharge of oily wastewater from industrial operations, both of which have resulted in catastrophic ecological devastation and enormous economic loss (Chen et al., 2021; Mondal and Gupta, 2018). Oil/water mixtures of varying types can be produced by a number of different industries, including the chemical, petroleum, manufacturing, and food industries. As a result, studies focusing on the separation of oil and water mixtures have received a lot of attention from researchers (Yeh et al., 2023). Traditional techniques have been utilized to control oily wastewater by thoroughly integrating physical, chemical, and biological approaches, including centrifugal separation, air flotation, gravity separation, ultrasonic separation, biological treatment, and coagulation as well as membranes produced using different surface modification techniques such as chemical etching, and chemical vapor deposition. However, the low effectiveness, high resource requirements, susceptibility to secondary pollutants, and absence of a structural hierarchy of these technologies significantly hinder their widespread use (Chauhan et al., 2019; Gupta et al., 2015b). When it comes to separating oil/water mixture based on molecular size, pressure-driven filtration operations, have their limitations due to constraints in working conditions, for example, low throughput, faster membrane contamination, and membrane damage at high pressures. Furthermore, the method of separating oil and water mixtures has received much attention in recent years by employing substances with unique wettability characteristics. The wettability of a solid surface is a distinctive feature that is governed by the chemical composition and the surface characteristics of the material. Therefore, it is possible to develop materials with exceptional wettability by modifying the surface energy and structure of the material (Gupta et

al., 2018; Yong et al., 2016). However, water removing materials are not the ideal option for oil/water separation because the accumulation of heavy oil on the surface of the material tends to build a barrier that prevents water absorption (Cheng et al., 2017; J. Li et al., 2016). As a result, oil removing materials seem to be the best choice for oil/water separation.

Recent developments in membrane technology have focused on achieving superior separation performance compared to chemical separation processes (Wen et al., 2023; Yan et al., 2023b). Membranes offer higher oil separation efficiency, are simple to manufacture, and possess features and functionalities that overcome the difficulties described previously (Tanudjaja et al., 2019; Zhu et al., 2014). Various techniques are employed to fabricate and modify separation membranes, including phase separation, templated synthesis, sol-gel, and surface grafting (Yan et al., 2023a). Each of these approaches has its own merits and plays a significant role in the realm of oil/water separation. However, as applications expand and the issue of oil contamination becomes more pressing, certain challenges related to structural efficiency have emerged. These challenges include issues like limited reusability, weak mechanical strength, and complex preparation methods. Amidst these considerations, electrospinning emerges as a notably straightforward technique (J. J. Li et al., 2016). It allows the production of NFs from various polymer solutions, including blends and composites. Electrospinning is also efficient in preparing membranes; it is less susceptible to contamination, offers excellent modifiability, and maintains consistent permeate flow even after repeated usage (Ma et al., 2018; Ni et al., 2022). These NFs, however, have low efficiency, mechanical strength, and WCA values (N. Zhang et al., 2022). As a result, different nanoparticles were typically added to the polymer precursor solution to improve porosity, WCA, adsorption ability, and surface area, resulting in composite NFs membranes that outperformed other pristine NFs membranes. Recently, significant research focused on the synthesis and use of carbonaceous nanomaterials such as nanoparticles, nanofibers, and nanotubes. Candle soot (CS) is an interesting material because of its low cost of synthesis and uniform particle size (Singh et al., 2021). These remarkable properties compel several researchers to explore the use of carbon soot in numerous fields, including energy storage, solar cells, heavy metal detectors, microbial fuel cells, and oil/water separation (Esmeryan et al., 2019; Xi et al., 2014; Yibowei et al., 2021). Furthermore, CS has hydrophobic and oleophilic properties due to the low surface energy functional groups such as hydrocarbon and methyl groups. CS has remarkable properties, but their poor adhesion and difficulty in recovery limit their use for oil/water separation (Kakunuri and Sharma, 2015). To overcome these challenges, CS could be deposited on surfaces based on PDMS, paraffin wax, or methyltriethoxysilane, or combined with a polymer precursor solution before electrospinning to develop stable hydrophobic surfaces (Thota et al., 2023). For example, Baig et al. developed a carbon nanofiber (CNF) embedded styrofoam (SF) for hexane/water separation (Baig et al., 2019). Ieamviteevanich et al. prepared a magnetic carbon nanofiber (MCNF) aerogels as an effective and reusable oil absorbent material (Ieamviteevanich et al., 2020). Because of its hydrophobic and oleophilic properties, MCNF aerogel does not require any post surface treatment to directly absorb oils. Therefore have an absorption performance in between 37 to 87/g for different oil/organic mixtures.

The study demonstrates the effective separation of oil/water mixtures using a TiS_2 /CS:CNF membrane. Although several studies on CNF membranes have been published, no studies on TiS_2 anchored CS:CNF membrane for effective removal of oils with low absolute viscosity from oil/water mixtures have been found in the literature. Further, the work is divided into three sections. Basic introduction and the need for an oil/water separation system; method and materials for preparing CS:CNF and TiS_2 /CS:CNF membranes with experimental characterization information, and finally the oil/water separation results.

7.1.2 Materials and Methods

Polyacrylonitrile (PAN, molecular weight: 150,000; Catalog number: 181315) was purchased from Sigma Aldrich, Germany, and N,N Dimethylformamide (DMF; Catalog number: 1.03053.2511) was purchased from VWR, Germany. Wax candles for the candle-soot collection were purchased from local supermarkets in Karlsruhe, Germany. TiS_2 nanoparticles (NPs) were

prepared using thio-urea ($\text{CH}_4\text{N}_2\text{S}$), titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$), all these chemicals were brought from Sigma Aldrich. The oil samples such as gasoline, diesel, turpentine, and castrol oil were purchased from Hindustan Petroleum and Gulf Oil companies, in India.

(a) Preparation of CS:CNF membrane

The procedure to obtain CS:CNFs includes electrospinning of a CS-PAN solution, followed by carbonization (see Figure 7.1). The CS-PAN solution features a CS to PAN wt% ratio of 1:10. To prepare the solution, CS particles are first collected from the tip of the flame of a wax candle on a glass slide. The CS particles are then added to the DMF solvent and sonicated in an ultrasonication machine for 10 mins to achieve a homogenous dispersion. PAN powder was added to the dispersion and stirred on a magnetic stirred overnight to achieve a solution concentration of 10% PAN. The CS-PAN solution is electrospun on a silicon wafer for around 2 hours in a custom-built electrospinning setup. The parameters for electrospinning are electric voltage = 10 kV, the distance between the spinneret and collector = 10 cm, and flow rate = 7.5 $\mu\text{L}/\text{min}$. After the collection of the nanofibers, the nanofibril mat was peeled off from the silicon substrate to obtain a free-standing mat, which was stabilized in an oven for 2 hours at 400°C. The stabilized mat was carbonized in a tube furnace in an Ar environment to obtain the CS:CNF mats. The carbonization process involves three steps: heating up to 900°C from room temperature with a heating rate of 5°C/min, dwelling at 900°C for 1 hours, and cooling down to room temperature using natural cooling.

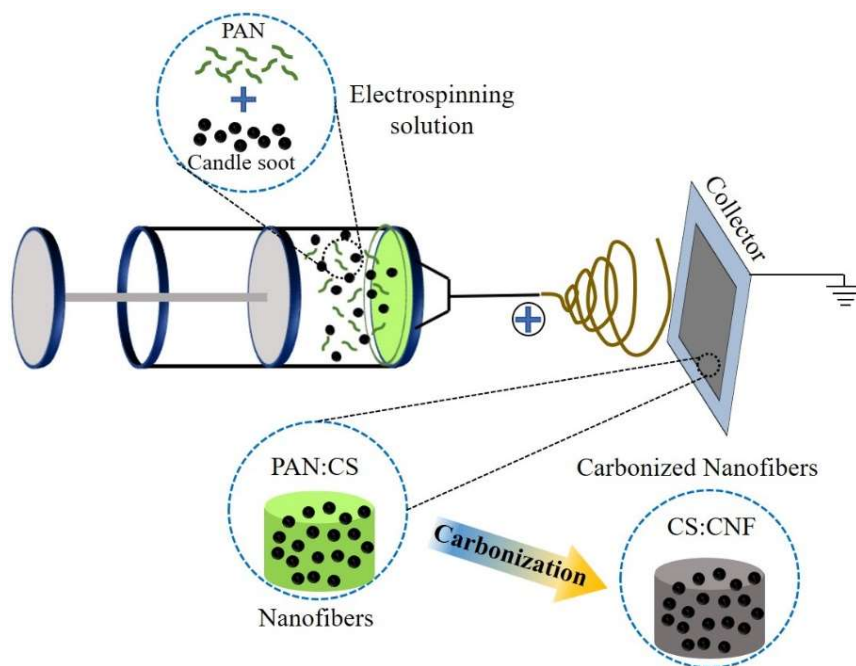


Figure 7.1: Schematic showing preparation steps of electrospun CS:CNF membrane

(b) Preparation of TiS_2 /CS:CNF membrane

The synthesis of TiS_2 NPs starts with the preparation of $\text{CH}_4\text{N}_2\text{S}$ solution in 10 mL of $\text{C}_2\text{H}_5\text{OH}$ via ultrasonication at ambient temperature. Another solution is prepared using a continuous stirring of $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ and $\text{C}_2\text{H}_6\text{O}_2$ at ambient temperature. Both the solutions are then added to the Teflon stainless steel autoclave and placed in an electric oven at 150°C for 16 hours. Following the synthesis, the temperature of the autoclave was allowed to cool down to ambient temperature. After washing the precipitate, it was dried at 150°C for 6 hours to produce pure TiS_2 NPs. The TiS_2 powder was next combined with 20 mL of $\text{C}_3\text{H}_8\text{O}$ and ultrasonicated for 30 mins.

To produce the TiS₂/CS:CNF membrane, the as-prepared CS:CNFs membrane was immersed in the above solution for 2 mins and dried at 70°C for 20 mins.

(c) Experimental setup for oil/water separation

Three experimental setups were designed to separate the oil and water mixtures. First, the gravity driven approach was used, with both the CS:CNF and TiS₂/CS:CNF membranes attached to a funnel and placed on top of a 100 mL glass beaker. The experiment begins by passing 20 mL of oil through the NFs membrane; as the NFs membrane is oleophilic, it attracts oils, making them permeable. Following that, an equal quantity of water was introduced into the experimental setup to test the NFs membrane's ability to trap water. Second, a 45° tilted experimental setup was developed for oil-water separation. The NFs membrane was securely positioned between two 16 mm diameter plastic tubes. A mixture of oil and water was then passed through tubes to test the effective separation efficiency. Finally, the absorption and cleaning performance of an NFs membrane were evaluated by checking the absorption ability of spilled oil on a glass slide and cleaning in ethanol. The parameters for analyzing oil/water separation were further investigated by permeation flux (J) and water rejection rate (WRR (%)). The following equations (7.1, and 7.2) show the permeation flux of oil and water rejection rate, respectively.

$$J = L/m^2xh \quad (7.1)$$

$$WRR (\%) = \left(1 - \frac{A_1}{A_0}\right) \times 100 \quad (7.2)$$

Where, L , m^2 and h are the total volume of oil penetrated, CS:CNF nanofibers membrane area, and total experimental time, respectively. We evaluated the permeation flux for 20 mL of different oils and a fixed 1.5 cm² TiS₂/CS:CNF membrane area at atmospheric pressure. Equation 2 was used to compute the WRR of TiS₂/CS:CNF membrane, where A_0 and A_1 , are initial and final water concentrations present in the oil, respectively.

7.1.3 Result and Discussion

(a) Characterization of TiS₂/CS:CNF membrane

Figure 7.2 (a, b, d, e) displays the SEM images of the CS:CNF and with TiS₂ NPs anchored CS:CNF membrane. During electrospinning, the carbon soot NPs orient along the driving voltage, forming 'streamlines' in the PAN/DMF solution. As a consequence, carbon soot NPs became parallel with the long axis of the individual fibers, resulting in a slightly deformed cylindrical shape of the NFs. During the process of TiS₂ NPs deposition, the larger NPs are maintained in the initial layers of the nanofibrous membrane, frequently in the form of aggregates. On the other hand, the smaller NPs have entered at deeper layers and anchored themselves on the underlying nanofibers. Under either of the two conditions of the process, the fibers have an average diameter of 260.24 nm (see Figure 7.2 (c)). The EDS analysis revealed information about the elemental composition of TiS₂/CS:CNF membrane. Figure 7.2 (f) evidently shows the presence of major elements such as C, O, S, and Ti.

The XRD diffraction spectrum of as-prepared NFs is shown in Figure 7.3 (a). The XRD result demonstrated a prominent broad peak with a low intensity centered at ~15°, which is attributed to the polymer phase of PAN (Saud et al., 2016). Whereas the broad peaks at $2\theta = 25^\circ$, and 42° were indexed to the (002), and (100) crystal planes of carbon soot NPs, respectively, and were matched to JCPDS number 41-1487 (Gangadharan et al., 2020). The (002) peak shows the formation of a turbostratic graphite structure with randomly aligned layers of graphitic carbon. While the (100) peak is associated with the π - π interactions of carbon atoms stacked on the same plane (Shokrani Havigh and Mahmoudi Chenari, 2022). Figure 7.3 (b) depicts the XRD spectra of TiS₂ NPs. Several notable peaks for the plane were reported, including (001) at 15.4° , (011) at 34.54° , (102) at 44.2° , (110) at 53.8° , (004) at 65.3° , and (022) at 72.1° , all of which are attributable to the hexagonal phase of TiS₂ and show a high level of relevance to the standard JCPDS card No.

01-088-1967 (Parvaz et al., 2018). Table 7.1 presents the structural characteristics of the as-prepared NFs computed. According to the Debye-Scherrer calculation, as the precursor's cyclization increases, the d(002) spacing decreases and the graphite crystallites increase. The d(002) spacing for CS:CNF was calculated and found to be 0.2960 nm. The average crystallite size of CS:CNF was found to be 1.3645 nm.

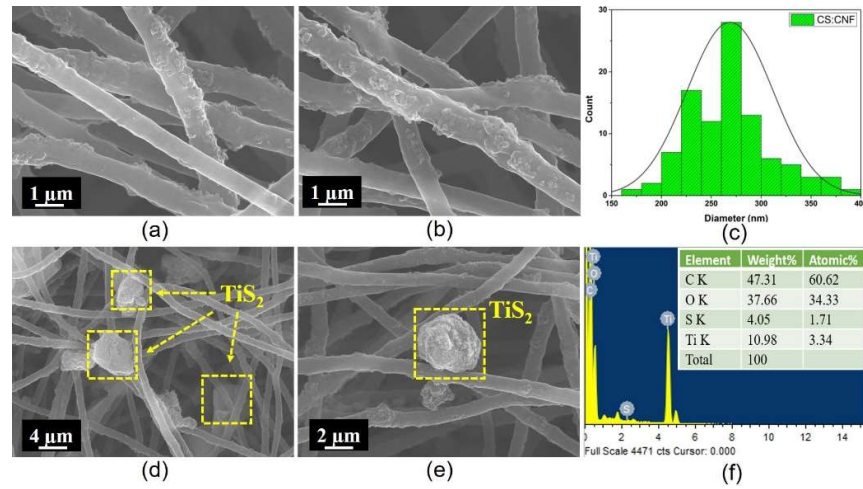


Figure 7.2: (a, c) SEM and (c) Histogram representation for an average diameter of CS:CNF membrane, and (d, e) SEM and (f) EDS results of TiS₂/CS:CNF membrane

Table 7.1: Presents structural characteristics of as-prepared nanofiber computed from Bragg's law and the Debye-Scherer formula

Nanofibers	2 θ	FWHM	Crystallite size D(nm)	Average size (nm)	d spacing (nm)
CS:CNF	15.12	6.579	1.2180	1.3645	0.5853
	30.16	6.523	1.2613		0.2960
	42.88	5.287	1.6141		0.2107

The Raman spectrum of as-prepared carbonized NFs is shown in Figure 7.3 (c). The degree of graphitization was determined by comparing the intensity ratios (I_D/I_G) of two significant peaks centered at 1343 cm⁻¹ and 1590 cm⁻¹. These ratios were found to be 0.97 for the CS:CNF with sonication. The D band is attributed to the A_{1g} mode, which was only seen for disordered graphite, and the G band corresponds to the first-order scattering of the E_{2g} mode reported for sp² domains (Ferrari and Robertson, 2000). This demonstrates that the carbon soot NPs are evenly incorporated in the nanofiber, considerably improving the graphitization of the nanofiber.

