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Development of PCL/PMMA and PCL/PEG Polymeric Film as Potential for Algae Removal

(Pembangunan Filem Polimer PCL/PMMA dan PCL/PEG Berpotensi sebagai Penyingkiran Alga)

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ABSTRACT

Human activities generate excess nutrients that can lead to harmful algal blooms (HABs), which are increasing in number and severity worldwide, causing significant ecological problems and substantial economic losses. Cost-effective polymeric films with ease of operation represent a promising and sustainable alternative to traditional HABs mitigation methods in various aquatic systems. In this study, composite polymer films, specifically polycaprolactone with poly(methyl methacrylate) (PCL/PMMA) and polycaprolactone with polyethylene glycol (PCL/PEG), were employed for algae mitigation. To the best of our knowledge, no prior studies have explored the application of PCL/PMMA and PCL/PEG composite polymer films for algae mitigation. These films were prepared using solvent casting methods. The successfully prepared film ratios were 1:0.2, 1:0.4, and 1:0.6. ATR-FTIR analysis confirmed the successful preparation of PCL/PMMA and PCL/PEG by detecting characteristic functional group peaks corresponding to each pure polymer, suggesting the possibility of non-covalent bond interactions between the polymers in the composites. Thermal analysis (TGA) indicated increased thermal stability for all film ratios. Algae mitigation studies form light microscope analysis showed the presence of algal cells within the composite. Removal efficiency improved with higher ratios of these composite polymer films, with PCL/PMMA outperforming PCL/PEG. Notably, the 1:0.4 PCL/PMMA film exhibited highly efficient algae removal, with interactions between microalgae cells and the film observed within a shorter time. This film achieved the highest removal efficiency of 10.6% within a 15-min interval compared to others. From this preliminary study, the composite polymer films show good potential and promising candidate for mitigating algae-related issues.

Keywords: Harmful algal blooms; mitigation; PCL; PEG; PMMA; polymeric films

ABSTRAK

Nutrien berlebihan hasil aktiviti manusia telah mengakibatkan peningkatan kembangan alga berbahaya (HABs) yang dilihat semakin parah di seluruh dunia. Keadaan ini menyebabkan masalah ekologi yang ketara dan kerugian ekonomi yang besar. Sebagai alternatif kepada kaedah tradisi mitigasi HABs dalam pelbagai sistem akuatik, kajian ini memfokuskan pada penggunaan polimer filem yang kos berkesan dengan kemudahan operasi. Filem polimer komposit, khususnya polikaprolakton dengan poli(metil metakrilat) (PCL/PMMA) dan polikaprolakton dengan polietilena glikol (PCL/PEG), diuji sebagai satu kaedah penyelesaian yang berpotensi dan mampan bagi masalah pertumbuhan alga. Menurut carian kami, kajian dalam mengeksplorasi penggunaan filem polimer komposit PCL/PMMA dan PCL/PEG dalam mitigasi alga masih belum pernah dijalankan. Filem-filem ini telah disediakan melalui kaedah acuan pelarut dengan filem berjaya disiapkan pada nisbah 1:0.2, 1:0.4 dan 1:0.6. Analisis ATR-FTIR telah mengesahkan keberhasilan penyediaan PCL/PMMA dan PCL/PEG dengan kehadiran puncak kumpulan berfungsi yang sepadan dengan setiap polimer tulen dengan ini menunjukkan interaksi ikatan bukan kovalen antara polimer dalam komposit filem yang dihasilkan. Analisis termal (TGA) menunjukkan peningkatan kestabilan termal untuk semua nisbah filem. Kajian mitigasi alga daripada analisis mikroskop cahaya mendedahkan kehadiran sel alga dalam komposit filem. Kecekapan penyingkiran meningkat dengan nisbah filem komposit yang lebih tinggi dengan PCL/PMMA melebihi PCL/PEG. Filem PCL/PMMA, 1:0.4 menunjukkan keberkesanan penyingkiran alga yang tinggi dengan interaksi antara sel mikroalga dan filem berlaku dalam waktu yang lebih singkat. Dalam tempoh 15 minit, filem ini mencapai kecekapan penyingkiran tertinggi sebanyak 10.6% berbanding dengan nisbah lain. Daripada kajian awal ini, dapat disimpulkan bahawa filem polimer komposit memperlihatkan potensi yang besar dalam menangani isu berkaitan dengan pertumbuhan alga dan merupakan calon berkemampuan untuk aplikasi lebih lanjut.

Kata kunci: Filem polimer; mitigasi; PCL; PEG; pertumbuhan alga merbahaya; PMMA

Introduction

Algae serve as the primary producers in various types of water bodies and play a significant role in water pollution through several mechanisms. Enrichments of organic effluents can selectively stimulate the growth of specific algal species, leading to massive surface growths or 'blooms' that contribute to the deterioration of water quality (Sen et al. 2018). Harmful algal blooms (HABs) occur when colonies of algae, which are simple plants inhabiting both saltwater and freshwater environments, proliferate uncontrollably, resulting in toxic or harmful effects not only on aquatic life but also on local ecosystems and human health (Imai, Inaba & Yamamoto 2021).

The deterioration of water quality is becoming increasingly significant, primarily due to harmful algal blooms (HABs). These blooms, known for their toxicity, can lead to fish kills, contaminate seafood sources with toxins, and disrupt ecosystems in ways that humans perceive as harmful (Balaji-Prasath et al. 2022). In addition to their detrimental effects on aquatic ecosystems, this decline in water quality can reduce the availability of potable water for consumption and industrial use (Panagopoulos 2021). The toxicity produced by these phenomena also results in economic damage to the fisheries industry, threats to coastal environments, and adverse effects on human health, especially in relation to the consumption of aquatic and water sources (Belin, Soudant & Amzil 2021).

Mitigation measures involving the removal of algae in wastewater treatment are crucial for addressing environmental concerns, particularly in the context of aquatic ecosystems. Harmful algae can cause extensive damage to the environment, especially to aquatic species, as they rapidly degrade aquatic environments, deplete oxygen, block out sunlight, and create dead zones where no life can thrive. The toxins produced by these algae can lead to a decline in aquatic life, particularly when consumed by fish. Reduced fish production impacts the livelihoods and economic conditions of fish farmers (Ghosh et al. 2021). Therefore, the removal of harmful algae is of paramount importance in protecting the productivity and growth of aquatic life.

