

Article

Plasma-Induced Graft Polymerization of Polyethylenimine onto Chitosan/Polycaprolactone Composite Membrane for Heavy Metal Pollutants Treatment in Industrial Wastewater

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Abstract: The present study manifests an innovative and green approach to graft metal ion adsorbent, polyethylenimine (PEI), onto an electrospun chitosan (CS)/polycaprolactone (PCL) composite membrane via atmospheric pressure nitrogen plasma grafting polymerization. FTIR absorption peak at around 1690 cm^{-1} was attributed to the bending vibration of N-H from PEI. Since the plasma exposure time is a dependent factor of -NH bond formation, an increased nitrogen content up to 3.3% was observed with an extensive reaction time under plasma treatment. In addition, N1s spectra showed a clear PEI dominating characteristic at 401.7 eV, which suggested a successful grafting of PEI onto the CS/PCL membrane. According to the EDX analysis, a significant amount of copper ions was detected in PEI-CS/PCL membranes. This study showed that a greener wastewater treatment can be realized with the developed plasma synthesis technology.

Keywords: polycaprolactone (PCL); chitosan (CS); polyethylenimine (PEI); atmospheric pressure nitrogen plasma (APNP); electrospinning; adsorption



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1. Introduction

Over the past two years, Taiwan, like Korea and other semiconductor manufacturing countries, has played an indispensable role and carried the burden in producing microchips in extremely high demand for industries across the globe amid unprecedented disruption brought by the pandemic [1], and the worsened conflicts in many economic centers [2,3]. Concurrently, the semiconductor manufacturing industries are required to develop strategic plans to reduce or reuse potential pollutants to align with the United Nations Sustainable Development Goals (SDGs). Thus, a different and cleaner approach in handling heavy metals in wastewater is pivotal.

Nickel, zinc, silver, lead, iron, chromium, copper, arsenic, and cadmium are some of the heavy metals often found in industrial wastewater [4–7]. Copper, among most heavy metals, is commonly identified in wastewater due to its wide range of applications [8–10]. Several conventional methods, including electrocoagulation [11], chemical precipitation [12–14], oxidation [15], ion exchange [16,17], adsorption [18,19], and membrane separation [20,21] have been applied to remove heavy metal ions. However, the methods mentioned above may have several drawbacks, such as high operating costs, insufficient removal efficiencies, and the production of large amounts of toxic secondary waste residue [22,23]. Adsorption, compared with these treatment methods, has many merits, and offers high removal efficacy, practical operation, and an affordable cost [24].

The use of biomass for adsorption of copper ion is considered a relatively environmentally friendly route [25–28]. Nevertheless, lack of physical and chemical stabilities

from biomass substance, and requiring complicated processing of biomass may limit their practical use. Polycaprolactone (PCL) has been used widely in biomedical research for its biocompatibility, biodegradability, non-toxicity, and superior mechanical properties [29,30]. These properties are favorable for environmental research such as air [31,32] and water treatment [33,34]. For instance, Maio et al. showed that graphene oxide-decorated polycaprolactone membranes possessed sorption capacity of phenol molecules on its nano-surfaces, and can offer a cost-effective approach for water treatment [35]. Meanwhile, Nivedita et al. prepared polyethylene glycol tailored PCL/TiO₂ nanocomposites, which can effectively filter proteins in effluents from the dairy industry [36].

Chitosan (CS), a polycationic natural polymer extracted from crustaceans, has been used in conjunction with PCL to fabricate composites with advantageous properties of antimicrobial [37], high sorption [38], and processability. Together with chitosan, the amino-rich polyethylenimine (PEI) composites have been used to boost copper ion scavenging effectiveness and selectivity [39–42]. Furthermore, the feasibility of cold plasma treatment on hybrid chitosan-SiO₂/PCL membranes [43], and amine functionalization by plasma polymerization on polypropylene surface were also reported by Mangindaan et al. [44].

