

## Development of PCL/PEG/TiO<sub>2</sub> Composite Membranes for Mitigation of Harmful Algal Blooms: A Preliminary Insight

(Pembangunan Membran Komposit PCL/PEG/TiO<sub>2</sub> untuk Mitigasi Ledakan Alga Berbahaya: Suatu Pandangan Awal)

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### ABSTRACT

Harmful algal blooms (HABs) have emerged as a significant environmental issue, threatening aquatic biodiversity, human health, and economic stability. Conventional mitigation methods, such as chemical, physical, and biological treatments, present several drawbacks, including secondary pollutants and ecological disruption. Photocatalytic degradation using titanium dioxide (TiO<sub>2</sub>) nanoparticles offers a promising alternative due to its oxidative capability and stability. However, TiO<sub>2</sub> nanoparticles often agglomerate, reducing effectiveness and complicating recovery. To overcome this, immobilizing TiO<sub>2</sub> nanoparticles onto polymeric supports has gained attention. In response to these challenges, this study developed a novel composite membrane by immobilizing TiO<sub>2</sub> nanoparticles onto a biodegradable polymeric matrix composed of polycaprolactone (PCL) blended with polyethylene glycol (PEG). The composite membranes were fabricated using a modified phase inversion method, and different molecular weights of PCL were evaluated to identify the optimal formulation. The results demonstrated that incorporating PEG significantly improved membrane hydrophilicity, surface porosity, and overall functional performance, enabling effective interaction with algal cells. FTIR analysis confirmed the successful integration of TiO<sub>2</sub> and PEG, maintaining structural integrity. TGA indicated enhanced thermal stability with increasing TiO<sub>2</sub> content, highlighting the contribution of inorganic filler to improved thermal resistance. The optimized PCL/PEG/TiO<sub>2</sub> composite membrane formulation (1:0.2:0.2 ratio) exhibited superior mechanical stability and maintained structural coherence during application. This novel approach provides an environmentally sustainable and efficient solution for HAB management in eutrophic water bodies.

Keywords: Harmful algal bloom; polycaprolactone; polyethylene glycol; titanium dioxide

### ABSTRAK

Ledakan alga berbahaya (HABs) telah berkembang menjadi isu alam sekitar yang signifikan, mengancam kepelbagaian biologi akuatik, kesihatan manusia dan kestabilan ekonomi. Kaedah mitigasi konvensional seperti rawatan kimia, fizikal dan biologi mempunyai beberapa kelemahan, termasuk penghasilan pencemar sekunder dan gangguan ekologi. Degradasi fotokatalitik menggunakan nano zarah titanium dioksida (TiO<sub>2</sub>) menawarkan alternatif yang berpotensi kerana keupayaan pengoksidaannya dan kestabilan yang tinggi. Walau bagaimanapun, nano zarah TiO<sub>2</sub> sering mengalami pengaglomeratan yang mengurangkan keberkesannya dan menyukarkan proses pemulihan. Untuk mengatasi masalah ini, teknik pengimobilisasian nano zarah TiO<sub>2</sub> pada penyokong polimerik telah mendapat perhatian. Sebagai tindak balas kepada cabaran ini, kajian ini telah membangunkan membran komposit baharu dengan mengimobilisasikan nano zarah TiO<sub>2</sub> pada matriks polimer biodegradasi yang terdiri daripada campuran poli(kaprolakton) (PCL) dan polietilena glikol (PEG). Membran komposit ini telah difabrikasi menggunakan kaedah inversi fasa yang diubah suai dan pelbagai berat molekul PCL telah dinilai bagi mengenal pasti formulasi yang optimum. Hasil kajian menunjukkan bahawa penambahan PEG telah meningkatkan sifat hidrofilik, keporosan permukaan dan prestasi fungsi keseluruhan membran, membolehkan interaksi yang lebih berkesan dengan sel alga. Analisis FTIR mengesahkan integrasi TiO<sub>2</sub> dan PEG tanpa mengganggu integriti struktur. Analisis TGA pula menunjukkan peningkatan kestabilan terma seiring dengan peningkatan kandungan TiO<sub>2</sub>, membuktikan sumbangan pengisi inorganik terhadap rintangan haba yang lebih baik. Formulasi membran komposit PCL/PEG/TiO<sub>2</sub> yang dioptimumkan pada nisbah 1:0.2:0.2 menunjukkan kestabilan mekanikal yang tinggi dan mengekalkan koherensi struktur semasa aplikasi. Pendekatan inovatif ini menyediakan penyelesaian lestari dari segi alam sekitar dan berkesan untuk pengurusan HAB dalam persekitaran air eutrofik.