According to Cotruvo (2015), conventional wastewater treatment methods such as electromagnetic radiation and chlorine disinfection could effectively remove most algal cells. However, they posed problems in toxin removal, were associated with high costs, and had limited effectiveness since they lacked reactivity towards toxins. The removal of algal cells by filtration before the addition of any oxidant, such as chlorine, had its drawbacks, as the oxidant would lyse the cells and release the toxins into the water (Qi et al. 2021). Traditional wastewater treatment methods, including chemical precipitation, physical adsorption, and ion exchange, have been in used for an extended period (Rajasulochana & Preethy 2016). Finding a cost-effective treatment process capable of removing or limiting algae growth without causing cell damage would be the ideal solution (Chekli et al. 2016). Algae treatment typically uses a prechlorination process with inorganic coagulants to improve treatment of algae-rich water (Ghernaout 2020). However, during algae blooms, increasing chlorine and coagulant dosages not only raises costs but also leads to higher concentrations of chlorinated by-products and residuals in treated water after sedimentation (Niu et al. 2017). Another method to separate algae from the water system is sedimentation, which is done using gravitational force, where algae are separated from a liquid due to differences in their densities (Joh et al. 2011). However, the difference between algae cell and water density is relatively small, making the process rather slow (Joh et al. 2011).

In modern times, organic, inorganic, synthetic, or natural polymer materials with hydrophilic or hydrophobic properties, incorporated into membranes or films, play a crucial role in improving environmental conditions, particularly in wastewater treatment applications (Mansoori et al. 2020). Therefore, polymeric membranes are the primary choice for algae removal in wastewater treatment due to their cost-effectiveness, ease of operation, pore size control, low energy consumption, and their ability to efficiently separate contaminants, yielding high-quality treated water (Sonawane et al. 2021). These excellent characteristics lead them to act as a hosting component for other organic or inorganic components to give a wide scaled applicable composite. A composite film composed of polyether block amide (PEBA) and cyclodextrin (CD) shows promise for algae removal. However, incorporating CD, while necessary to enhance the film's properties, also reduces its cost-effectiveness (Hooman et al. 2021).

In this study, we employed cost-effective solvent casting methods to produce enhanced composite films comprising polycaprolactone (PCL) with poly(methyl methacrylate) (PMMA) and polycaprolactone (PCL) with polyethylene glycol (PEG) for algae removal. To the best of our knowledge, a comprehensive literature search showed no prior investigations into the application of PCL/PMMA and PCL/PEG composite polymer films for algae mitigation. In this preliminary exploration of the potential of newly developed composite films, the choice of PCL, PMMA, and PEG—each having received FDA approval - was guided by their exceptional biocompatibility and biodegradability, rendering them highly suitable for application in wastewater treatment (Naser et al. 2021). These composite polymers exhibit promising properties as synthetic, biocompatible, and biodegradable materials in aqueous environments and interactions with microorganisms. They can be utilized in the production of compostable polymeric materials (Bhagabati 2020).

METHODS

LIST OF CHEMICALS USED

Polycaprolactone (M_n 45,000) (PCL) from Sigma-Aldrich United States, Polyethylene glycol 10000 (PEG) from Sigma-Aldrich United States, Polymethyl methacrylate (PMMA) from Sigma-Aldrich United States, Dichloromethane (DCM) from Merck USA, Deionized (DI) water, *Nannochloropsis* stock culture, Seawater, Conway medium, and 70% ethanol. All chemicals were used as received without further purification.

PREPARATION OF POLYMER FILMS

The fabrication of different ratios of composite PCL/PMMA and PCL/PEG polymer film, respectively, have been prepared by the solvent casting method based from Ibrahim et al. (2022) with some modifications. The amount of each polymer used to synthesize the PCL/PMMA and PCL/PEG composite polymer membranes on different ratios is followed in Table 1.

TABLE 1. Amounts of polymers used for PCL/PMMA and PCL/PEG composite

Ratios	Amount of polymers (g)		
	PCL	PMMA	PEG
1:0.2	0.25	0.05	0.05
1:0.4	0.25	0.10	0.10
1:0.6	0.25	0.15	0.15
1:0.8	0.25	0.20	0.20
1:1	0.25	0.25	0.25

The weighted polymers, in different ratios for each composite polymer's films, were mixed and dissolved in 10 mL of DCM by stirring and heating for 15 min to produce a homogeneous film-forming solution. Subsequently, the film-forming solution was poured into a 60 × 15 mm petri dish. The films were dried in an oven at 50 °C overnight. After being left in the oven overnight, the polymer film was carefully peeled off. All polymer films were then placed in the oven at 50 °C for a few minutes to complete the drying process.

MITIGATION OF *Nannochloropsis* VIA POLYMER FILMS

The mitigation of algae was carried out based on previous study by Ibrahim et al. (2022) using the physical method with some modification. Briefly, in a 100 mL beaker containing 50 mL of the cell culture, placed on a table in static conditions. Each film sample was cut to the same size (diameter 2.5 cm) and put into the reaction medium. Approximately 1 mL of the sample from 2 cm below the solution surface was taken at each specific time interval of 5 min, 15 min, 30 min, 1 h, 4 h, and 8 h. The pH of the control and each culture solution was measured after each time interval. The cells were counted using a hemocytometer under a light microscope at 10× magnification. The effectiveness of the polymer films in mitigating algae removal was determined by the removal efficiency (RE), calculated using Equation (1). All RE data were expressed as the mean ± standard deviation (S.D.).

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

INSTRUMENTATIONS

Fourier transform infrared (FTIR) spectra were recorded with Perkin-Elmer Spectrum 400FTIR/FT-NIR spectrometer. Solid samples were ground with anhydrous potassium bromide (KBr) and compressed into thin pallet. Thermogravimetric TGA/DTG analysis of the synthesized polymers was carried out using Hitachi Simultaneous Thermogravimetric Analyzer (STA 7200). The temperature used is in the range of 30 °C to 600 °C, under nitrogen (N_2) with a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

DEVELOPMENT OF POLYMER FILMS

The preparation of different ratios of PCL/PMMA and PCL/PEG polymer blend films involved the solvent casting method. Dichloromethane (DCM) was used as the solvent to dissolve the PCL/PMMA and PCL/PEG polymer blend, resulting in a homogeneous mixture. The polymer films of PCL/PMMA and PCL/PEG polymer blend with ratios of 1:0.2, 1:0.4, and 1:0.6 were successfully prepared by solvent casting exhibited homogeneous and smooth features. However, the polymer blend films with ratios of 1:0.8 and 1:1 did not form films. Further increasing the PMMA and PEG content in the films was not possible due to decreased compatibility between them and PCL, without the addition of any additives (Li et al. 2013; Pekdemir et al. 2021). The increased content of these polymers rendered them insoluble or incompatible with PCL, disrupting the blending process and preventing the formation of homogeneous films (Pekdemir et al. 2021).

ATR-FTIR spectra is used to investigate the incorporation of PCL into the PMMA and PEG composite polymers. Figures 1 and 2 show the ATR-FTIR absorption spectra of PCL/PMMA and PCL/PEG polymer blend films, respectively. In both figures, the PCL spectrum displays characteristic peaks of C=O stretching vibrations at 1721 cm^{-1}, CH_2 asymmetric stretching at 2925 cm^{-1}, and C-O-C stretching vibrations yield peaks at 1168 cm^{-1}. The bands at 1168 cm^{-1} and 1046 cm^{-1} are assigned to C-O and C-C stretching in the amorphous and crystalline phases, respectively (Elzubair et al. 2006). However, the hydroxyl group (-OH) not detected by FTIR may be due to the low content/concentration of OH end groups as there are only one hydroxyl group per PCL chain (Li et al. 2021).

