

Nonwoven Bio-Based Membranes for Removal of Micropollutants from Aqueous Water

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Abstract: *The aim of this paper is to obtain two types of bio-based membranes by electrospinning process: one based on polylactic acid (PLA), and PLA/polyhydroxybutyrate (PHB), and the second by coating the PLA/PHB membrane with chitosan (CS) and CS/activated coal (AC), respectively for removal of micropollutants from aqueous water. The designed bio-based electrospun membranes were analyzed through scanning electron microscopy (SEM), attenuated total reflectance (ATR) - Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), the removal of solid suspension and Pb (II) from aqueous water. The quality of filtrates was evaluated by physical-chemical methods, while the retaining of Pb (II) from wastewaters was reported.*

Keywords: *bio-based polymers, chitosan, activated coal, electrospinning, membrane, micropollutant, heavy metals*

1. Introduction

The rapid growth of global population, generation of large quantities of wastewaters from industrial activities as well its needs for safe drinking water have become a critical issue that the world is facing. To obtain an acceptable quality of treated wastewaters, the removal of undesirables components, such as: conventional pollutants (suspended solids, colloids, inorganic salts and toxic substances and pathogens), and emerging contaminants (pharmaceuticals, personal care products, pesticides, degradation by-products of detergents, and endocrine disrupting compounds) should be provided [1-2]. Organic and inorganic pollutants found in wastewaters are bioactive and persistent contaminants, non-biodegradable, which cannot be completely removed with traditional wastewater treatment methods. The presence of micropollutants in wastewater can lead to long-term hazards, as contaminants accumulate and can even form new mixtures in water [3]. It was found that the filtration membranes can be successfully used to retain contaminants from water. There are known three main types of membrane filtration systems: ceramic, metal and polymeric membranes [4]. Based on their separation principles, the filter membranes are classified in: reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), and microfiltration (MF) [5]. Depending on the particle retention diameter, the pore diameter of the filter membranes are ranged from 0.05 to 10 μm for MF, 0.1 to 0.005 μm for UF, 0.5 to 5 nm for NF and 0.1 up to 1 nm for RO.

Microfiltration polyurethane–cellulose acetate membrane with a pore dimension of 0.86 μm was studied for removal of Direct Blue dye (DB) from water [6]. The polysulfone type ultrafiltration membrane filtration process was used to evaluate the efficiency of removal of TiO_2 , ZnO and CeO_2 nanoparticles with dimensions in the range of 10 nm to 21 nm from aqueous suspensions [7]. An efficiency of 72.3-98.6% was reported for the retention of the investigated nanoparticles.

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Polymeric nanofibers produced by the electrospinning process are the best materials for a variety of high value applications, including filtering pollutants from water [8-9], materials for optical and chemical detection [10], photovoltaic cells [11], tissue engineering [12] and drug controlled release [13], due to their very fine size and high surface-to-volume ratio.

Furthermore, the nanofibrous polymer membranes show higher porosity, interconnected pore structure, less energy for their producing and reduced cost of filtration as compared to conventional membranes [14]. It has been reported that the nonwoven polymeric membranes could be used both in filtration and adsorption of heavy metals [15-16]. For example, polymeric membranes with a diameter of about 100 nm obtained from recycled polyethylene terephthalate (PET) designed for water filtration have been obtained by electrospinning [17]. In another paper, the filtration efficiency of PET membranes was evaluated for retaining of latex beads, with dimensions ranging between 30 nm to 2000 nm. It has been reported that over 99% of latex beads smaller than 500 nm were retained using gravitational filtering. Furthermore, a commercial polysulfone membrane was used to retain organic pollutants generated by residues from fish feed, manure and/or microorganisms in aquaculture systems [18]. Kampalanonwat and Supaphol [19] described the preparation of polyacrylonitrile (PAN) nanofiber mats by electrospinning, their modification with diethylenetriamine (DETA) and the successfully adsorption of Cu (II), Pb (II), Fe (II) and Ag (I) ions.