Kata kunci: Ledakan alga berbahaya; polietilena glikol; polikaprolakton; titanium dioksida

## INTRODUCTION

Harmful algal blooms (HABs) have become an escalating environmental challenge across freshwater and marine ecosystems worldwide. Characterized by the rapid proliferation of toxin-producing algal species, HABs severely degrade water quality, diminish aquatic biodiversity, disrupt fisheries and aquaculture industries, and pose serious health risks to both humans and animals (Anderson et al. 2021; Paerl & Otten 2016). The toxins released by HABs such as microcystins, saxitoxins, and domoic acid which not only impair aquatic food webs but also contaminate drinking water sources and bioaccumulate in seafood, endangering public health. Furthermore, these blooms contribute to significant economic losses in sectors including tourism, water treatment, and commercial fishing (Sanseverino et al. 2016). In addition to the direct toxicity of algal blooms, their impact on dissolved oxygen levels is a major concern. When algal biomass decays, microbial respiration depletes oxygen, leading to hypoxic or even anoxic conditions that are lethal to aquatic organisms (Wurtsbaugh, Paerl & Dodds 2019).

Conventional techniques to mitigate HABs include chemical treatments (algaecides), physical methods (ultrasonication and UV irradiation), and biological controls (algicidal bacteria). While these methods have shown effectiveness in specific contexts, their broader application is often limited by several drawbacks, including high energy consumption, operational complexity, generation of harmful by-products, and lack of selectivity (Brenckman et al. 2025; Tripathy et al. 2021). Moreover, chemical and biological approaches can introduce secondary pollutants or disrupt non-target organisms, raising concerns over ecological safety.

Photocatalytic degradation using titanium dioxide ( $\text{TiO}_2$ ) offers a promising alternative due to its robust oxidative power, chemical stability, low toxicity, and affordability. Upon exposure to ultraviolet (UV) light,  $\text{TiO}_2$  generates electron-hole pairs that react with water and oxygen to form reactive oxygen species (ROS), such as hydroxyl radicals and superoxide anions, which can oxidize and break down a wide range of organic pollutants and microbial contaminants (Chen et al. 2020). This mechanism renders  $\text{TiO}_2$  an effective tool in environmental remediation, including the inactivation of harmful algal cells.

Despite its advantages,  $\text{TiO}_2$  presents practical limitations especially when used in dispersed nanoparticle form,  $\text{TiO}_2$  tends to agglomerate in aqueous solutions, reducing surface reactivity and complicating post-treatment recovery. Free nanoparticles can accumulate in aquatic environments, posing long-term ecological and toxicological risks to aquatic organisms (Rocha, Felix & Farias 2024; Sibiyi et al. 2025). Consequently, immobilization strategies have been developed to address these challenges, with polymeric membranes emerging as a promising support matrix.

To address this, the use of biodegradable polymers, such as polycaprolactone (PCL), has gained increasing attention. PCL is a semi-crystalline, biocompatible, and environmentally friendly polymer with good mechanical properties and slow degradation rates under natural conditions (Emadi et al. 2023). Embedding  $\text{TiO}_2$  into polymeric matrices enables better dispersion of nanoparticles, prevents aggregation, and facilitates easier recovery and reuse of the photocatalyst. Immobilization not only preserves the photocatalytic function of  $\text{TiO}_2$  but also minimizes the release of free nanoparticles, thus reducing environmental risk. Polymers can act as scaffolds that provide mechanical stability and enhance interaction between  $\text{TiO}_2$  and target contaminants.

Although  $\text{TiO}_2$ -embedded membranes have been widely investigated for the degradation of dyes, pharmaceuticals, and other organic pollutants (Ikrari et al. 2024), their potential for mitigating harmful algal blooms remains unexplored. To address this gap, this preliminary study evaluates the initial feasibility and baseline performance of a novel  $\text{TiO}_2$ -PCL composite membrane. Our primary objective was to strictly isolate and evaluate the algal bloom mitigation effects resulting simply from the physical presence of  $\text{TiO}_2$  in the membrane. By establishing this baseline, this research introduces a sustainable, cost-effective platform that combines the high adsorption capacity of PCL with the potential of  $\text{TiO}_2$  for advanced aquatic remediation and the management of eutrophic water bodies.

## MATERIALS AND METHODS

### CHEMICALS

Polycaprolactone ( $\text{PCL}_{14\text{K}}:M_w$  14,000 and  $\text{PCL}_{80\text{K}}:M_w$  80,000) and polyethylene glycol (PEG,  $M_w$  10,000) were purchased from Sigma-Aldrich. Dimethylformamide (DMF), sodium nitrate ( $\text{NaNO}_3$ ), calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), magnesium sulfate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), dipotassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ), monopotassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), sodium chloride ( $\text{NaCl}$ ), and EDTA stock solution were obtained from Merck (USA). All chemicals were used as received without further purification.

