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Improved Oil-Water Separation Performance of Polylactic Acid by Halloysite Nanotube Incorporation

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Abstract: In this study, polylactic acid (PLA)-based nanocomposite membranes were prepared and used for the purification of simulated oil/water based wastewater. The lubricant oil (lubricating oil) was chosen as model oil. In order to increase the hydrophilicity of the membrane and improve its filtration performance, 0-20 wt.% of Halloysite nanotubes (HNT) were added into the PLA matrix. The effects of the HNT ratio on the oil/water swelling ratios (adsorption ratio), water flux, and oil rejection were determined. According to the results, optimal flux-oil rejection results were obtained with 5 wt.% of HNT incorporated nanocomposite membranes. The highest oil rejection of 94.9% was obtained using 5 wt.% of HNT incorporated membrane with a flux value of 1542.9 LMH.

Keywords: Nanocomposite membrane, polylactic acid membrane, halloysite nanotube, oil- water separation, lubricating oil.

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INTRODUCTION

Depending on the environmental impact of the global population rise and industrialization, the consumption of earth resources is increasing. Although three-quarters of the earth's surface is covered with water, the amount of freshwater that is suitable for human use is limited. Rapid urbanization, industrialization, and agricultural developments lead to consumption of large amounts of freshwater. Therefore, water production from natural sources or wastewater treatment technology becomes essential (1).

Industrial wastewater contains many contaminants, including heavy metals, dissolved salts, polymeric fibers, metals, alloys, and oils. These contaminants must be kept in limit values and must be cleaned before discharging. Wastewater treatment consists of many stages and each component is disposed of at a different stage. The nature of the wastewater treatment system varies depending on the content of the wastewater to be cleaned. One of the basic components found in industrial wastewater is oil. While the vegetable and animal oils present in the discharging of the food sector, lubricating and motor oils include in the wastewater of machinery containing sectors. Petrochemical-based oils and other industrial oily wastewaters pollute water resources irreversibly.

Waste oils must be handled appropriately. Oil/water mixes are classified into three types based on the droplet size of the dispersed phase: oil/water emulsion, free oil/water mixture, and oil/water dispersion (2, 3). Compared to emulsified oils, it is easy to remove free oil and dispersion from the water. For the removal of emulsified oil, advanced techniques are used (4). Well-known oil-water treatment techniques are gravity separation, dissolved air flotation, coagulation-flocculation (5), adsorption (6), biological treatment (7,8), electrochemical treatment (9), and membrane filtration (10). Membrane-based technology is prominent for treating oily wastewater due to its simplicity, ease of use, and low energy consumption. The separation efficiency of the membrane-based system is directly related to the structure and property of the membrane. Intensive studies are carried out to prepare high-performance membranes for the oil/water separative membranes.

Membranes used in the oil-water treatment are classified as polymeric (organic), inorganic and mixed (composite) membranes according to their structures. According to the material affinity they can be defined as hydrophilic, hydrophobic, oleophilic, oleophobic, etc. (11). It is essential to use appropriate material with the appropriate pore size for filtration experiments. In the literature, MF and UF membranes are prepared with polyvinylidene fluoride (PVDF) (12), polyacrylonitrile (PAN), polydimethyl siloxane (PDMS) (13), cellulose acetate (CA) (14), polysulfone (PS), polyethersulfone (PES) (15) polymers are widely used in oil-water treatment studies (16). Composite membranes have recently attracted great interest in oil-water separation studies. By incorporating different inorganic fillers into the polymeric (organic) membrane matrix, higher flux and selectivity values, longer lifetime, less contamination, and better performance can be achieved (17-19).

In this study, a hydrophobic polylactic acid membrane was prepared for oily water separation. The main polymer matrix, polylactic acid, is a bio-based polymer. It can be obtained from natural sources such as corn starch, sugar cane, and other renewable biomass products or waste. They have high strength and can be used in biomedical applications and a wide variety of engineering applications. There are limited studies in which this polymer is used in oil-water separation (20, 21). In the present study, in order to enhance the water separation capability of the membrane, halloysite nanotubes (HNT) were added to the PLA matrix at different ratios. Halloysite nanotubes have multi-walled structures, and their morphology is like carbon nanotubes (22, 23). Since the attraction force between the particles of HNTs is lower than those of carbon nanotubes, they can be easily distributed homogeneously in a polymeric matrix (24). HNTs are environmentally friendly nanoparticular materials. Bioplastics and membranes can be produced by adding HNTs to biodegradable polymers (25). There are several studies in the literature in which HNT was added to PLA polymer except for separation membranes (21, 26, 27)

