

Article

Removal of Heavy Metals from Wastewater Using Novel Polydopamine-Modified CNTs-Based Composite Membranes

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Abstract: The presence of major heavy metals including Pb^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , Cr^{6+} , Cd^{2+} , and Zn^{2+} in water is of great concern because they cannot degrade or be destroyed. They are toxic even at very low concentrations. Therefore, it is necessary to remove such toxicants from water. In the current study, polydopamine carbon nanotubes (PD-CNTs) and polysulfone (PS) composite membranes were prepared. The structural and morphological features of the prepared PDCN composite membranes were studied using FTIR, XRD, SEM, and EDS. The potential application of PDCNs for heavy metal removal was studied for the removal of Pb^{2+} , Cr^{6+} , and Cd^{2+} from wastewater. The maximum removal efficiency of 96.1% was obtained for Cr^{6+} at 2.6 pH using a composite membrane containing 1.0% PD-CNTs. The removal efficiencies decreased by 64.1 and 73.4, respectively, by enhancing the pressure from 0.50 up to 0.85 MPa. Under the same circumstances, the percentages of Pb^{2+} removal at 0.49 bar by the PDCNS membranes containing 0.5% and 1.0% PD-CNT were 70 and 90.3, respectively, and decreased to 54.3 and 57.0, respectively, upon increasing the pressure to 0.85 MPa. The results showed that PDCNS membranes have immense potential for the removal of heavy metals from water.

Keywords: CNTs; polydopamine; heavy metals; adsorption; removal percentage



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1. Introduction

Heavy metals are environmental contaminants in unclean wastewater, and they have become the cause of serious public health issues [1]. The key cause of various types of metal contamination in natural water is industrial wastewater [2]. The main source of these pollutants is manufacturing industries, such as manufacturers of batteries, pesticides, mining, electroplated metal parts, alloys, textiles, dyes, and paints. Pb^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , Cr^{6+} , Cd^{2+} , and Zn^{2+} are some of the common metals that can easily bioaccumulate in living organisms [3]. These heavy metal ions cannot be degraded or destroyed over the years and hence become permanent pollutants in the environment. Even a very low concentration of heavy metals can result in various physiological conditions, such as high blood pressure, abdominal pain, nephritis, vomiting, nausea, and various developmental issues [4]. Therefore, most countries are developing very high standards to control

the discharge of heavy metals into fresh water, which offers enormous demand for the development of modern technologies for the treatment of wastewater [5].

Extensive techniques have been introduced for the removal of heavy metals from water, which include nanofiltration, precipitation, reverse osmosis, adsorption, and coagulation. In recent years, the preparation of organic polymer in organic nanocomposite membranes has been extensively studied. Nanomaterials offer a great systematic pore structure, surface area, and ease of tunable surface properties [6].

There are a range of polymers that are used to prepare membranes for wastewater treatment purposes [7–9]. Polysulfone has several significant mechanical and thermal characteristics that make it attractive to membrane scientists [10,11]. The continuous care of the membrane, and also the high mechanical strength of the films, enable the establishment of penetrating networks within the mixtures while maintaining the thermal and mechanical properties. However, due to the hydrophobic nature of the PSF membrane, its applications are often limited [12]. The performance of PSF membranes results in low water flux and severe fouling of the membrane due to its hydrophobic properties. It was found that the thermodynamic, rheological, and adsorption properties change significantly through the induction of inorganic charges [13].

Nanomaterials, including organometallic structure (MOF) carbon-based materials (carbon and graphene nanotubes) [14], nanoscale zero-valence iron (nZVI), and graphitic carbon nitride (gC_3N_4) [15], have revealed a promising ability to remove heavy metal ions [16]. Due to the high stability and mechanical strength, relatively low price, and strong interaction with pollutant molecules, carbon nanotubes (CNTs) are widely used to remove various pollutants from wastewater. By anchoring the functional groups on the surface of CNTs, such as $-NH_2$ and $-SH$, these modified nanomaterials show improved adsorption abilities for heavy metal ions [17]. Although, at present, various studies are focused on the preparation of CNT-based composite, many disadvantages are associated with them, such as agglomeration, difficult separation, and recycling. Therefore, modification of CNTs is necessary before induction into the polymer matrix. The modification of CNTs is a simple, suitable, and effective way to eliminate these disadvantages for practical applications [18].

A variety of CNT-based composites have been prepared and applied in different fields. For example, polymer CNT composite membranes have been fabricated and applied for high gas transportation [19]. Poly(ether urethane) filled with CNTs grafted on isophorone diisocyanate was used to achieve the high water vapor penetrability [20]. It has been described that functionalized polyamide/CNT nanocomposite membranes fabricated by interfacial polymerization [21] can be used for the removal of solutes of brilliant blue R and safranin O from aqueous and methanol solutions.

Nanocomposite membranes with carbon nanotubes with a single wall in a matrix of polysulfone have high permeability and diffusivity for hydrogen, oxygen, and carbon dioxide. Several studies investigating the improvement of pore structure, size control, and flow have put together polysulfone/CNT composite membranes, a motivating area for purification [22]. The functionalized nanotubes have been observed to have significant affinity for metals, such as lead, copper, and cadmium. The large surface area and nano diameter of CNTs could be used effectively to modify the polysulfone membrane, which enhances the removal of metal ions in precarious applications.