### FABRICATION OF PCL/PEG/ $\text{TiO}_2$ MEMBRANE

The fabrication of PCL/PEG/ $\text{TiO}_2$  composite membranes was carried out using a modified phase inversion method based on the procedure reported by Nivedita and Joseph (2020) with modification. Two types of PCL with different molecular weights were used to evaluate their effects on  $\text{TiO}_2$  dispersion and the mechanical stability of the membranes. The specific ratios of each polymer used in the synthesis are detailed in Table 1. Initially,  $\text{TiO}_2$  nanoparticles were dispersed in DMF via ultrasonication. Subsequently, PCL with a molecular weight of 14,000 g/

TABLE 1. Amounts of polymers used for chitosan/TiO<sub>2</sub> and PCL/TiO<sub>2</sub> composite membranes

Types	Amount used (g)		
	PCL	PCL	PEG
PCL/PEG (1:0.2)	1	0.2	-
PCL/PEG/TiO <sub>2</sub> (1:0.2:0.2)	1	0.2	0.2
PCL/PEG/TiO <sub>2</sub> (1:0.2:1)	1	0.2	1

mol (PCL<sub>14K</sub>) was added to the solution and dissolved by heating at 75 °C for 2 h. Once fully dissolved, 0.2 g of PEG was incorporated, and the mixture was stirred until the PEG was completely melted and homogeneously mixed. The resulting polymer solution was cast onto a glass plate and immersed in a water bath to induce phase separation. The same procedure was applied to prepare membranes using PCL with a molecular weight of 80,000 g/mol (PCL<sub>80K</sub>).

#### PCL/PEG/TiO<sub>2</sub> MEMBRANE CHARACTERIZATION

Composite membrane characterization was performed using FTIR, TGA, and SEM. FTIR (PerkinElmer Frontier) was used to confirm the chemical structure and successful incorporation of TiO<sub>2</sub> through the presence of Ti–O stretching vibrations. Spectra were collected from 400 to 4000 cm<sup>-1</sup> using KBr pellets prepared at a 1:20 sample-to-KBr ratio under 10 tons of pressure. Thermal stability and decomposition behavior were assessed using a Shimadzu TGA-50, with temperature ramped from 25 °C to 700 °C at 10 °C/min under a 50 mL/min inert gas flow.

#### SCENEDESMUS GROW CULTURE

Initially, Bold's Basal Medium (BBM) stock solution was prepared. To approximately 900 mL of deionized water (dH<sub>2</sub>O), 10 mL each of sodium nitrate, calcium chloride, magnesium sulfate, dipotassium sulfate, monopotassium sulfate, and sodium chloride were added. Subsequently, 0.05 mL each of EDTA stock, iron stock, boron stock, and Bold's trace element stock were introduced. Distilled water was then added to adjust the total volume to 1 L. The prepared medium was transferred into a borosilicate bottle and sterilized by autoclaving. The procedure continued by autoclaving two 1-L conical flasks. Each flask was filled with 200 mL of BBM and 200 mL of *Scenedesmus* stock culture. Aeration was supplied to both flasks, which were covered with cotton wool and aluminum foil to prevent contamination. The cultures were incubated undisturbed for one week to allow algal growth. Algal cell density was monitored using a hemocytometer.

#### SCENEDESMUS MITIGATION VIA NEWLY DEVELOPED MEMBRANE

The algae mitigation experiment was conducted in sterilized 100 mL beakers, each containing 50 mL of *Scenedesmus* culture. The cultures were maintained under a continuous 24-h light cycle at a stable temperature of approximately 27 °C. Membrane samples of PCL/PEG/TiO<sub>2</sub> were cut into uniform dimensions of 1.5 cm × 1.5 cm and tested in triplicate. A control group without a membrane was included for comparison. The membranes were carefully placed into the beakers containing the *Scenedesmus* culture, as shown in Figure 1.

At designated time intervals, approximately 1 mL of the culture was withdrawn. Prior to each sampling, the beakers were gently swirled to ensure uniform cell distribution. Algal cell concentration (Figure 2) was determined using a hemocytometer under a light microscope at 100× magnification.

For each replicate, two 1 mL aliquots were counted, and the mean value was used. The removal efficiency (RE) of each membrane in mitigating algal growth was calculated using Equation (1).

$$RE (\%) = 1 - \left( \frac{\text{Number of final cells in test}}{\text{Number of cells in control}} \right) \times 100\% \quad (1)$$

#### RESULTS AND DISCUSSION

##### PCL/PEG/TiO<sub>2</sub> MEMBRANE PREPARATION

The fabrication of PCL/PEG/TiO<sub>2</sub> composite membranes was investigated using different polymer molecular weights and TiO<sub>2</sub> loadings. Initially, low molecular weight PCL<sub>14K</sub> was tested with varying TiO<sub>2</sub> ratios. At a 1:1 ratio (PCL:TiO<sub>2</sub>), using the phase inversion method, the membrane failed to form as the polymer solution dispersed upon immersion in the water bath. An alternative approach using solvent evaporation at room temperature also proved unsuccessful, resulting in a brittle, powder-like material rather than a coherent membrane. Reducing the TiO<sub>2</sub> content to 1:0.2 improved dispersibility but still resulted