In the present study different amounts of HNTs (from 1 wt.% to 20 wt.%) were added to the PLA matrix to remove the water from emulsified oil-containing water solution. Lubricant oil was chosen as the model oil in the present study. Lubricating oil, in other words lubricant, is a type of synthetic oil that is used to reduce the friction between the engine and parts of vehicles. The use of lubricating oils is increasing in proportion to the number of vehicles. Lubricant oil is refined from crude oil or is synthesized in the laboratory. It is used in most important machines and vehicles (28).

Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to investigate the physical and chemical structures of nanocomposite membranes. The affinity of the composite membranes to the oil and water was determined using water-oil uptake studies. Vacuum filtration experiments were conducted to determine the filtration capability of the membranes. The effect of HNT concentration in the matrix, oil types, and the downstream pressure on the water flux and oil rejection were investigated. According to the author's knowledge, HNT loaded PLA membranes were first time prepared as a membrane and were used for oil-water separation.

EXPERIMENTAL SECTION

Polylactic acid (PLA) was supplied from the Turkish distributor of Nature Works (2003D)., N, N-dimethylformamide (DMF, with >99% purity), chloroform, and methanol (>99% purity) were purchased from Merck Chemicals. Halloysite nanotube was kindly supplied from the ESAN, Eczacıbasi, Turkey.

Membrane Preparation

For the preparation of the plain PLA membrane, a DMF/chloroform solution containing 10% PLA was prepared. The membrane solution was stirred at 50 °C for four hours until a homogeneous mixture was obtained. The mixture was poured onto a Teflon sheet and semi-dried at room temperature for an hour. Then the casting solution was immersed in a water bath for two minutes. The membrane was taken from the bath and washed for a couple of times. Parameters such as the temperature of the water bath and the retention time affect the pore structure of the membrane.

For the preparation of the HNTs loaded nanocomposite membrane, 5-20 wt.% of HNTs were dissolved in 10 mL of DMF in an ultrasonic bath for 10 minutes. Then, the well-mixed HNTs-DMF solution was mixed with the PLA-DMF-chloroform solution containing 10% PLA. The solution was stirred for 2 hours at room temperature and was poured onto a Teflon layer. The casting solution was dried at room temperature for an hour. It was immersed in a water bath for two minutes.

Fourier transform infrared spectroscopy (Perkin Elmer) was used to determine the chemical properties of nanocomposite membranes (FTIR-Perkin Elmer). The test was carried out in the range of 4000–650 cm^{-1} wavelength.

Oil/Water Uptake

The affinity of all prepared membranes to water and oils was determined by adsorption tests. For the uptake test, 1 cm^2 of membrane samples were kept in water and lubricating oil for 24 hours. The weights of the membranes were recorded hourly and were waited to reach constant weight. The uptake percentage was calculated from the weight of the dry (W_i) and swollen membranes (W_f). The calculation is given in Equation 1.

$$Uptake(\%)=\frac{W_f-W_i}{W_i*100} \quad (1)$$

Vacuum filtration test
The schematic representation of the vacuum filtration test system is shown in Figure 1a. The prepared membranes are seen in Figure 1b. The experiments were carried out at room temperature by preparing lubricating oil-water emulsions containing 1 wt.% oil. Prior to the vacuum filtration experiments, the oil-water emulsion was sonicated for one hour and a milk-like color was obtained as shown in Figure 1c. Experiments were done at room temperature with 100 mL of oil-water solution. The time-dependent permeate weight was recorded and the concentration of the permeate sample was analyzed using a UV-visible spectrophotometer (Shimadzu, 1800) at 420 nm.

The volumetric flow rate or flux (F) (L/m^2.h) was calculated from the volume of the permeate (Equation 2) and the oil rejection (R)(%) was calculated from the oil concentrations of the feed and permeate (Equations 3).

$$F=\frac{M}{t.A} \quad (2)$$

$$R(\%)=\frac{C_f-C_p}{C_f*100} \quad (3)$$

where L (Liter) represents the volume of the permeate, t (h) represents the duration of filtration, and A (m^2) represents effective membrane area. On the feed and permeate sides, C_f and C_p are the concentrations of the oil-water solution.