Nowadays, a considerable attention is paid towards the development of advanced filtering systems based on environment-friendly polymers in order to achieve high micropollutant removal efficiency. In addition to their biodegradation, the bio-based polymers such as polylactic acid (PLA) [20] and poly(hydroxybutyrate) (PHB) [21] have been studied for manufacturing of electrospun membranes with high mechanical strength, thermal stability and chemical resistance. PLA is obtained from the controlled depolymerization of the lactic acid monomer resulting from the fermentation of corn, sugars, starches, etc. It is one of the most promising biopolymers, biodegradable and compostable, with high transparency, water solubility resistance and good mechanical properties [22]. However, its dissolving in proper solvents and processability by electrospinning need to be improved. For this purpose it is recommended to blend PLA with other polymers or plasticizers [23]. PLA-based biomembranes and polyethylene glycol (PEG) were reported by electrospinning process and used for the absorption of pollutants found in drinking water [24]. Hydrophobic PLA nanofibers were found to have high efficiency for oil/water separation [25].

PHB belongs of the polyhydroxyalkanoate family (PHA) and it is an intensely designed polyester for environmental applications. It is totally biodegradable, partially crystalline, with a high melting temperature (175°C) and a high degree of crystallinity [26-27]. PLA and PLA/PHB nonwoven polymeric membranes were also reported for oil adsorption from aqueous media [28].

Chitosan (CS) is a natural polymer obtained from crustaceans, showing biocompatibility, biodegradability, antimicrobial and antifungal activity [29]. Chitosan is insoluble in water and alkaline medium due to its rigid and compact crystalline structure and strong intra and intermolecular hydrogen bonds, but it is soluble only in acidic aqueous solutions with a pH of less than 6.5. Its chemical stability should be improved by the use of crosslinking agents, such as: glutaraldehyde, glycolic ether diglycidyl ethylene and epichlorohydrin [30]. The adsorption properties of chitosan were proved by our team for removal of Cr (VI) [31] and Pb (II) [32].

Activated carbon (AC) is used for water filters due to the fact that it is a natural and effective product for removing many toxins from water, such as volatile organic compounds and chlorine, without the need to use chemicals or remove mineral salts from the water.

The present study presents the obtaining of symmetric (PLA, PLA/PHB) and antisymmetric (PLA/PHB/CS, PLA/PHB/CS/AC) nonwoven polymeric membranes in order to retain either the solid suspensions or heavy metals from aqueous water.

2. Materials and methods

2.1. Materials

All used materials were analytical grade, thus:

- polylactic acid, PLA type 4032D (NatureWorks, Resinex SRL, Romania)
- polyhydroxybutyrate (PHB) in powder form (Biomer, Germany)
- chitosan powder with a deacetylation degree of 75% (Aldrich-Sigma)
- activated carbon powder, 100-400 mesh (Sigma Aldrich).

Also solvents such as: dimethyl formamide (DMF), chloroform, acetic acid and a crosslinking agent - 50% glutaraldehyde (Alfa Aesar, Germany).

2.2. Preparing of Electrospun Bio-Based Membranes

Polymeric solutions for electrospinning were obtained as follows:

- 10% PLA solution (wt/vol) was obtained by dissolving of PLA pellets in a mixture of solvents consisting of 90 wt.% chloroform and 10 wt.% DMF using a hot table with magnetic stirring at 90°C, for 6 h and 600 rpm;

- 2.5% PHB solution (wt/vol) was obtained by dissolving PHB powder in a mixture of 90 wt.% chloroform and 10 wt.% DMF solvents using a hot table with magnetic stirring for 3 h at 50°C.

- 1.5 wt% chitosan solution was obtained by dissolving of chitosan powder in 85% (vol/vol) acetic acid solution.

PLA/PHB solution was obtained by mixing 10% solution of PLA with 2.5% solution of PHB, as above prepared. The weight ratio between the PLA solution and that of PHB was 3:1.