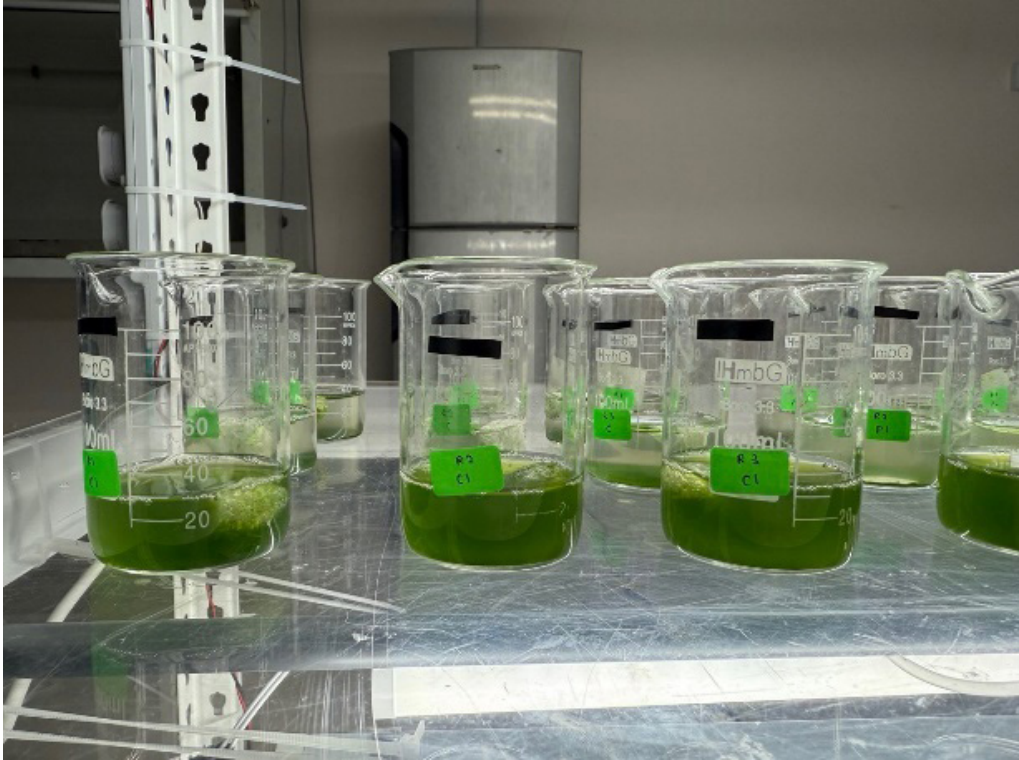


FIGURE 1. 100 mL beakers that contain 50 mL of *Scenedesmus* culture with the composite membranes

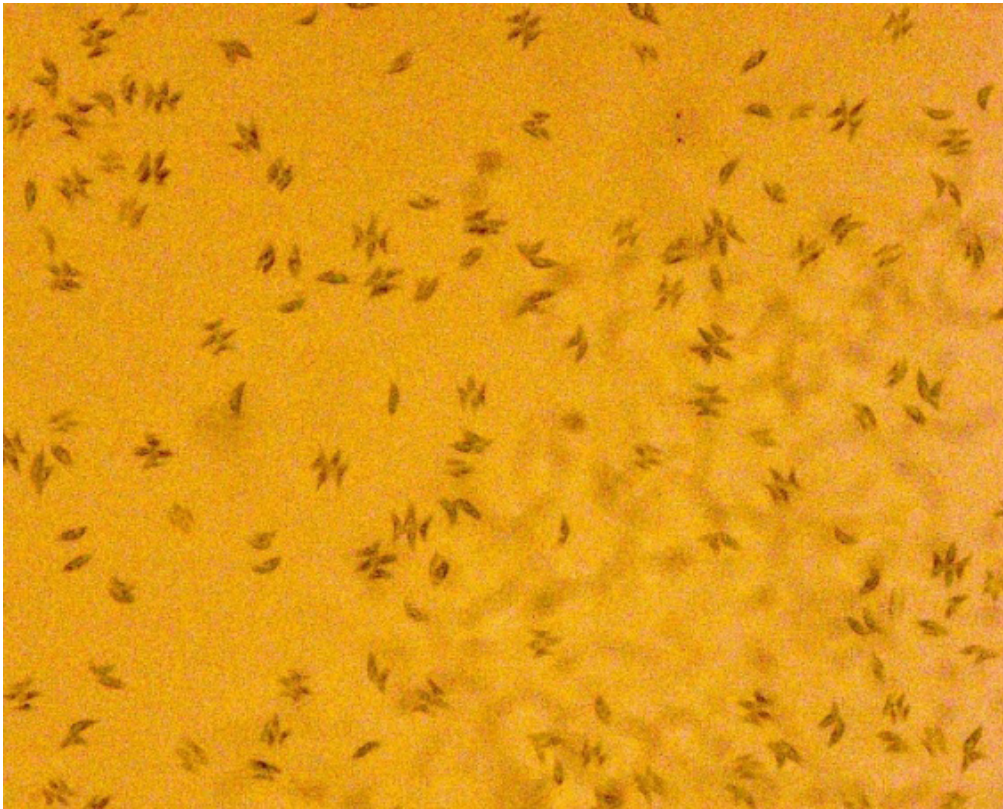


FIGURE 2. *Scenedesmus* microalgae under light microscope at 100x magnification

in a fragile, cracked membrane. These results suggest that  $\text{TiO}_2$  content alone was not the primary factor affecting membrane formation.