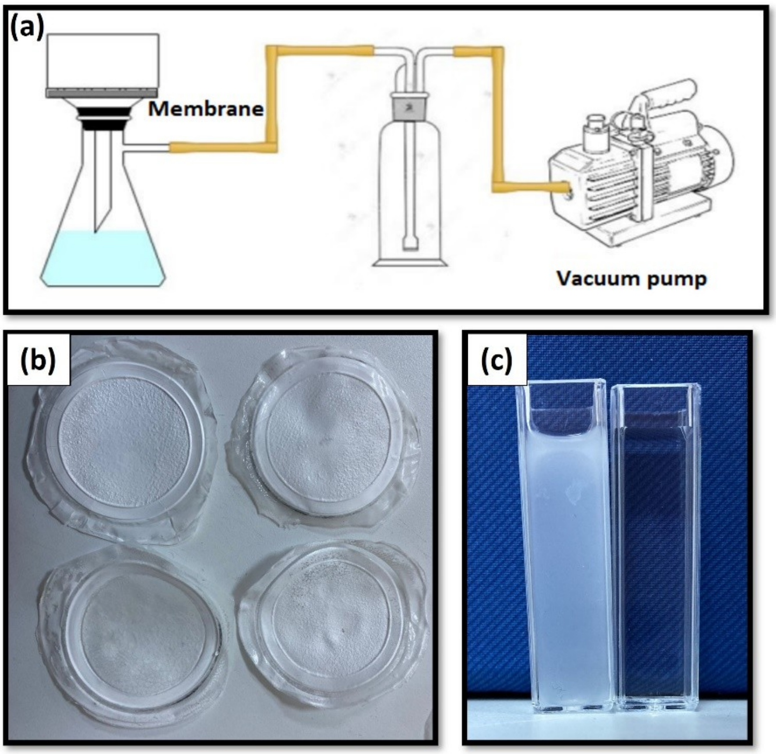

Figure 1: Vacuum filtration test unit (a), prepared nanocomposite membranes (b), and the oil-water mixture before (left) and after (right) vacuum filtration (c).

RESULTS AND DISCUSSION

Membrane Characterization
FTIR spectroscopy was used to investigate the chemical structures of plain PLA and HNT-PLA nanocomposite membranes. Figure 2 shows the spectra of unfilled and nanocomposite membrane. PLA has asymmetric and symmetric –CH groups, which have stretching vibration peaks around 2998 cm^{-1} and 2922 cm^{-1}, respectively. The place of -CH stretching peaks are shifting 2996 cm^{-1} and 2945 cm^{-1} due to HNT addition into PLA. The C=O bond strains in PLA is observed about 1750 cm^{-1}. The asymmetric and symmetric $–CH_3$ groups have bending frequencies of 1450 cm^{-1} and 1385 cm^{-1},

respectively. The absorption peak at 910 cm^{-1} is corresponding to Al–O–OH bending of HNT (29, 30).