The following experimental variants were prepared (Table 1).

Table 1. Experimental variants proposed for obtaining nonwoven bio-based membranes

Sample	PLA (wt%)	PHB (wt%)	CS (wt%)	AC (wt%)
PLA	100			
PLA/PHB	75	25		
PLA/PHB/CS	74.25	24.75	1	
PLA/PHB/CS/AC	73.5	24.5	1	1

The nonwoven polymeric membranes were fabricated using a commercially TL-Pro-BM Electrospinning equipment (Tong Li Tech Co., Ltd., Bao An, Shenzhen, China), which consists of a syringe pump (TONG LI TECH device) with a volume of 50 mL, a high-voltage power supplier, and a grounded conductive drum collector covered with aluminum foil. The optimal experimental conditions for obtaining of electrospun polymeric membranes are shown in Table 2.

Table 2. Optimal parameters of the electrospinning process for obtaining of nonwoven polymeric membranes

Sample	Negative electrode voltage (kV) / positive electrode voltage (kV)	Solution flow rate (mL/h)	Distance between the needle to collector (cm)	Drum rotation (rpm)	Drum rate (m/s)
PLA	-7.04/15.17	0.9	12	250	10
PLA/PHB	-8.42/24.02	3.9	10	50	10
PLA/PHB/CS	-10.4/21.37	0.9	10	-	-
PLA/PHB/CS/AC	-12.95/21.75	0.7	10	-	-

The experiments took place in the following environmental conditions: the temperature ranging from 20 to 28°C and a relative humidity of 27% RH. The membranes containing PLA/PHB/CS and PLA/PHB/CS/AC, respectively, were obtained by the depositing of 1% solution of CS, and 1:1 CS/AC, respectively onto the PLA/PHB membrane, previously obtained. The fabricated PLA/PHB/CS and

PLA/PHB/CS/AC membranes were crosslinked by keeping them in contact with glutaraldehyde vapors (sol. 50%) for 4 h. Smooth polymeric membranes with a length of ~12 cm and width of ~6 cm were obtained by electrospinning.

2.3. Characterization of Electrospun Bio-Based Membranes

The polymeric membrane surfaces were investigated using a QUANTA 450 FEG (FEI, Eindhoven, The Netherlands) equipped with a field emission gun at a 1.2 nm resolution. Fourier transform infrared spectroscopy (FT-IR) with attenuated total reflectance (ATR) (Interspec 200-X Spectrophotometer, Interspectrum, Estonia) were applied to observe the functional groups presented in the electrospun polymeric membranes. Differential Scanning Calorimetry (DSC) measurements were determined using a Mettler Toledo (Model DSC 823^e, Calorimeter (Greifensee, Zürich, Switzerland).

