Surface functionalization of nylon 66 membrane using para-phenylenediamine and carboxylic functionalized multi-walled carbon nanotubes for removal of calcium ions from aqueous solution

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\textbf{ABSTRACT}

Nylon 66, which is an important membrane class used in manufacturing of chitin and chitosan, have a number of features that can be improved by surface functionalizations into a novel composite structure with support of ultrasound and silica gel (SiG) catalyst in a doubled amidation reaction. Firstly, nylon 66/para-phenylenediamine thin film composite (NP-TFC) is prepared from commercial nylon 66 membrane in an ultrasound assisted hydrolysis-amidation reaction. Secondly, carboxylic functionalized multi-walled carbon nanotubes (MWCNT-COOH) are grafted on the NP fiber in an ultrasound assisted/SiG-catalyzed amidation reaction, where para-phenylenediamine (pPD) role is cross-linking. As an excellent result confirmed by either Fourier transform infrared (FTIR), Raman spectrometry or scanning electron microscopic (SEM), bundled MWCNTs bridges are easily built in SiG-catalyzed ethanol media to connect nylon 66 fibers at distances of 0.3–1 µm. The vacuum filtration test confirmed that as-prepared nylon 66/pPD/MWCNTs structure has superior Ca\textsuperscript{2+} rejection efficiency to that of original nylon 66.

\textbf{GRAPHICAL ABSTRACT}

1. Introduction

In knowledge of literatures, crustacean shell is an important raw material for processing of valuable nutrition products including chitin, chitosan, glucosamine, … [1–4]. In particular, shrimp shells are extremely rich source of chitin and chitosan [1–3]. Studies on manufacturing processes to extract chitin and chitosan from a shrimp shells are important in improving value of using seafood waste and contributing to environmental protection [4]. In food industry, raw shrimp shell materials are crushed and dissolved to form the initial protein solution. The chitin in solution is then separated or enriched by several cycles of hydrolysis in acid...
media, neutralization with alkali solution and filtration. In acidic hydrolysis steps, some minerals in shrimp shells, such as calcium carbonate and/or calcium phosphate are dissolved, leading to increased concentration of Ca\(^{2+}\) ion in protein solution [2,3]. Thereafter, neutralization steps with base solution further increase the concentration of alkaline ion, including Ca\(^{2+}\), K\(^{+}\), Na\(^{+}\), leading to reduced quality of products. Such alkaline ions then can be removed in filtration process by ultrafiltration, or nanofiltration or reverse osmosis technologies. Among them, the ultrafiltration and nanofiltration are usually used for early steps to separate and/or purify chitin from raw protein solution. Commonly used membranes in these methods are porous polymeric films or the thin film composites (TFCs) based on them [6–16]. Liquid flows, including semi-finished or finished liquids, washing water, wastewater, are pumped and returned to high pressure in the production line [9–12]. Depending on wettability of polymers, permeable components through hydrophilic membrane are solvents, such as water or alcohol, or is a slightly or absolutely insoluble ingredient such as lipids, amino acids, proteins with different sizes [3,5,6]. Such organic components often precipitate on the surface of membrane or on side wall of its pores, leading to fouling as well as reducing efficiency, productivity and life time of membranes.