Yang et al. presented a simple and adaptable modification technology that employs dopamine as a potent modifying agent [23]. Dopamine is a catecholamine with both catechol and primary amine functional groups in its structure. Dopamine can self-polymerize in aqueous solution under oxidizing circumstances, resulting in the formation of poly-dopamine (PDA).

According to Jiang et al., PDA could cling strongly to a variety of solid substrates, including titanium oxide nanoparticles, clay materials, and graphene oxide. The hydrophilicity and antifouling ability of the substrate along with the interfacial contacts between nanomaterials and polymer matrices are improved by the hydroxyl and amine groups in the PDA layer [24]. According to Hansen et al., both the bonding force and

membrane performance are improved by the PDA bonding technique [25]. Wang et al. reported that the numerous functional groups of polydopamine-functionalized graphene display great surface assimilation capabilities against a wide range of pollutants, including organic impurities, synthetic dyes, and heavy metals [26]. Mesoporous silica coated with PDA, zeolites, carbon nanotubes, nanoparticles, etc. was also used as a sorbent material to remove contaminants from wastewater [27].

The current study was conducted with the objective of producing a new nanocomposite membrane with a PD-modified multi-walled carbon material as a stabilizer for the removal of selected heavy metals. Nevertheless, to the best of our knowledge, no previous studies have been carried out on the removal of metal ions from wastewater using PD-CNT/and sulfonated polysulfone composite membranes. An operating material (PD-CNTs) was made by self-polymerizing dopamine under basic system conditions. The amine and catechol groups (having a tendency to strongly bind to hazardous metal ions) in the PDA matrix are sufficient in the PDA-based adsorbents. Chromium, lead, and cadmium ions were selected as distinctive heavy metal contaminants to assess the removal capability of -CNTs/PS membranes, and the produced composite membranes were evaluated using the FTIR, XRD, SEM, and TGA techniques.

2. Materials and Methods

2.1. Synthesis of PD-CNT-Based Composite Membranes

The synthesis of PD-CNT-based composite membranes consists of several steps illustrated in the following paragraphs.

2.1.1. Nanotube Surface Cleaning and Washing

The purified commercially available MWNTs are nevertheless coupled with amorphous carbon and residues of metal ions that come into contact with these nanotubes during their manufacture. In the current study, the amorphous carbon soot and nearly all heavy metals found in the as-purchased CNTs were removed using a modified approach to clean the surface. In total, 3 g of these nanotubes were sonicated for roughly 3 h with 600 mL of 1% Brij 98 (non-ionic surfactant). The sonicated solution was left to settle for 7 h. The sediments were removed in the form of soot linked with CNTs. The CNTs were extracted from the mother liquor after centrifugation and 10 min of sedimentation at 3000 rpm. To obtain clean nanotubes, this process was repeated 3–4 times.

By alternating washing with water and brine solution, the surfactant associated with the nanotubes could be easily removed. Following this, some of the heavy metals that may have remained on to the CNTs' surface were eliminated by reducing them to their soluble metal chlorides in a 50% HCl solution. The yield was only about 35% of the raw CNTs used. The rest could be amorphous and other undesirable carbonaceous material, as well as heavy metal traces. In contrast to uncleaned pure CNTs, which include Fe, Co, Ni, and other trace metals and are attracted to the magnetic bar, the produced nanotubes are not attracted to the magnetic needle. Purification and washing remove undesirable carbonaceous material and metal ions, and the washed and dried nanotubes are then treated with various functionalizing agents.

2.1.2. Oxidation of Carbon Nanotubes

In total, 2 g of washed CNTs were treated with a 3:1 mixture of strong nitric and sulfuric acid (50 mL) for 1 day at 33 °C to introduce a carboxylic group (-COOH) onto the surface. The resultant mixture was then transferred to a 500 mL round-bottom flask and kept at 100 °C for one day with vigorous shaking. After, the substance was chilled and blended at room temperature with DI liquid. The oxidized CNTs (O-CNTs) were rinsed with DI water to remove the excess HNO₃. The O-CNTs were then dried in a vacuum oven at 80 °C overnight [10,28].

2.1.3. Dopamine-Coated Carbon Nanotubes

About 12 g of dopamine were added to a round-bottom flask and heated to 80 °C to functionalize CNTs with dopamine. Then, 3 g of CNTs were added to the mixture and mixed for around 20 min. At pH 8.5, a few drops of H₂SO₄ were added to speed up the process. Under a nitrogen environment, the process was conducted for 4 h. To eliminate excess dopamine from the supernatant solution, the resulting combination was precipitated with petroleum ether. The precipitated modified polydopamine (PD-CNTs) was then washed in acetone and dried under vacuum at 80 °C overnight.