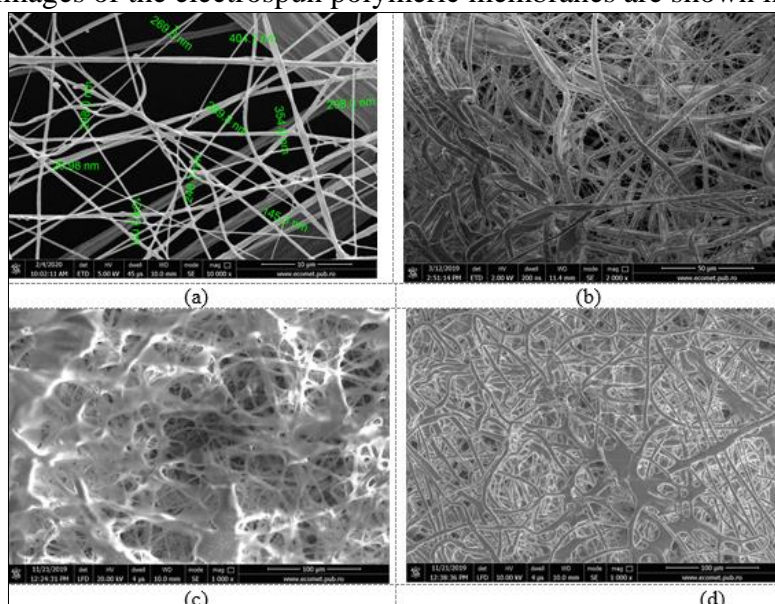
Specimens with dimensions (length x width) of (6 x 6) cm² were taken out from the PLA and PLA/PHB electrospun membranes and used for filtration of 25 mL solid suspension solution that contain 1% fine sand. This suspension is characterized by a pH value of 5.72 and electrical conductivity of 12.56 $\mu\text{S}/\text{cm}$. The filtrates from each electrospun polymeric membrane were collected and analyzed for the water quality constituents: the conductivity of the solution was measured using a Consort C862 equipment, pH was carried out by a Consort C831 Multiparameter analyzer, under laboratory conditions, on duplicate, total content of dissolved soluble salts and transmittance measured using an UV-VIS Spectrometer (Alpha Helios, Thermospectronic). An analytical balance (accuracy 0.1 mg) was used to determine the filtration efficiency. Distilled water was used for comparison tests.

Adsorption capacity of PLA/PHB/CS and PLA/PHB/CS/AC electrospun membranes was investigated by contacting 100 mg of adsorbent with 100 mL of Pb (II) solution at a concentration of 1 mg L⁻¹, with stirring (200 rpm) at room temperature, for a maximum time of 120 min. After reaching of equilibrium, the solutions were filtered (Whatman filter paper No. 1) and the Pb (II) concentration in the filtrate was detected at 217 nm wavelength by an atomic absorption spectrometer (GBC 932 AB PLUS, from GBC Scientific Equipment PTY Ltd., Australia) with acetylene flame.

3. Results and discussions

3.1. Scanning electron microscope (SEM) measurement

Structural investigation of the polymeric membranes obtained by the electrospinning process was performed by electron microscopy (SEM) analysis. In order to ensure the filtration of solutions contaminated with visible particles with the naked eye (with dimensions between 1 mm and 5 mm) it is necessary that the pores of the membrane to be relatively evenly distributed and have an optimum diameter. The SEM images of the electrospun polymeric membranes are shown in Figure 1.