In contrast, high molecular weight  $\text{PCL}_{80\text{K}}$  exhibited significantly improved membrane-forming properties. A control sample with no  $\text{TiO}_2$  successfully formed a robust membrane. When  $\text{TiO}_2$  was incorporated at a 1:0.2 ratio, the membrane remained stable and intact, demonstrating that higher molecular weight PCL could effectively support  $\text{TiO}_2$  incorporation. According to Shen et al. (2023), low molecular weight PCL lacks sufficient chain entanglement required for forming stable membrane, a critical factor in membrane cohesion and mechanical integrity. High molecular weight PCL offers several advantages for membrane fabrication. The longer polymer chains provide increased chain entanglement, which contributes to greater mechanical strength and elasticity. Additionally, higher molecular weight leads to higher solution viscosity, which is essential for controlled phase separation during the phase inversion process. This prevents premature dispersion of the polymer in the non-solvent bath and promotes the formation of a continuous membrane structure. Collectively, these properties explain the successful formation of  $\text{PCL}_{80\text{K}}$  membranes, while highlighting the limitations of  $\text{PCL}_{14\text{K}}$  for membrane applications. Based on these findings, three  $\text{PCL}_{80\text{K}}$ -based membranes with different  $\text{TiO}_2$  ratios were successfully fabricated using the phase inversion technique, offering mechanically stable and reproducible composite membranes suitable for environmental remediation applications.

To enhance the membrane's hydrophilicity and functional performance for aquatic based applications, polyethylene glycol (PEG) was incorporated as a polymeric additive. PEG improves water absorption capacity by increasing the surface hydrophilicity of PCL membranes, thereby enhancing their interaction with aqueous media which is an important characteristic for algae mitigation applications (Arbade et al. 2020; Xia et al. 2024).

Furthermore, PEG also acts as a pore-forming agent during membrane fabrication, promoting a more porous structure. This enhanced porosity facilitates mass transfer and allows for more effective capture and adsorption of algal cells (Xia et al. 2024). The resulting PEG-modified  $\text{PCL}/\text{TiO}_2$  membranes are thus expected to offer improved performance in environmental applications by combining mechanical robustness, water compatibility, and enhanced algae removal efficiency.

#### PCL/PEG/ $\text{TiO}_2$ MEMBRANE CHARACTERIZATION

The FTIR spectra of pure PCL, 1:0.2:0.2 PCL/PEG/ $\text{TiO}_2$ , and 1:0.2:1 PCL/ $\text{TiO}_2$  composite membranes are presented in Figure 4. The PCL spectrum exhibits characteristic absorption bands, including a strong carbonyl ( $\text{C}=\text{O}$ ) stretching vibration at approximately  $1660\text{ cm}^{-1}$ ,  $\text{C}-\text{H}$  stretching vibrations near  $2935\text{ cm}^{-1}$ , and  $\text{C}-\text{H}$  bending vibrations around  $1390\text{ cm}^{-1}$ . Additionally, the bands at  $1255\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  correspond to  $\text{C}-\text{O}$  and  $\text{C}-\text{C}$  stretching vibrations, which are associated with the amorphous and crystalline regions of the PCL polymer chain, respectively (del Ángel-Sánchez et al. 2019). These peaks were observed in all samples, indicating that the structural integrity of PCL was preserved after the incorporation of PEG and  $\text{TiO}_2$ .

The incorporation of  $\text{TiO}_2$  was confirmed by the appearance of a new absorption band in the region of  $414-408\text{ cm}^{-1}$ , attributed to the  $\text{Ti}-\text{O}$  stretching vibration (Plermjai et al. 2019). This peak becomes more pronounced with increasing  $\text{TiO}_2$  content, indicating successful integration and improved dispersion of  $\text{TiO}_2$  nanoparticles within the polymer matrix. The presence of  $\text{TiO}_2$  may also cause slight shifts or changes in peak intensities, reflecting interactions between the inorganic filler and polymeric chains.