2.1.4. Membranes Casting PD-CNTs/SPS (PDCPS) Nanocomposite

The phase inversion method was used to create PDCPS membrane mixed matrix membranes. A selected amount of PD-CNTs (0.5 wt.% to 1.0 wt.%) [F. Altaf, R. Gill, R. Batool, Z.-U.-Rehman, H. Majeed, G. Abbas, K. Jacob, Synthesis and applicability study of novel poly(dopamine)-modified carbon nanotubes based polymer electrolyte membranes for direct methanol fuel cell], was dispersed in a sufficient volume of NMP solvent and agitated at room temperature for 90 min. Sulfonated polysulfone (SPS) (overall 20 wt.% percent of the polymer concentration in the final casting solution) and 2% of the invariable pore formation agent PVP were added to the aforesaid dispersion solution. The solution was then agitated for 18 h at 65 °C to obtain a homogenous casting. To remove any air bubbles, the solution was vacuumed for 15 h before being cast on a petri dish. To complete the phase inversion, the membranes were immersed in a water bath at 20 °C for one day. There were no visible signs of PD-CNTs leaching from the cast membranes.

2.2. Characterization of PD-CNT-Based Composite Membranes

The Fourier Transform Infrared Spectra (FTIR) were obtained using Nicolet Magna 550 series II FTIR in order to find out the presence of functional groups in all prepared samples (PD-CNTs, PDCNS). The FTIR of all samples were done by making direct contact between the ATR tip and samples and 64 scans were obtained in the range 4000–400 cm⁻¹. The crystallographic arrangements of all samples were analyzed using PANalytical X-Pert Pro X-ray Diffractometers (XRDs) employing Cu K α radiation at $\lambda = 1.540598 \text{ \AA}$. SEM micrographs of the prepared samples were obtained by employing LEO 1530 and Hitachi SU8010 equipped with EDS to study the elemental composition of the samples. TEM micrographs of the samples were obtained using a Tecnai G2 F20 S-Twin microscope operated at 200 kV.

2.3. Removal Efficiency Determination by Atomic Absorption Spectrometry

The metal removal efficiency of the prepared samples was analyzed by preparing a salts solution of heavy metals and ultrapure water. The chromium and lead stock solutions of (1000 mg/L) were prepared by adding 3 g of K₂Cr₂O₇, 2 g of Pb(NO₃)₂, respectively, in 1000 mL of DI water. The cadmium solution was prepared by adding 1 g of Cd metal in HCl and increased to 1000 mL by adding DI water. The metal removal efficiencies were checked at pH 2.6 (acidic medium), 6.8, and 9.5. The pH was adjusted to 6.8 and 9.5 by adding 0.1 N solution of NaOH. The acidic and basic solutions of all metal ions except Cr⁺⁶ exhibited formation of hydroxide and hydrolysis and therefore it was concluded that such pH conditions were not appropriate for metal removal analysis by the prepared membranes. The experiments were conducted at different pH values of 2.6, 6.8, and 9.5 for Cr⁺⁶ ions and at pH 2.6 only for other metal ions. The optimum pressure of 0.50 MPa and pH of 2.6 were set for the metal removal analysis. The concentration of heavy metals in the solutions was determined by Atomic Absorption Spectrometry (AAS), using an FAAS (Model: SpectraAA300 + Varian, Australia) in oxy-acetylene flame. Volumes of up to 1000 mL of metal ions were passed through the column at a flow rate of 4–10 mL/min. The wavelengths were selected on the basis of the most sensitive value for every metal.

3. Results and Discussion

In Figure 1, the FTIR spectra of PD, PDCNTs, OCNTs, CNTs (panel a), and PS, PDCNS (panel b) composite membranes are reported. The FTIR spectrum of (PD) dopamine illustrated in Figure 1a shows few distinguishing features. The presence of a broad peak in the range of 2912 to 3431 cm^{-1} is associated with catechol groups. The presence of aromatic rings is fully confirmed by the sharp peak at 1614 cm^{-1} while another sharp peak at 1293 cm^{-1} can be ascribed to the C-O stretching vibration. The oxidized MWNTs (O-CNTs) denotes a spectrum with key bands, while the purified MWCNTs membranes do not show any significant peak. The peak present at 1462 cm^{-1} is a characteristic feature of the carboxylate anion. The stretching patterns of the C-O carboxylic group are evident due to the presence of a sharp peak at 1618 cm^{-1} , whereas the band at 3500 cm^{-1} can be associated with the hydroxyl (-OH) group.

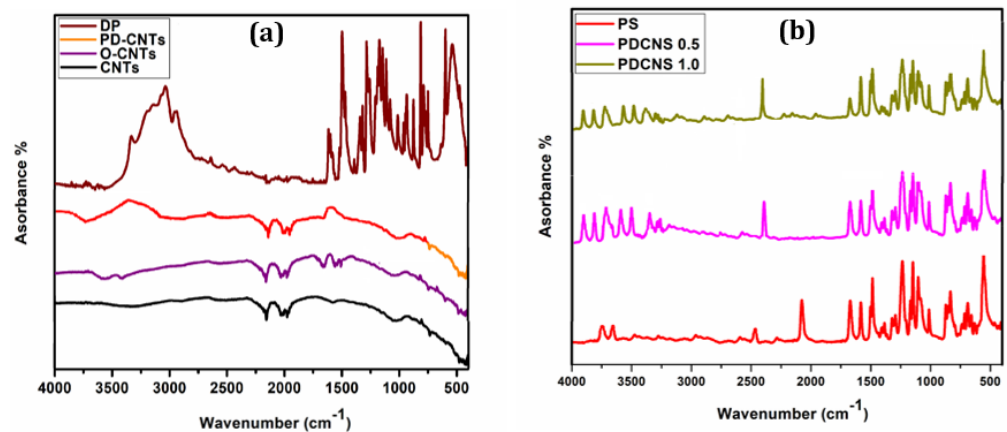


Figure 1. FTIR spectra of (a) PD, PDCNTs, OCNTs, CNTs (b) PS, and PDCNS composite membranes.