As shown in Figure 1, there are characteristic three peaks of PMMA that appear which the absorption band at 1142, 1723, and 2995 cm^{-1} are assigned to O—CH_3 stretching, C=O stretching, and C—H asymmetric stretching vibrations in PMMA, respectively. All ratios (1:0.2, 1:0.4, and 1:0.6) of PCL/PMMA composite polymer films have identified bands at about 2945, 2945, and 2948 cm^{-1} which are the C—H stretching bands. Meanwhile, the C=O stretching vibrations at 1722, 1723, and 1722 cm^{-1}. The absorption band of 1159, 1163, and 1148 cm^{-1} represent C—O —CH_3 stretching. Therefore, from the spectrum, it shows good compatibility between PCL and PMMA (Abdelrazek et al. 2016). In Figure 2, the ATR-FTIR spectra of PCL, PEG, and PCL/PEG blends are presented. It is shown one of the PCL absorption bands which is the C=O carbonyl stretching, at around ~1721 cm^{-1} visible homopolymer PCL and the PCL/PEG polymer blend film; 1723, 1723, and 1724 cm^{-1}, respectively. The peak at around ~1095 cm^{-1} is attributed to ether groups for the homopolymer PEG and it is also present in the spectra of PCL/PEG blends; 1104, 1103, and 1102 cm^{-1}, respectively (Mansur, Oréfice & Mansur 2004). Homopolymer PCL has also shown a peak at 2880 cm^{-1} representing C-H asymmetric stretching vibrations. All ratios (1:0.2, 1:0.4, and 1:0.6) of PCL/PEG composite polymer films have C-H stretching bands at about 2942, 2942, and 2943 cm^{-1}. The absorption band of 1169, 1180, and 1175 cm^{-1} represent C-O-CH3 stretching. Thus, the composite of PCL/PMMA and PCL/PEG was successfully prepared as the presence of peaks corresponding to each pure polymer in the blend composition indicates the possibility of non-covalent bond interactions between the polymers in the composites (Douglas et al. 2016; Repanas et al. 2015).

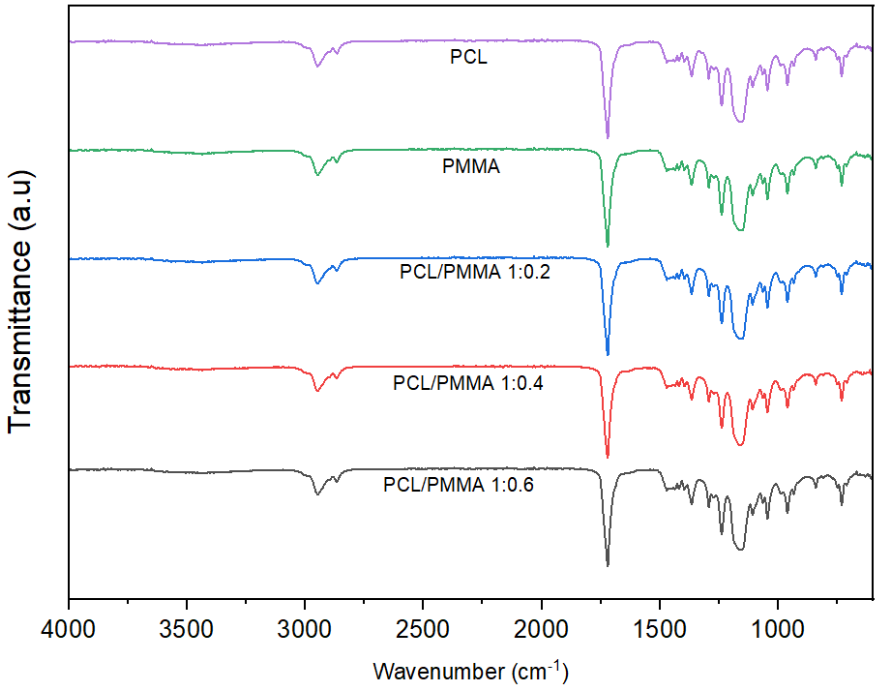

FIGURE 1. ATR-FTIR PCL/PMMA polymer films

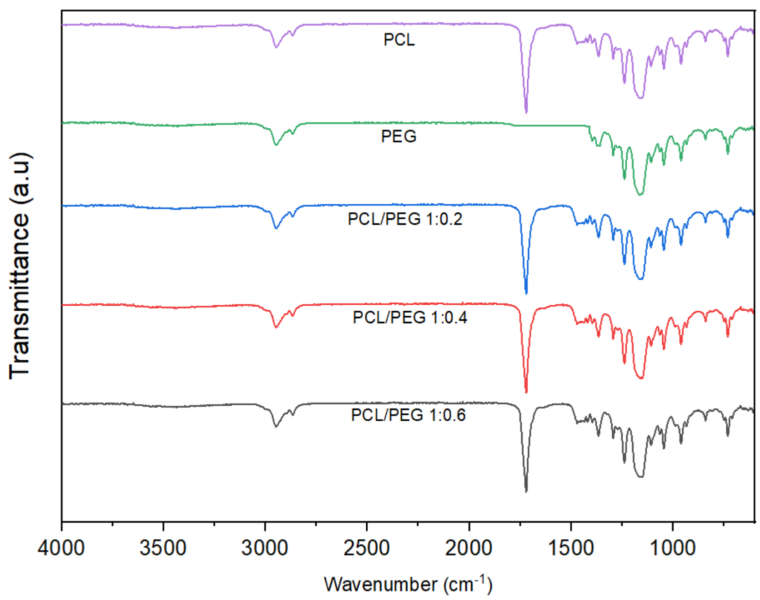

FIGURE 2. ATR-FTIR PCL/PEG polymer films

POLYMER FILMS THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis (TGA) is used to investigate the thermal decomposition of polymer and to determine the order of reaction of the thermal decomposition which can be used to obtain a better understanding of the thermal stability. The characteristic TGA curves of the pure PCL and PMMA and PCL/PMMA of each ratio are shown in Figure 3. The onset decomposition of the homopolymer PCL and PMMA occurred around 340.19–422.83 and 314.47–384.91 °C, respectively. The thermal behavior is attributed to the PCL decomposition of methyl pentanoate, water, and carbon dioxide (Del Ángel-Sánchez et al. 2019). The weight loss of PMMA indicated the degradation of the side groups in the polymeric structure and thermal degradation of the PMMA (Ulu, Köytepe & Ates 2016). It involves homolytic cleavage of the C– C bond β to the vinyl group and random chain scission of the PMMA backbone (Huang et al. 2012). The 1:0.2 PCL/PMMA and 1:0.4 PCL/PMMA have onset decomposition around 372.21-415.89 °C and 340.32-415.92 °C, respectively. The 1:0.6 PCL/PMMA have onset decomposition around 318.04-415.96 °C. The samples started to lose weight due to the moisture evaporation and the solvent evaporated (Abdelrazek et al. 2021). This correspondent to the structural decomposition of polymer blends. PMMA is known to have a higher glass transition temperature (T_g). The addition of PCL to PMMA increases the thermal stability of the blend as the higher T_g of PMMA indicates that it can withstand higher temperatures without undergoing significant softening or degradation (Pekdemir et al. 2021). By incorporating PMMA into the PCL matrix, the thermal stability is improved.