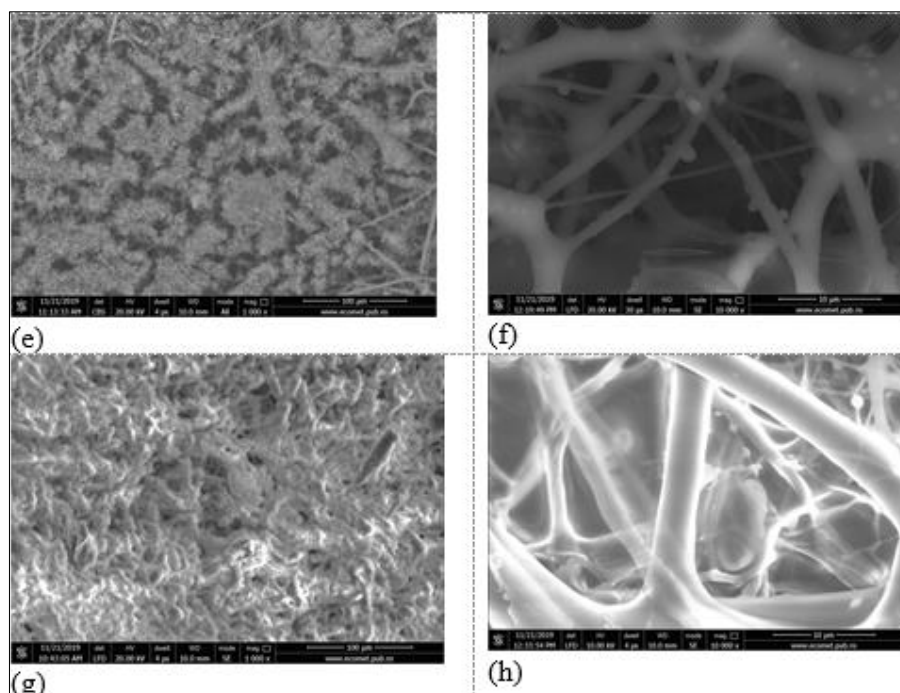


Figure 1. SEM images of the electrospun polymeric membranes: (a) PLA; (b) PLA/PHB; (c) PLA/PHB/CS; (d) PLA/PHB/CS crosslinked (b) with glutaraldehyde; (e), (f) PLA/PHB/CS/AC; (g), (h) PLA/PHB/CS/AC crosslinked with glutaraldehyde

Consistency and diameter control, absence of any surface defects such as pores and "beads" as well as the continuity of unique nanofibers as much as possible represent optimal morphological characteristics that are achieved only by adjusting the electrospinning parameters. The large diameter of electrospun fibers and the beads formation are related to the viscosity of solution. The right choice of ratio of 9:1 between chloroform and DMF solvents, the concentration of polymer solutions of 10% in the case of PLA and 2.5% in the case of PHB together with the selecting of electrospinning parameters according to Table 2 led to fabricate symmetric bio-based polymeric membranes. According to the SEM examination, it can be seen that the investigated polymeric membranes show a network of yarns with three-dimensional structure and intercalated pores. In the case of the PLA membrane (Figure 1 (a)) the nanofibers with a size diameter between 26-400 nm are observed. The pores have a size of $\sim 10 \mu\text{m}$, which will ensure the retention of solid suspensions larger than $10 \mu\text{m}$. A dense structure of nanofibers can be observed in the case of PLA/PHB membrane (Figure 1(b)). Large pores with diameter $\sim 20 \mu\text{m}$ were observed in the case of asymmetric polymeric membranes, by deposition of CS and CS/AC, respectively, in the form of small spheres onto the PLA/PHB membrane (Figures 1(e-g)). The morphology of asymmetric membranes with large pores will allow the retention of micropollutants (heavy metals) only at the upper layer [33].

3.2. Fourier Transform Infrared Spectroscopy (FT-IR)

The ATR-FTIR spectra and optical images of polymeric nonwoven membranes are shown in Figure 2.

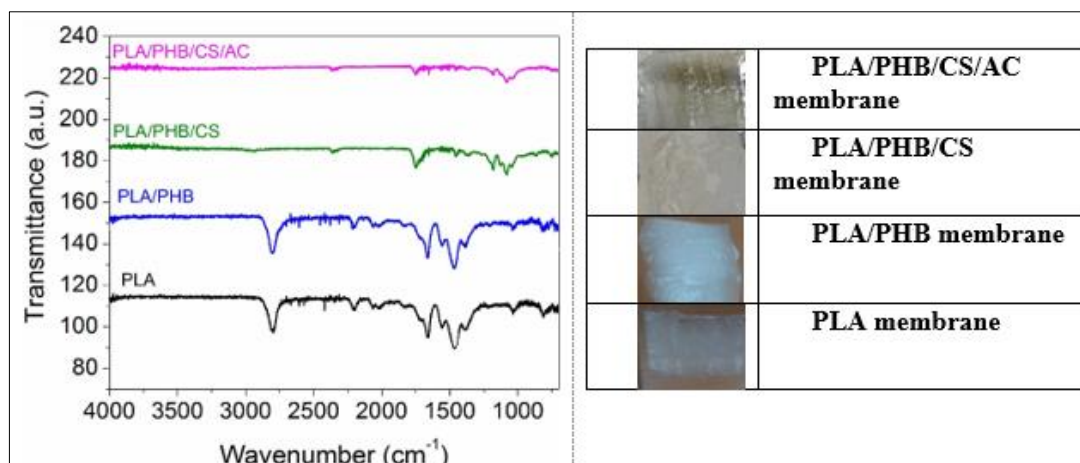


Figure 2. ATR-FTIR spectra and the optical images for the electrospun polymeric membranes: PLA membrane; PLA/PHB membrane, PLA/PHB/CS membrane, and PLA/PHB/CS/AC membrane