In the spectra of PD-functionalized CNTs, a new band is found at 1601 cm^{-1} related to the C=C stretching vibration within the aromatic ring. The detailed spectrum obtained as a result of PDA coating shows an intense peak at 3421 cm^{-1} reflecting the stretching vibration of O-H and N-H, whereas the strong peak at 2830 cm^{-1} confirms the presence of a long alkyl dopamine chain. All these unique peaks in the spectrum of PD-CNTs are the outcome of dopamine coating, which was accomplished through a simple oxidative polymerization procedure.

The FTIR spectrum of PS is shown in Figure 1b. The characteristic absorption band appearing at 1014 cm^{-1} is due to aryl groups while the bands at 1152 and 1174 cm^{-1} are due to symmetric vibration at O=S=O. The bands due to C-O stretching vibration appear at 1237 cm^{-1} . Asymmetric stretching vibration due to the O=S=O group is observed at 1294 and 1325 cm^{-1} , whereas consecutive bands at 1486, 1503, and 1582 cm^{-1} reflect the in-ring C-C vibration. The symmetric and asymmetric stretching vibration due to CH₃ and CH₂ are found between 2898 and 3000 cm^{-1} and finally C-H stretching vibration from aryl groups is observed at 3000–3105 cm^{-1} . The spectra of all prepared composite membranes shown in Figure 1b depict the presence of the same elementary polysulfone (PS) polymer structure, which is found in all composite membranes [29]. The peak at 2981 cm^{-1} represents the hydroxyl groups of PS and polydopamine and hence confirms their presence in the composite membranes. The fall in the bands' intensities at 1152 and 1246 cm^{-1} is an indicator of the formation of another layer over the polysulfone support. The broad band found within the range of 1442–1624 cm^{-1} is due to absorption by the C-O and C-N groups of the composite membranes while the bands in the region of 1670–1744 cm^{-1} are associated with amide linkage (CONH). The bands obtained at 1693 and 1372 cm^{-1} are due to the imide group in the plane whereas the imide group out of the plane is characterized by the presence of another peak at 1732 cm^{-1} .

The lower intense band at 1682 cm^{-1} is an indicator of polydopamine N-H in all composite membranes [30,31]. The above data strongly suggests the formation of co-

polyamide coating on the polysulfone support. The lowering of the band intensity at higher contents of PD-CNTs in the composite membranes corroborates the formation of hydrogen bonds between PD-CNTs and PS.

The dispersion pattern of the particles within the polymer matrix and the interlayer space of PD-CNTs was analyzed using the XRD technique. In Figure 2a, the XRD patterns of O-CNT and PD-CNT membranes compared to pure PD and CNTs are reported. The two peaks at 26° and 44° typical of the CNT structure are slightly less intense in the PD-CNTs material. This effect is associated with the formation of polydopamine coating on the CNT surface as demonstrated by TEM analysis. This finding also provides evidence that CNT functionalization was positively reached.

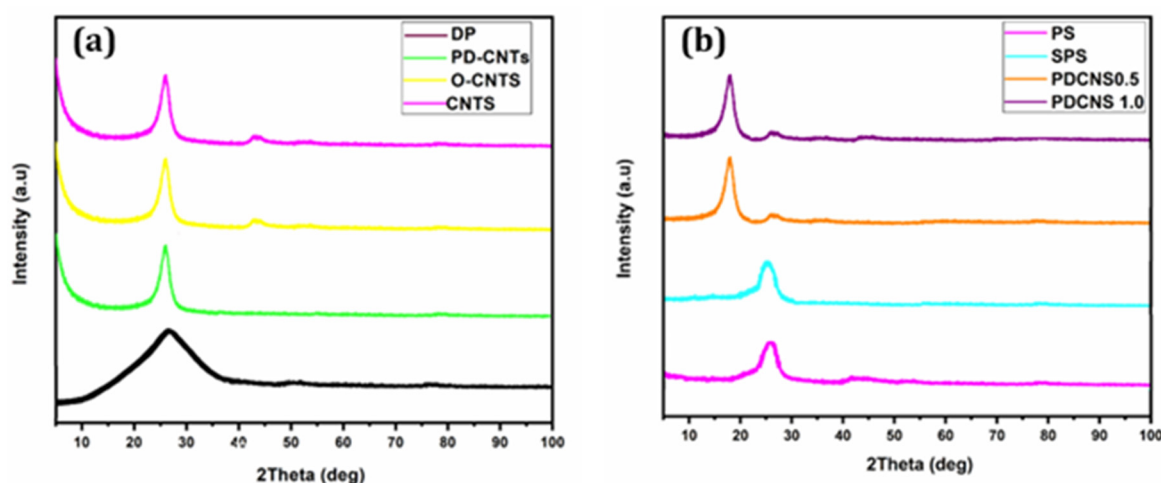


Figure 2. XRD patterns of (a) DP, PD-CNTs, OCNTs, CNTs, and (b) PS, PDCNS composite membranes.