Polyethylene glycol (PEG), included at a fixed ratio in all composite membranes, is known for its hydrophilicity and plasticizing effect. Although PEG has

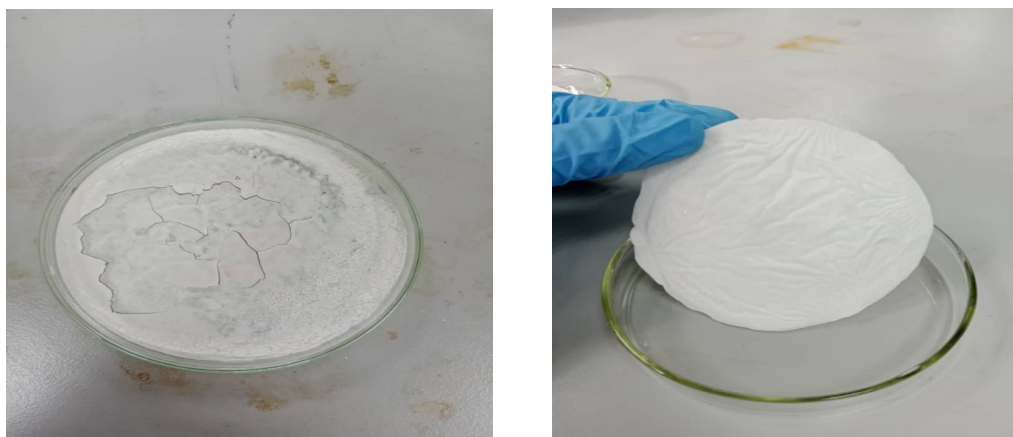


FIGURE 3. PCL/PEG/ $\text{TiO}_2$  (1:0.2:0.2) using (a)  $\text{PCL}_{14\text{K}}$  and (b)  $\text{PCL}_{80\text{K}}$

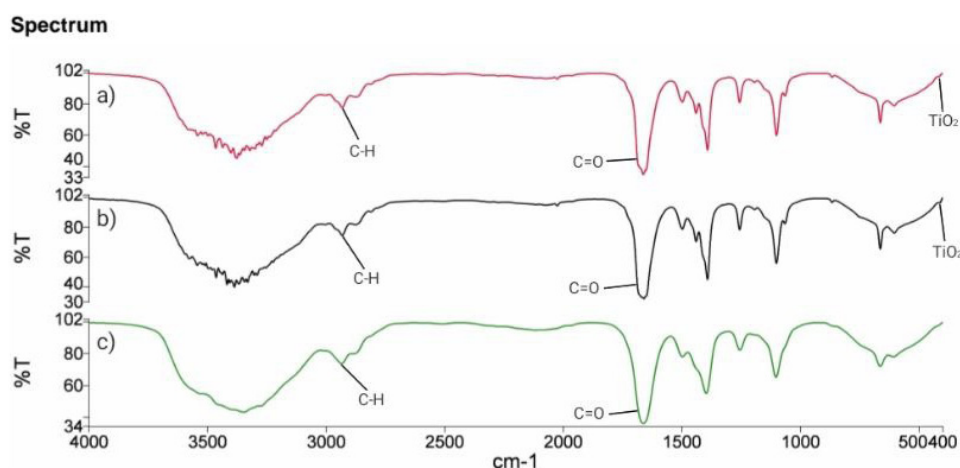


FIGURE 4. FTIR spectra for PCL/PEG/TiO<sub>2</sub> (a) 1:0.2:1 (b) 1:0.2:0.2 and (c) 1:0.2:0

overlapping functional groups with PCL, such as C–O and –OH stretching vibrations, its presence may cause subtle broadening or intensity changes in the region of 3300–3500 cm<sup>-1</sup> due to –OH stretching, and in the fingerprint region (~1050–1150 cm<sup>-1</sup>), where ether linkages are observed (Guastaferrero et al. 2022). The integration of PEG can increase segmental mobility and facilitate the formation of more porous membrane structures, enhancing water affinity and pollutant interaction. Overall, the FTIR analysis confirms the successful incorporation of both TiO<sub>2</sub> and PEG into the PCL matrix, with retention of the key structural features of each component. The interactions among PCL, PEG, and TiO<sub>2</sub> contribute to the functional performance of the membrane by enhancing hydrophilicity, stability,

Thermogravimetric analysis (TGA) of the PCL/PEG membrane (Figure 5) showed an onset degradation temperature of 400.86 °C and an endset temperature of 426.62 °C, corresponding to a total weight loss of 96.43%. This result aligns with findings reported by Herrera-Kao et al. (2018), who observed that PCL/PEG undergoes a single-step thermal degradation process, with an onset near 300 °C and maximum decomposition temperature around 430 °C. Similarly, Hoidy, Al-Mulla and Al-Janabi (2010) noted that PCL begins to degrade at approximately 224 °C and is fully decomposed by 444 °C. The primary degradation pathway of PCL involves chain scission resulting in the release of volatile products such as methyl pentanoate, carbon dioxide, and water (del Ángel-Sánchez et al. 2019).

The incorporation of titanium dioxide (TiO<sub>2</sub>) into the PCL/PEG matrix resulted in a significant enhancement in thermal stability. The 1:0.2:0.2 PCL/PEG/TiO<sub>2</sub> composite membrane exhibited a reduced weight loss of 77.87%, while the 1:0.2:1 PCL/PEG/TiO<sub>2</sub> membrane showed the lowest weight loss at 70.38%. This progressive reduction in thermal degradation with increasing TiO<sub>2</sub> content indicates that the inorganic filler contributes to the thermal resistance of the composite. TiO<sub>2</sub> nanoparticles are known to act as

effective thermal insulators and can hinder the mobility of polymer chains, thereby delaying decomposition (de S.B. Monteiro & Tavares 2018).