The main target of the current study is to utilize atmospheric pressure plasma as a green and simple technique to hybridize the superior qualities of PCL, CS, and PEI into a membrane with copper ion adsorption capability. The conditions of CS/PCL fiber formation were investigated. The effects of atmospheric pressure nitrogen plasma on CS/PCL and grafting of PEI onto CS/PCL were evaluated. Moreover, the adsorption of copper ion was also assessed with SEM and EDX analyses.

2. Materials and Methods

2.1. Materials

The polyethylenimine (PEI) used in this work was EPOMIN[®], purchased from MPES (Taipei, Taiwan); it is a cationic water-soluble polymer suitable for chelation of metal ions. High quality natural polymer chitosan (CS) by Chang Chun Petrochemical Co., Ltd. (Taipei, Taiwan) was added to the polycaprolactone (PCL), acquired from Sigma-Aldrich (St. Louis, MO, USA), matrix to enhance structural stability and functionality.

2.2. Membranes Fabrication

PCL-based membranes, containing different amounts of chitosan (from 2 up to 30 wt.%), were dissolved in a mixture of formic acid and acetic acid solvent [45], and fabricated by electrospinning with voltage and flowrate in the range of 15 to 25 kV, and 0.4 to 1.5 mL·h^{−1}, respectively. The prepared CS/PCL membranes were activated via an atmospheric pressure nitrogen plasma (APNP) with operating voltage, air flowrate, distance between the tip of the plasma torch and membranes, and exposure time of 6 kV, 15 L·min^{−1}, 1 cm, and 5 to 380 s, respectively. The grafting of PEI onto CS/PCL was carried out by injecting 7 wt.% PEI mist into nitrogen plasma torch, of the same plasma parameters, while limiting the exposure time to only one minute. All samples were kept in a desiccator for two days before performing characterizations.

2.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was essential to assessing the surface topography after each treatment, especially after nitrogen plasma exposure. The surface of the prepared CS/PCL and PEI grafted CS/PCL membranes were investigated by Hitachi (S-3400N, Tokyo, Japan) scanning electron microscope at an accelerating voltage between 5 and 20 kV, and mounted with energy dispersive X-ray analysis (EDX). The samples were sputter-coated with gold prior to microscopy to prevent charge build-up.

2.4. Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier-transform infrared (FT-IR) spectra were recorded using a Fourier-transform infrared spectrophotometer (Thermo Nicolet iS5 FTIR, Waltham, MA, USA), and collected

over the range 4000–400 cm^{-1} . All the FT-IR measurements were repeated three times for each sample and are well reproducible.

2.5. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was carried out on a PHI 5000 VersaProbe supplied by ULVAC-PHI Inc. (Chigasaki, Japan), equipped with a monochromatic Al $K\alpha$ X-ray irradiation ($h\nu = 1486.6$ eV). The take-off angle of the photoelectron was fixed at 45° . The spectra were recorded from at least three different locations on each sample, with a $1\text{ mm} \times 1\text{ mm}$ area of analysis. For a wide-scan survey, spectra were recorded in 0.25 eV steps with 80 eV pass energy, while high resolution spectra were in 0.1 eV steps with 20 eV pass energy. The binding energies were calibrated with reference to the C1s main peak at 284.5 eV [46].

3. Results and Discussion

3.1. Characterizations of CS/PCL Nanofibers

FT-IR spectroscopy was performed to detect the presence of CS in the fabricated PCL fibers (Figure 1). The main peaks of the spectrum of chitosan included 3400 cm^{-1} and 1580 cm^{-1} , which were assigned to the -OH and -NH stretching, and the amide II bands of chitosan [47]. A strong peak at 1750 cm^{-1} , was attributed to the C=O stretching, and distinctive peaks at 2940 cm^{-1} and 2861 cm^{-1} were ascribed to the CH_2 stretching in PCL [48]. The feature peaks of PCL were not seen in CS, and their intensity decreased with increasing CS content. The FT-IR results showed that CS and PCL were compounded successfully without any new chemical bonds being identified.