In Figure 2b, the XRD patterns of pristine PS, SPS, and PD-CNTs composite membranes are reported. The two diffraction peaks observed at $2\theta = 18^\circ$ and 45° are attributed to the amorphous character of the pure PS polymer membrane in agreement with the literature [32]. The intensity of the peaks is increased when the PD-CNT content is increased while retaining the actual positions of each characteristic peak of PS and CNTs, indicating conservation in the orientation of the PS chains and the structure of CNTs during the synthesis [33]. However, after the addition of CNTs, the two peaks at 18° and 45° are less intense, indicating that the nanocomposite crystallinity is dependent on the amount of CNTs contained in the membranes. The peaks relating to PS are less intense in the composite membrane, suggesting possible interactions between PS and PD-CNTs [32].

It is known that free volume cavities can be produced in the polymer support by the induction of nanofillers; however, aggregation takes place due to the high PD-CNTs content of up to 1 wt.% in the newly synthesized composite membrane. The crystallinity of the membranes can be decreased by the increase of the PD-CNT content because of the formation of bonds between PD-CNTs and the SPS matrix. The presence of unbonded crystalline PD-CNTs also contributes to the improved crystallinity [34].

The growth of a uniform PD layer on the CNT substrate was confirmed by TEM analysis. This layer is an ultimate outcome of the strong association between the polydopamine aromatic ring and MWCNTs [35]. TEM and SEM images of the functionalized MWNTs were collected through the opened tips of nanotubes before the blending of polysulfone membranes. Rupturing can be seen in the outer layer of the composite membrane as a side effect of cleaning process done through oxidation and amide treatment. This rupturing is restricted only to the outer layer and the internal surface remains unharmed. It illustrates the advantage of having multiwall nanotubes. MWCNTs can maintain their structure even after surface medication, which is not true in the case of SWCNTs. This is the major reason why most research and development are devoted to MWCNTs. Surface treatment also involves cutting of the nanotubes. Surface treatment of nanotubes reduces their length

from 5–9 to 4–6 nm. Variation in the texture and size is clearly observed through TEM analysis as reported in Figure 3a. It shifts from smooth to rough due to dopamine treatment. It is also reported that PD at CNTs also provides high polymer matrix dispersion [36]. Figure 3b reports the SEM images of the synthesized membranes. The morphology of the polysulfone (PS) membranes exhibits a small finger-like pore structure well separated by a honeycomb-like framework in agreement with the literature [37]. However, the SEM morphology of the SPS image reveals that pores are separated by a denser porous medium. The different pore sizes are due to the occurrence of sulfonic groups (SO_3H) in the polymer chain.