The improved thermal stability is also attributed to the barrier effect of TiO<sub>2</sub>, which limits the diffusion of volatile degradation products and heat transfer within the polymer matrix. Additionally, the possible formation of hydrogen bonds and interfacial interactions between TiO<sub>2</sub> and the polar functional groups in PEG and PCL such as ester carbonyls and ether linkages contribute to increased structural rigidity and reduced chain scission during thermal exposure (Visan et al. 2020). The dispersion of TiO<sub>2</sub> within the matrix may also induce changes in PCL crystallinity, influencing both the melting behavior and degradation kinetics of the composite. PEG, acting as a plasticizer, may initially lower the thermal resistance slightly; however, its compatibility with TiO<sub>2</sub> and ability to facilitate better dispersion offsets this effect in the presence of TiO<sub>2</sub>.

#### ALGA MITIGATION

Algae mitigation performance was evaluated using six different membrane formulations, including control experiments without membranes. Each membrane was tested in triplicate, and *Scenedesmus* microalgae cultivated in Bold's Basal Medium (BBM) served as the target species. Cell counts were taken at 0 min, 30 min, 1 h, 4 h, and 8 h to assess the removal efficiency over time. Additionally, pH measurements of the algal culture were recorded before and after membrane addition. No significant changes in pH were observed, with values remaining between 6.0 and 7.0 throughout the experiment, indicating that the membranes did not significantly alter the acidity or alkalinity of the culture medium.

The removal efficiency of *Scenedesmus* using 1:1, 1:0.2:0.2, and 1:0.2:1 PCL/PEG/TiO<sub>2</sub> composite membranes is presented in Table 2, with the trend illustrated in Figure 6. The PCL/PEG membrane without TiO<sub>2</sub> (1:0) exhibited a moderate algae removal efficiency

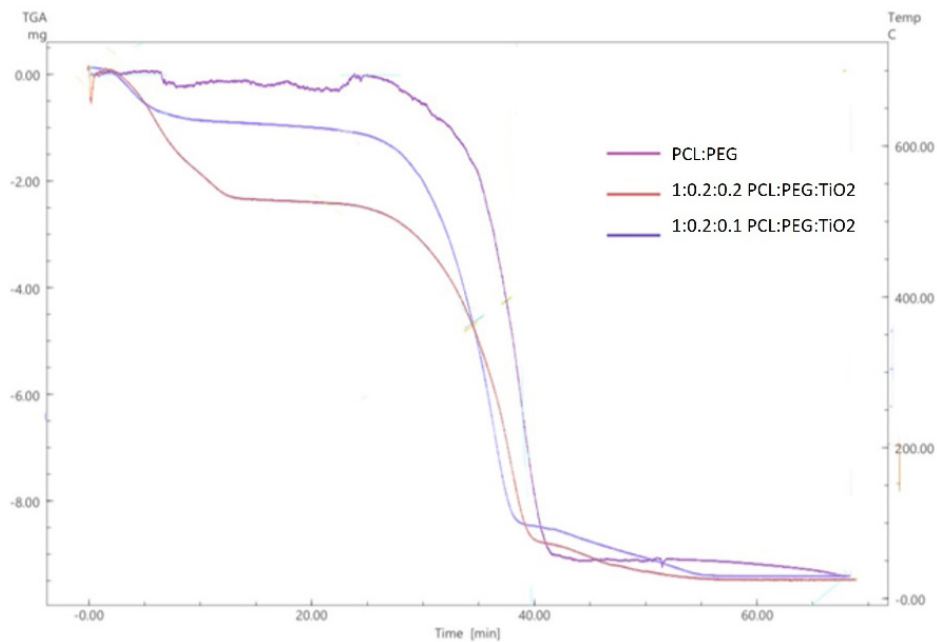


FIGURE 5. Thermal analysis spectra for the developed membrane

TABLE 2. *Scenedesmus* removal efficiency of PCL/TiO<sub>2</sub> composite membranes

Types	Removal efficiency (%)				Average
	30 min	1 h	4 h	8 h	
PCL/PEG	23.43(±0.95)	25.14(±0.72)	42.09(±0.92)	43.31(±0.87)	33.49
PCL/PEG/TiO <sub>2</sub> (1:0.2:0.2)	12.50(±0.86)	32.30(±0.94)	53.23(±0.91)	39.46(±0.72)	34.37
PCL/PEG/TiO <sub>2</sub> (1:0.2:1)	5.27(±0.97)	37.57(±0.87)	52.58(±0.90)	36.22(±0.79)	32.91