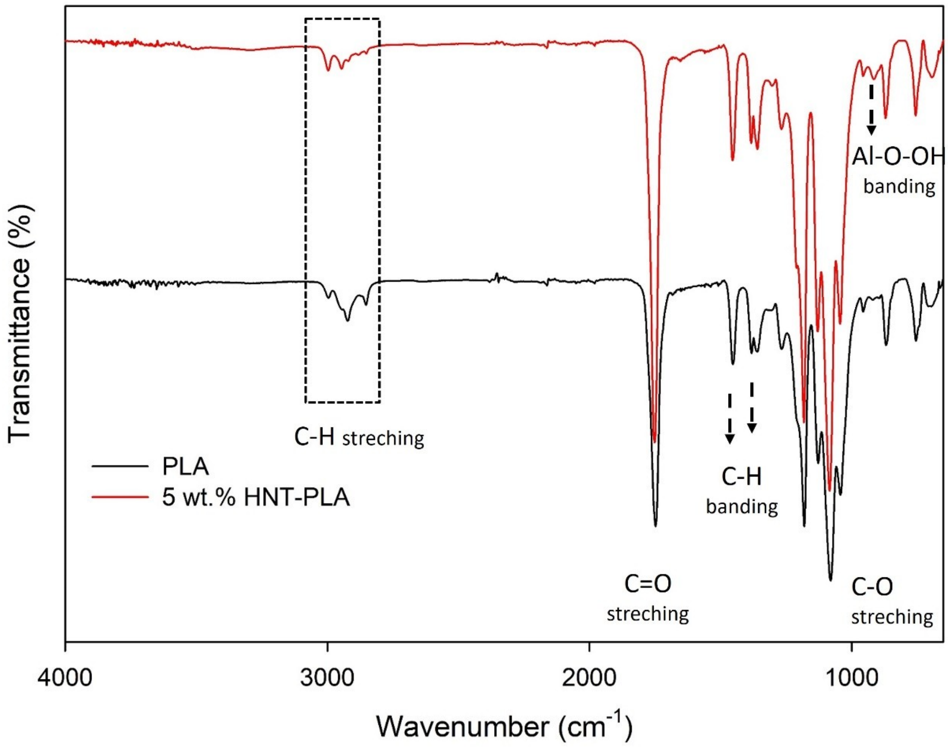

Figure 2. FTIR analysis of the plain PLA-and HNT-filled nanocomposite membranes.

Figure 3a and Figure 3b show the pore size and distribution of the plain and HNT loaded PLA membranes. The pore size of the plain PLA membrane varying between 1 µm to 3 µm. Unlike the plain membrane, the number of pores decreased, and the size of the pores increased in the nanocomposite membrane. The possible reason for this is the strong interaction between the PLA matrix and HNT. This interaction may cause a decrease in the density of pore formation during the phase inversion stage. HNT particles are clearly seen within the polymer matrix. it is seen that HNT changes the membrane's structure. The distribution of HNT in the matrix is homogeneous.

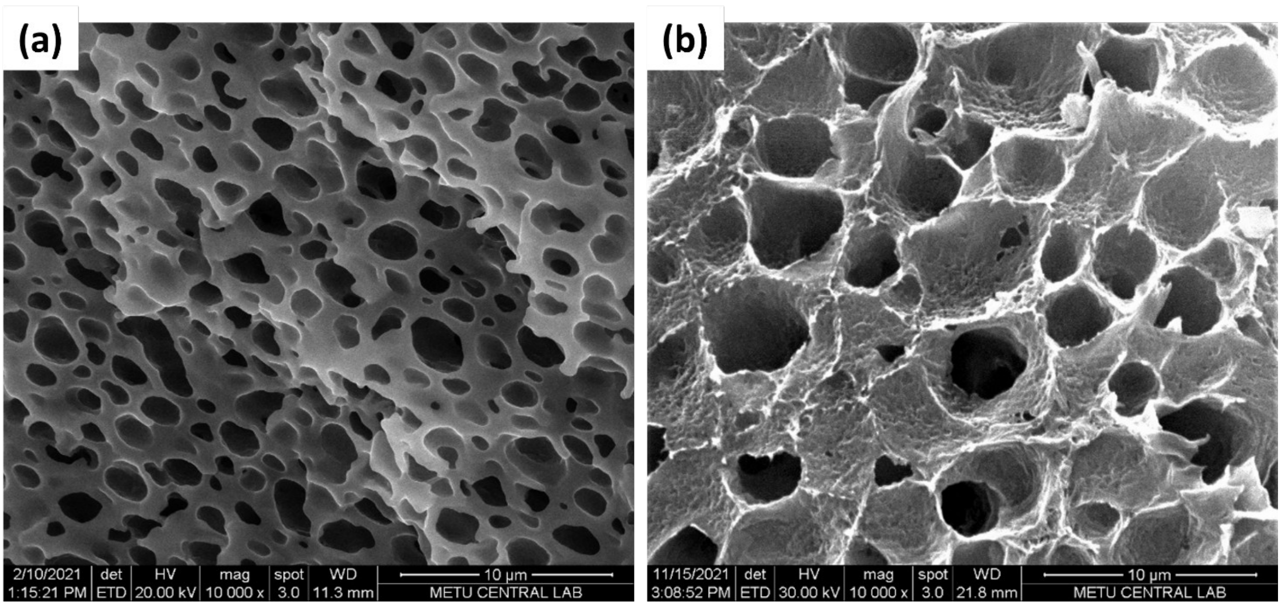

Figure 3. Cross-sectional SEM micrographs of the plain PLA (a)- and 5 wt.% of HNT-loaded PLA membranes.