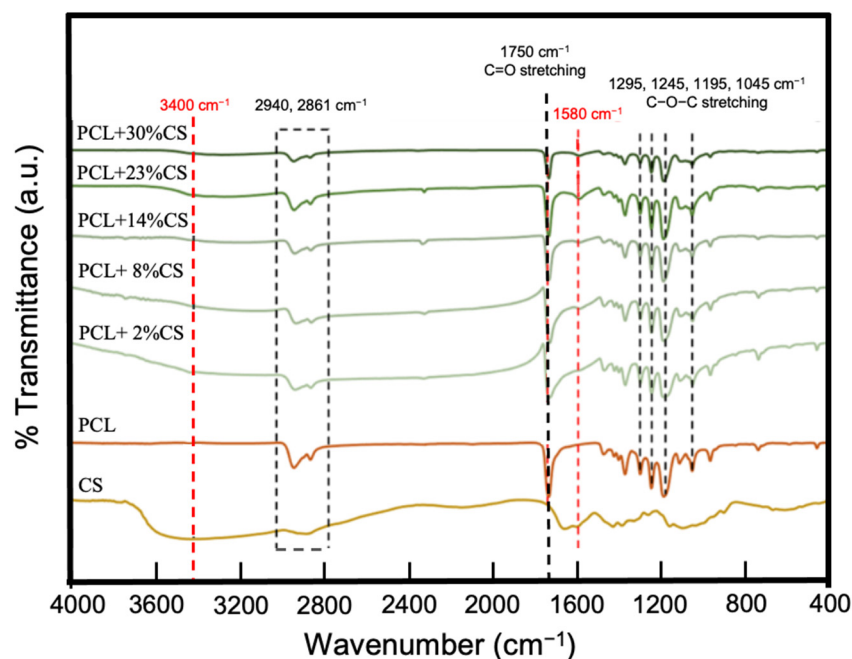


Figure 1. FT-IR spectra for CS, PCL, and CS/PCL nanofibers of various chitosan weight percentages.

PCL fibers produced at 15, 18, and 25 kV with CS addition in the range of 2 to 30 wt.% are shown in Figure 2a. For CS/PCL blends, the average diameter is affected by CS concentration. Reduction of the fiber diameter in higher CS concentration is observed because of increasing electrical conductivity in the polymeric solution [49]. Multiple beads are seen across the fibrous membranes for incompletely dissolved (2, 8, 14 wt.%) and excessive amounts (30 wt.%) of CS due to low viscosity [45] and clogging of the needle [49]. At 23 wt.% CS, less or zero-bead nanofibers were obtained. In general, the increase of the electric field from enhanced applied voltage would lead to reduction in fiber diameter [50].

In our case, using CS/PCL blends at a higher voltage (18 and 25 kV), a strong electrical interaction between the jet and the electric field encouraged the formation of thinner secondary jet split fibers [51]. These branching fibers then formed smaller beads along several main fibers. At the balance of surface tension (23 wt.% CS) and the electrical field (15 kV), bead-free CS/PCL fibers ranging from 58 to 131 nm were obtained (Figure 2b).