Figure 4 shows the TGA curve of pure PCL and PEG, and PCL/PEG on each ratio. The homopolymer PEG shows onset decomposition around 232.13-325.01 °C. Pardeshi and Mungray (2019) described that the thermal decomposition of simple linear-chain-bond structure PEG is assumed to occur at both -C-O- and -C-C bonds of the backbone chain. The onset decomposition of 1:0.2, 1:0.4, and 1:0.6 PCL/PEG composite are 281.66-376.44, 265.23-456.70, and 318.36-441.81 °C, respectively. Higher ratios contribute to the increase of indicating small but synergistic thermal stability of the combined polymers (Douglas et al. 2016). The addition of PCL to PEG increases the decomposition temperature of the copolymer.

MITIGATION OF *Nannochloropsis* USING NEWLY DEVELOPED FILMS

The prepared polymer blends, PCL/PMMA and PCL/PEG, were used to study their effectiveness in algae removal. The purpose of these studies were to explore the potential application of the polymer blends as materials for mitigating or removing algae. The samples were monitored over time to assess the extent of algae reduction. The cell density of algae before and after the mitigation process was measured to determine the removal efficiency of the polymer blends. The pH of the

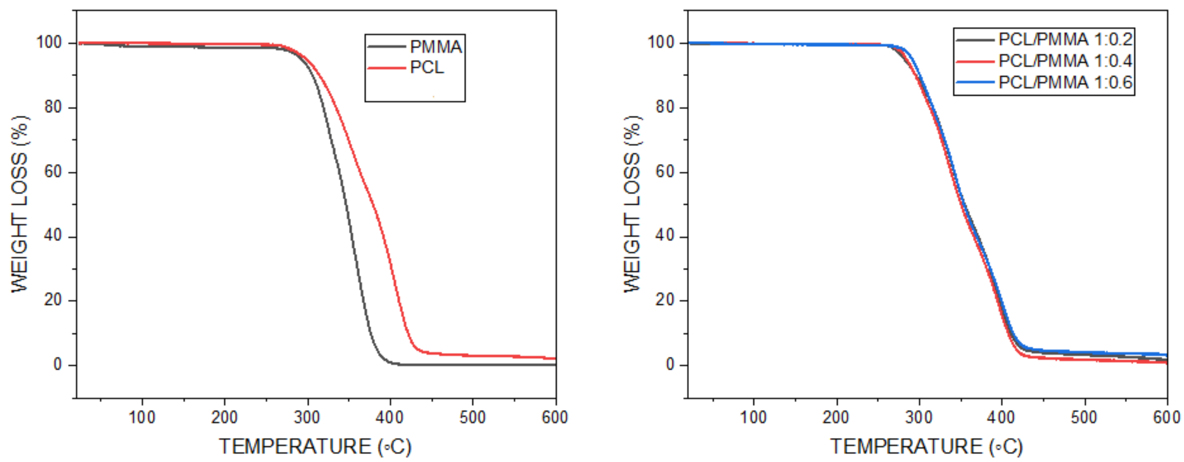

FIGURE 3. TGA curve results (a) pure PCL and PMMA (b) PCL/PMMA

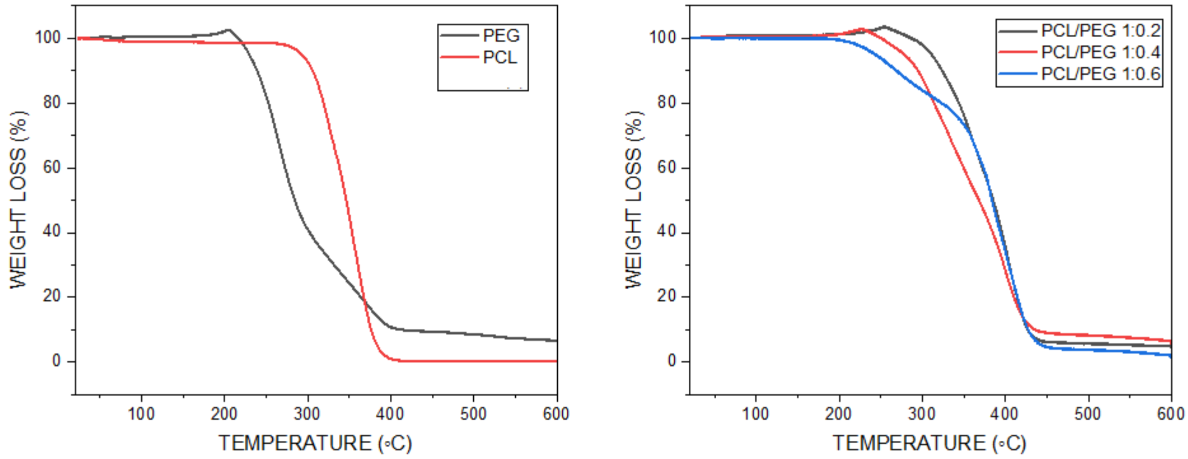

FIGURE 4. TGA curve results (a) pure PCL and PEG (b) PCL/PEG

culture was also measured to determine pH changes before and after the addition of polymer films to the microalgae culture. However, no significant pH changes occurred; the pH remained in the range of 8 to 9, which represents the optimal pH for *Nannochloropsis* microalgae growth (Osama, Hosney & Moussa 2021). The cell density of microalgae used in this study was between 5×10^4 and 13×10^4, as it was considered a suitable cell density for measuring the effectiveness of the polymer film samples in algae removal.

Light microscopy analysis depicts the physical appearance of PCL/PMMA and PCL/PEG before and after their application for algae removal, observed under a light microscope at 10x magnification, as shown in Figures 5 and 6, respectively. In Figure 5(a), the appearance of the blend indicates the formation of a composite between the semicrystalline PCL and the amorphous PMMA, while in Figure 6(a), the physical appearance shows the composite of semicrystalline PCL and PEG (Niu et al. 2014; Pekdemir et al. 2021). In Figures 5(b) and Figure 6(b), we can observe the attachment of algae to the polymer films. Additionally, from the optical images of PCL/PEG polymer films, it is evident that after adding the film to the microalgae culture, the film structure enlarges due to the high water-swelling nature of the PEG hydrophilic polymer matrices (Yang & Zhao 2022). This enlargement is attributed to the high water-swelling property of the PEG hydrophilic polymer matrices present in the film. PEG is known for its hydrophilic nature, which means it has an affinity for water and can absorb significant amounts of it. When the PEG-containing film comes into contact with a microalgae culture, the water present in the culture is absorbed by the PEG matrices within the film. This water absorption causes the PEG polymer matrices to swell, leading to an increase in the size or volume of the film structure.