The FT-IR spectrum for the PLA type membrane indicated the presence of the absorption bands at 1721 cm^{-1} attributed to the symmetrical vibration of the C=O bond, a small shoulder at 1755 cm^{-1} related to the amorphous state of polyester, 2867 cm^{-1} and 2941 cm^{-1} due to the symmetrical and antisymmetric stretching vibration of the C-H bond. In the case of PLA/PHB membrane, the same absorption peaks like PLA membrane are observed, highlighting the polyester nature of PHB. The presence of the absorption band at 1748 cm^{-1} attributed to the stretching vibration of the C=O bond of the ester group [34], and 1458 cm^{-1} assigned to the bending vibration of the CH_3 group from polyesters [35] are observed in the case of PLA/PHB/CS and PLA/PHB/CS/AC membranes. The presence of chitosan was highlighted by the absorption peaks due to the acetamide groups located at 1382 cm^{-1} [36] for PLA/PHB/CS and 1378 cm^{-1} in the case of PLA/PHB/CS/AC. However, the functional groups from polyesters can not be observed in the case of the coating PLA/PHB membrane with CS and CS/AC, respectively, maybe due to the thick coating layers.

3.3. Differential Scanning Calorimetry (DSC)

Figure 3 shows the DSC curves for PLA and PLA/PHB electrospun polymeric membranes.

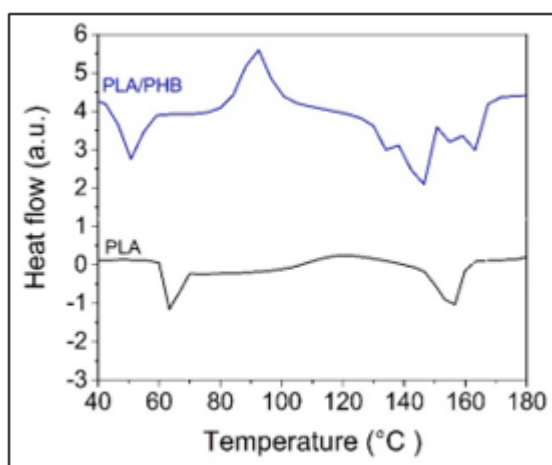


Figure 3. DSC curves for PLA and PLA/PHB membranes (first heating run)

Nonwoven PLA membrane is characterized by a glass transition temperature (T_g) of 62°C , a small cold crystallization temperature (T_{cc}) of 120°C and a melting temperature (T_m) of 157°C . Approximately the same DSC parameters were reported for PLA prepared by melt processing [37]. DSC curve for the PLA/PHB membrane shows one single T_g at 52°C meaning the miscibility of components and enhancing in the flexibility of polymeric chains compared with the PLA, and an evident T_{cc} at 92°C .

A similar decrease in T_g and T_{cc} compared with PLA was reported by Arrieta et al. 2015 [38] in the case of PLA/PHB (75:25) electrospun mat, explained by the capacity of PHB to re-crystallize the PLA matrix. The melting temperature for PLA/PHB membrane retains the characteristics of PLA and PHB respectively, showing one first maxim melting peak located at 148°C with a shoulder at 132°C, associated to melting of PLA, followed by another at 167°C with a shoulder at 154°C due to the melting of PHB.

3.4. Filtration of Suspended Solid Solution

In order to test the PLA and PLA/PHB polymeric membranes for retaining suspensions from the water, 1% fine sand solution was prepared.