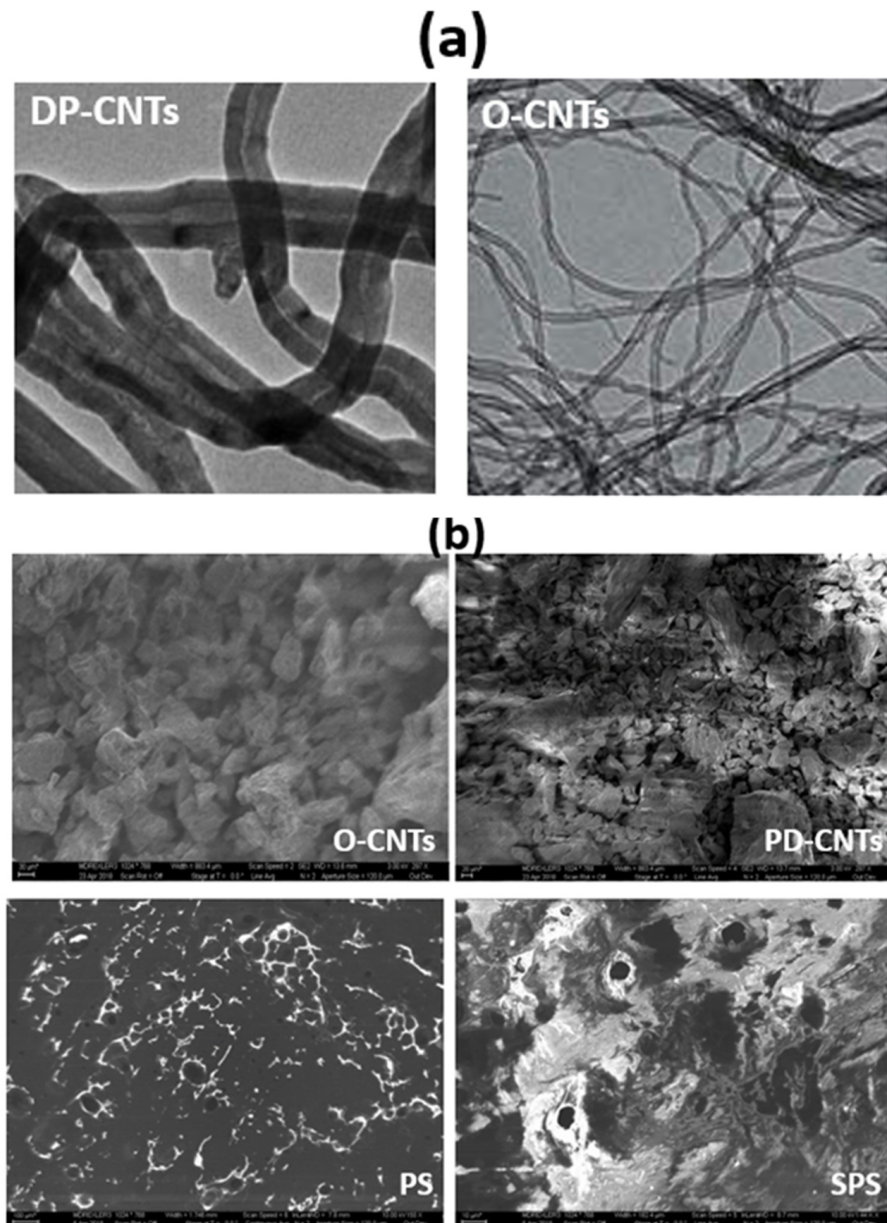


Figure 3. Cont.

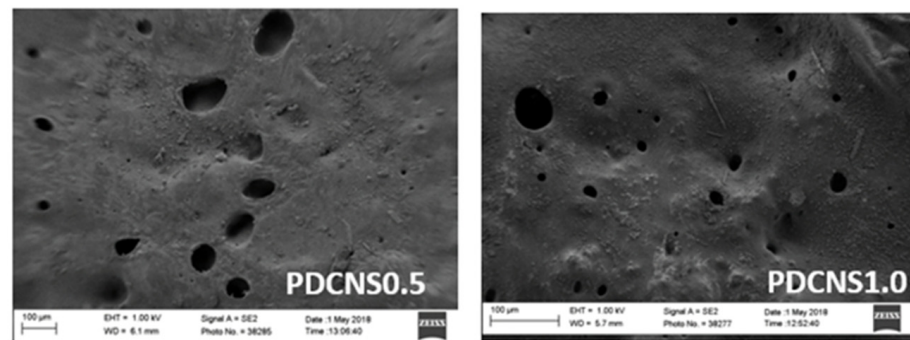


Figure 3. (a) TEM images relating to O-CNT and PD-CNTs membranes. (b) SEM micrographs of O-CNTs, PS, CNTs, and PD-CNTs composite membranes.

The porosity of the synthesized membranes is influenced by the introduction of modified fillers that trigger CNTs, forming physical bonds between PD-CNTs and the PS matrix. The porosity of the PS polymer matrix increases after the introduction of PD-coated CNTs. The composite membranes become more porous compared to the pristine membrane. This is associated with a fast exchange between the non-solvent and solvent during the phase inversion process [38]. The porosity decreases with the increase of the PD-CNT loading from 0.5 to 1.0 wt.%, resulting in a denser framework of the sublayer, which consequently delays the phase separation [39]. The physical bonds between PD-CNTs and SPS polymer and/or between PD-CNTs themselves may be responsible for the higher viscosity because of steric interferences. As a consequence, during the cycle of phase inversion, undesired linking inside the membrane forms, resulting in a roughening of the surface caused by the formation of PD-CNTs beads or to surface overhang [36].

In Figure 4, the energy-dispersive X-ray spectroscopy (EDS) analysis of PD-CNTs composite membranes is reported. In Figure 4a, the EDS analysis of PDCNS0.5 confirms the expected presence of C, O, S, and N. Due to the presence of CNTs, the carbon proportion is found to be high, i.e., 78.99% [40], while the presence of oxygen and sulfur is due to sulfuric acid in SPS. The EDX spectrum of PDCNS 1.0 shown in Figure 4b displays the same elemental peaks as for PDCNS0.5, but the proportion of carbon is slightly higher, which is coherent with the major CNTs content. Although, the presence of N is related to the presence of polydopamine on the CNT surface in agreement with previous results [35].

The effect of PD-CNTs in the polysulfone matrix was also studied by TGA analysis. The data represented in Figure 5 show the great thermal stability of the blended membranes, which further increases by increasing the concentration of PD-CNTs (from 0.5–1.0 wt.%) as compared to a polysulfone membrane without PD-CNTs coating. In the case of the pure PS base membrane, the first degradation starts at 310 °C. While in the case of the composite membrane with 0.5 wt.% of PD-CNTs, the first degradation begins at a higher temperature of 368 °C. The first degradation starts at 376 °C by increasing the concentration of PD-CNTs PD from 0.5 to 1.0 wt.%. Based on the above findings, we can conclude that the introduction of functionalization in nanotubes made them more compatible with polysulfone membranes, thereby enhancing their thermal stability.

The use of a PD-CNT concentration greater than 1 wt.% results in an increased density, i.e., pore size decrease, and steric hindrance with higher hydrophilicity. While the electrostatic interactions between modified CNTs and polysulfone increase, part of the MWNTs aggregate in an undesired way in the membrane during the phase inversion. Due to these undesired effects arising from the high content of PD-CNTs, the maximum value is selected to be 1 wt.%.