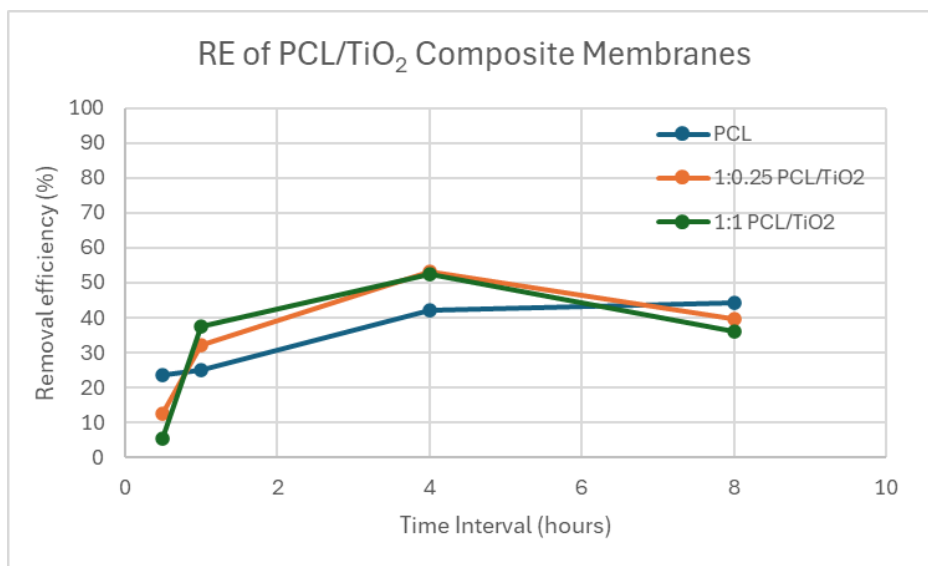


FIGURE 6. *Scenedesmus* removal efficiency of PCL/PEG/TiO<sub>2</sub> composite membranes

of 33.49%, increasing gradually over time. This result suggests that algae removal was primarily driven by physical adsorption, as polycaprolactone (PCL) and polyethylene glycol (PEG) form a semi-crystalline matrix with limited surface reactivity. The addition of PEG improves membrane hydrophilicity and porosity, thereby enhancing surface contact and interaction with algal cells; however, the absence of photocatalytic components limits its degradation capabilities.

Incorporating TiO<sub>2</sub> into the PCL/PEG matrix was expected to improve algae removal efficiency through photocatalytic degradation. The 1:0.2:0.2 PCL/PEG/TiO<sub>2</sub> composite membrane achieved a slightly higher efficiency of 34.37%, indicating a marginal improvement due to the generation of reactive oxygen species (ROS) under ambient light exposure. These ROS, including hydroxyl and superoxide radicals, are capable of disrupting algal cell walls and promoting degradation. However, contrary to expectations, the 1:0.2:1 PCL/PEG/TiO<sub>2</sub> membrane exhibited the lowest removal efficiency at 32.91%. This decrease may be attributed to TiO<sub>2</sub> nanoparticle aggregation at higher loading levels, which reduces the available active surface area and light penetration required for efficient photocatalysis (Ainali et al. 2021). Excessive TiO<sub>2</sub> content can also disrupt membrane homogeneity, negatively affecting porosity and interaction with algal cells. Therefore, the 1:0.2:0.2 membrane likely represents an optimal balance between the photocatalytic activity of TiO<sub>2</sub> and the structural integrity of the PCL/PEG matrix.

To the best of our knowledge, there are currently no published studies that specifically investigate PCL/PEG/TiO<sub>2</sub> composite membranes for algae mitigation. However, Shabuddin et al. (2024) reported algae removal efficiencies of 21.7% and 25.8% for PCL/PMMA and PCL/PEG membranes, respectively, against *Nannochloropsis* after 8 h. Comparatively, the 1:0.2:0.2 PCL/PEG/TiO<sub>2</sub> membrane in this study achieved a higher removal efficiency, suggesting that TiO<sub>2</sub> incorporation enhances performance. This improvement may result from the synergistic effect between TiO<sub>2</sub>'s photocatalytic degradation mechanism and the structural attributes of the PEG-modified PCL membrane, including its porosity and hydrophilicity, which facilitate better algal contact and interaction with reactive sites.

#### CONCLUSION

In conclusion, this preliminary study successfully developed PCL/PEG/TiO<sub>2</sub> composite membranes using a modified phase inversion method to mitigate harmful algal blooms. The incorporation of TiO<sub>2</sub> nanoparticles significantly improved algal removal, although excessive TiO<sub>2</sub> content led to nanoparticle aggregation and a subsequent reduction in membrane performance. Overall, these membranes offer a promising, eco-friendly, and effective baseline approach for managing eutrophic aquatic environments. Future

research will focus on the optimization of TiO<sub>2</sub> content, the integration of UV light exposure to thoroughly evaluate the membrane's photocatalytic degradation capabilities, and detailed morphological analyses to better understand the impact of TiO<sub>2</sub> distribution on algal bloom mitigation.

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