The AFM technique is used to investigate the surface roughness of both the nanofibril membranes. The AFM images demonstrate that the roughness of the surface of TiS₂ anchored CS:CNFs is slightly increased in contrast to the surface of a CS:CNFs membrane as shown in Figure 7.4 (a, b). The root means square roughness values for the CS:CNF and TiS₂/CS:CNF surface are calculated as 179.943 nm and 290 nm, respectively. When compared to the geometric area, the actual wetted surface area is larger if the surface is rough. As a result, there is an overall increase in surface energy, which indicates that the surface becomes less hydrophilic. Therefore, as the surface roughness of TiS₂/CS:CNF increases due to the presence of micro/nano hierarchical structure leading to an increase in the WCA (see Figure 7.4 (c, d)). This increased WCA leads to trapping the water droplets more on the surface of NFs membrane and enhances the WRR.

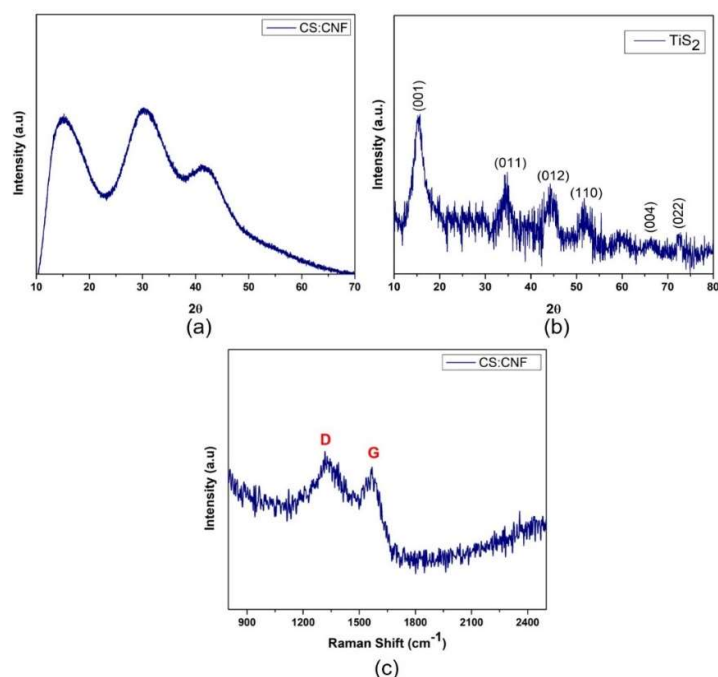


Figure 7.3: XRD of (a) CS:CNF, (b) TiS₂ NPs, and Raman spectra of (c) CS:CNF membrane

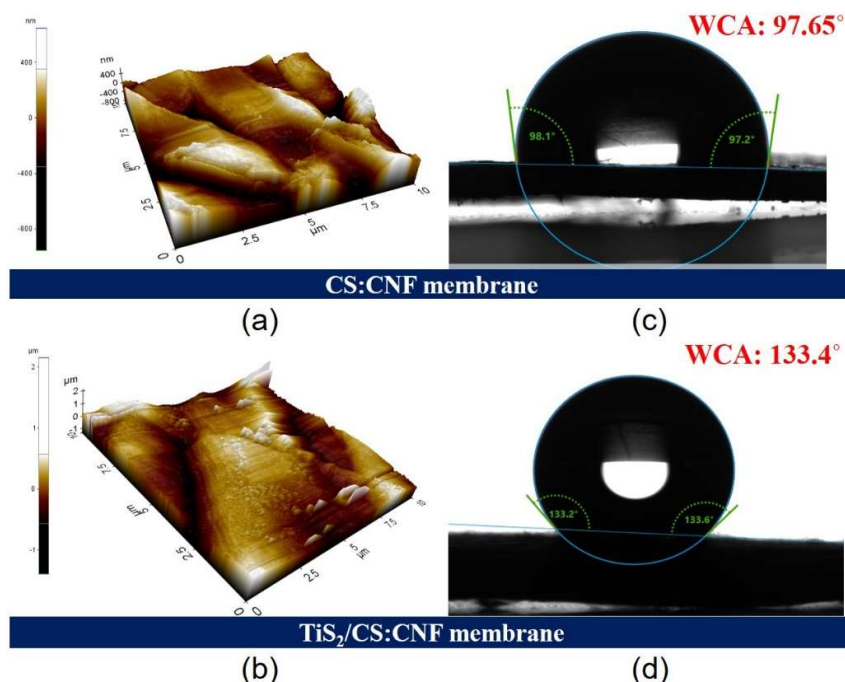


Figure 7.4: AFM and WCA results for (a, c) CS:CNF, and (b, d) TiS₂/CS:CNF membrane

(b) Oil/water separation

The experiment used four different viscosity oils: gasoline, diesel, turpentine, and castrol oil. Since oil and water have different densities and oil frequently floats on the surface of the water, the gravity-driven experiment was started with 20 mL of oil. The oil sample was collected in the beaker below after easily passing through the oleophilic TiS₂/CS:CNF membrane. The experimental setup was then filled with an equal amount of water. The water sample was retained on the surface of the TiS₂/CS:CNF membrane due to the presence of micro/nano hierarchical structures. To improve visibility, a methylene blue dye was added to the water during the experiment. Figure 7.5 depicts the photograph of a gravity-driven experimental setup

for oil/water separation. The values of oil permeation flux are significantly influenced by the viscosity of the oils. The low viscous oils such as gasoline, diesel, and turpentine show a high permeation flux (see Figure 7.5 (a, c, e)). According to Table 7.2, low-viscosity gasoline, diesel, and turpentine each showed oil permeation flux values of 6707.378 ± 262 L/(m² h), 1616.146 ± 44 L/(m² h), and 1197.292 ± 9 L/(m² h), respectively, whereas highly viscous castrol oil shows a permeation flux of 299.493 ± 4 L/(m² h) (see Figure 7.7 (a)). Furthermore, adding water to the membrane results in a small stress concentration in the membrane, causing it to move downward in the direction of the funnel and become stuck, preventing further water passage (see Figure 7.5 (b, d, f)).

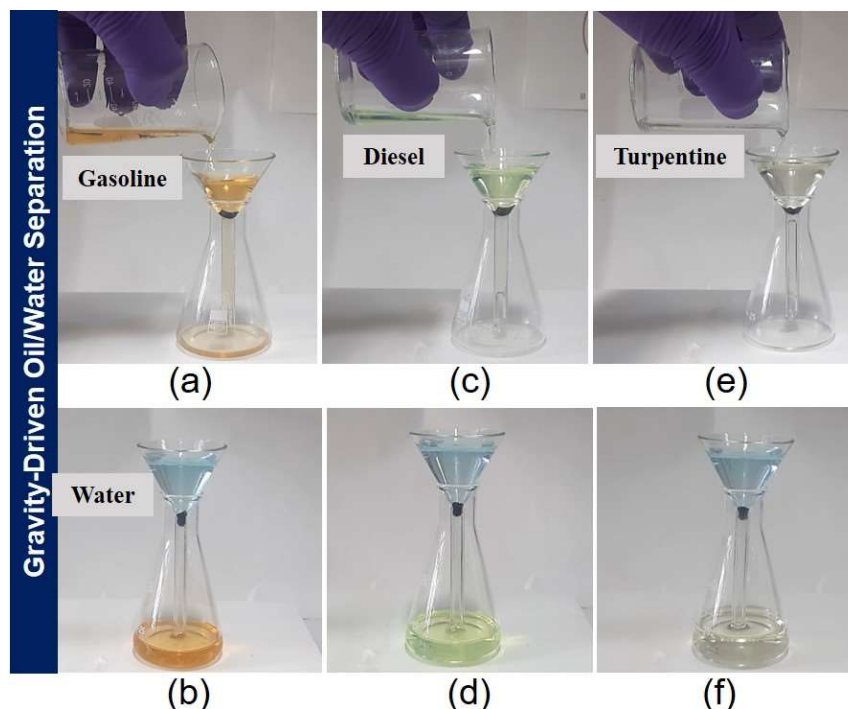


Figure 7.5: An experimental setup for gravity-driven oil/water separation; (a, c, e) before and (b, d, f) after the separation of different oil samples through TiS₂/CS:CNF membrane

Table 7.2: Comparison table for oil permeation flux, water rejection rate of CS:CNF and TiS₂/CS:CNF membrane

Nanofibers Membrane	Oil	Standard Absolute viscosity (cP)	Oil Permeation Flux J [L/(m ² .h)], setup installed at 90°	Oil Permeation Flux J [L/(m ² .h)], setup installed at 45°	WRR%
CS:CNF	Gasoline	0.5-0.6	6009.21±239	1297.76±219	97.36±0.8
	Diesel	2.4-2.5	1559.74±20	334.94±9	95.09±0.7
	Turpentine	2.0-2.5	1168.29±18	249.48±12	94.84±0.7
	Castrol oil	140-420	291.61±24	49.11±7	86.43±1.1
TiS ₂ /CS:CNF	Gasoline	0.5-0.6	6707.378±262	1394.14±186	97.63±0.3
	Diesel	2.4-2.5	1616.146±44	374.94±23	95.34±0.3
	Turpentine	2.0-2.5	1197.292±9	257.67±15	95.09±0.4
	Castrol oil	140-420	299.493±4	58.322±6	86.86±1.4

In the second experiment, the whole experimental set-up was slanted at a 45° angle (see Figure 7.6). Using the ultrasonication method, the oil and water mixture is first prepared with a ratio of water to oil (4:8). During the experiment, the low viscous oils such as gasoline, diesel, and turpentine show a high permeation flux. According to Table 7.3, low-viscosity gasoline, diesel, and turpentine, each showed oil permeation flux values of 1394.14 ± 186 L/(m² h), 374.94 ± 23 L/(m² h), and 257.67 ± 15 L/(m² h), respectively, whereas highly viscous castrol oil shows

permeation flux of $58.322 \pm 6 \text{ L}/(\text{m}^2 \cdot \text{h})$ (see Figure 7.7 (b)). Because of this, the tilted experiment exhibits a low permeation flux and a relatively slow separation time.

It was also observed that the $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane was effective in separating gasoline, diesel, and turpentine with a higher WRR due to the lower viscosity of these oils. However, because castrol oil has such a high viscosity, it has a lower WRR. This can be understood by considering the possibility that the smaller drop of water will become entangled with the more viscous oil as it travels through the smaller pore size of the $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane. This experiment demonstrates the $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane's ability to effectively remove low viscous oil from the mixture while simultaneously preventing water from passing through the NFs membrane, resulting in effective separation of oil/water mixtures.

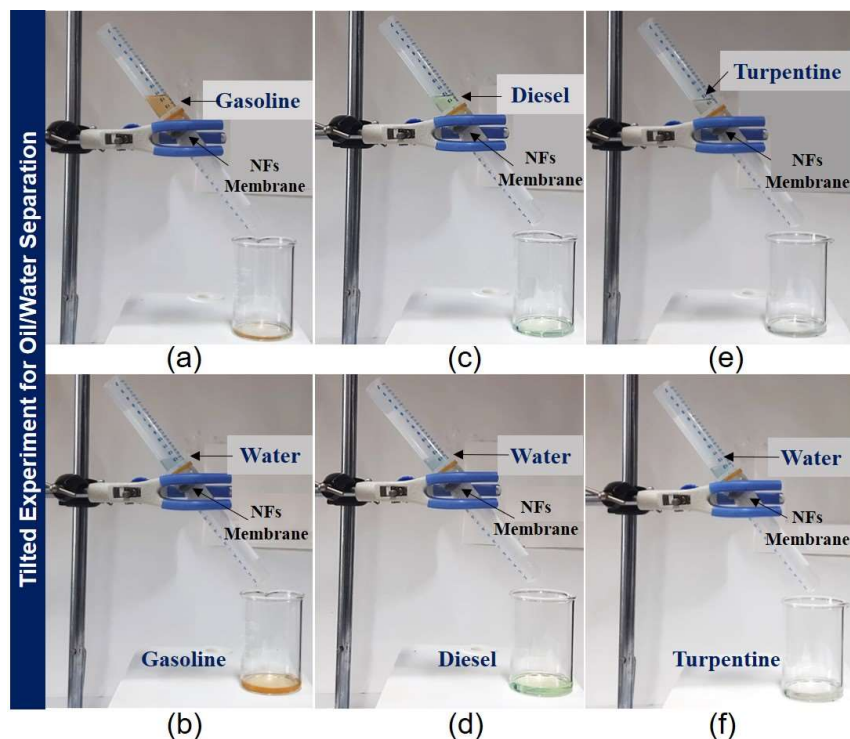


Figure 7.6: Tilted experiment for oil/water separation; (a, c, e) before, and (b, d, f) after the separation of different oil samples through $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane

The percentage mass ratio of each oil before and after the separation process was compared to determine the separation efficiency. The separation efficiency of NFs membrane for various types of oils is shown in Figure 7.7 (c). After a first trial, the $\text{TiS}_2/\text{CS}:\text{CNF}$ membrane had an efficiency of 99.1%, 96.6%, 95.01%, and 83.57% for gasoline, diesel, turpentine, and castrol oil, respectively. However, the separation efficiency of all oil samples decreases moderately as the number of separation cycles increases. Because of the porous structures and rough surface of the NFs membrane, it shows excellent multi-cycle efficiency, and consistent hydrophobicity, and can efficiently help in blocking water during the separation of the oil/water mixtures.