According to the data showed in Table 3 it is observed that the PLA/PHB polymeric membrane allows the filtration of distilled water with the highest flow (0.1595 mL/s), while the PLA polymeric membrane recorded a flow of 0.1079 mL/s. This could be explained by the flexibility and, maybe, the thickness of the electrospun polymeric membranes. In the case of the solid suspension filtration, the filter flow is equal for these membranes types (0.053 mL/s), but the amount of retained sand was different. It is possible that some pores of the PLA membrane to be clogged with fine sand particles, which led to a less amount of contaminant retained (248 mg). The filtration efficiency was high when used filter membranes based on PLA. After filtering the contaminant solutions with 1% sand, it was found that the pores of the membranes were clogged, which indicates that the filtrate solution contains particles equal in size to the pores of the membrane. Also, larger solid particles were retained on the surface of the filter. However, the membrane architecture of PLA and PLA/PHB allows a good pore distribution such that to obtain efficient filtration of suspended solid solution. The utility of bio-based polymeric membranes can be extended to other suspensions present in water, as well to the retention of microplastics from rivers.

Table 3. Flow rate and filtration efficiency of a 1% solid suspension solution using PLA and PLA/PHB polymer membranes

Electrospun bio-based membrane	Distilled water	1% solid suspension solution		
	Filter flow (mL/s)	Filter flow (mL/s)	Amount of sand suspension retained (mg)	Filter efficiency (%)
PLA	0.1079	0.053	248	99.2
PLA/PHB	0.1595	0.053	251	98.4

Table 4 shows the physical characteristics of filter solutions through polymeric membranes: pH , electroconductivity and total soluble salt content. The water resulting from the retention of the suspended solid solution is characterized by a pH value between 5.6 and 6.3, very close to the value of distilled water (pH value ~ 6).

Table 4. Characteristics of solutions filtered through polymeric membranes.

Electrospun bio-based membrane	Filtered solution pH	Electroconductivity of the filtered solution ($\mu S/cm$)	Total content of soluble salts (mg/L)
PLA	5.6	11.65	7.456
PLA/PHB	6.3	18.05	11.55

Compared to the conductivity value recorded by the distilled water sample (2.67 $\mu S/cm$), from Table 4 it is observed that the solutions obtained by filtration with the help of polymeric membranes had a higher conductivity, due to the dissolution of some existing salts. The total content of soluble salts is in good correlation with the electroconductivity of the filtered solutions. The total soluble salt content is highest in the case of the PLA/PHB polymer membrane (11.55 mg/L), in correlation with the filtration

efficiency shown in Table 3. The transmittance of water resulted from the filtration process with bio-based membranes is shown in Figure 4.

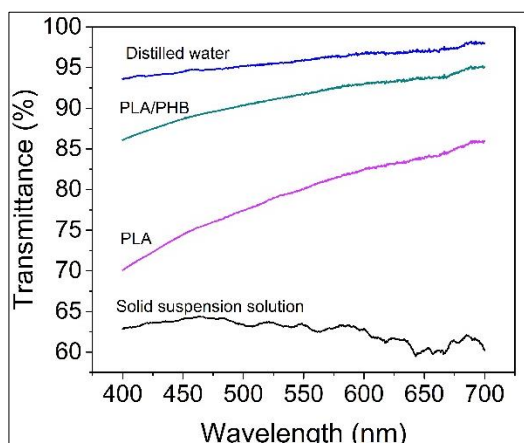


Figure 4. Transmittance for PLA and PLA/PHB membranes compared with distilled water and solid suspension solution

In all membranes tested, the resulting water was clearly, which reveals the importance of the filtration process (Figure 4).

3.5. Removal efficiency

In order to evaluate the adsorption capacity, the two membranes were tested in aqueous solutions with Pb as heavy metal with high impact on aquatic environment. The role of membranes was established by analyses before and after immersion into solution with 1 mg/L Pb (II). The pollutant removal (as percentage) during 120 min contact time is presented in Figure 5.