Oil and water uptake

In this study, it was aimed to improve the separation performance of the PLA membrane by adding HNT to the matrix. HNT is an environmentally friendly material that exhibits biocompatible hydrophilicity, stable dispersion in the polymer, and high water adsorption capacity. In the literature, it was reported that the hydrophilicity of the PLA-based materials was strongly increased by the addition of HNT depending on the hydroxyl groups in its structure (31). It was also reported that the separation performance of membranes in water-oil solution was significantly improved by HNT addition (32). A dramatic improvement in hydrophilicity and separation performance of membranes have been achieved depending on the HNT modification.

In Figure 4, the effect of HNT addition on uptake values is illustrated. The HNT concentration was varied from 0 wt% to 20 wt%. The highest oil uptake results were obtained by using the plain PLA membrane. The plain membrane did not adsorb water. As the HNT concentration increased from 3 wt.% to 20 wt.%, the water uptake capacity of the plain membrane gradually increased. According to these results, it could be concluded that the HNT significantly increased the water uptake capacity of the hydrophobic PLA membrane. Halloysite clay is a mineral of volcanic origin consisting of layered aluminosilicate with a high surface area and aspect ratio (26). Like other kaolinite minerals, it adsorbs water, but unlike montmorillonite, this ratio is not high and does not cause an increase in polymer volume (swelling effect). As seen in the figure, the addition of HNT increased the water uptake only after 3% addition. However, swelling values in oily waters decreased significantly as the HNT content increased. According to these results, it can be predicted that the HNT could improve the water flux and oil rejection, simultaneously.

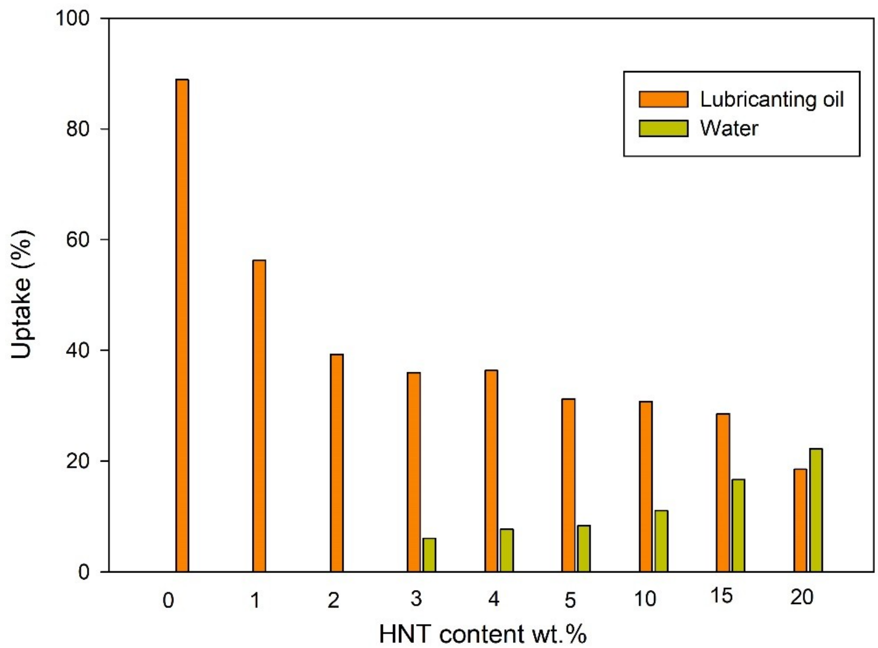

Figure 4. Effect of HNT ratio on uptake.

Filtration performance of membranes

The flux and rejection results of the lubricant oil-water emission as a function of HNT content are shown in Figure 5. Very high flux values were obtained with the prepared membranes. Fluxes were remarkably improved by the addition of HNT. Flux increases occurred due to the high water holding and transfer capacity of HNT. When the HNT ratio was increased from 0 wt.% to 1 wt.%, flux increased from 1330.9 LMH to 3566.5 LMH when the vacuum pressure was 10 mbar (985 mbar gauge pressure). However, after this loading, a significant decrease in flux was observed. This decrease is attributed to the closing of active separation sites by overloading of HNT. The pore-blocking effect may be occurred due to the highest amount of HNT which was also reported in the literature (32). Additionally, decrease in flux is also related to the reduced the number of the pores depending on the HNT addition as also confirmed by SEM image.