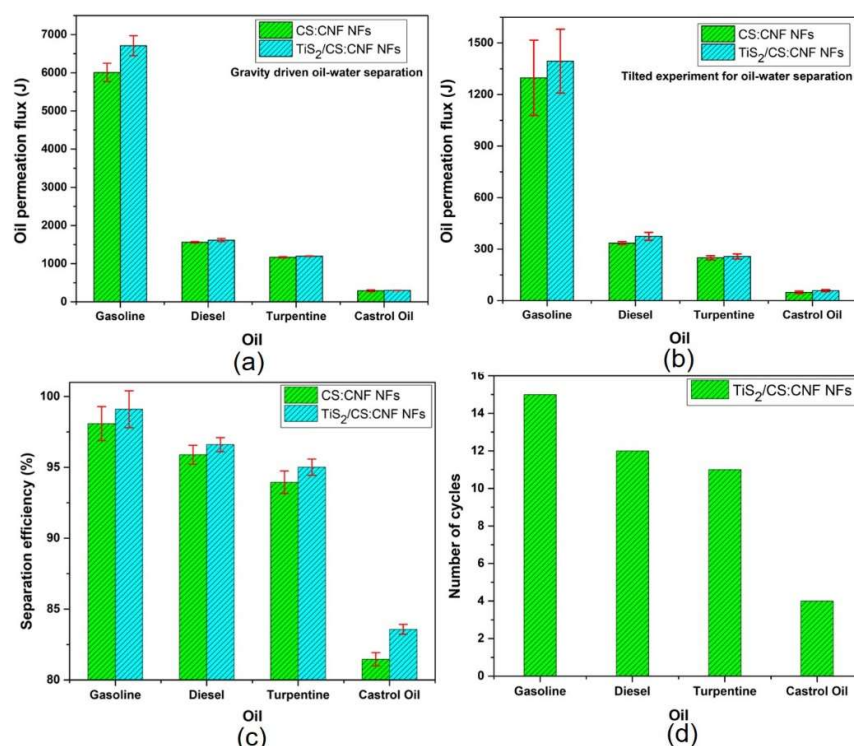


Figure 7.7: Oil permeation flux for (a) gravity-driven, (b) tilted experiment for oil/water separation, (c) separation efficiency, and (d) repeatability of NFs membrane

Experiments on oil/water separation were carried out multiple times so that the $\text{TiS}_2/\text{CS:CNF}$ membrane recovery could be evaluated for its accuracy (see Figure 7.7 (d)). Furthermore, the adsorption performance of the $\text{TiS}_2/\text{CS:CNF}$ membrane was evaluated in another experiment, as shown in Figure 7.8 (a-d). Here, the ability of the NFs membrane to absorb a mixture of gasoline and Rhodamine B (RhB) dye (to increase visibility) that had been spilled on the glass slide was evaluated. The result shows that the NFs membrane performs well in absorbing the oil layer, leading to the desired oil absorption effect. The cleaning efficiency of the prepared NFs membrane is further evaluated as depicted in Figure 7.8 (e-h). The NFs membrane is immersed in an ethanol solution after absorbing oil in order to remove the oil from the membrane. The result after 1 min of ethanol immersion shows that the NFs membrane was effectively cleaned. Table 7.3 shows the comparative analysis of previously published papers based on an oil/water separation system using a nanofiber membrane.

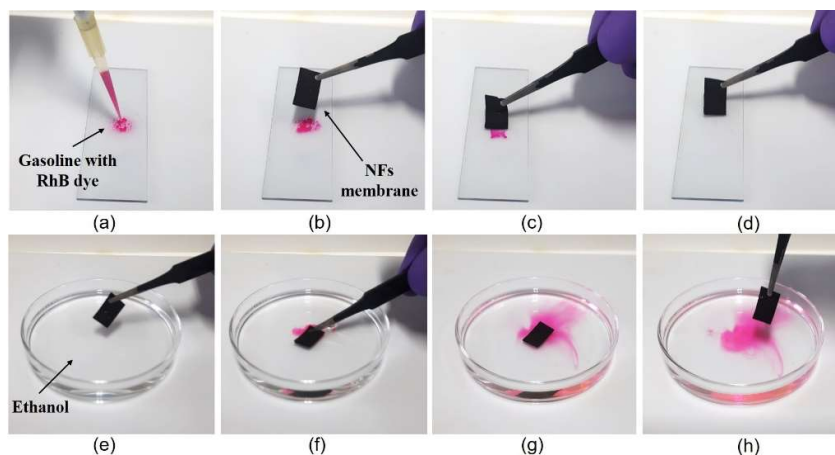


Figure 7.8: (a-d) The adsorption performance of the NFs membrane was evaluated using the absorption of gasoline that had been spilled on the glass slide, (e-h) cleaning efficiency of NFs membrane in ethanol.

Table 7.3: Comparative table based on previously used nanofiber membrane for separation of different oil/water mixtures

Nanofiber membrane	WRR (%)	Separation efficiency (%)	Active membrane area (cm ²)	Average roughness of membrane	Oil Permeation flux (%) (L/m ² .h)
CS:PVDF (Li et al., 2017)	-	99%	-	53.3 nm	70 (gravity)
PVA-PVDF (Gu et al., 2021)	-	95%	-	-	1471 (gravity)
PVDF NFs (Ding et al., 2019)	-	96.3%	2.0	-	18,482.7±287.3 (gravity)
Zn@GF membrane (Huang et al., 2018)	-	98%	-	384 nm	280 (gravity)
PAN@ZIF-8 (M. Wu et al., 2022)	97%	99.5%	-	2.22 µm	1720 (gravity)
TiS ₂ /CS:CNF (Current work)	97.63±0.3%	99.1%	1.5	290 nm	6707.378±262 (gravity)
					1394.14±186 (tilted experiment)

7.1.4 Summary

The study describes a simple and efficient technique used to fabricate a TiS₂/CS:CNF membrane. The prepared NFs membrane had exceptional hydrophobic and oleophilic characteristics, with a water contact angle of ~133° and an oil contact angle of ~3°, respectively. The oil/water separation capabilities of the NFs membrane were evaluated using permeation flux (*J*), water rejection rate (*WRR* (%)), and separation efficiency. Different oil samples such as gasoline, diesel, turpentine, and castrol oil were mixed with water and were subsequently separated using an experiment namely, gravity-driven and tilted oil/water separation. Moreover, the adsorption performance of the TiS₂/CS:CNF membrane was evaluated when gasoline spilled on the glass slide was adsorbed by the NFs membrane. The experimental results suggest that an oil/water mixture can be effectively separated using any oil with low absolute viscosity. It is possible that in the future, the overall cost of the oil/water separation process might be considerably lowered by adopting such an easily accessible NFs membrane, which also offers an environmentally benign option.

7.2 NATURE INSPIRED FICUS RELIGIOSA LEAF MESH COATED WITH ANTIBACTERIAL NANOCOMPOSITE FOR SEPARATION AND WATER PURIFICATION

In this study, we fabricate a nature inspired *Ficus religiosa* leaf mesh with a micro/nano hierarchical structure utilizing the ZnO/PANi@PMMA nanocomposite having exceptional hydrophobic and oleophilic characteristics, with a water contact angle of ~130° and an oil contact angle of ~2°, respectively. Different oil/water mixtures were subsequently separated using the mesh. Further the mesh is demonstrated to successfully degraded the methylene orange (MO) dye solution in the presence of sunlight, envisioning its potential use in water purification applications.

7.2.1 Introduction

A large quantity of refractory oily and textile wastewater has been produced as a consequence of the extraction and transportation of crude oil, offshore crude oil spills, and large-scale textile production, etc., leading to a number of issues with human health, the environment, and the economy (Gupta et al., 2015b; Zhang et al., 2013). Attempts to efficiently separate

water/oil from oily wastewater sources have sparked considerable public and government concern, and hence have become a pressing issue (Kintisch, 2010). With the course of industrialization, the discharge of oil-contaminated wastewater is continually rising yearly (L. Zhang et al., 2012). Accidental oil spills and the discharge of oily wastewater not only result in significant financial losses but also substantial water contamination and other ecological and environmental issues (Zhao et al., 2021). Traditional techniques have been utilized to control oily wastewater by thoroughly integrating physical, chemical, and biological approaches, including centrifugal separation, air flotation, gravity separation, ultrasonic separation, biological treatment, and coagulation (Hodges et al., 2018; Kota et al., 2012; Yue et al., 2019). For example, mechanical skimmers are often used to recover oil/water mixture after spills, but this mixture is still challenging to handle. Contrarily, physical adsorption materials for oil-water separation like activated carbon, linoleum, sponge, cloth, porous materials, and metal wire mesh present the drawbacks of small absorption capacity, low absorption rate, and constrained recyclability because water absorption exerts a lot of pressure on recovery and recycling (Ma et al., 2016). However, these systems have historically been challenging to utilize because of their poor separation efficiency, production of secondary pollutants, and large size, which has prompted researchers to come up with more efficient approaches (Yuying Deng et al., 2020; Y. X. Wang et al., 2019).

In addition, wastewater that is released as a by-product of textile/production industries not only comprises oily wastewater but also contains water-soluble organic color contaminants, which necessitates additional treatment. Therefore, an environmentally friendly, and economically viable approach for the simultaneous separation of oil/water mixture and wastewater degradation using materials with unique wettability characteristics is required (Padaki et al., 2015; Qiu et al., 2020; Wang et al., 2014). Fabrication of absorbent or filtration materials has made use of a wide variety of porous substrates. These substrates include metallic meshes, sponges, filter paper, fibers, fabrics, and aerogel (Nie et al., 2022; Zhu et al., 2014). Recently, researchers have focused on the development of efficient mesh materials with oleophilic and hydrophobic characteristics that can be utilized as "oil-removing" materials due to their ability to allow oil to penetrate while simultaneously repulsing water (N. Zhang et al., 2020). Additionally, these mesh materials become contaminated by various organic substances present in the oil-water mixture during real-time operation, thus lowering the separation flux and decreasing the filtration efficiency. Therefore, it is essential to develop a multifunctional mesh that can both separate oil-water mixtures and degrade organic contaminants. Most research initiatives have primarily concentrated on oil-water separation, frequently ignoring the degradation of contaminants that persist in the filtrate water. There are few reports on the development of antibacterial coated mesh that can efficiently separate oil-water mixtures while also promoting contaminant degradation. Metal oxides such as zinc oxide (ZnO), tin oxide (TiO₂), etc., are proven to have antibacterial properties (Chauhan et al., 2019; Peng et al., 2023b; M. Wang et al., 2023). These metal oxides are often incorporated into mesh materials to enhance their oil adsorption and water removal capabilities by tailoring oleophilicity and hydrophobicity characteristics while also enabling the degradation of organic pollutants when exposed to light (Dwivedi et al., 2017; Gupta et al., 2018; Mensah et al., 2018; Mondal et al., 2019). However, pristine ZnO may have limitations in terms of photocatalytic effectiveness. Among the numerous reports focusing on improving the photocatalytic efficiency of ZnO, polyaniline (PANi) has received a lot of attention for improving the photocatalytic performance of ZnO by broadening the spectrum of light absorption, optimizing charge carrier separation, increasing material stability, and selectively breaking down organic dyes in aqueous environments (Ameen et al., 2011; Saravanan et al., 2016; Yadav et al., 2021). These advantages make ZnO/PANi suitable for use in a wide range of separation and water purification applications. For example, Vijayalakshmi et al. synthesized a ZnO/PANi composite by varying the weight percentages of ZnO (1% and 10%) in the PANi matrix to assess its photocatalytic efficiency in degrading methylene blue (MB) dye under sunlight exposure (Vijayalakshmi et al., 2021a). The result demonstrated that the 10wt% PANi/ZnO composite exhibited excellent conductivity properties and achieved the

highest photocatalytic activity, with a rate constant (k) of 14.77×10^{-3} /min for MB dye degradation. Similarly, Sahu et al. synthesized an orthophosphoric acid-doped PANi/ZnO composite for MB dye degradation. The results showed that 30wt% ZnO in an orthophosphoric acid-doped PANi matrix resulted in enhanced MB dye degradation with $k = 0.01 \times 10^{-3}$ /min (Sahu et al., 2019).

Fabricating inexpensive and effective naturally available materials to combat significant industrial organic pollutants and oil spills is required for environmentally benign solutions that are easy to scale up (Peng et al., 2023a). Therefore, this work focuses on developing a low-cost, nature-available material for water purification and oil/water separation systems using *Ficus religiosa* leaf mesh coated with an antibacterial ZnO/PANi@PMMA nanocomposite.

7.2.2 Materials and Methods

The leaves for the experiment were collected from the *Ficus religiosa* tree. The polymer-based coating was prepared using aniline, hydrochloric acid (HCl), ammonium persulfate (APS) which were purchased from Otto Chemicals. The ZnO nanowires (NWs) were grown using zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$), isopropyl alcohol (IPA), hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$), which were purchased from Sigma Aldrich. Similarly, other chemicals, such as poly(methyl methacrylate) (PMMA), Luria Bertani (L.B) media, methylene blue (MB), methylene orange (MO), rhodamine-B (Rh-B), and chloroform, were also purchased from Sigma Aldrich. The oil samples such as diesel, gasoline, and turpentine oil were purchased from Hindustan Petroleum and Gulf Oil companies, in India.

(a) Synthesis of PANi

PANi NPs were synthesized using aniline, HCl, APS, and DI water. 1 mL of aniline was ultrasonicated in 0.1 M HCl for 40 mins. Another solution of 2.4 g of APS was prepared in 20 mL of 0.1 M HCl and ultrasonicated for 30 mins and was added to the previously prepared solution in a dropwise manner, and magnetically stirred at 5°C for 2 hours to obtain a blackish green color precipitate. After polymerization completion, the blackish-green product was separated through centrifugation and washing several times with double distilled water. The resulting products were dried under vacuum at 90°C for 8 hours. The PANi precipitate was collected after the synthesis for characterization.

(b) Preparation of ZnO/PANi@PMMA coated *Ficus religiosa* leaf mesh

To initiate the preparation of a *Ficus religiosa* leaf mesh, the first step involves immersing the leaf in hot water for a duration of 24 hours. Subsequently, the leaf was maintained in a water soak for 15 days. This is succeeded by a thorough washing of the leaf to eliminate any pulp and dust adhering to its surface, thereby facilitating the extraction of a skeleton. Once the cleansed skeleton leaf mesh was obtained, it is left to air dry at room temperature until it was ready to use. The $3 \times 3 \text{ cm}^2$ leaf mesh was cut and used for the deposition of polymer-based composite coating. Figure 7.9 shows the schematic representation of the preparation of hydrophobic and oleophilic leaf mesh. The synthesis began with the dissolving of 4 g of PMMA in 40 mL of chloroform, which was followed by 45 mins of magnetic stirring. Then 0.40 mg of prepared PANi NPs are added, followed by 15 mins of ultrasonication. Finally, the leaf mesh was immersed for 2 mins in a PANi@PMMA prepared solution before drying in an oven at 70°C for 40 mins.

Furthermore, ZnO NWs were grown in the PANi@PMMA coated leaf mesh. Firstly, the ZnO seed layer was prepared using zinc acetate in IPA solution, and PANi@PMMA coated leaf mesh was immersed for the initial growth of ZnO seed on the PANi@PMMA leaf mesh. For the growth of ZnO NWs, a solution containing $\text{Zn}(\text{NO}_3)_2$ and $(\text{CH}_2)_6\text{N}_4$ in a ratio of 1:5 in DI water and ultrasonicated for 30 mins. The PANi@PMMA coated leaf mesh was then immersed in the ZnO solution for 7 hours at 90°C in the electric oven for the hydrothermal growth of ZnO NWs. After the reaction was completed, the ZnO NWs grown PANi@PMMA coated leaf mesh and the leftover ZnO precipitate (in the solution) were collected for characterization.



Figure 7.9: Photograph of *Ficus religiosa* leaves and leaf mesh with the (1-6) showing preparation of ZnO/PANi@PMMA coated leaf mesh

(c) Antibacterial characteristic of coated leaf mesh

To determine the zone of inhibition against the bacteria, antibacterial testing has been carried out utilizing the agar well diffusion method (Chauhan et al., 2018b). *Ficus religiosa* leaf mesh was employed in the experiment in four different combinations: bare (or pure) leaf mesh, PMMA coated leaf mesh, ZnO seed on PANi@PMMA leaf mesh, and ZnO/PANi@PMMA leaf mesh with a diameter of 1 cm each, against the *E. coli* bacteria (dh-5 α strain). The *E. coli* bacterium has been grown on the Luria Bertani (L. B) agar medium. The 100 μ L of *E. coli* were added to the L.B. media using a micropipette after the agar patri plate had been formed, and they were then spread out using an L-shaped glass rod spreader (Chauhan et al., 2018a). The bare leaf mesh, PMMA coated leaf mesh, ZnO seed on PANi@PMMA leaf mesh, and ZnO/PANi@PMMA leaf mesh were kept after the bacteria had fully absorbed into the patri plate. The patri plate was then kept in the incubator at 37°C for a day. The zone of inhibition against the *E. coli* bacteria was observed and measured via the measuring scale.