In addition to light microscopy, this study also involved the observation of the condition of the polymer film samples and the culture after 8 h. The sample sizes of both the 1:0.6 PCL/PMMA and PCL/PEG polymer films decreased over an 8-h period, indicating that this ratio of composite polymer films slowly dissolves in the culture. The increased amount of PMMA in these films leads to a gradual dissolution in seawater (Donell n.d.). Furthermore, the increased amount of PEG in the films contributes to excellent water solubility, resulting in the dissolution of the film during the experiment (Prasopchai et al. 2019). The culture containing the 1:0.6 PCL/PMMA ratio at 8 h showed a green layer at the bottom of the beaker. This green layer indicates algal death, which typically results in a layer of dead cells at the bottom of the culture vessel, despite the slow dissolution of the film (Tang et al. 2018). The green color of the layer is primarily due to the pigments present in the algal cells, such as chlorophyll (Molnar & Gair 2019).

REMOVAL OF *Nannochloropsis* USING PCL/PMMA FILMS

When *Nannochloropsis* cells were introduced, they were observed to interact with the PCL/PMMA films. The removal efficiency (RE) values at various time intervals (5 min, 15 min, 30 min, 1 h, 4 h, and 8 h) for different

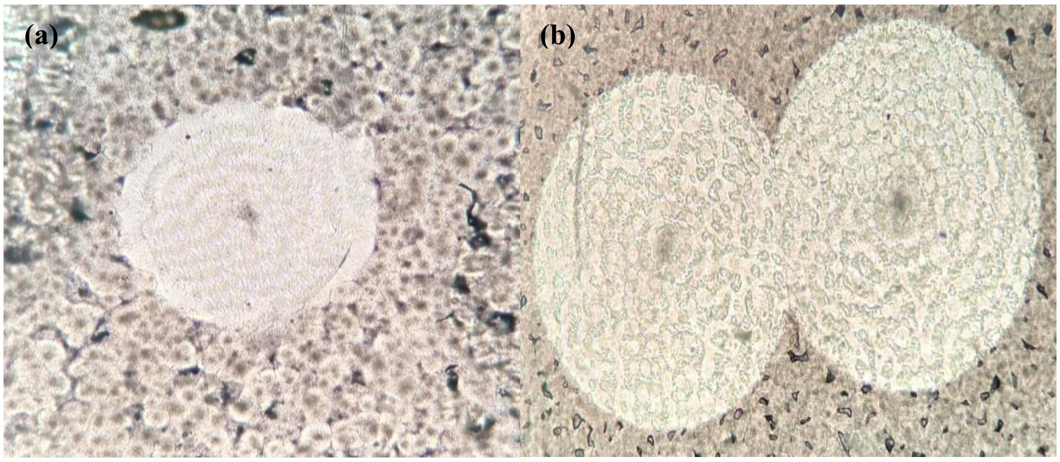

FIGURE 5. PCL/PMMA polymer film physical appearance (a) before and (b) after being added into microalgae culture (Magnification 10x)

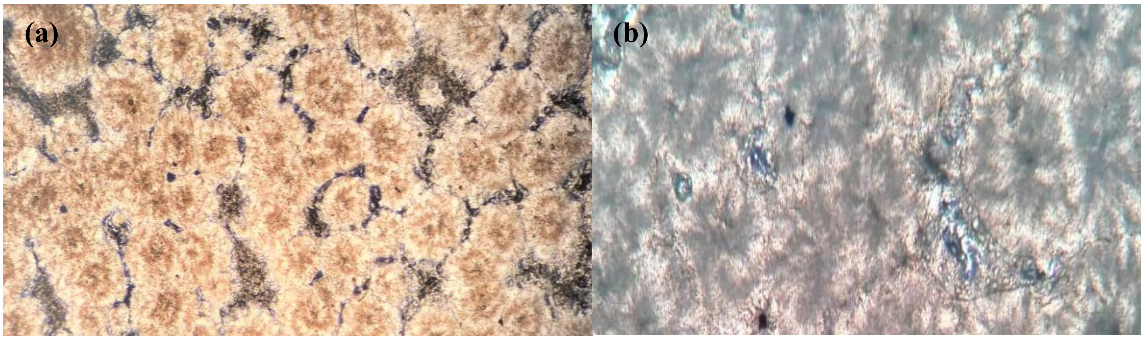

FIGURE 6. PCL/PEG polymer film physical appearance (a) before and (b) after being added into microalgae culture (Magnification 10x)

ratios of composite PCL/PMMA films are displayed in Figure 7. The figure illustrates a gradual increase in RE for each ratio of PCL/PMMA films. The 1:0.2, 1:0.4, and 1:0.6 films exhibited the highest RE values after 8 h, which were 18.9%, 21.7%, and 28.1%, respectively. Notably, the 1:0.6 film achieved the highest RE value at 8 h, reaching 28.1%, surpassing the others, even though the film slowly dissolved in the culture. This exceptional RE value was attributed to the properties of PMMA, which are harmful to algae but not to the marine environment, resulting in algal death (Venâncio et al. 2019).

The 1:0.6 PCL/PMMA polymer film has the best increasing trend of RE with the highest RE values at the most each time interval compared to other ratios. According to Ren et al. (2021), higher amounts of polymer ratios in films blending increase the likelihood of microalgae cell absorption onto the polymers. This increased absorption capability contributes to the higher removal efficiency (RE) of microalgae. Mousavian's research group (2023) also supported this by stating that larger ratios of films provide a greater surface area to which microalgae can attach. Furthermore, the results showed that the PCL/PMMA film with the lowest ratio takes the longest time to remove microalgae, which is 8 h. However, it demonstrates the highest removal efficiency value at 18.9%. This indicates that the film shows interaction with the algae but requires a longer contact time for algae removal. On the other hand, the 1:0.4 PCL/PMMA film, which has a higher ratio, shows highly efficient removal of algae. It exhibits interactions between the microalgae cells and the film in a shorter time, specifically 15 min. Additionally, it demonstrates the highest removal efficiency values within the 15-min time interval, reaching 10.6% compared to other ratios.