The thin film nanocomposites (TFNs), which are believed to be capable of solving such fouling problems, are developed with attention with difference structures and compositions. Recently, TFN membranes are gaining attention for their ability to meet the above requirements. Multilayered TFN membranes are often casted from nanocomposites or formed directly during the polymerization of the precursors. Nanomaterials are dispersed in thin films to generate or improve mechanical, chemical and special properties combined from different groups of materials (such as hydrophilic properties, creating interactive forces, static electricity, adsorption capacity, specific surface area, …) [7,10,13–24]. Therefore, multilayered TFN membranes have a diverse range of segregation, according to the purpose of use, and enhanced anti-fouling features. Now, such TFN membranes have begun to appear on the market with a wide range of features and applications. A number of researches focus on solving these two problems by using new materials and their composites, including flexible polymeric thin films [12–14] or inorganic porous solids [13,19]. Polymeric membranes are more widely developed than the rest of the materials due to their low production costs, mass production and flexible applications [5,19]. Types of polymer materials commonly used to make membranes include polytetrafluoroethylene (PTFE) [21,23], polyvinylidene fluoride (PVDF) [9,11,13,23], polyamide (PA) [14,15,17,19,21], polysulfone (PSF) [14,15,17,24], polyethersulfone (PES) [15,19,20], polyetherimide (PEI) [11,15,24], polystyrenes (PS) [14], polyvinyl alcohol (PVA) [14,16], … Among such materials, PA based thin-film nanocomposite (PA-TFC) are commonly used as either forward osmosis (FO) or reverse osmosis (RO) membranes due to their high separation efficiency, high mechanical strength and environmental friendliness [23,24]. However, the fouling is easily caused by hydrophobicity of the active PA layer as well as uncertain retention time of components on rough walls of pores. Such reasons lead to hindering the separation process, thereby reducing the overall filtration efficiency of membranes. To overcome the disadvantages, surface modification methods such as using additional absorbent polymer layers; photo-grafting polymerization [25–27]; nanoparticle coating [28–31]; group-functionalization [32,33]; carbon-based nanomaterials grafting [34–37], … have been considered to make the membrane surface more hydrophilic, smoother and reduce the interoperability between the membrane surface and clogging particles. Carbon nanotubes (CNTs) based TFN membranes are expected to be a breakthrough in the field of membrane fabrication used for ion separation. The highly durable tube structure and a relatively wide adjustable diameter allow the CNTs to act as highly isolated ion channels. CNTs surface can be functionalized with either hydrophilic or hydrophobic groups, making it possible for CNTs to isolate organic molecules of different sizes. Some hydrophilic groups are commonly functionalized on the surface of CNTs are hydroxyl (–OH), carboxylic (–COOH), amino (–NH\(_2\)), … [22–25]. TFN membrane with such functionalized CNTs has created new properties for the membrane such as high strength, hydrophilic properties, porosity, charge density on and within the membrane as well as creating frictionless and straight-structured nanotransmitters within the membrane [26–30]. The TFN membrane based on CNTs is a product capable of separating both organic and ionic compounds at the same time, saving energy consumption in the multi-level filtration system. TFN membrane based on polyamide combined with single-walled carbon nanotubes (SWCNTs) with a concentration of 0.59 wt% has a 1.5% increase in permeability of the membrane compared to traditional TFN membranes with a slight decrease in NaCl salt selectivity [22]. It is explained by the water flow through the frictionless membrane flowing inside a carbon tube 1 nm in diameter. Some types of CNT-TFN membranes have a water permeability of about 1.3 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), a filtration efficiency of 98.6% NaCl, much higher than commercial TFNs.
(with a permeability of 0.3 L m⁻² h⁻¹ bar⁻¹, NaCl filtration efficiency 97.6%) [23]. Some TFNs containing functionalized and dispersed CNTs with a content of 0.01 wt% in the polyamide matrix improved membrane water yield up to 41.4 L m⁻² h⁻¹ and 96.7% of SO₂⁻⁻ and Na⁺ ions filtration efficiency when operating at a pressure of 6 bar [24]. Such cation extraction indices are important for separation of alkaline ions from protein solution.

The TFN membranes made from above studies are mostly synthesized by adding carbon-based reinforcement in polymerization process. In this study, a novel method is proposed of attaching reinforcing carbon nanotubes to an existing porous polyamide membrane. This method aims to directly functionalize the microfilters, with pore sizes ranging from 0.1 to 1 μm, and to enhance it alkaline ion rejection efficiency without changing its skeleton structure. The three main steps of this method are proposed as follows:

i. partial hydrolysis of polyamide skeleton fibers in the membrane to reveal amino and carboxylic groups;

ii. graft para-phenylenediamine (pPD) as branch on hydrolyzed polyamide fiber by amidation between carboxylic groups of the fiber with amino group of pPD;

iii. graft the carboxylic functionalized multi-walled carbon nanotubes (MWCNT-COOH) on pPD grafted polyamide fiber by amidation between free amino groups of pPD and carboxylic group of MWCNT-COOH.