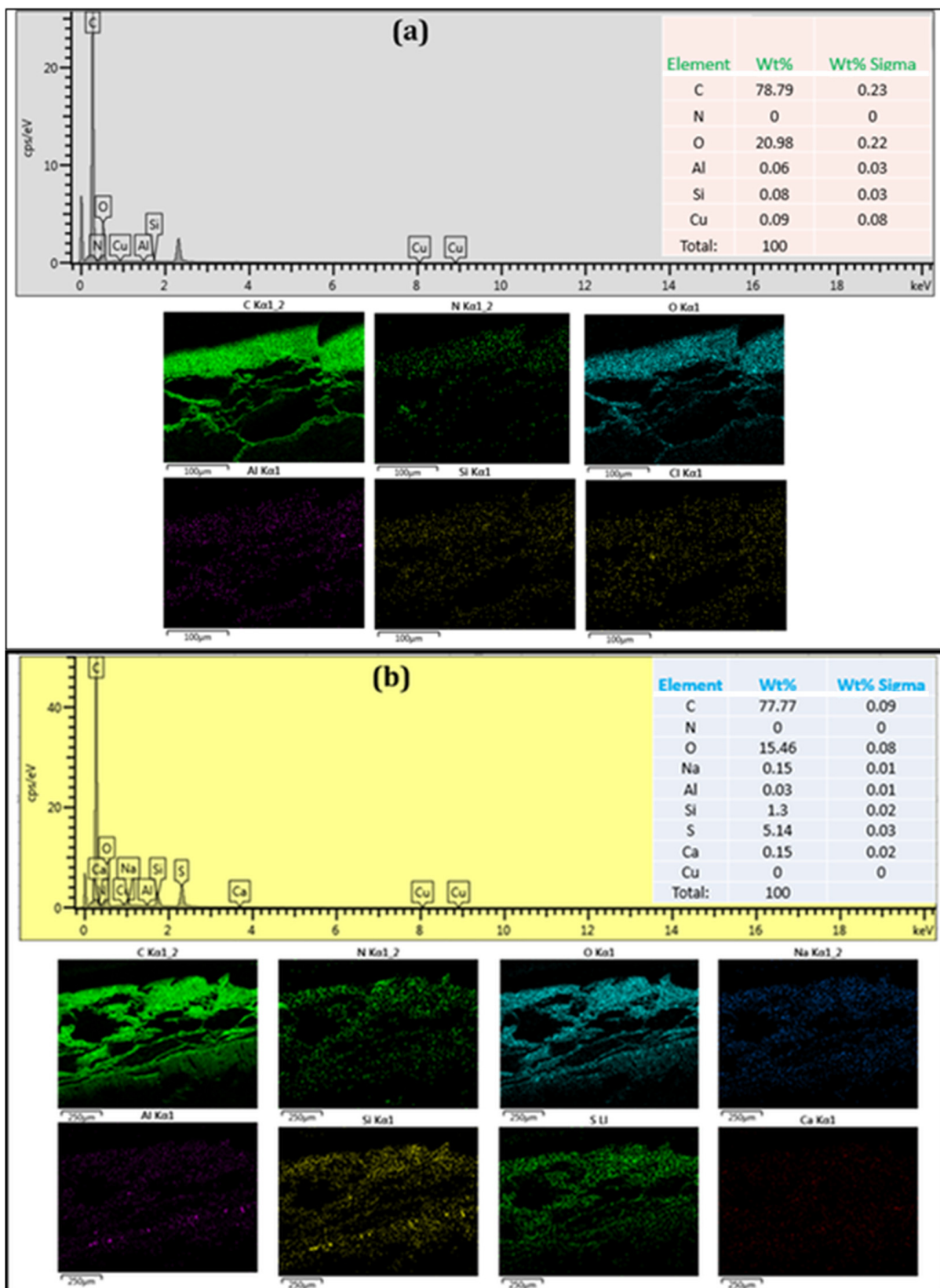


Figure 4. Elemental analysis of (a) PDCNS0.5 and (b) PDCNS1 composite membranes.

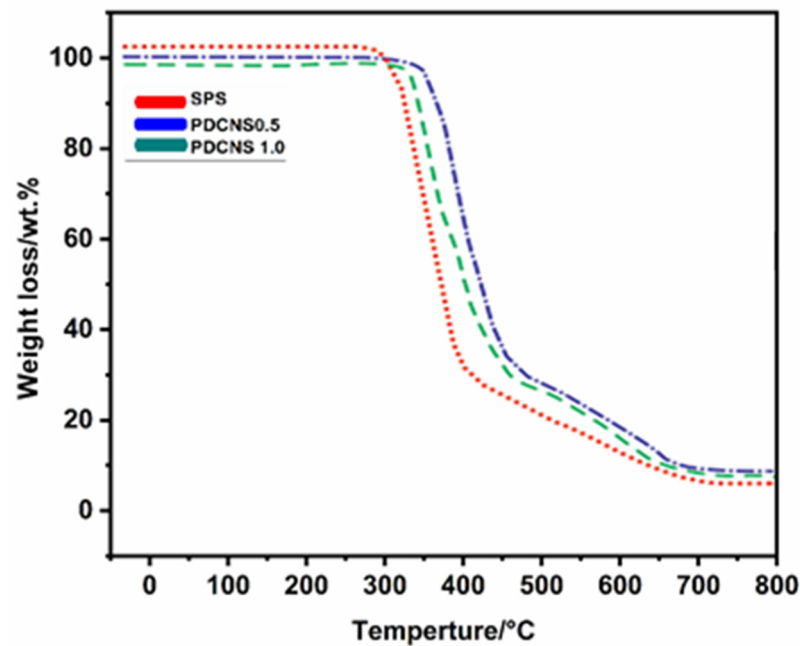


Figure 5. TGA relating to PS and PDCNS composite membranes.