REMOVAL OF *Nannochloropsis* USING PCL/PEG FILMS

In Figure 8, the mitigation ability of PCL/PEG films toward algae removal is presented. The results show that the 1:0.2 PCL/PEG film yield negative removal efficiency (RE) values until the 8-h time interval. Similarly, the 1:0.4 PCL/PEG film also exhibited poor algae removal performance, with negative RE values obtained for most of the time intervals, including after 8 h. This is because of cell density increased due to algae culture growth, and few interactions between the algal cells and the films for removal (von Sperling, Verbyla & Oliveira 2020). Both ratios of the PCL/PEG polymer films (1:0.2 and 1:0.4) were found to be inefficient in removing algae. Negative removal efficiency (RE) values were obtained for most of the time intervals, including after 8 h, indicating that the films did not effectively mitigate or remove the algae.

Among the different ratios tested, the 1:0.6 PCL/PEG film demonstrated better removal efficiency, achieving the highest RE value of 14.2% within a short period of 30 min. Furthermore, this film exhibited the highest RE value of 25.8% at the 8-h time interval compared to the other ratios. However, RE values of PCL/PEG films were lower compared to PCL/PMMA films. This difference in performance can be attributed to the hydrophilicity of the PCL/PEG film, which provided fewer interactions between the composite film and the algal cells (Wang et al. 2018).

Therefore, the composite film of PCL/PMMA generally exhibits better algae removal compared to PCL/PEG for each ratio. The PCL/PMMA films consistently show higher removal efficiency (RE) values in most time intervals. The 1:0.4 PCL/PMMA film stands out as a highly efficient film for algae removal, as it demonstrates fast adsorption between the algal cells and the film within 15 min which achieves a high RE value of 10.6%. The 1:0.6 PCL/PMMA film shows a significant increase in RE values with the lengthening of the time interval, reaching the highest value of 28.1% at 8 h, despite the dissolution

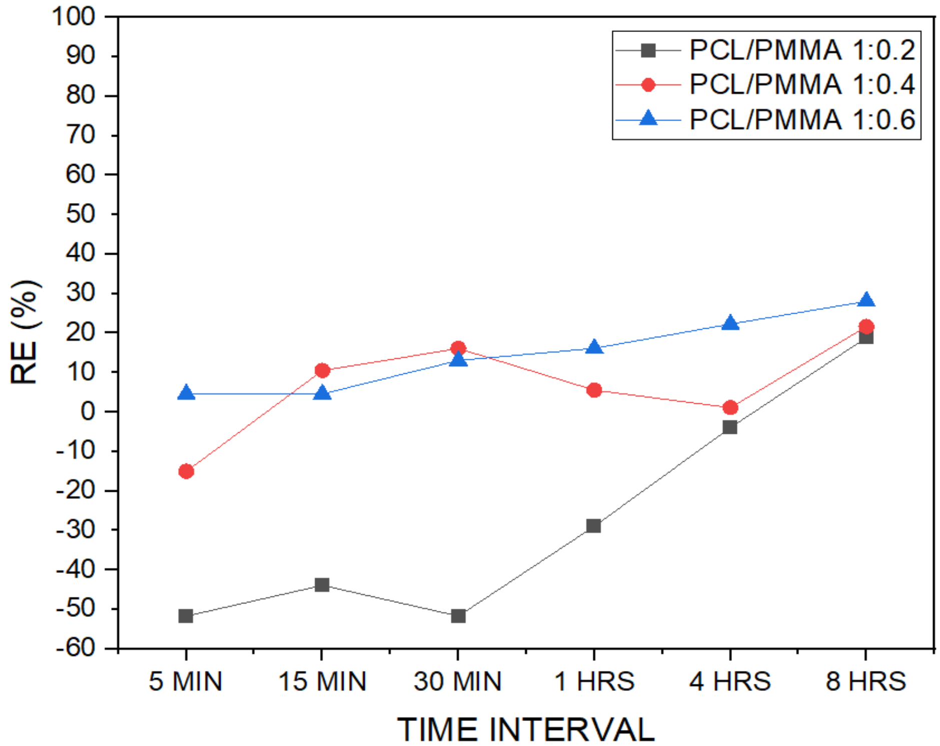

FIGURE 7. *Nannochloropsis* removal efficiency (%) of PCL/PMMA polymer films

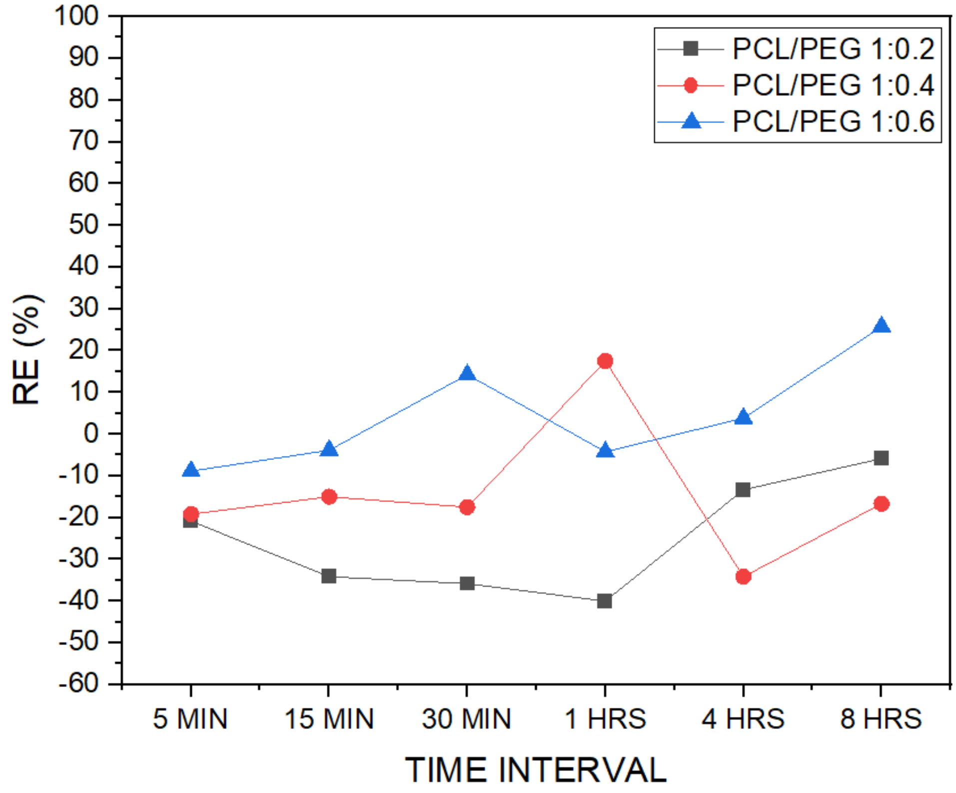

FIGURE 8. *Nannochloropsis* removal efficiency (%) of PCL/PEG polymer films

of the film, as the toxicity of PMMA contributes to the death of algal cells. Larger ratios of PCL/PMMA films enhance the removal efficiency of algae cells, as the film result in more surface area of PCL/PMMA exposed to the algae, thereby enhancing the absorption and trapping of algae within the polymeric film. Overall, increasing the ratios of the PCL/PMMA films demonstrates positive effects in the mitigation application of algae removal.