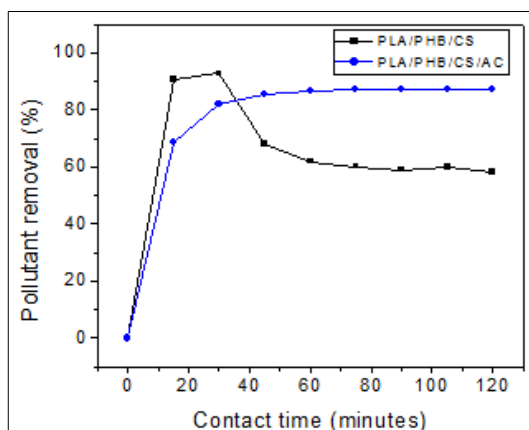


Figure 5. Effect of contact time on the adsorption of Pb (II) ions by the nonwoven PLA/PHB/CS and PLA/PHB/CS/AC membranes.

Experimental conditions: the amount of adsorbent of 500 mg was dispersed into 100 mL solution of Pb (II) pollutant at 1 mg/L under gentle stirring conditions at room temperature and 200 rpm, and at maximum 120 min contact time

After 15 min, the highest pollutant retention efficiency of the PLA/PHB/CS adsorbent material (94.6%) was observed, after that it decreased with the increasing contact time up to 120 min, to about 53% (Figure 5). This behaviour can be explained by the competition between Pb (II) ions to fill the vacancies sites in the first 15 min and the repulsive force that decreases the adsorption rate of Pb (II) from 30 to 120 min. In the case of PLA/PHB/CS/AC membrane, >60% efficiency is reached in the first 15 min, following that the equilibrium to be reached after 50 min (the maximum value being of 85%). This demonstrates the complementary performance and synergy occurred between the chitosan and activated carbon, as well as the role of nanofiber dimensions on the heavy metal adsorption process. The results indicate possibility of membrane use in Pb retention and removal from aqueous systems, thus future experiments will be developed for different concentrations of Pb and membranes quantities in order to be established the retention mechanism and maximum retained Pb quantity onto studied membranes.

4. Conclusions

Symmetric and asymmetric bio-based polymeric membranes were fabricated by the electrospinning process. The efficiency of the PLA and PLA/PHB membranes was proved by performing the filtration of a solid suspension solution, and the adsorption of Pb (II) in the case of PLA/PHB/CS and PLA/PHB/CS/AC membranes.

SEM analysis revealed that the thickness of fibers was of maximum 400 nm, and the size of the membrane pores was $\sim 20 \mu\text{m}$, which is suitable for retaining of solid suspension from water with the same dimension. The thermal transitions highlighted by the DSC analysis show the characteristic peaks of polyesters and the improved in the flexibility in the case of PLA/PHB membrane. The FTIR results confirmed the chemical structure of the membranes.

The results showed that the PLA and PLA/PHB polymeric membranes led to the filtration efficiency of 99.2 and 98.4%, respectively for 1% sand solution and good physical characteristics of the filtered solutions. The PLA/PHB/CS membrane recorded 94.6% efficiency for removing Pb(II) from wastewater for the first 15 min, while the PLA/PHB/CS/AC membrane reached 85% efficiency after 50 min. The electrospun polymeric biomembranes are promising for further investigated at industrial scale to replace membranes made of petrochemical plastic materials.

Acknowledgments: The work has been funded by the European Union through POC Program, Project ID: P_40_253, Contract 130/23.09.2016, SMIS 105558, Subsidiary Contract 5048/23.03.2018, and Subsidiary Contract 25501/18.12.2018. The FTIR analysis on INTERSPEC 200-X Spectrophotometer was possible due to European Regional Development Fund through Competitiveness Operational Program 2014-2020, Priority axis 1, Project No. P_36_611, MySMIS code 107066, Innovative Technologies for Materials Quality Assurance in Health, Energy and Environmental - Center for Innovative Manufacturing Solutions of Smart Biomaterials and Biomedical Surfaces – INOVABIOMED.

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Manuscript received: 4.09.2020