In order to reduce the interfacial energy during the phase inversion process, hydrophilic PD-CNTs migrate impulsively to the membrane–liquid interface. The hydrophilic behavior of membranes is found to be proportional with the amount of PD-CNTs. The viscosity of the blend solution also follows the same pattern, allowing the solvent/non-solvent exchange process to be slower, and allowing smoothing of the surface of the membranes.

As shown in Figure 6a,b, the prepared PDCNS membranes containing 0.5 wt.% and 1.0 wt.% PD-CNT exhibited percentage removals of 82.3 and 96.1% for Cr^{+6} at 2.6 pH, respectively. The removal efficiencies decreased by 64.1 and 73.4, respectively, by enhancing the pressure from 0.50 up to 0.85 MPa. Under the same circumstances, the percentages of Pb^{+2} removal at 0.49 bar by the PDCNS membranes containing 0.5% and 1.0% PD-CNT were 70 and 90.3, respectively, and decreased to 54.3 and 57.0, respectively, upon increasing the pressure to 0.85 MPa. In the case of Cd, the removal efficiency of the composite membrane with 0.5% and 1.0% PD-CNT was reduced from 73 to 77 to 58 to 64% by increasing the pressure from 0.50 to 0.85 MPa.

In PDCNs composite membranes, the presence of functional sites results in the complexation of metal ions and thus enhances the metal removal efficiencies. Such functional groups are absent in pure polysulfone membranes. Additionally, in acidic conditions, protons also tend to compete with the heavy metal ions, improving the removal efficiency. The PD-CNT-based composite membranes showed increased percentage removal of heavy metals upon increasing the concentration of PD-CNTs. This higher removal percentage corroborates with the reduction of the pore size in the composite membranes and with the availability of more active sites on the membrane surface. By increasing the filler content, the pore size is reduced, providing a decreased flow rate and reduced flux. All such conditions support heavy removal. On the other hand, the pristine PS membrane (without filler) shows a very low or negligible removal capacity (10.5% for Cr^{+6}).

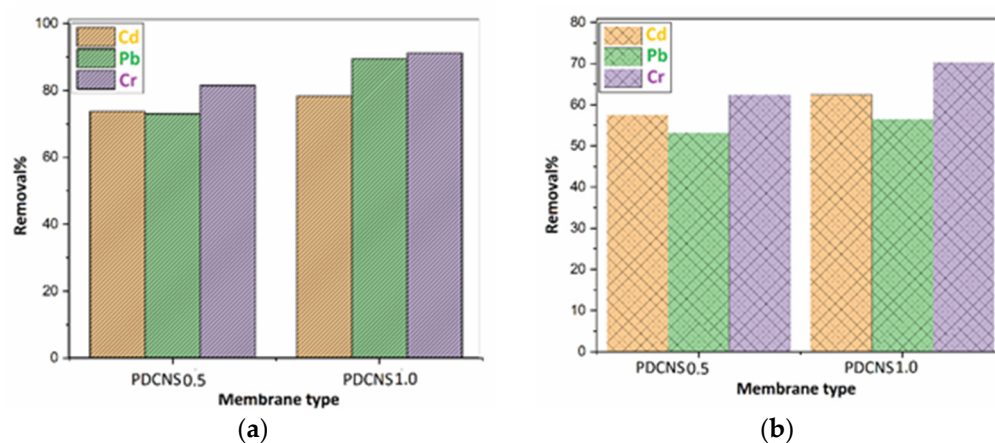


Figure 6. Heavy metal removal percentage of prepared PDCNS composite membranes at pH = 2.6 and (a) 0.50 and (b) 0.85 MPa.

4. Conclusions

In the current study, modified carbon nanotube-based composite membranes were prepared and analyzed for potential removal of heavy metals from wastewater. Initially, CNTs were modified using polydopamine as a modifying agent. In subsequent steps, various percentages of PD-CNTs were added to the sulfonated polysulfone matrix to synthesize composite membranes using the phase inversion process. The presence of functional groups on the surface and the structure of the composite membranes were analyzed using FTIR and XRD. SEM and EDS studies showed that upon increasing the percentages of PD-CNTs, the porosity of the PDCN membranes was reduced. The prepared PDCN membranes were studied for the removal of heavy metal ions by using solutions of metal salts and atomic absorption spectroscopy. A maximum removal efficiency of 96.1% was obtained for Cr^{+6} at 2.6 pH using a composite membrane containing 1.0% PD-CNTs. The results showed that composite membranes can be used as a potential candidate for the removal of heavy metals from wastewater.

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