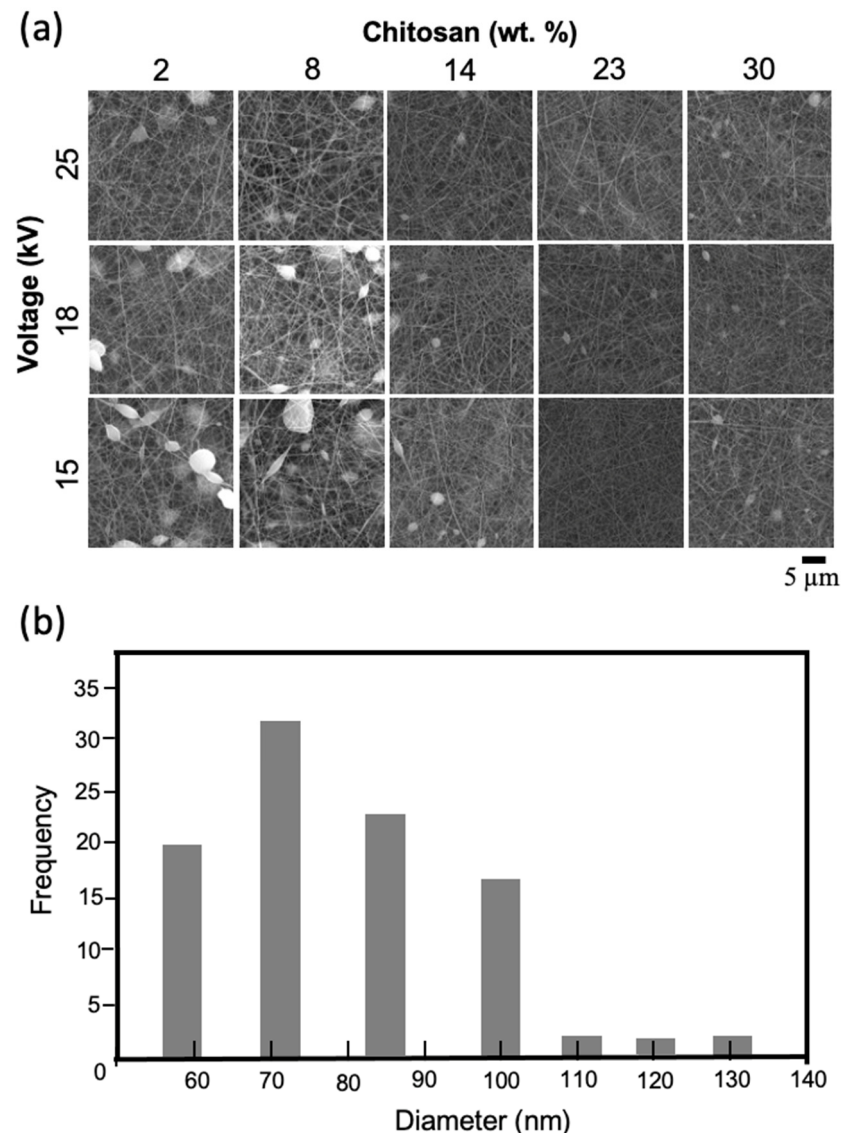


Figure 2. SEM images of (a) CS/PCL nanofibers with different chitosan concentration (wt.%) and applied voltage; and (b) fiber diameter distribution of CS/PCL produced at applied voltage of 15 kV with 23 wt.% CS.

3.2. Characterizations of CS/PCL Nanofibers after APNP

Electrospun CS/PCL nanofibers were subjected to atmospheric pressure nitrogen plasma (APNP) for fiber activation. In Figure 3, a noticeable decrease of intensity in -NH bending vibration (assigned to 1580 cm^{-1}) when increasing the plasma exposure time, while significant increase in C-O-C stretching bands (1295 , 1245 , 1195 , 1045 cm^{-1}) are observed [52]. Sites originally with amino functional groups are being replaced with newly formed ether, secondary alcohol, methyl functional group or even crosslinking from activated hydrogen, oxygen, and other free radicals [53]. In our prior study, amine-terminated peptide bonds were being grafted and removed as the result of simultaneous activation and etching reactions during plasma process [54]. This competing phenomenon

is also observed in the two enlarged regions (-NH stretching and in C-O-C stretching) such that the correlation of plasma exposure time and the change in functional group intensities is not easily identifiable.