Conclusion

The analysis of removal efficiency (RE) indicates that higher ratios of films lead to increased RE values. Larger ratios offer more surface area for exposure to algae, thereby enhancing algae absorption. PCL/PMMA exhibits superior algae removal compared to PCL/PEG at each ratio. Despite the dissolution of the 1:0.6 PCL/PMMA film after 8 h, the properties of PMMA results in the death of algal cells, consequently boosting RE values. Therefore, between PCL/PEG and PCL/PMMA, the latter proves to be more suitable as a composite polymer for algae mitigation due to its biocompatibility, biodegradability, and cost-effectiveness. This preliminary study can serve as a foundation for further research on the effectiveness of composite films in mitigating Harmful Algal Blooms (HABs).

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References

Abdelrazek, E.M., Hezma, A.M., El-khodary, A. & Elzayat, A.M. 2016. Spectroscopic studies and thermal properties of PCL/PMMA biopolymer blend. *Egyptian Journal of Basic and Applied Sciences* 3(1): 10-15. https://doi.org/10.1016/j.ejbas.2015.06.001

Balaji-Prasath, B., Wang, Y., Su, Y.P., Hamilton, D.P., Lin, H., Zheng, L. & Zhang, Y. 2022. Methods to control harmful algal blooms: A review. *Environmental Chemistry Letters* 20: 3133-3152. https://doi.org/10.1007/s10311-022-01457-2

Belin, C., Soudant, D. & Amzil, Z. 2021. Three decades of data on phytoplankton and phycotoxins on the French coast: Lessons from REPHY and REPHYTOX. *Harmful Algae* 102: 101733. https://doi.org/10.1016/j.hal.2019.101733

Bhagabati, P. 2020. Biopolymers and biocomposites-mediated sustainable high-performance materials for automobile applications. In *Sustainable Nanocellulose and Nanohydrogels from Natural Sources*, edited by Mohammad, F., A. Al-Lohedan, H. & Jawaid, M. Elsevier. pp. 197-216. https://doi.org/10.1016/b978-0-12-816789-2.00009-2

Chekli, L., Eripret, C., Park, S.H., Tabatabai, S.A.A., Vronska, O., Tamburic, B., Kim, J.H., & Shon, H.K. 2016. Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride ($TiCl_4$) and ferric chloride ($FeCl_3$) in algal turbid water. *Separation and Purification Technology* 175: 99-106. https://doi.org/10.1016/j.seppur.2016.11.019

Cotruvo, J. 2015. Treating algal blooms and algal toxins in drinking water. *Opflow* 41(2): 16-17. https://doi.org/10.5991/opf.2015.41.0008

Del Ángel-Sánchez, K., Borbolla-Torres, C.I., Palacios-Pineda, L.M., Ulloa-Castillo, N.A. & Elías-Zúñiga, A. 2019. Development, fabrication, and characterization of composite polycaprolactone membranes reinforced with TiO_2 nanoparticles. *Polymers* 11(12): 1955. https://doi.org/10.3390/polym11121955

Donell, M. (n.d.). *The Dissolution of Polymethylmethacrylate (PMMA) in Salt Water.* https://Www.ozmo.io/. Retrieved June 24, 2023, https://www.ozmo.io/the-dissolution-of-polymethylmethacrylate-pmma-in-salt-water/

Douglas, P.S., Albadarin, A.B., Sajjia, M., Mangwandi, C., Kuhs, M., Collins, M.N. & Walker, G. 2016. Effect of poly ethylene glycol on the mechanical and thermal properties of bioactive poly(ε-caprolactone) melt extrudates for pharmaceutical applications. *International Journal of Pharmaceutics* 500(1-2): 179-186. https://doi.org/10.1016/j.ijpharm.2016.01.036

Elzubair, A., Elias, C.N., Miguez, C., Lopes, H.P. & Vieira, B. 2006. The physical characterization of a thermoplastic polymer for endodontic obturation. *Journal of Dentistry* 34(10): 784-789. https://doi.org/10.1016/j.jdent.2006.03.002

Ghernaout, D. 2020. Water treatment coagulation: Dares and trends. *Open Access Library Journal* 7: e6636. https://doi.org/10.4236/oalib.1106636

Ghosh, S., Chatterjee, S., Shiva Prasad, G. & Pal, P. 2021. Effect of climate change on aquatic ecosystem and production of fisheries. In *Inland Waters - Dynamics and Ecology,* edited by Devlin, A., Pan, J. & Manjur Shah, M. IntechOpen. https://doi.org/10.5772/intechopen.93784

Hooman, M., Sajjadi, N., Marandi, R., Zaeimdar, M. & Akbarzadeh, N. 2021. Design of a novel PEBA/CDs polymeric fibrous composite nanostructure in order to remove *navicula* algal and improve the quality of drinking water. *Polymer Bulletin* 79(9): 7459-7477. https://doi.org/10.1007/s00289-021-03852-1

Huang, N., Li, S., Liu, H. & Wang, J. 2012. Thermal stability and degradation kinetics of poly(methyl methacrylate)/sepiolite nanocomposites by direct melt compounding. *Journal of Macromolecular Science, Part B: Physics* 52(4): 521-529. https://doi.org/10.1080/00222348.2012.716318

Ibrahim, N.H., Iqbal, A., Mohammad-Noor, N., Razali, R.M., Sreekantan, S., Yanto, D.H.Y., Mahadi, A.H. & Wilson, L.D. 2022. Photocatalytic remediation of harmful *Alexandrium minutum* bloom using hybrid chitosan-modified TiO_2 films in seawater: A lab-based study. *Catalysts* 12(7): 707.

Imai, I., Inaba, N. & Yamamoto, K. 2021. Harmful algal blooms and environmentally friendly control strategies in Japan. *Fisheries Science* 87(4): 437-464. https://doi.org/10.1007/s12562-021-01524-7

Joh, G., Choi, Y.S., Shin, J.K. & Lee, J. 2011. Problematic algae in the sedimentation and filtration process of water treatment plants. *Journal of Water Supply: Research and Technology-Aqua* 60(4): 219-230. https://doi.org/10.2166/aqua.2011.035

Li, M., Pu, Y., Chen, F. & Ragauskas, A.J. 2021. Synthesis and characterization of lignin-grafted-poly(ε-caprolactone) from different biomass sources. *New Biotechnology* 60: 189-199. https://doi.org/10.1016/j.nbt.2020.10.005

Li, Y., Ma, Q., Huang, C. & Liu, G. 2013. Crystallization of poly (ethylene glycol) in poly (methyl methacrylate) networks. *Materials Science* 19(2). https://doi.org/10.5755/j01.ms.19.2.4430

Mansoori, S., Davarnejad, R., Matsuura, T. & Ismail, A.F. 2020. Membranes based on non-synthetic (natural) polymers for wastewater treatment. *Polymer Testing* 84: 106381. https://doi.org/10.1016/j.polymertesting.2020.106381