Steps (i) and (ii) can occur sequentially in a one-pot reaction. This method does not destroy the fibrous structure, as well as retain both porosity and permeability of polyamide membranes. To increase the interaction rate between precursors and polyamide fiber, catalyst and ultrasound is added during reaction periods. The ultrasound also helps to remove residual precursors from amidation reaction.

2. Experimental

2.1. Materials

Reagent grade chemicals are included: sodium hydroxide (NaOH, 98%) was purchased from Alfa Aesar; pPD (C₆H₄(NH₂)₂, 98%), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Mo-catalyst core reagent type, 99.98%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, catalyst reagent type, 99.95%), aluminum oxide (Al₂O₃, 99.99%) were purchased from Sigma-Aldrich. Analytical grade chemicals are included: toluene (99.95%), ethylene glycol (EG, 99.5%) were purchased from RCI Labscan; ethanol (EtOH, 99.7%) was purchased from Chemsol; silica gel (SiG, mesh of 230–400, particle size of 37–53 μm) was purchased from HiMedia. Nylon 66 syringe filters (pore size of 0.45 μm, diameter of 25 mm, non-sterile, polypropylene (PP) housing) were purchased from Membrane Solutions.

The production, purification and functionalization of MWNTs and MWCNT-COOH and their characterizations were given elsewhere [38,39]. Summary of such processes are as follows: (i) the raw MWNTs (r-MWNTs, diameter of 20–30 nm) are produced via Mo–Fe/Al₂O₃ catalyzed reaction of toluene in a fluidized bed chemical vapor deposition (FBCVD) system; (ii) the r-MWNTs then purified by heat treatment at 460 °C with air supply and acid treatment in HNO₃ and HCl at 60 °C [38]; (iii) carboxyl radicals were generated on outer wall of the purified MWNTs (p-MWNTs) in solution of HNO₃/H₂SO₄ to produce MWCNT-COOH. The MWCNT-COOH was centrifuged and vacuum filtered to obtain dry powder [39].

2.2. Surface treatment of nylon 66 membrane by hydrolysis and amidation with pPD

The solution was prepared by dissolving 30 mmol of NaOH and 9 mmol of pPD in 30 mL of distilled water. The polyamide based membranes (nylon 66) were taken from the syringe filter by removing the PP housing, followed by rinsing with distilled water and drying at 85 °C for 20 min. The clean nylon 66 membranes were immersed in glass beakers containing 30 mL of as-prepared pPD/NaOH solution. Such a beaker was soaked in an ultrasonic bath with 37 kHz of frequency, at 55 °C for 30 min. As-prepared nylon 66/pPD TFC (labeled as NP-TFC) was ultrasonicated in distilled water for 6 min to remove residual precursors, followed by drying at 85 °C for 60 min.

2.3. Amidation of NP-TFC with MWCNT-COOH

Amidation of NP-TFC with MWCNT-COOH was carried out in three different solvents: distilled water, EG and EtOH. A 30 mg of MWCNT-COOH and 30 mg of SiG were added to 30 mL of each solvent, followed by sonication at room temperature for 30 min. The NP-TFC was immersed in a glass beaker containing 30 mL of prepared solvents. Such a beaker was soaked in an ultrasonic bath with 37 kHz of frequency, at 50 °C for 10 h. As-prepared nylon 66/pPD/MWCNTs TFC (labeled as NPM-TFC) was sonicated in distilled water for 6 min to remove residual precursors, followed by drying at 85 °C for 20 min. The reactions were repeated in solvents
without SiG as references. The resulting NPM-TFCs were labeled as shown in Table 1.

### 2.4. Characterizations

The chemical structures of as-prepared TFCs were characterized using Fourier transform infrared (FTIR) and Raman spectroscopies using PerkinElmer Spectrum™ 3 FT-IR spectrometer and Horiba XploRA ONE™ spectrometer, respectively. Surface and cross-section morphologies of such TFCs were observed by (FESEM) using JEOL JSM-7401F microscope.