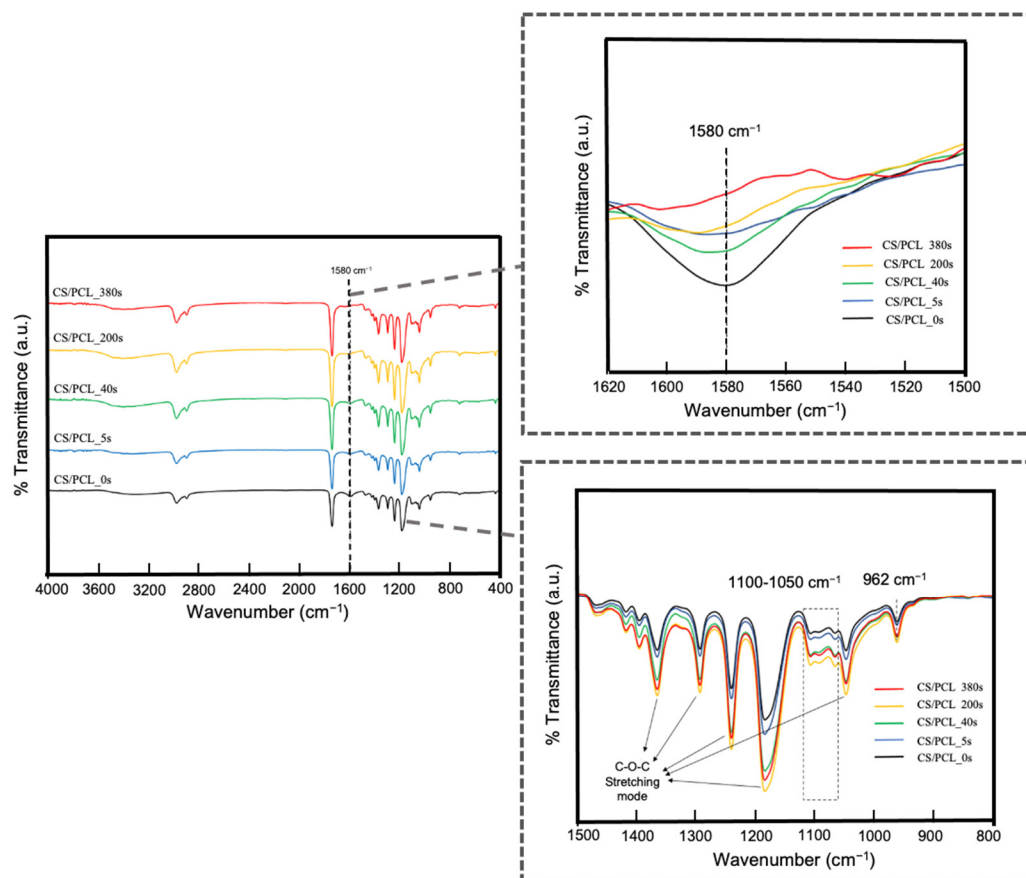


Figure 3. FT-IR spectra of CS/PCL with various APNP exposure time.

As shown in Figure 4, notable change in fiber morphologies is observed as plasma exposure time increase from 5 to 380 s. No obvious change is observed for CS/PCL nanofibers underwent 5 and 40 s exposure time (Figure 4a,b). At an extended exposure time of 200 s (Figure 4c), fiber fusion starts to take place as result of crosslinking between fibers. Plasma-initiated surface can create numerous active sites for rapid reactions, and thus junction fusion continues to expand horizontally and vertically under prolonged plasma exposure time (Figure 4d) [55].

3.3. Characterizations of PEI Grafted CS/PCL Nanofibers

In Figure 5, an identifiable characteristic absorption of bending vibration of N-H at 1690 cm^{-1} is clearly seen in PEI-CS/PCL with 30 and 60 s plasma exposure time. The intensity of the 1690 cm^{-1} peak is slightly reduced after the washing off of unreacted PEI on the fiber surface. It is worth noting that the absorption band at 1750 cm^{-1} , assigned to the C=O stretching, is not perceptible in the PEI grafted samples, but showing a weak shoulder peak next to (short wavenumber side) the 1690 cm^{-1} absorption peak after washing. Can-Herrera et al. reported that superficial changes caused by plasma treatment was not observed mainly because of the physical detection limit of FTIR-ATR [56].