Mansur, H.S., Oréfice, R.L. & Mansur, A.A.P. 2004. Characterization of poly(vinyl alcohol)/poly(ethylene glycol) hydrogels and PVA-derived hybrids by small-angle X-ray scattering and FTIR spectroscopy. *Polymer* 45(21): 7193-7202. https://doi.org/10.1016/j.polymer.2004.08.036

Molnar, C. & Gair, J. 2019. *Overview of Photosynthesis.* https://opentextbc.ca/biology/chapter/5-1-overview-of-photosynthesis

Mousavian, Z., Safavi, M., Salehirad, A., Azizmohseni, F., Hadizadeh, M. & Mirdamadi, S. 2023. Improving biomass and carbohydrate production of microalgae in the rotating cultivation system on natural carriers. *AMB Express* 13: 39. https://doi.org/10.1186/s13568-023-01548-5

Naser, A.Z., Deiab, I., Defersha, F. & Yang, S. 2021. Expanding poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) applications: A review on modifications and effects. *Polymers* 13(23): 4271. https://doi.org/10.3390/polym13234271

Niu, Z.G., Hu, Z.P., Zhang, Y. & Sun, Y.Y. 2017. Effect of chlorine dosage in prechlorination on trihalomethanes and haloacetic acids during water treatment process. *Environmental Science and Pollution Research* 24: 5068-5077. 10.1007/s11356-016-8265-x

Niu, Y., Dong, W., Wang, H., Bi, D., Zhu, G., Tang, S., Wei, J., Yang, L. & Yao, X. 2014. Mesoporous magnesium silicate-incorporated poly(ε-caprolactone)-poly(ethylene glycol) poly(ε-caprolactone) bioactive composite beneficial to osteoblast behaviors. *International Journal of Nanomedicine* 9(1): 2665-2675. https://doi.org/10.2147/ijn.s59040

Osama, A., Hosney, H. & Moussa, MS. 2021. Potential of household photobioreactor for algae cultivation. *Journal of Water and Climate Change* 12(6): 2147-2180. https://doi.org/10.2166/wcc.2021.261

Panagopoulos, A. 2021. Study and evaluation of the characteristics of saline wastewater (brine) produced by desalination and industrial plants. *Environmental Science and Pollution Research* 29(16): 23736-23749. https://doi.org/10.1007/s11356-021-17694-x

Pardeshi, P.M. & Mungray, A.A. 2019. Photo-polymerization as a new approach to fabricate the active layer of forward osmosis membrane. *Scientific Reports* 9: 1937. https://doi.org/10.1038/s41598-018-36346-8

Patrojanasophon, P., Pitaktunskul, B., Ngawhirunpat, T., Akkaramongkolporn, P., Opanasopit, P. & Nattapulwat, N. 2019. Effect of polyethylene glycol on cellulose acetate films designed for controlled porosity osmotic pump systems. *Indian J. Pharm. Sci.* 81(1): 117-123. https://doi.org/10.4172/pharmaceutical-sciences.1000486

Pekdemir, M.E., Öner, E., Kök, E. & Qader, I. 2021. Thermal behavior and shape memory properties of PCL blends film with PVC and PMMA polymers. *Iranian Polymer Journal* 30(6): 633-641. https://doi.org/10.1007/s13726-021-00919-8

Rajasulochana, P. & Preethy, V. 2016. Comparison on efficiency of various techniques in treatment of waste and sewage water - A comprehensive review. *Resource-Efficient Technologies* 2(4): 175-184. https://doi.org/10.1016/j.reffit.2016.09.004

Repanas, A., Wolkers, W.F., Gryshkov, O., Muller, M.A. & Glasmacher, B. 2015. PCL/PEG electrospun fibers as drug carriers for the controlled delivery of dipyridamole. *Journal of In Silico and In Vitro Pharmacology* 1(2): 1-10. https://doi.org/10.21767/2469-6692.10003

Qi, J., Ma, B., Miao, S., Liu, R., Hu, C. & Qu, J. 2021. Pre-oxidation enhanced cyanobacteria removal in drinking water treatment: A review. *Journal of Environmental Sciences* 110: 160-168. https://doi.org/10.1016/j.jes.2021.03.040

Ren, X., Yu, Z., Qiu, L., Cao, X. & Song, X. 2021. Effects of modified clay on *Phaeocystis globosa* growth and colony formation. *International Journal of Environmental Research and Public Health* 18(19): 10163. https://doi.org/10.3390/ijerph181910163

Sen, B., Tahir, M., Sonmez, F., Turan Kocer, M.A. & Canpolat, O. 2018. Relationship of algae to water pollution and waste water treatment. In *Water Treatment*, edited by Elshorbagy, W. & Chowdhury, R.K. IntechOpen. https://doi.org/10.5772/51927

Sonawane, S., Thakur, P., Sonawane, S.H. & Bhanvase, B.A. 2021. Nanomaterials for membrane synthesis: Introduction, mechanism, and challenges for wastewater treatment. In *Handbook of Nanomaterials for Wastewater Treatment,* edited by Bhanvase, B., Sonawane, S., Pawade, V. & Pandit, A. Elsevier. pp. 537-553. https://doi.org/10.1016/b978-0-12-821496-1.00009-x

Tang, C.Y., Yang, Z., Guo, H., Wen, J.J., Nghiem, L.D. & Cornelissen, E. 2018. Potable water reuse through advanced membrane technology. *Environmental Science & Technology* 52(18): 10215-10223. https://doi.org/10.1021/acs.est.8b00562

Ulu, A., Köytepe, S. & Ates, B. 2016. Synthesis and characterization of PMMA composites activated with starch for immobilization of L-asparaginase. *J. Appl. Polym. Sci.* 133(19): 43421. https://doi.org/10.1002/app.43421

Venâncio, C., Ferreira, I., Martins, M.A., Soares, A.M., Lopes, I. & Oliveira, M. 2019. The effects of nanoplastics on marine plankton: A case study with polymethylmethacrylate. *Ecotoxicology and Environmental Safety* 184: 109632. https://doi.org/10.1016/j.ecoenv.2019.109632

von Sperling, M., Verbyla, M.E. & Oliveira, S.M.A.C. 2020. *Assessment of Treatment Plant Performance and Water Quality Data: A Guide for Students, Researchers and Practitioners.* IWA Publishing.

Wang, K., Saththasivam, J., Yiming, W., Loganathan, K. & Liu, Z. 2018. Fast and efficient separation of seawater algae using a low-fouling micro/nano-composite membrane. *Desalination* 433: 108-112. https://doi.org/10.1016/j.desal.2018.01.032

Yang, Y. & Zhao, H. 2022. Water-induced polymer swelling and its application in soft electronics. *Applied Surface Science* 577: 151895. https://doi.org/10.1016/j.apsusc.2021.151895

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