7.2.3 Results and Discussion

(a) Characterization of hydrophobic/oleophilic leaf mesh

At an accelerating voltage of 5 kV, a field emission scanning electron microscope and an energy dispersive spectrometer were used in order to investigate the surface morphological characteristics and elemental composition of all of the prepared hydrophobic/oleophilic leaf mesh. Figure 7.10 shows the FESEM images of the (a) uncoated leaf mesh with an inset showing a magnified image, (b) PANi@PMMA coated leaf mesh, (c) ZnO seed coated PANi@PMMA leaf mesh, (d) ZnO/PANi@PMMA coated leaf mesh with inset showing a magnified image of ZnO nanowires (NWs). The lack of PANi NPs in the composite coating was easily discernible according to the FESEM images. This can be because the PANi NPs were trapped in the PMMA structure and became less visible. On the other hand, a thin layer of PANi NPs deficient composite coating was reported to be smooth and homogeneous throughout the *Ficus religiosa* leaf skeleton. The prepared coated leaf mesh has a water contact angle (WCA) of $\sim 129.4^\circ$ and an oil contact angle (OCA) of $\sim 2^\circ$; thus demonstrating a hydrophobic and oleophilic nature of the coating (see Figure 7.11 (c)). The growth of ZnO NWs on the PANi@PMMA composite coating may be able to give the desired rough micro- and nanostructure, this may be because the ZnO seed has high

surface energy despite its small size. When the leaf mesh is immersed in a solution containing $(\text{Zn}(\text{CH}_3\text{CO}_2)_2)$ and IPA, a thin film of evenly distributed seed adheres to the leaf mesh. This thin film of seed attracts Zn^{2+} and O^{2-} ions from another growth solution containing $\text{Zn}(\text{NO}_3)_2$ and $((\text{CH}_2)_6\text{N}_4)$, which in turn reduces the surface energy. Due to the ideal growth temperature, these ions have sufficient energy to unite and arrange themselves into a hexagonal shape in the (002). As a consequence, ZnO NWs are grown on the surface of the leaf mesh.

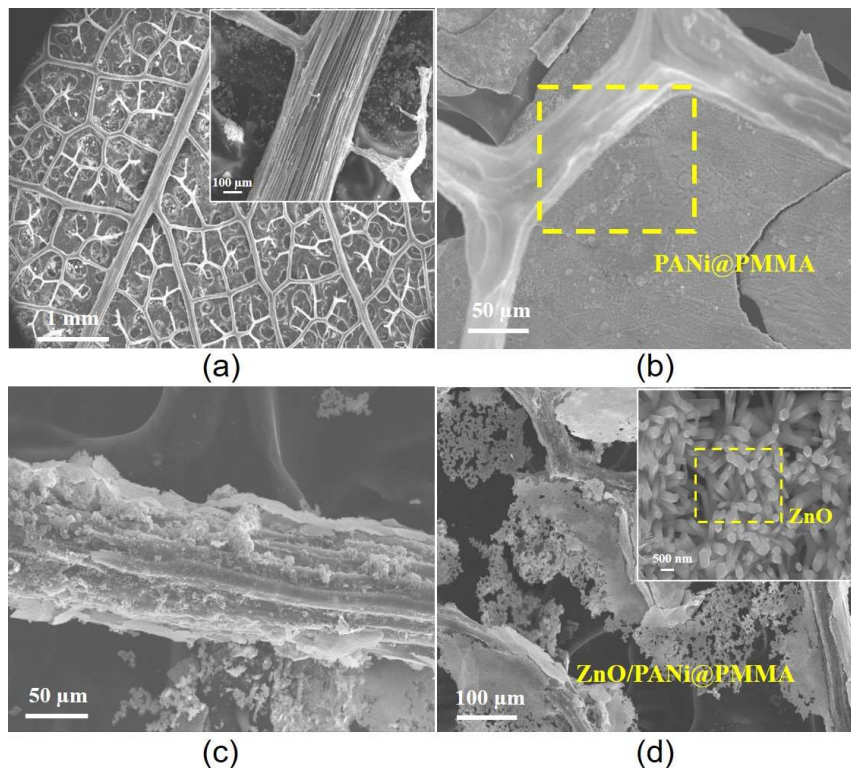


Figure 7.10: FESEM images of (A) uncoated leaf mesh with inset showing a magnified image, (B) PANi@PMMA coated leaf mesh, (C) ZnO seed coated PANi@PMMA leaf mesh, (D) ZnO/PANi@PMMA coated leaf mesh with inset showing a magnified image of ZnO nanowires

In the presence of ZnO NWs with micro/nano hierarchical structures, water molecules may be trapped in these structures, resulting in a composite water/solid interface. These structures will have difficulty interacting with oil as the water gets confined in these hierarchically rough surfaces. The trapped water acts as a barrier to stop oil droplets from penetrating the surface, resulting in a water-resistant surface. Therefore in the gravity-driven experiment of oil/water separation, the oil is transferred to the leaf mesh first, and then the water is transferred. The composition analysis of PANi@PMMA and ZnO/PANi@PMMA coated leaf mesh is shown in Figure 7.11 (a, b). The elements C, O, Al, and Cl are present in the PANi@PMMA coated leaf mesh which is consistent with the previously published articles (Niranjana et al., 2016; Wankasi and Dikio, 2014), whereas C, O, and Zn are reported for ZnO/PANi@PMMA coated leaf mesh. Furthermore, XRD characterization of the PANi@PMMA and ZnO/PANi@PMMA coated leaf mesh is difficult because X-ray exposure caused these coated leaf mesh to burn. The XRD spectrum of individual PANi and ZnO NPs is shown in Figure 7.11 (d). Cu K1 α radiation with an energy of 1.54059 Å was used to record the diffraction patterns across a 2θ range of 20-80°. The XRD pattern of PANi showed a broad peak at 23°, which demonstrates that PANi has amorphous characteristics. Similarly, several prominent peaks are apparent in the XRD pattern of ZnO NPs, and these peaks correspond to hexagonal wurtzite ZnO crystal planes that were indexed in Figure 7.11 (d). These peaks include (100), (002), (101), (102), (110), and (200), which indicates a strong relation to the standard JCPDS card No. 00-036-1451 (Marouf et al., 2017).

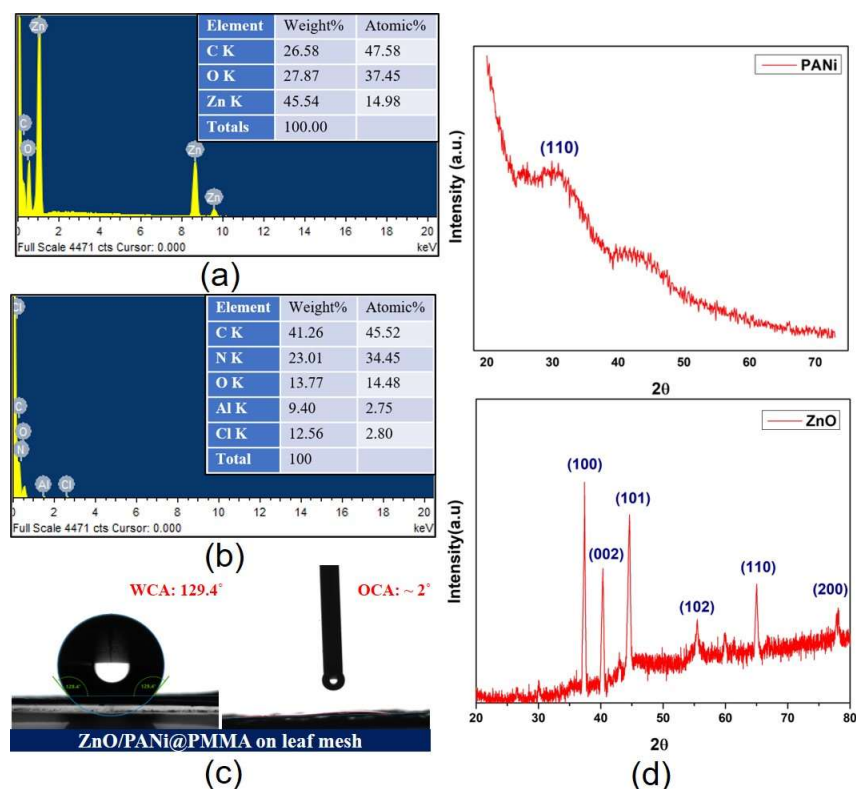


Figure 7.11: (a, b) EDS results for PANi@PMMA, and ZnO/PANi@PMMA, (c) Contact angle results of ZnO/PANi@PMMA coated leaf mesh, and (d) XRD of PANi and ZnO NPs

(b) Oil/water separation

In order to prepare the experimental setup for gravity-driven oil/water separation, a hole of 2 cm in diameter is made into the bottom of 50 mL of a plastic beaker. The leaf mesh samples are then attached to the two beakers while they are arranged at a 180° angle from one another. The parameters for analyzing oil/water separation of materials are investigated by permeation flux (J) and separation efficiency (η (%)). We evaluated the permeation flux for 20 mL of different oils and a fixed 2.5 cm² leaf mesh area at atmospheric pressure. A methylene blue dye was added to the water during the experiment to enhance its visibility. For the experiment, three oils with different viscosities were used, including gasoline, diesel, and turpentine. Due to the fact that oil and water have different densities and that oil often floats on the surface of the water, 20 mL of oil was fed through the gravity-driven experiment first, followed by an equal amount of water (see Figure 7.12). The oil sample was readily passed through the oleophilic leaf mesh and was collected in the beaker beneath. While the water sample was retained on the surface of the leaf mesh owing to the presence of micro/nano hierarchical structures of ZnO/PANi@PMMA nanocomposite. Table 7.4 summarises the results of permeation flux and separation efficiency. The percentage mass ratio of each oil before and after the separation process was compared in order to determine the separation efficiency. The separation efficiency of all oil samples decreases moderately as the number of separation cycles increases (see Figure 7.12). Due to their rapid penetration through the micro/nano hierarchical structure of the mesh, diesel, and gasoline displayed separation efficiencies of $\sim 96.86 \pm 0.8\%$ and $\sim 93.09 \pm 0.9\%$ respectively, as shown in Figure 7.13 (a). This efficiency was maintained for 8 and 5 separation cycles, respectively. However, turpentine oil, because of its relatively high viscosity, partly remains trapped in the mesh, causing a reduced separation efficiency of $\sim 89.14 \pm 0.4\%$ which severely impacts the separation cycle's capacity to 4 (see Figure 7.13 (b)).

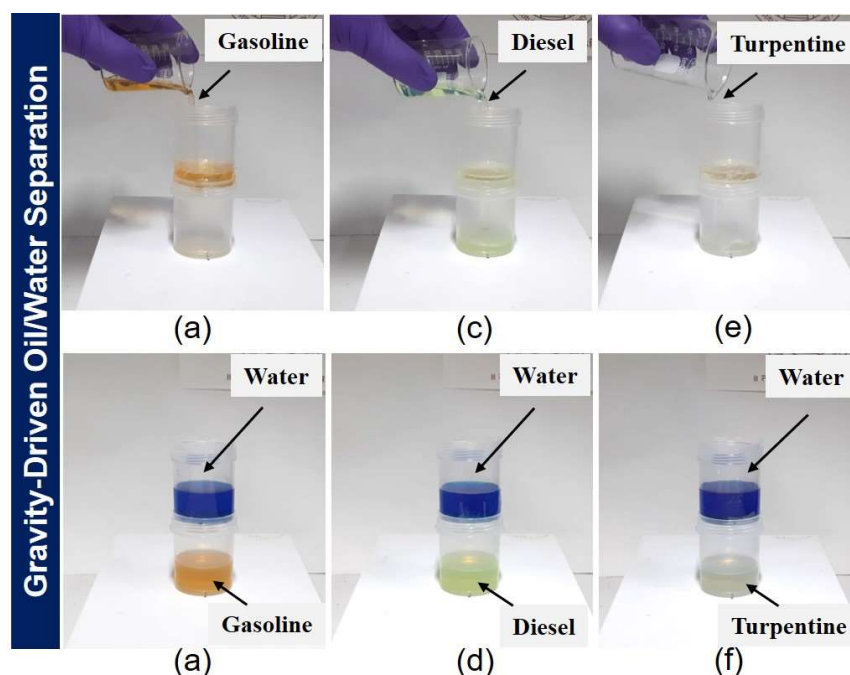


Figure 7.12: Gravity-driven experiment of ZnO/PANi@PMMA coated leaf mesh for oil/water separation

Table 7.4: Comparison table for oil permeation flux, the separation efficiency of ZnO/PANi@PMMA nanocomposite coated leaf mesh

Material	Oil	Absolute viscosity (cP)	Oil Permeation Flux J [L/(m ² .h)]	Separation efficiency (%)
ZnO/PANi@PMMA coated leaf mesh	Gasoline	0.5-0.6	3800.44±199.56	96.86±0.8
	Diesel	2.4-2.5	1764.86±53.32	93.09±0.9
	Turpentine	2.5-3	1494.83±20.32	89.14±0.4

Moreover, due to oil evaporation loss, fractional wetting of the beakers, and partial mesh structure absorption, the ideal separation efficiency could not be achieved. Furthermore, after a maximum of 8 cycles of oil/water separation, the separation efficiency significantly decreased. This is assumed to be a result of the coated ZnO/PANi@PMMA nanocomposite being gradually removed after each cycle and being replaced by the inherent leaf mesh structure. Furthermore, the absorption performance of the ZnO/PANi@PMMA coated leaf mesh is evaluated in another experiment, as shown in Figure 7.14 (a). These experiments consisted of the absorption of gasoline mixed with rhodamine B (RhB) dye to increase the visibility that had been spilled on the glass plate. The coated leaf mesh is then allowed to absorb the oil layer, and the oil layer quickly absorbs the gasoline-RhB to produce the desired effect of absorbing the oil. Because the surface is extremely hydrophobic/oleophilic, it is able to achieve a good level of selective absorption of the coated leaf mesh. The cleaning efficiency of the ZnO/PANi@PMMA coated leaf mesh is shown in Figure 7.14 (b). After the coated leaf mesh is absorbed the oil, is then submerged in an ethanol solution for 120 sec in order to remove the oil from the coated leaf mesh. The cleaned leaf mesh after every 30 sec is shown in Figure 7.14 (e).