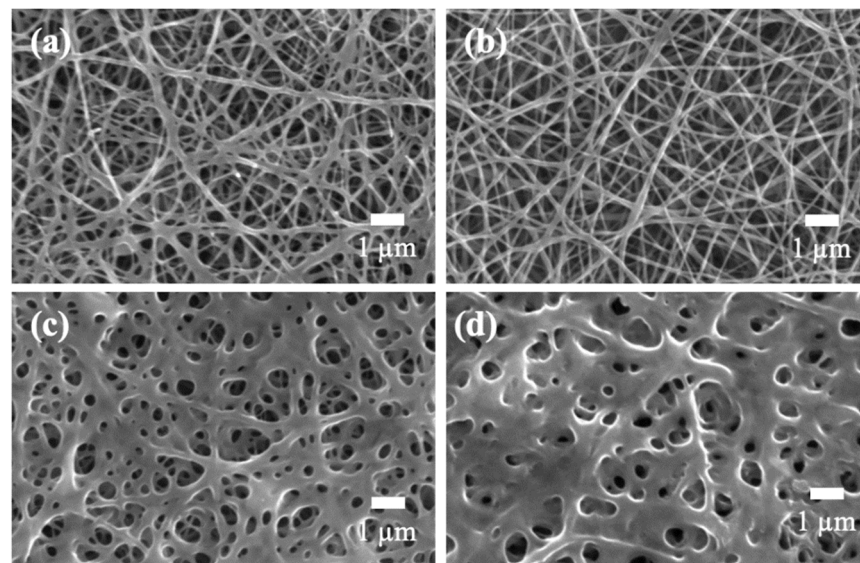


Figure 4. SEM images of CS/PCL nanofibers expose to APNP for (a) 5; (b) 40; (c) 200; and (d) 380 s.

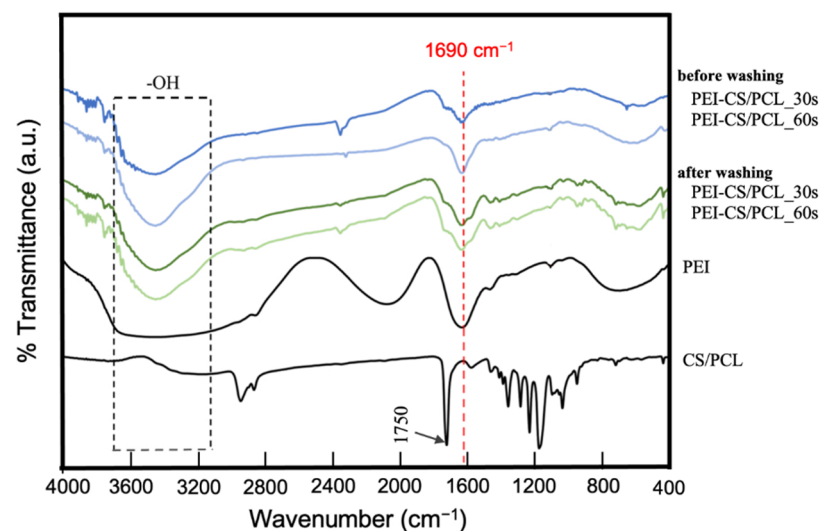
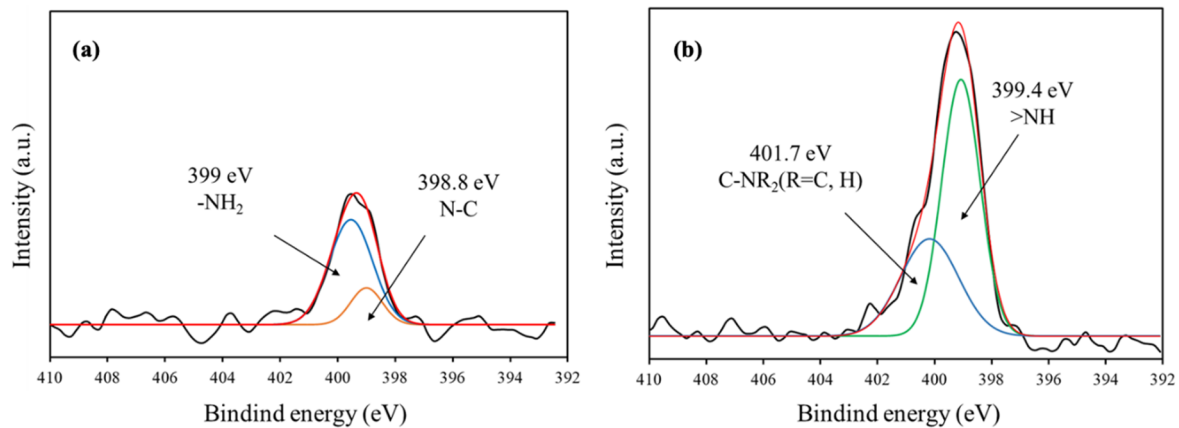