Extraction efficiency of Ca\(^{2+}\) ion from water was carried out in vacuum filtered through as-prepared membrane. The solution was prepared by dissolving of 0.5 g CaCl\(_2\) in 100 mL of distilled water. Time of each filtered cycle was recorded to calculate water flux using Equation (1). The Ca\(^{2+}\) rejection efficiency was calculated from concentration of Ca\(^{2+}\) ion in the input and output solution of Equation (2)

\[
W = \frac{V}{A \times t} \tag{1}
\]

where \(W\) is water flux, L m\(^{-2}\) h\(^{-1}\); \(V\) is volume of test solution, L; \(A\) is effective area of membrane, m\(^2\); \(t\) is average time of filtered cycle, h. The effective area of membrane has diameter of 25 mm

\[
E = \frac{C_{\text{in}}^{\text{Ca}^{2+}} - C_{\text{out}}^{\text{Ca}^{2+}}}{C_{\text{in}}^{\text{Ca}^{2+}}} \times 100\% \tag{2}
\]

where \(E\) is Ca\(^{2+}\) rejection efficiency, %; \(C_{\text{in}}^{\text{Ca}^{2+}}\) and \(C_{\text{out}}^{\text{Ca}^{2+}}\) are concentration of Ca\(^{2+}\) ion in the input and output solution, respectively, ppm.

### 3. Results and discussions

The appearance of functionalized TFCs are shown in Figure 1. Compared with TFCs obtained from admidation in distilled water, the ones from organic solvents (EG and EtOH) have significantly larger coverage areas of MWCNTs, shown by higher ratio

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**Table 1.** Labels and names of NPM-TFCs.

| TFC’s label | TFC’s name | Catalyst | Solvent |
|-------------|------------|----------|---------|
| NPM-H\(_2\)O | Nylon 66/pPD/MWCNTs, catalyst-free in distilled water | Catalyst-free | Distilled water |
| NPM-EG | Nylon 66/pPD/MWCNTs, catalyst-free in ethylene glycol | Catalyst-free | Ethylene glycol |
| NPM-EtOH | Nylon 66/pPD/MWCNTs, catalyst-free in ethanol | Catalyst-free | Ethanol |
| NPM-SiG/H\(_2\)O | Nylon 66/pPD/MWCNTs, silica gel catalyzed in distilled water | Silica gel | Distilled water |
| NPM-SiG/EG | Nylon 66/pPD/MWCNTs, silica gel catalyzed in ethylene glycol | Silica gel | Ethylene glycol |
| NPM-SiG/EtOH | Nylon 66/pPD/MWCNTs, silica gel catalyzed in ethanol | Silica gel | Ethanol |

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**Figure 1.** Images of NPM-TFCs: SiG-free amidation in (a) H\(_2\)O, (b) EG, (c) EtOH; SiG-catalyzed in (d) H\(_2\)O, (e) EG, (f) EtOH.
black area. Otherwise, the NPM-TFCs obtained from SiG-catalyzed amidation have larger and more uniform coverage of MWCNTs than from catalyst-free amidation. Such phenomena indicate that the presence of SiG is helping amidation of –COOH group on MWCNTs and –NH2 on NP-TFCs more easily and evenly. However, the role of SiG catalyst is reduced in reaction performed in distilled water because the amount of water molecules exceeds the absorption limit of SiG. Figure 1(f) shows the best appearance of NPM-TFCs obtained from amidation in EtOH. This can be explained by the difference in relative polarity of reaction solvents (Table 2) [40].

The solvents with strong polarity can form strong hydrogen bonds with MWCNT-COOH, allowing well dispersion of MWCNT-COOH in it but reducing the displacement of interaction between –COOH group from with solvent molecule to with –NH2 group on NP-TFC. However, nonpolar solvents cannot be selected because the reaction requires a stable dispersion of MWCNT-COOH. Therefore, ethanol – a solvents with medium polarity and not too low boiling point – is a good selection for reaction media.