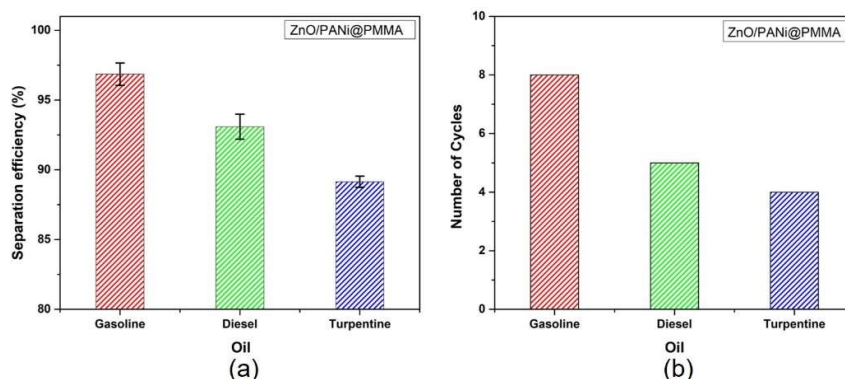


Figure 7.13: (a) Separation efficiency and (b) repeatability studies of coated leaf mesh

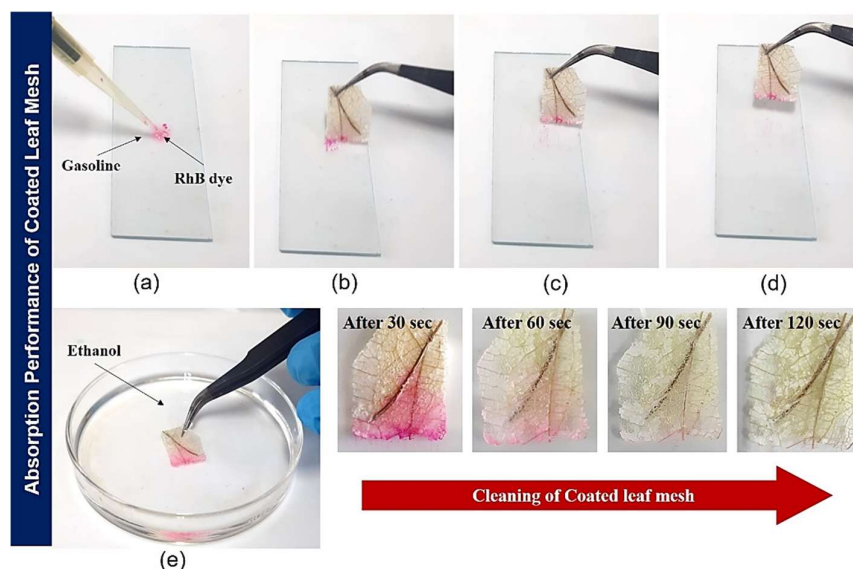


Figure 7.14: (a–d) The absorption performance of the ZnO/PANi@PMMA coated leaf mesh was evaluated using the absorption of gasoline/Rh-B that had been spilled on the glass slide, and (e) the cleaning efficiency of coated leaf mesh in ethanol

(c) Photocatalytic Degradation of Methylene Orange (MO) dye

The photocatalytic degradation of ZnO/PANi@PMMA leaf mesh was evaluated by analyzing the rate of degradation of MO dye in an aqueous solution with solar radiation. The digital images of the degraded MO dye are shown in Figure 7.15 (a). A concentration of 15 mg/L is prepared in 100 mL of MO dye solution, which is used to expose the coated leaf mesh in a small acrylic tank, and the solution is gradually stirred for 2 min. A 3 mL sample of the degraded MO dye solution is taken and recorded regularly for the UV-Vis absorption system to analyze the rate of MO dye degradation. The maximum peak intensity MO dye remained at 466 nm, after 140 min of observation. As time passes, the maximum peak intensity at 466 nm decreases significantly, which is attributed to MO dye degradation, demonstrating that ZnO/PANi@PMMA coated leaf mesh has strong degradation reactivity against the MO dye (see Figure 7.15 (a)). A decrease in the maximum normalized absorbance is shown as a function of time in Figure 7.15 (b). The breakdown of MO dye appears to follow a pseudo-first-order kinetic pattern, as seen in Figure 7.15 (c).

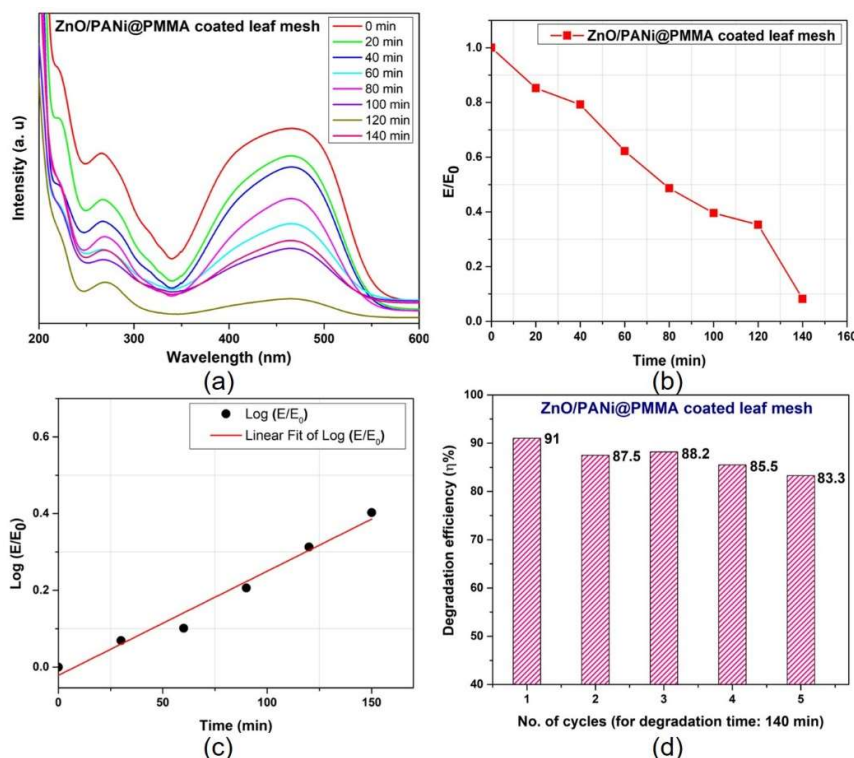
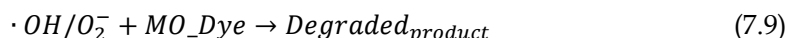
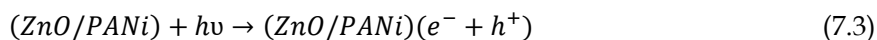


Figure 7.15: UV-vis spectrum of (a) ZnO/PANi@PMMA coated leaf mesh, (b, c) experimental and kinetics of photodegradation of MO dye, and (d) reproducibility of coated leaf mesh

The intermolecular interaction between ZnO and PANi absorbs photons as a consequence of being exposed to sunlight on the surface of PANi/ZnO nanocomposites, which results in the generation of electrons (e^-) and hole (h^+) pairs. In this particular system, the PANi is excited about the $\pi \rightarrow \pi^*$ transition, which led to the production of e^- and the subsequent transfer of e^- from the HUMO to the LUMO states (Asgari et al., 2019). Subsequently, the e_{VB}^- move from the valence band (VB) of ZnO to the conduction band (CB). A relative difference in the energy levels of PANi and ZnO will cause the e_{LUMO}^- of PANi to shift to the CB level of ZnO. The e_{CB}^- in the ZnO and the h_{HUMO}^+ in the PANi act synergistically with H_2O . It leads to the production of O_2^- or $-OH$ ions on the surface, which are responsible for MO dye degradation and result in the mineralization of dye to form CO_2 and H_2O (Vijayalakshmi et al., 2021b).



One of the possible photocatalytic degradation mechanisms of MO dye using coated leaf mesh is shown in Figure 7.17 (b, c). The possible degradation of MO dye follows the symmetric separation of the azo bond ($-N=N-$) present in MO structure, which resulted in the production of N,N-dimethyl-p-phenylenediamine, and sulfanilic acid which further helps to degrade the

intermediate products as shown in Figure 7.16 (c). These by-products are further degraded in the mineralization of dye to form CO_2 and H_2O in presence of $-OH$ (Kgatle et al., 2021). A recycling test for five repeatable cycles is carried out to investigate the reproducibility of the ZnO/PANi@PMMA leaf mesh for practical application (see Figure 7.15 (d)). The coated leaf mesh was collected and washed three times with DI water and IPA before being dried at $60^\circ C$ for 1 hr for the next photocatalytic degradation cycle. In the first cycle, the initial degradation efficiency is $\sim 91\%$. However, the efficiency gradually decreases to $\sim 83.3\%$ with each subsequent degradation cycle. Previous research has shown that some photocatalyst is released into the solution during the photocatalysis process, resulting in a decrease in degradation efficiency (Latthe et al., 2019). Similarly, the decrease in degradation efficiency of MO dye by coated leaf mesh after five cycles could be due to the release of a small amount of ZnO nanorods into the solution.

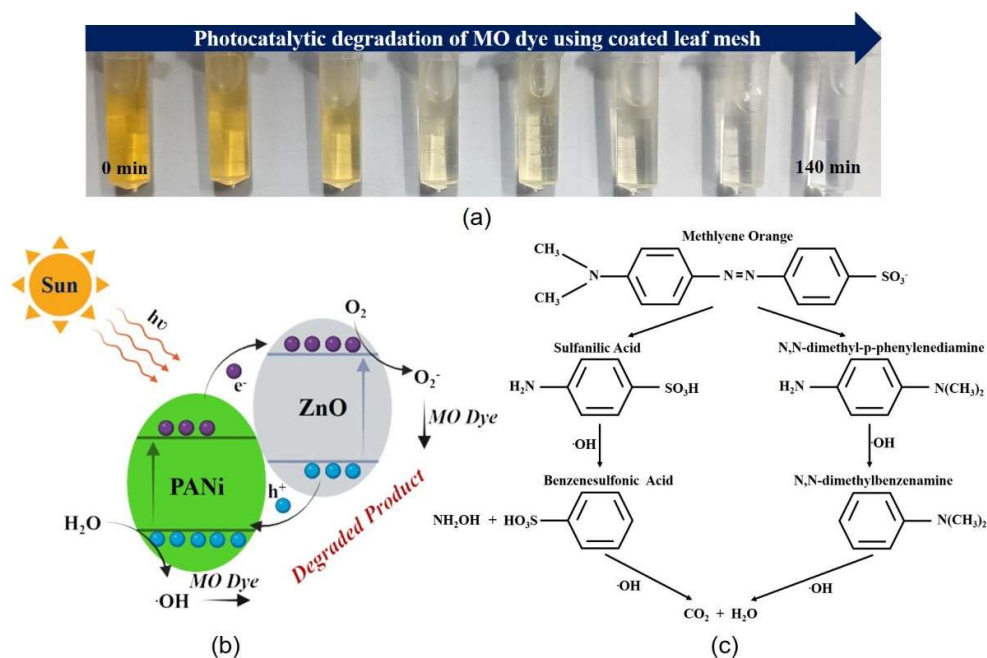


Figure 7.16: (a) Photograph of degraded MO dye, (b, c) Possible degradation mechanisms of MO dye using ZnO/PANi@PMMA coating on leaf mesh

(d) Antibacterial studies of ZnO/PANi@PMMA coated leaf mesh

All four combinations of bare and coated leaf mesh were tested for antibacterial properties against *E. coli* bacteria (see Figure 7.17 (a-c)). By following the traditional method, we measure the zone of inhibition using a physical ruler by positioning the scale above the petri dish and examining it with the naked eye. The zone of inhibition for the bare leaf mesh and PMMA-coated leaf mesh was not observed. The previously published article also supports that pristine PMMA and pristine PANi don't show antibacterial properties, however, PMMA coupled with nanoparticles or other materials resulted in its antibacterial characteristic (Abdel Rehim et al., 2020; Dimitrakellis et al., 2021; Karatepe and Ozdemir, 2020). Moreover, the other combination such as ZnO seed coated PANi@PMMA leaf mesh and ZnO NWs coated PANi@PMMA leaf mesh shows the zone of inhibition of 1.5 cm and 1.9 cm, respectively (see Figure 7.17 (c)). The possible reason for the enhanced antibacterial capabilities of coated leaf mesh is because of the growth of ZnO NWs over the PANi@PMMA, where these ZnO NWs combine with a conducting polymer (PANi), which helps to disrupt cell membranes and prevent bacterial colonies from forming on the surface of the plate (Falak et al., 2022).

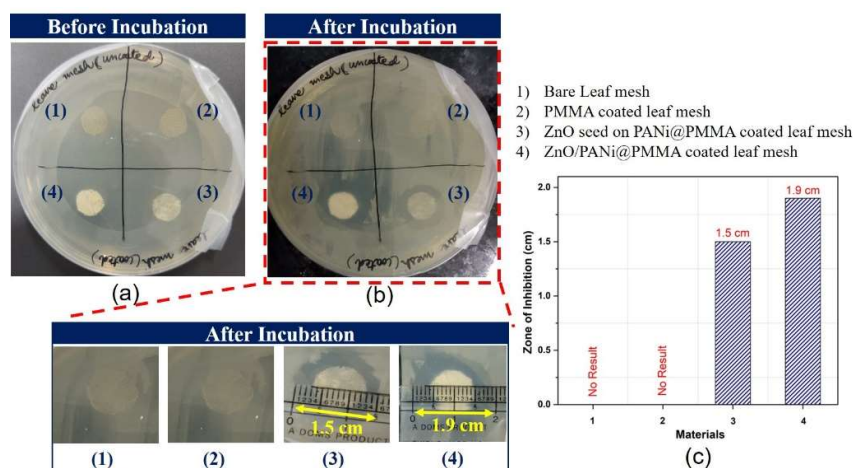


Figure 7.17: (a, b) Antibacterial testing using Agar-diffusion petri plate method, with photograph of before and after incubation, and (c) relationship between the zone of inhibition vs various coated leaf mesh

7.2.4 Summary

The study describes a simple and efficient technique used to fabricate a nature inspired *Ficus religiosa* leaf mesh with a micro/nano hierarchical structure utilizing the ZnO/PANi@PMMA nanocomposite. The prepared leaf mesh had exceptional hydrophobic and oleophilic characteristics, with a water contact angle of $\sim 130^\circ$ and an oil contact angle of $\sim 2^\circ$, respectively. Different oil/water mixtures were subsequently separated using the mesh, and after 8 cycles, the separation efficiency was recorded to be $\sim 96.86 \pm 0.8\%$ for gasoline. The experimental results suggest that an oil/water mixture can be effectively separated using any oil with low absolute viscosity. Moreover, in the presence of sunlight, the ZnO/PANi@PMMA coated leaf mesh degraded the MO dye solution in 140 min with a maximum $\sim 91\%$ degradation efficiency. The Agar diffusion petri plate method was employed to further analyze the inhibition efficiency of the coated leaf mesh, which indicates a zone of inhibition of ZnO/PANi@PMMA coated leaf mesh as 1.9 cm, higher than other combinations of bare and coated leaf mesh. It is possible that in the future, the overall cost of the oil/water separation process might be considerably lowered by adopting such easily accessible leaf mesh, which also offers an environmentally benign option. The reported composite material is found to be an excellent mesh for separating oil/water mixtures and photocatalytic degradation, and hence, can be envisioned as a potential material for water purification applications.

7.3 FABRICATION OF CONTINUOUS FLOW MICROREACTOR FOR EFFICIENT DYE DEGRADATION USING GRAPHENE QD@MOF (Ti) PHOTOCATALYST

This study presents an efficient approach to degrading Methylene blue (MB) dye, commonly used in the textile industry, within a cost-effective polydimethylsiloxane (PDMS) based continuous flow optofluidic microreactor. This microreactor combines graphene quantum dots (QDs) and $\text{NH}_2\text{-MIL-125}$ (MOF(Ti)) as a highly effective photocatalyst coating within its microchannels. By directly incorporating graphene QDs@MOF(Ti) into the microchannels, the photocatalytic medium is brought into close proximity with the flowing MB dye solutions, thereby reducing the necessary interaction time and enhancing purification efficiency. Additionally, the microfluidic reactor exhibits prolonged stability of the photocatalyst, enabling its reuse without significant efficiency loss. In addition, a comparative analysis, highlights the advantages of microreactor-based photocatalysis over traditional methods. These advancements in the features of the graphene QDs@MOF(Ti) nanocomposite substantiate their demonstrated superiority in degradation efficiency.