Figure 5. FT-IR spectra of CS/PCL, PEI, and PEI-CS/PCL before and after washing.

In order to gain better insight on the plasma-induced nitrogen containing functionalities, a deconvolution of high resolution N1s spectra is performed for CS/PCL and PEI grafted CS/PCL samples. The N1s envelope of the CS/PCL sample could be decomposed into two distinct peaks: a peak at 398.8 eV corresponds to N–C bonds, and a peak at 399 eV, which can be attributed to —NH_2 groups [57,58]. After plasma treatment for PEI grafting, one peak at 399.4 eV that can be ascribed to the presence of amine or imine groups, and another peak at 401.7 eV accredited to the protonated amines presented in PEI [59–61]. The results of increasing N1s percentage value with the increase in plasma treatment time in Table 1 not only align well with the results in Figures 5 and 6, but also highlight the role of plasma treatment in PEI grafting, and demonstrate that high concentrations of surface nitrogen can be translated into high contents of amine.

Table 1. XPS atomic concentration table for CS/PCL and PEI-CS/PCL.

	C1s	N1s	O1s
CS/PCL	74.4	1.5	24.2
PEI-CS/PCL_0s	72.2	1.8	26.0
PEI-CS/PCL_15s	70.5	2.0	27.5
PEI-CS/PCL_30s	70.3	2.1	27.7
PEI-CS/PCL_60s	70.1	3.3	26.6

**Figure 6.** High-resolution N1s peaks of (a) CS/PCL, and (b) PEI-CS/PCL.

3.4. Adsorption of PEI Grafted CS/PCL Nanofibers

The prepared PEI-CS/PCL_60s membrane was immersed in 100 ppm copper(II) sulfate pentahydrate solution up to two hours (Figure A1). The distinct color change on the prepared membranes from pale blue to azure (left to right) suggests the adsorption of copper ion (Figure A1a), while the solution bottles show a reverse color change in the same direction (Figure A1b). Reduction of copper ion concentration from 100 to 75.80 ppm is indicated, however the adsorption of copper ions merely reaches 19.1% after 120 min of contact time with the selected membrane (Table 2). This outcome may be attributed to the insufficient overall amine concentration on the membrane surface which shall be investigated further [62]. Curl and ball-like features are seen on the surface of PEI-CS/PCL membranes (Figure 7a), which may be shown in other polymeric fibers treated with plasma [63]. However, fibers produced from solvent-blended PEI/PCL via electrospinning would appear rather smooth otherwise [64]. After being exposed to copper-contained solution, a veil-like layer is observed on top of the prepared membrane (Figure 7b). The presence of copper ions is stipulated by the elemental mapping analysis in Figure 7c. Although a direct proof is not found, the literature suggests it can be complexes of PEI with copper(II) ions [65].

Table 2. Adsorption of copper onto PEI-CS/PCL_60s membrane.