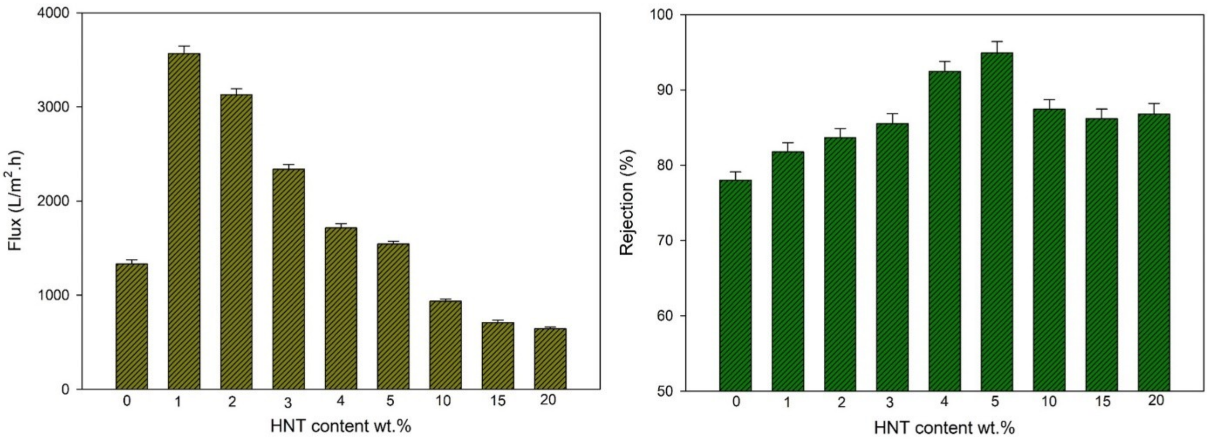

Figure 5. Effect of HNT content on the flux and lubricating oil rejection results.

The membranes also exhibited excellent rejection results for the water/lubricating oil emulsion. Although the flux values of membranes were improved compared to the plain membrane, there was no reduction in oil rejection values until the HNT loading ratio of 5 wt.%. Therefore, it can be assumed that the trade-off trend between the flux-rejection was overcome. The highest lubricating oil rejection of 94.9% was achieved with a flux of 1542.9 LMH using 5 wt.% of HNT loaded membrane. After that point, rejection decrease depending on the enlarged pore size of membrane which was confirmed by the SEM image.

Table 1 includes the results of oil-water separation studies. The cited studies are selected according to the high rejection results (greater than 90% oil rejection). When compared with the literature, it is seen that the results are quite good. Therefore, it is possible to consider that the produced membrane has the potential to be commercialized as a microfiltration membrane. Also, considering that both the polymer and the additive used are natural and cheap sources, promising results were obtained in the study.

Table 1. Comparison of the results with the literature.

Membrane	**Oil Type**	**Flux (LMH)**	**Rejection (%)**	**Reference**
Kaolin	-	123.8	97.3	(10)
PMDS/SiO_2	Kolza	1800	97.2	(4)
PMDS/SiO_2	Engine oil	1900	97.3	(4)
PS/PVA/Bentonite	Petroleum	312	97	(33)
PSf/PEG	-	120	95	(34)
Cellulose	Petroleum	1591	>96.5	(35)
PLA/TiO_2	Lubricating oil	963	99	(20)
PVDF/PVP/TiO_2	-	70.48	99.7	(36)
PSf		245	95.9	(37)
PVDF/Bentonite	Lubricating oil	1800	96.5	(38)
PLA/PDA	-	2664	98.4	(3)
PLA/HNT	Lubricating oil	1542.9	94.9	This work

CONCLUSION

In this study, bio-based PLA-HNT nanocomposite membranes were produced and their performance in oil-water separation was investigated. It has been seen in the SEM analyses that the HNT material can be added to the membrane homogeneously. Although the number of pores decreased in membranes with HNT added, they exhibited excellent water separation performances. A significant increase in water flux values was observed in HNT-loaded nanocomposite membranes. In addition, oil rejection values increased significantly. It has been observed that the most suitable HNT concentration was up to 5 wt. %, and the flux value was lower compared to the plain PLA after this ratio. When the HNT watio was 5 wt.%, the highest oil rejection of 94.8% and a reasonable flux value of 1542.9 LMH were obtained. These results were higher than many studies in the literature. As a result, it has been seen that the HNT-doped PLA membrane was very successful for separation of emulsified oily wastewater using microfiltration technique.

CONFLICT OF INTEREST

The author confirmed that there is no declaration of interest.

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