7.3.1 Introduction

Recently, the growth of industries combined with rising populations, has resulted in the release of toxic contaminants in the water bodies (Saucier et al., 2015). This increase in pollutants has led to a significant risk for both the environment and humanity. These contaminants even in low concentrations, can affect the essential aquatic life cycles by blocking light and oxygen from entering the water (Liu et al., 2017; Prashanth et al., 2021). Additionally, textile contaminants such as dyes are considered to be one of the harmful toxins that are difficult to break down under natural conditions (Gupta et al., 2015a). For example, Methylene blue (MB) dye based wastewater is extensively released pollutants from textile industries. Therefore, there is an essential requirement for advanced methods for eliminating these toxins from water sources. The literature reports the use of different methods for treating these toxins via techniques such as electrocoagulation, chemical oxidation, and adsorption (Anh Tran et al., 2021), etc. However, these methods are often unable to fully eliminate these modern pollutants; instead, they relocate the dye molecules rather than removing them. For instance, electrocoagulation frequently requires significantly higher cost and energy, and generates a substantial amount of sludge, thus contributing to the increase of secondary pollution and waste management issues. Similarly, chemical oxidation is an expensive method that results in incomplete dissociation of dyes and produces toxic byproducts. Furthermore, in the adsorption method, the dye is merely relocated in another form, necessitating an additional disposal process. In contrast, advanced technology such as photocatalysis is important, as it alters the dye molecules into harmless substances, effectively addressing the issue. Consequently, it presents a more efficient, sustainable, and environmentally friendly solution.

Additionally, with the advancement of technology, the use of optofluidic microreactors are increasingly utilized for wastewater treatment, as this technique combines the use of optics, microfluidics, and chemical reactions in compact yet smaller devices (Rambabu et al., 2022). As compared to traditional methods, these techniques have a higher surface-to-volume (S/V) ratio, which improves the photoinduced process (Parmar et al., 2015). Further, the presence of short transfer length along with uniform light distribution enables the spontaneous chemical reactions, thus improving the energy density within the microreactor (Li et al., 2014). The performance of the photocatalysis technique is determined by two factors: photocatalysis efficiency (light adsorption and charge transport within catalyst) and mass transfer efficiency (the interaction of catalyst and reactants, and removal of resultant byproducts) (H. Kim et al., 2022a). Additionally, the optofluidic microreactor is a cost-effective technology that requires only a minimal amount of photocatalyst to be coated on the internal channels, yet it achieves results comparable to conventional methods. Due to the small volume of solution that flow continuously in the microreactor's channels, light penetration is uniform across the reactor's depth, enabling rapid degradation of contaminants often within seconds, whereas traditional reactors may take several hours (Das and Srivastava, 2016). Despite their swift reaction rates, microreactors face challenges in meeting the demands of wastewater treatment facilities due to their limited throughput, which hinders their commercial potential. To address this issue, increasing the number of microchannels within a single device or utilizing parallel microchannel reactors can enhance operational efficiency and make the technology suitable for large-scale industrial use. Consequently, this advanced approach serves as a practical strategy to solve the limitations of traditional treatment methods, advancing waste purification technology to higher levels of enhanced effectiveness.

In recent years, the researcher has increased focus on designing photocatalysts in various 0D to 3D nanostructures, to maximize their S/V ratio to significantly enhance their photocatalytic degradation efficiency (Ahmadpour et al., 2020a; Wu et al., 2020). For example, titanium (Ti) based metal organic framework (MOF) materials with their unique features such as porous structure, customizable pore characteristics, and enhanced surface area, emerges as a suitable adsorption material for removal of organic dyes from wastewater (Roy et al., 2023; Yao et al., 2023). These porous structures not only enable them for excellent adsorption and diffusion but also enhance light trapping, resulting in the abundance of active sites (Bůžek et al., 2021; Zhu et al., 2016). Further, graphene quantum dots (QDs) offer a large surface area and excellent electron

transfer capabilities, which help reduce the recombination of electron/hole (e^-/h^+) pairs and improve charge separation, while also expanding the photocatalyst's light absorption into the visible range (Ibarbia et al., 2020; Lu et al., 2015). Moreover, the combination of graphene QDs and the MOF(Ti) composite has not yet been extensively explored for textile dye degradation. This novel composite is anticipated to offer enhanced electron mobility, broader light absorption, and more efficient generation of reactive oxygen species, all of which are expected to significantly accelerate and improve the degradation of MB dye.

The work aimed to demonstrate the fabrication of low cost optofluidic microreactor with graphene QDs@MOF(Ti) photocatalyst decorated microchannel for effectively degrading MB dye. The intricate porosity of the MOF(Ti) serves as a crucial facilitator, augmenting the dispersion and stability of graphene QDs, thereby supporting their effectiveness throughout the degradation process. Moreover, the integration of graphene QDs enhances the efficient transfer of photogenerated electrons (e^-), thereby amplifying the composite's degradation capabilities. These advancements in the features of the graphene QDs@MOF(Ti) nanocomposite substantiate their demonstrated superiority in degradation efficiency.

7.3.2 Experimental Section

Citric acid ($C_6H_8O_7$), 2-Aminoterephthalic acid (NH_2 -BDC; $C_8H_7NO_4$); dimethylformamide (DMF; C_3H_7NO), methanol (CH_3OH), titanium butoxide ($C_{16}H_{36}O_4Ti$) and sodium hydroxide (NaOH), Slygard 184 and curing agent were procured from Sigma Aldrich. All solutions were prepared in DI water with a high purity of 18.2 M Ω -cm.

(a) Fabrication of Microreactor

The continuous flow microreactor was fabricated on PDMS using double replication technique. Initially, the acrylic sheet (thickness: 4 cm) is ultrasonically clean using DI water. Subsequently, the design was precisely patterned on the acrylic sheet (master mold) using a laser micromachining technique. The pattern was then transferred to the PDMS. To achieve this, Slygard 184 and curing agent were mix in 10:1 and pour on the pattern acrylic sheet (Sheshkar et al., 2022). Followed by degassing in vacuum desiccator to remove trap air bubble and finally curing at 50°C for 3 hours. After curing, the PDMS was carefully peel off from the acrylic master, serving as a negative master for the subsequent PDMS double replication process. The PDMS negative master was then coated with a 10 nm of gold NPs, which acts as an anti-adhesive surface for the second PDMS mixture. Following the pouring of PDMS mixture, the mold was then cured at 50°C for 3 hours. Once cured, the positive PDMS pattern was peeled off and thermally bonded to a glass slide. Lastly, inlet and outlet holes are punched using a plunger, and tubes are attached to finalize the microreactor's assembly.

(b) Synthesis of MOF(Ti)

The MOF(Ti) was synthesized through a solvothermal reaction. The process commenced with the ultrasonication of 6mM $C_8H_7NO_4$ in a mixture of C_3H_7NO and CH_3OH , each 3.5 mL. Subsequently, 1.5 mM (0.5 mL) of $C_{16}H_{36}O_4Ti$ was mixed with the prepared solution and further ultrasonicated for 5 min. The resulting solution was then shifted to a Teflon-lined autoclave and subjected to a 16 hours reaction at 150°C, resulting in the formation of a yellowish precipitate. Post-reaction, the resulting precipitate was centrifuged and washed with C_3H_7NO to remove any unreacted organic ligands, followed by additional washing with CH_3OH . Finally, the product was dried under vacuum conditions to obtained MOF(Ti) powder (see Figure 7.18).

(c) Synthesis of Graphene QDs

The graphene QDs was synthesized through a direct pyrolysis method using citric acid. The procedure involved adding 2 g of $C_6H_8O_7$ into a 200 mL beaker. The beaker was then heated to 200°C, to start the process of liquification of $C_6H_8O_7$, which gradually turned to yellowish color over a 5 min. After 35 min of heating, an orange hue emerged, indicating the formation of

graphene QDs. Subsequently, the resulting orange liquid, containing graphene QDs, was carefully added drop by drop into a vigorously stirred solution of 10 μ M NaOH. Following pH adjustment to 8 using NaOH, the graphene QDs solution underwent dialysis in a 1k Da dialysis bag for 24 hours, with dialysate replacement every 8 hours, to eliminate residual chemicals. The purified solution of graphene QDs was then freeze dried for 24 hours.

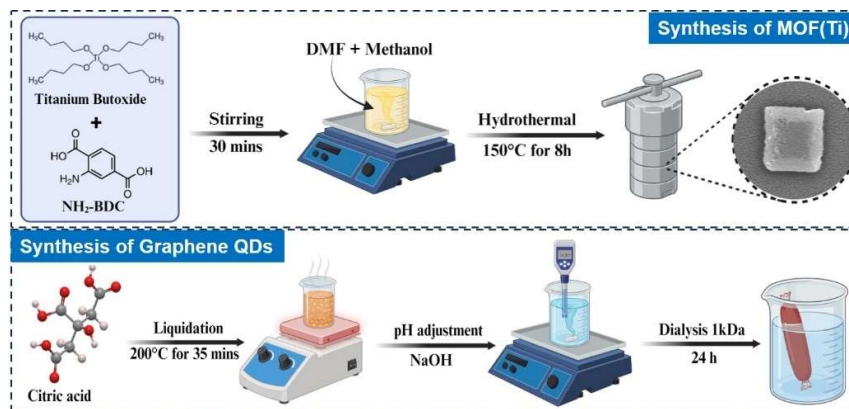


Figure 7.18: Schematic image for the synthesis of MOF(Ti) and graphene QDs

(d) Preparation of graphene QDs@MOF (Ti) photocatalyst

The graphene QDs@MOF(Ti) composite was prepared in two steps. First, 15 mg of MOF(Ti) powder is dissolved in DI water in two containers separately. Then, 2 mL and 4 mL of graphene QDs solution (0.2 mg/mL in DI) are added to the respective containers. The obtained solutions undergo 12 hours of ultrasonication, after which they are centrifuged and rinsed with DI water. Finally, it was collected after being dried at 80°C for 5 hours to obtain 2-graphene QDs@MOF(Ti) and 4-graphene QDs@MOF(Ti) composites, respectively.

(e) Photocatalysis Experiment

The photocatalytic performance of both MOF(Ti) and graphene QDs@MOF(Ti) was assessed by examining the MB dye degradation. Specifically, 0.01 g of each photocatalyst was dissolved separately in acetone. These photocatalyst solutions were then passed through the microchannel at a rate of 50 μ L min⁻¹ to uniformly coat the interior of the channel at 50°C. Finally, a 100W Xe lamp served as the visible light source for the experiment, positioned at a distance of 15 cm from the microreactor. The schematic view of the final optofluidic microreactor is depicted in the Figure 7.19. For the experiment, a stock solution of 10 μ M MB dye in DI water was prepared and subjected to continuous stirring and left in darkness for 30 min to reach absorption-desorption equilibrium before the start of the experiment under visible light. The degradation efficiency of prepared photocatalysts was evaluated by varying the flow rate of the MB dye solution (500, 200, 150, 100, and 50 μ L min⁻¹) in the microchannel. The treated dye solution is then collected and analyzed in UV-Vis spectrum (400-700 nm) to examine the relative absorbance of MB dye. As per the Beer-Lambert law, which establishes a linear correlation between concentration and absorbance, the normalized absorbance corresponds to the normalized concentration of the MB solution.

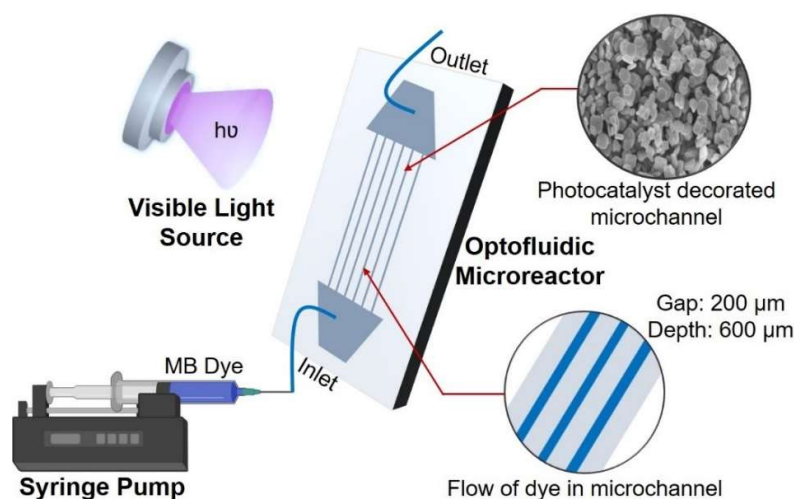


Figure 7.19: Schematic illustration of microreactor

7.3.3 Results and Discussion

(a) Characterization of both MOF(Ti) and graphene QDs@MOF(Ti) Photocatalyst

The morphology of MOF(Ti) was examined using FESEM imaging (see Figure 7.20 (a)). The FESEM images revealed that MOF(Ti) exhibited a truncated square bipyramid shape with an average size of ~ 531 nm. Furthermore, the morphology of graphene QDs, synthesized through the pyrolysis of citric acid, was analyzed using TEM (see Figure 7.20 (b)). Further, the particle size histogram, shown in the inset of Figure 7.20 (b), indicates an average size of 3.985 ± 1.3 nm. The HRTEM depicts distinct lattice fringes characterized by a spacing of ~ 0.24 nm, which corresponds to the (1120) lattice planes of graphene (see Figure 7.20 (c, d)). This observation provides additional evidence supporting the claim that the synthesized QDs exhibit graphene-like characteristics. These lattice fringes are also present in the graphene QDs@MOF(Ti) composite, suggesting that the graphene QDs were successfully integrated into the MOF(Ti) framework.