Contact Time (min)	Copper Ion Concentration (ppm)	Adsorption (%)
0	100	—
10	88.13	7.76
20	86.40	11.7
30	78.80	15.9
60	77.06	17.7
120	75.80	19.1

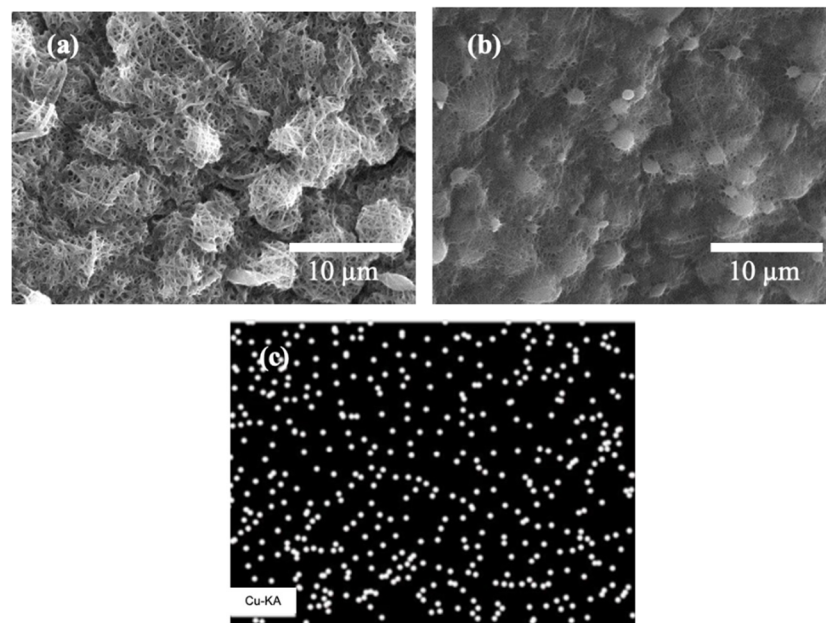


Figure 7. SEM images of PEI-CS/PCL_60s nanofibers: (a) before; and (b) after exposed to copper-containing solution, with (c) elemental mapping of Cu.

4. Conclusions

An innovative method to graft PEI onto electrospun CS/ PCL membranes was proposed. The results showed that nitrogen plasma activated membranes have a distinct structural feature of a fibrous network at 5 and 40 s of plasma treatment time. FT-IR and XPS results suggest that via the nitrogen plasma-assisted approach, PEI can be grafted onto CS/PCL without the use of any solvent. Consequently, copper ions were detected on the PEI-CS/PCL membranes with the confirmation of EDX analysis. The findings of the adsorption results reveal that the fabricated membranes have the potential to be a sustainable solution for removing heavy metal ions.

Author Contributions: Conceptualization, validation, supervision, writing, J.H.C.Y., C.-K.C. and S.-C.S.; methodology, formal analysis, S.-L.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

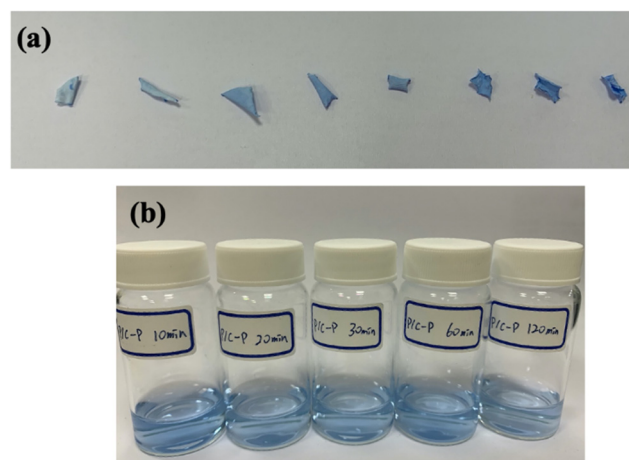


Figure A1. Sorption of 100 ppm copper(II) sulfate pentahydrate onto PEI-CS/PCL_{60s} membranes. Color changes of (a) PEI-CS/PCL and (b) copper-contained solution with increasing immersion time.

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