FTIR spectra of MWCNT-COOH, nylon 66 membrane NP- and NPM-TFCs are shown in Figure 2. The spectrum of MWCNT-COOH shows a wide band located at about 3410 cm\(^{-1}\), which attributes to stretching vibration of –OH groups. The wide bands located at about 2870 cm\(^{-1}\) are attributed to overlapping signals of asymmetric methyl stretching and methylene stretching. Generally, such groups are located at the defects on side wall of MWCNTs. The presence of –COOH group can be observed by the appearance of characteristic bands of C=O (1730 cm\(^{-1}\)), –COO (1240 cm\(^{-1}\)) and C–O–C (1100 cm\(^{-1}\)).

The spectrum of nylon 66 membrane is similar to results commonly seen with the appearance of characteristic bands, including N–H (3300 and 695 cm\(^{-1}\)), C=O (1640 cm\(^{-1}\)), C–C (1540 cm\(^{-1}\)), C–N (1270 cm\(^{-1}\)). Compared with nylon 66, the spectrum of NP-TFC shows the same position of such peaks. Intensity of the C–N and N–H bands is slightly higher in spectrum of NP-TFC, shows that pPD was grafted on nylon 66 fiber in hydrolysis-amidation step. The spectra of catalyst-free NPM-TFCs are almost constant compared to spectrum of NP-TFC, proving that the amidation with MWCNT-COOH did not occur or occurred insignificantly. It is consistent with non-uniform appearance of such TFCs.

The spectrum of NPM–SiG/H\(_2\)O–TFC shows a wide and intensive peak at about 3440 cm\(^{-1}\), which attributes to overlapping signals of Si–OH stretching and O–H of physically absorbed water [25]. The characteristic peak about 1150 cm\(^{-1}\) attributes to the asymmetric stretching of Si–O–Si cage [25]. It indicates that SiG is present in NPM–SiG/H\(_2\)O–TFC. The reason is that SiG particles absorb large amounts of water during the reaction, causing them to swell and become trapped in the pore of NP-TFC. SiG insertion into pore also hindered the interaction between MWCNT-COOH and NP fibers. The spectra of NPM–SiG/EG–TFC and NPM–SiG/EtOH–TFC clearly show the presence of MWCNT-COOH according to the appearance of C=O and C=O bands at the same position compared with MWCNT-COOH. Characteristic peaks of nylon 66 and amide bonds clearly appear in the spectrum of NPM–SiG/EG–TFC. The intensity of such peaks in NPM–SiG/EG–TFC spectrum are lower than in NP–TFC and NPM–EG–TFC, while the intensity of MWCNT-COOH attributed peaks are high. It shows that MWCNTs were grafted on fiber during amidation of MWCNT-COOH and NP fiber in NPM–SiG/EG–TFC. Shape of C=O (1640 cm\(^{-1}\)) and C=C (1540 cm\(^{-1}\)) attributed peaks are wide and caused by overlapping signals of MWCNT-COOH. NPM–SiG/EtOH–TFC spectrum shows the most clearly the overlapping bands of C–O (of carboxylic group) and C=O (of carboxylic and amide groups), caused by high amidation rate of MWCNT-COOH and NP fiber in NPM–SiG/EtOH–TFC.

Raman spectra of NPM-TFCs are shown in Figure 3. Spectrum of MWCNT-COOH shows intensity peaks at about 1340, 1570 and 2680 cm\(^{-1}\), which are attributed to D-, G- and 2D-band of MWCNTs [26,27]. Normally, the appearance of the 2D-band depends on either the excitation wavelength or interaction of laser source to graphene layers [28], which were torn off the side wall of MWCNT during functionalization in acidic media. In spectra of pPD/MWCNTs, NP- and NPM-TFCs, the disappearance of the 2D-band shows that graphene were not participate in the amidation step and were washed away by ultrasound. Comparing spectra of NPM-TFCs with NP-TFC and pPD-MWCNTs, the background of spectra are similar to that of nylon 66 with different intensity of D- and G-band.