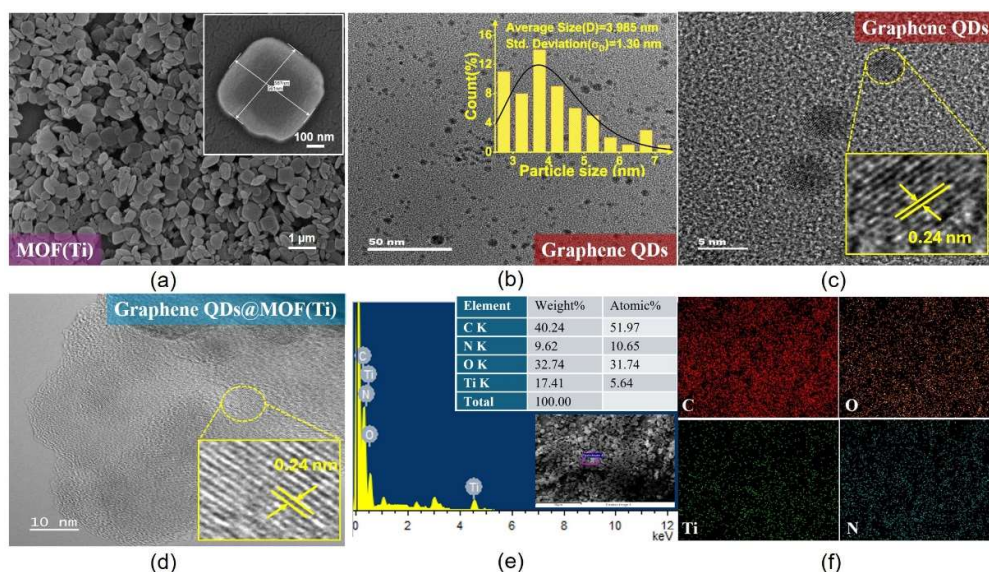


Figure 7.20: (a) FESEM images of MOF(Ti), (b) TEM image of graphene QDs, (c, d) HRTEM images of graphene QDs and graphene QDs@MOF(Ti), (e, f) EDS and elemental mapping of graphene QDs@MOF(Ti)

To confirm the coexistence of graphene QDs with MOF(Ti), EDS and elemental mapping analysis were performed (Figures 7.20 (e, f)). The EDS spectrum and elemental mapping images revealed a homogeneous distribution of carbon (from the graphene QDs) along with Ti, O, and

N within the graphene QDs@MOF(Ti) nanocomposites. The crystalline structures of graphene QDs, MOF(Ti), and graphene QDs@MOF(Ti), were analyzed using XRD, as illustrated in the Figure 7.21 (a). The XRD spectra of MOF(Ti) were found to be consistent with previously reported results, confirming successful synthesis (Fu et al., 2021). Additionally, the XRD spectra of graphene QDs revealed a broad peak, corresponding to the (002) peak, in good agreement with the JCPDS No. 41-1487 (Kumar et al., 2017). In the case of the graphene QDs@MOF(Ti) nanocomposite, the XRD peaks of the MOF shift towards higher 2θ values due to the disturbance in the MOF lattice parameters caused by the QDs. The tensile stress exerted by the graphene QDs on the MOF results in a decrease in the d-spacing of the MOF (Khelifi et al., 2022). Further, the full XPS spectrum, shown in the Figure 7.21 (b), indicates that the primary elements present in both samples are C, N, O, and Ti. This finding is consistent with the results from elemental mapping, confirming the composition. Figure 7.21 (c) shows the C1s spectrum of graphene QDs@MOF(Ti), highlighting three significant peaks at 283.5, 284.9, and 287.7 eV. These peaks correspond to the carbon-containing functional groups within the graphene QDs and MOF(Ti), specifically attributed to C=C, C-N, and C=O bonds, respectively (Shi et al., 2023). Although the C=C peak is observed at 284.9 eV slightly higher than the typical range for C=C bonds (284.4-284.5 eV) this shift can be attributed to the electron interaction between the graphene QDs and the MOF framework. The red shift in the deconvoluted C1s spectrum indicates an increase in electron density in the graphene QDs due to charge transfer from the MOF(Ti). The Ti 2p spectrum in the Figure 7.21 (d) exhibits symmetric peaks at 457.4 and 463.3 eV, corresponding to Ti2p_{3/2} and Ti 2p_{1/2}, respectively (Wang et al., 2015). This indicates the presence of Ti(IV) within the titanium oxygen-cluster (Ti-O). After incorporating graphene QDs into the MOF(Ti), the Ti 2p peaks shift towards higher binding energy, indicating an increase in electron density around the Ti atoms due to the interaction between the GQDs and the MOF(Ti). The deconvoluted O1s XPS spectra of graphene QDs@MOF(Ti), shown in the Figure 7.21 (e), display characteristic peaks at 531.36, 530.28, and 528.76 eV. These peaks correspond to oxygen atoms in the Ti-O, C=O (Qingjuan Wang et al., 2019), and O-H. In the deconvoluted O1s spectra, the Ti-O and O-H peaks exhibit a blue shift, while the C=O peak shows a red shift, further confirming electron redistribution within the graphene QDs@MOF(Ti) composite. Additionally, the N1s spectra, as shown in Figure 7.21 (f), reveals peaks at 397.8 and 401.5 eV, corresponding to N-C=O and N-H groups, respectively. Both peaks exhibit a blue shift after incorporating graphene QDs into the MOF.

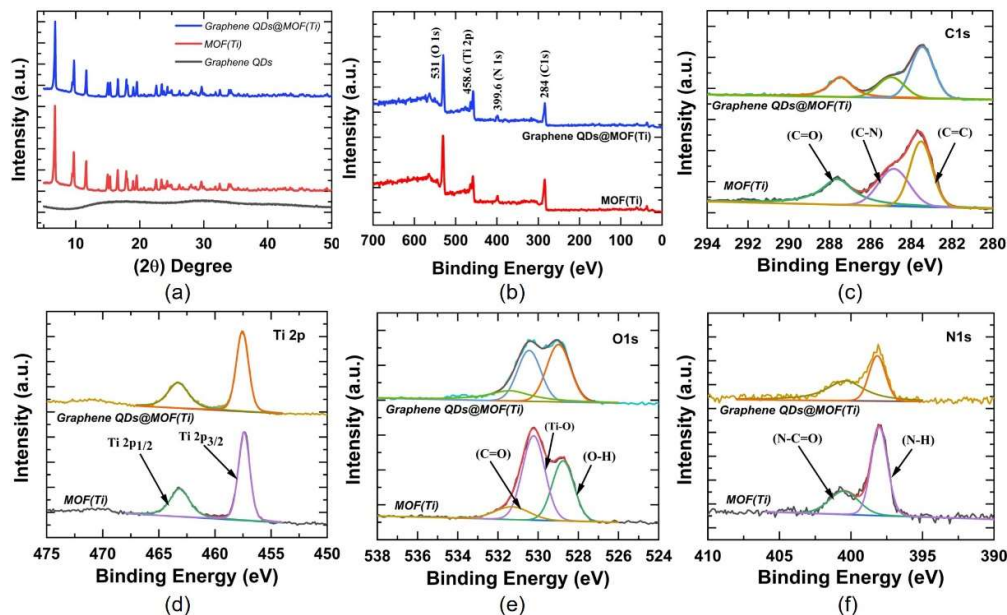


Figure 7.21: (a) XRD and (b-f) XPS spectrum of MOF(Ti) and graphene QDs@MOF(Ti)

The high specific surface area of a catalyst significantly enhances its adsorption and photocatalytic abilities by promoting interfacial reactions and exposing more active sites to

reactants. The N_2 adsorption-desorption isotherm of graphene QDs@MOF(Ti) exhibits a type IV isotherm, indicating its mesoporous nature (Kumar et al., 2017). According to BET study (see Figure 7.22 (a)), the specific surface areas of graphene QDs@MOF(Ti) and MOF(Ti) are 904.8 and 1134.8 $m^2 g^{-1}$, respectively. The notable decrease in the surface area of graphene QDs@MOF(Ti) is accredited to the presence of graphene QDs. Furthermore, Figure 7.22 (b) demonstrates that the pore size distribution of both graphene QDs@MOF(Ti) and MOF(Ti) remains relatively unchanged, predominantly ranging from 2-4 nm. Moreover, Figure 7.22 (c) presents the UV-vis spectra of both MOF(Ti) and graphene QDs@MOF(Ti). The results reveal an absorption peak ~ 400 nm for MOF(Ti). In contrast, graphene QDs@MOF(Ti) exhibits an enhanced response not only in the visible light region but also in the near-infrared region. This improved performance is attributed to the optical absorption properties of the graphene QDs. Furthermore, based on the tauc plot depicted in the Figure 7.22 (d), the bandgaps were determined to be 2.59 eV for MOF(Ti) and 2.52 eV for graphene QDs@MOF(Ti). This suggests that incorporating graphene QDs onto MOF(Ti) effectively reduces its bandgap, thereby extending its light absorption range.

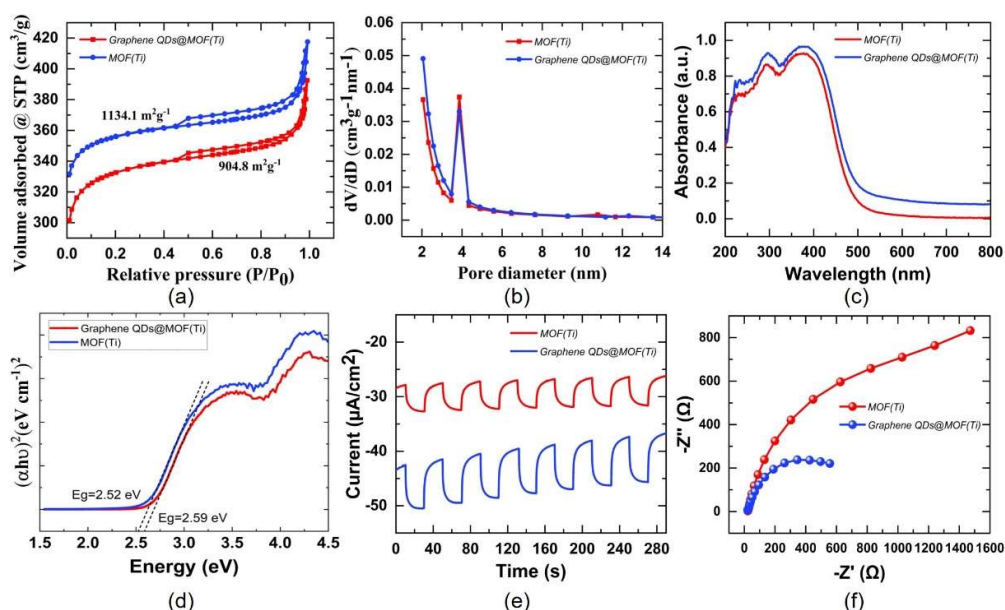


Figure 7.22: (a, b) BET and pore size distribution, (c, d) UV-Vis and tauc plot, (e, f) photocurrent and Nyquist plot for both MOF(Ti) and graphene QDs@MOF(Ti)

The transient photocurrent response and electrochemical impedance spectroscopy (EIS) of graphene QDs@MOF(Ti) based nanocomposite were further analyzed. Figure 7.22 (e) illustrates the photocurrent responses of the photocatalyst electrodes during on-off cycles under visible light irradiation. The graphene QDs@MOF(Ti) composite exhibited a significantly higher photocurrent response compared to MOF(Ti). Additionally, the photocurrent of graphene QDs@MOF(Ti) remained stable at 45 μA after six cycles, which is a 12% increase over MOF(Ti). Several factors contribute to the enhanced photocurrent observed. The integration of conductive graphene QDs with MOF(Ti) reduces the electrical resistance and impedance of the MOF(Ti), thereby accelerating the electron transfer rate and improving electron-hole (e^-/h^+) separation efficiency. Furthermore, the graphene QDs@MOF(Ti) composite demonstrated a substantial increase in light absorption, particularly in the visible light spectrum (Figure 7.22 (c)). The graphene QDs act as mediators for photogenerated charge separation and migration, facilitating the transfer of electrons from the conduction band (CB) of MOF(Ti) to the fluorine-doped tin oxide (FTO) substrate. This process reduces the recombination rate of e^-/h^+ pairs in graphene QDs@MOF(Ti), thereby enhancing the photoelectrochemical performance and resulting in higher photocurrent. To gain deeper insights into the charge transfer resistance and separation efficiency at the photocatalyst-electrolyte interface, EIS measurements were conducted, as shown in Figure

7.22 (f). The semicircle observed in the high-frequency range (10^5 – 10^3 Hz) represents the charge transfer resistance (R_{ct}), indicating the electron transfer between the electrode and the electrolyte. The arc radius of MOF(Ti) is almost indistinguishable, characteristic of electric double-layer capacitor (EDLC) materials. Conversely, the graphene QDs@MOF(Ti) composite exhibits a smaller arc radius than MOF(Ti), confirming more effective e^-/h^+ pair separation and rapid interfacial charge transfer in graphene QDs@MOF(Ti).

(b) Degradation of MB Dye

For comparison, conventional method is used to assess the photocatalytic degradation of both MOF(Ti) and graphene QDs@MOF(Ti). The dye solution was stirred continuously and placed in a dark environment to achieve absorption-desorption equilibrium for 30 min. Following this, visible light was then turned on for the subsequent 60 min. Throughout this period, a volume of 1.25 mL of the MB solution was collected at regular intervals of 10 min to conduct absorption measurements. The spectral images of a gradual reduction in the intensity of the characteristic absorption peak at 663 nm with increasing visible light exposure time. The attenuation of MB dye due to visible light exposure is evident from the inset of Figure 7.23 (a-c). The rate constant (k) was determined as $8.56 \times 10^{-3} \text{ min}^{-1}$, $10.1 \times 10^{-2} \text{ min}^{-1}$ and $12.9 \times 10^{-2} \text{ min}^{-1}$, derived from the slope of the linear plot of $\log(C_0/C)$ versus time for the MOF(Ti), 2- and 4-graphene QDs@MOF(Ti), respectively, which affirmed the adherence to the first-order degradation kinetic model (see Figure 7.22 (d, e)). The experiment revealed that the degradation efficiency of the MOF(Ti) is found to be 70.32%, while the 2- and 4-graphene QDs@MOF(Ti) exhibited an enhanced degradation efficiency of 74.95% and 83.8% respectively, after 60 min of visible light irradiation (see Figure 7.22 (f)).

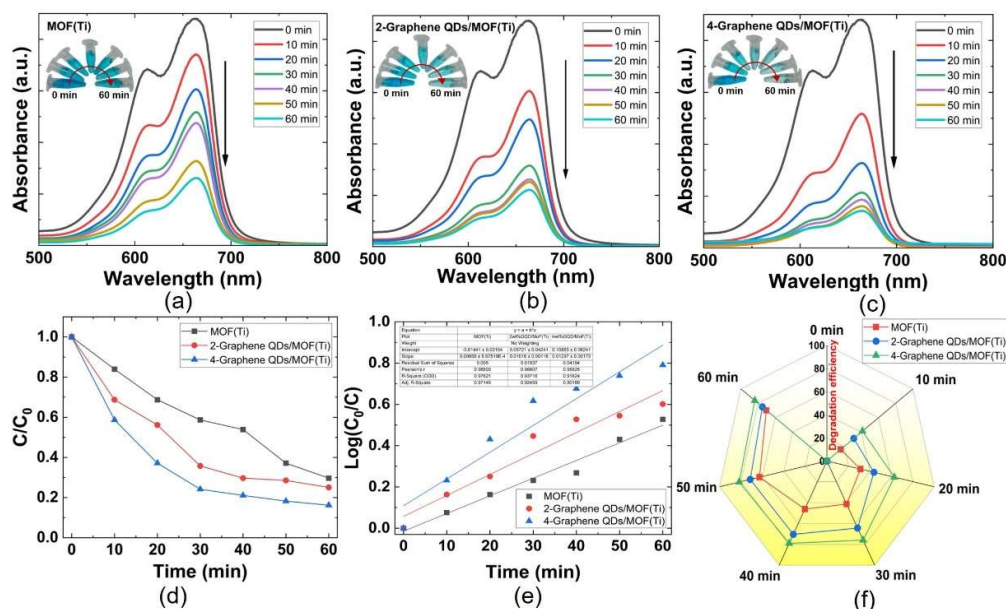


Figure 7.23: (a-c) Degradation of MB dye using conventional beaker method using MOF(Ti), 2-Graphene QDs/MOF(Ti) and 4-Graphene QDs/MOF(Ti), respectively, (d, e) experimental and kinetics study results, and (f) comparative degradation results of MB dye

The efficacy of the photocatalyst in degrading MB dye solutions can be influenced by varying the flow rate and catalyst concentrations (Roy et al., 2022) in the microreactor. Therefore, it is important to investigate the photocatalytic capabilities of both MOF(Ti) and graphene QDs@MOF(Ti) under these situations. The initial experiment involved measuring the photocatalytic activity of MOF(Ti), and 2-graphene QDs@MOF(Ti) under visible light irradiation inside microreactor. This was done at various flow rates using a syringe pump in a continuous flow microchannel. The photocatalytic activity of both photocatalysts was measured by analyzing the absorbance of MB solution exiting the channels. Figure 7.24 (a, b) demonstrates the relative

decrease in MB absorption intensity as flow rates are reduced, indicating a decrease in dye concentration in the solution. The attenuation of MB dye due to visible light exposure at different flow rates is evident from the inset of corresponding Figure 7.24 (a, b). The relative alteration in dye concentration was determined by comparing it with the blank dye concentration using equation 3, as depicted in the Figure 7.24 (e). It is important to note that the MB dye solution flowing through the microchannel exist the microreactor after 8 min at $50 \mu\text{L min}^{-1}$, but it takes a total of 52 min to completely fill 1.25 mL, the minimum volume required to measure the absorption of degraded MB dye. Similarly, all results also encompass the total time taken to collect 1.25 mL at different flow rates. As illustrated in the Figure 7.24 (d), it becomes apparent that a flow rate of $50 \mu\text{L min}^{-1}$ yields optimal degradation of MB dye. This heightened efficiency at a lower flow rate could be ascribed to the prolonged interaction time between the photocatalyst and MB dye. Previous studies have demonstrated similar findings in research focused on contaminant degradation at low flow rates (Eskandarloo and Badiei, 2015; Meng et al., 2013; Shukla et al., 2021). Additionally, it was observed that at higher flow rates ($500 \mu\text{L min}^{-1}$), the MOF (Ti) shows slightly better efficiency compared to the 2-graphene QDs@MOF(Ti) composite. This reduction in the composite's performance may be attributed to higher flow rates causing disturbances in the microreactor, potentially compromising the stability of the composite. Thus the 2-graphene QDs@MOF(Ti) within the microchannel can result in it being washed away with the dye solution, further lowering the degradation efficiency.

The efficiency of the photocatalytic degradation of the reactant heavily relies on the concentration of photocatalyst within the microreactor channel's wall. To quantitatively explore the impact of different concentrations of graphene QDs in MOF(Ti) on dye degradation, a comparative photocatalytic test was conducted (see Figure 7.24 (c)). As shown in the Figure 7.24 (d), under the same operating conditions, the efficiency of MB degradation consistently increased with 4-graphene QDs@MOF(Ti). The shift in the overall conversion efficiency can be attributed to the heightened absorption of photons with higher concentrations of graphene QDs in MOF(Ti). This leads to an increased production of e^-/h^+ pairs, enabling more active participation in the degradation reactions. The experiment revealed that the degradation efficiency is significantly enhanced, reaching 98.76% under visible light irradiation at a $50 \mu\text{L min}^{-1}$ using 4-graphene QDs@MOF(Ti) photocatalyst.

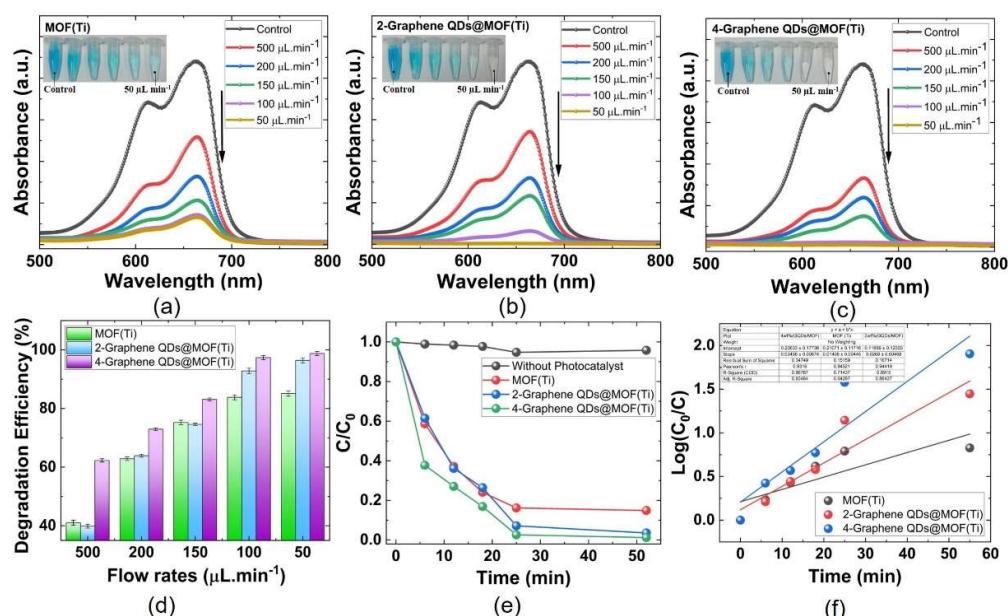


Figure 7.24: UV-Vis spectra for degradation of dye using (a) MOF(Ti), (b) 2-graphene QDs@MOF(Ti), (c) 4-graphene QDs@MOF(Ti) at different flow rate under visible light exposure respectively, (d) comparative analysis of degradation efficiency, (e, f) experimental and kinetics study results for all combination of photocatalyst

The graphene QDs@MOF nanocomposite possess various features that enable them for the proven enhanced degradation efficiency. The abundant active sites present on porous MOF (Ti) surface, along with the graphene QDs, promotes the O_2 absorption capabilities thus enhances the generation of reactive oxygen species. Additionally, the presence of graphene QDs enhances the sufficient transfer of photogenerated e^- , which further magnifies the degradation ability of the composite. Figure 7.25 shows the possible degradation mechanism of MB dye using graphene QDs@MOF composite. Initially, a significant quantity of MB dye molecules is adsorbed onto the surface of the graphene QDs@MOF photocatalyst upon exposure to visible light. Upon this absorption, e^-/h^+ pairs are generated, where the e^- are excited to the CB and thereafter transferred to the graphene QDs, while the h^+ remain in the valence band (VB). This pivotal step significantly enhances the efficiency of the photogenerated e^-/h^+ pairs, thus driving the degradation mechanism forward. Furthermore, the CB potential of the graphene QDs@MOF composite measured at -0.45 V is more negative than the reduction potential of O_2/O_2^- (-0.33 V vs NHE) (Shi et al., 2023; Xia et al., 2017). This favorable energetic arrangement enables the photogenerated e^- residing on the CB of the graphene QDs@MOF composite to effectively react with the O_2 molecules adsorbed on the surface of the composite photocatalyst, leading to the formation of O_2^- . Additionally, it is observed that the VB potential of graphene QDs@MOF, measured at 2.14 V vs NHE, slightly exceeds the oxidation potential of $OH^-/\cdot OH$ (1.99 V vs NHE) (Huang et al., 2021; Yang et al., 2023). Consequently, within the reaction system, the presence of OH^- can undergo oxidation by h^+ to generate $\cdot OH$ (see Equations 7.10 to 7.16).

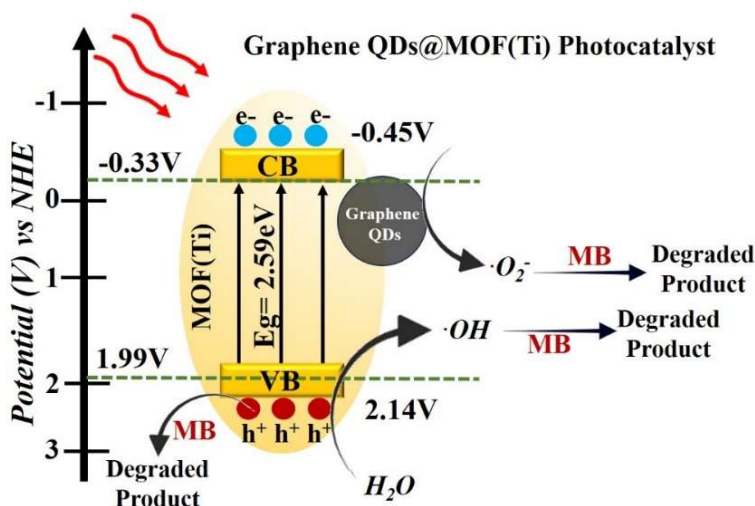
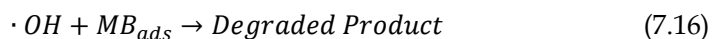
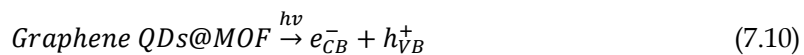


Figure 7.25: The mechanisms of MB dye degradation using graphene QDs@MOF(Ti) composite

The degradation of MB in aqueous phase were also analysed using comparative ^1H NMR spectroscopy. ^1H NMR spectrum of MB and graphene QDs@MOF(Ti) degraded MB solution (at

50 $\mu\text{L min}^{-1}$) are shown in Figure 7.26. The presence of various protons are marked on the structure of MB dye. The ^1H NMR spectra of MB exhibits a sharp singlet signal at δ 3 ppm, corresponding to aliphatic protons (designated as H_a), and three doublet signals between δ 6.7 and δ 7.5 ppm, which are attributed to aromatic protons (H_b - H_d), encompassing six distinct chemical protons. After photocatalytic treatment, the signals in the aromatic region disappear, indicating the loss of aromaticity. Additionally, the sharp peak associated with the 12 methyl protons also vanishes. New peaks emerge in the region, indicating the formation of intermediate products after photocatalytic degradation. This NMR analysis confirms the complete degradation of MB molecules, as evidenced by the disappearance of proton signals in the aromatic regions.

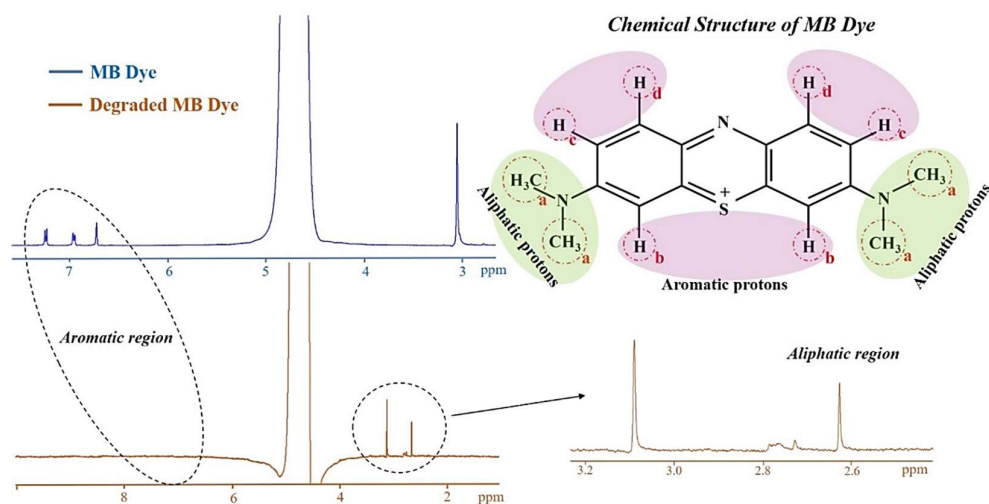


Figure 7.26: Chemical structure and ^1H NMR spectra of MB dye before and after degradation

Moreover, assessing the reusability of the photocatalyst is crucial in determining its recyclability. Therefore, we conducted a thorough examination of 4-graphene QDs@MOF(Ti) by subjecting it to repeated degradation processes within an optofluidic microreactor. With the identical photocatalyst coating maintained within the channels, it's apparent that the initial cycle achieved a degradation efficiency of up to 98.61% at 50 $\mu\text{L min}^{-1}$. However, subsequent cycles witnessed a gradual decline in efficiency, recording at 97.70%, 96.97% and 95.54% for the following three consecutive cycles, respectively. Consequently, even after four cycles, the degradation efficiency of MB remained only marginally reduced. This finding serves as evidence of the superior reusability exhibited by the 4-graphene QDs@MOF(Ti) photocatalyst (see Figure 7.27 (a)). Additionally, the long-term stability of the 4-graphene QDs@MOF(Ti) is examined through experiments conducted over a period of 7 days (see Figure 7.27 (b)). Following the experiments, despite a decrease in degradation efficiency, it still persists at 87.21%, underscoring the admirable stability of the prepared 4-graphene QDs@MOF(Ti) photocatalyst.

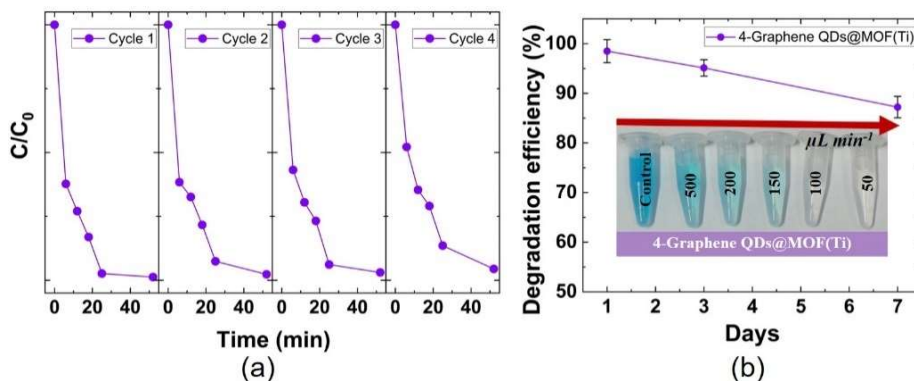


Figure 7.27: (a) repeatability study, (b) long term stability

Table 7.5: A comparison with the previously published composite based on MOF(Ti) for dye degradation

Photocatalyst	Synthesis Route	Method	Light source	Dye	Time	η (%)
MIL-125-NH ₂ @BiVO ₄ (Fu et al., 2022)	Solvothermal method	Beaker method	300W Xe lamp	MB	120 min	97.6
NH ₂ -MIL125(Ti)/ Polysulfone (Ahmadi et al., 2020)	Hydrothermal method	Beaker method	LED floodlight (6W)	MB	300 min	49.2
Ca/TiO ₂ /NH ₂ -MIL-125 (Ahmadpour et al., 2020b)	Solvothermal process	Beaker method	300W Xe lamp	MO	140 min	86.22
7wt% NH ₂ -MIL-125(Ti)/Bi ₂ WO ₆ (Yin et al., 2020)	Hydrothermal method	Beaker method	300W Xe lamp	RhB	120 min	95.85
4-Graphene QDs@MOF(Ti) (This work)	Solvothermal method	Beaker method	100W Xe lamp	MB	60 min	79.42
		Optofluidic microreactor		MB	52 min @ 50 μ L/min	98.61

Table 7.5 summarizes the comparison of previously published works on MOF(Ti) based composites for the degradation of various organic dyes. The comparative results show that the graphene QDs@MOF(Ti) decorated microreactor demonstrates superior efficiency in degrading MB dye compared to other reported MOF based photocatalysts (Ahmadi et al., 2020; Ahmadpour et al., 2020b; Fu et al., 2022; Yin et al., 2020). Additionally, while recent studies have explored other reactors using photocatalysts such as ZnO, ZnS and TiO₂ however, these systems tend to be more expensive to fabricate and exhibit lower degradation efficacy, and requiring more time to break down dyes (Han et al., 2013; H. Kim et al., 2022b; Martin et al., 2022; Prakash et al., 2020; Satuf et al., 2019). Thus the fabricated graphene QDs@MOF(Ti) decorated microreactors used in this study offer a high S/V ratio, and uniform light distribution to the photocatalyst resulting in significantly improved photocatalytic degradation performance for MB dye.

7.3.4 Summary

This study presents a cost-effective method for fabricating an optofluidic microreactor, featuring graphene QDs@MOF(Ti) photocatalyst decoration within the channels for MB dye degradation. Additionally, the presence of graphene QDs enhances the sufficient transfer of photogenerated e⁻, which further magnifies the degradation ability of the composite. The direct integration of graphene QDs@MOF(Ti) into the microchannels ensures intimate contact with the MB dye solutions, minimizing interaction time and maximizing purification efficacy of 98.61% under visible light exposure at a flow rate of 50 μ L min⁻¹. Moreover, the optofluidic microreactor showcases prolonged stability of the photocatalyst, enabling its repeated use without significant efficiency decline. These advancements underscore the superior degradation efficiency of the graphene QDs@MOF(Ti) nanocomposite, validating its remarkable potential for practical applications.

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