### Table 2. Properties of solvents [40].

| Solvent          | Formula          | Boiling point (°C) | Normalized empirical solvent polarity parameter |
|------------------|------------------|-------------------|-----------------------------------------------|
| Water            | H\(_2\)O         | 100.0             | 1.000                                         |
| Ethylene glycol  | C\(_2\)H\(_4\)OH\(_2\) | 197.5             | 0.790                                         |
| Ethanol          | C\(_2\)H\(_5\)OH  | 78.3              | 0.654                                         |
Spectra of NPM–SiG/EtOH and NPM–SiG/EG have intensity ration of G-band to D-band ($I_G/I_D$) similar to that of pPD/MWCNTs spectrum shows that amide bonds were significantly formed between NP-TFC and MWCNT-COOH. The $I_G/I_D$ ratio in spectra of NPM–SiG/EtOH and NPM–SiG/EG are slightly higher than that of MWCNT-COOH due to the overlapping signal of G-band with peaks attributed to C–C of bezenoid or quinoid ring, which must be present at about 1510 and 1580 cm$^{-1}$ [29]. In the spectrum of NPM–SiG/EG, the appearance of 2D-band centered at lower Raman shift is attributed to less-layered graphene [30], which was trapped in NPM–SiG/EG-TFC. This can be explained by high viscosity of EG, which reduces the washout effect of ultrasound during amidation step. Spectra of the NPM-TFCs from catalyst-free amidation and NPM–SiG/H$_2$O–TFC have a significantly higher ratio of $I_G/I_D$ than spectra of pPD/MWCNTs and MWCNT-COOH, indicating that the presence of MWCNT in such TFCs was very low. Thus, Raman spectra confirm the discussion from FTIR spectroscopy that SiG catalyst can enhance amidation efficiency between –NH$_2$ and –COOH groups on NP fibers and MWCNT-COOH, respectively.

Surface morphology of nylon 66 membrane and NP-TFC are shown by SEM (Figure 4). Due to the hydrolysis reaction, nylon 66 fibers are truncated.

Figure 2. FTIR spectra of MWCNT-COOH, nylon 66 membrane, NP–TFC and NPM–TFCs.
the cross-linker via pPD bridges in amidation. This circulation allows the fibers to bond more tightly and reduces the average pore size. The surface of the pristine nylon 66 membrane surface (Figure 4(a, b)) is very rough, shown through large cavities on the surface with a diameter of about 2–3 μm. After treatment with pPD, the number of cavities is significantly reduced as well as their diameter reduced to about 1–2 μm (Figure 4(c, d)). Such reductions are believed to help retain MWCNT on the surface and control the amount of MWCNT entering the pores. However, the pPD bridge only connects adjacent nylon 66 fibers on the wall of pore. Therefore, the morphology of NP-TFC is less changed compared to the pristine nylon 66 membrane. The membrane functionalized method in this study shows that connections between distant polyamide fibers can be used with long-fiber structured materials such as MWCNT-COOH via a multi-steps amidation.

The cross-section morphologies of NPM-TFCs in SEM images (Figures 5–7) are used to clarify the linking effects of MWCNTs in structures of NPM-TFCs. Figure 5(a, b) shows the structure of NPM-SiG/H₂O–TFC with medium appearance of MWCNTs. Figure 5(c) shows the connection between nylon 66 fibers with a distance of about 300 nm using MWCNTs bridges. The amide bonds
Figure 4. SEM images of (a, b) nylon 66 membrane and (c, d) NP–TFC.

Figure 5. Cross-section morphologies of as-prepared NPM–SiG/H₂O–TFC by SEM.

Figure 6. Cross-section morphologies of as-prepared NPM–SiG/EG–TFC by SEM.
between –NH₂ groups of NP fibers are formed with –COOH groups at the ends of MWCNTs. In addition, the sonication cleaning step had completely removed residual MWCNTs in the last amidation step. The SEM images in Figures 6 and 7 show the higher density of loaded MWCNTs bridges in structures of NPM–SiG/EG–TFC and NPM–SiG/EtOH–TFC, respectively, compared with NPM–SiG/H₂O–TFC. However, Figure 6(b) shows the matrix of NP and NPM fiber in NPM–SiG/EG–TFC with smooth and rough side wall, which indicate that amidation reaction of MWCNT-COOH and NP fibers occurred. Contrastively, such amidation reaction in NPM–SiG/EtOH–TFC occurred almost completely, leading to the highest density of loaded MWCNTs in its structure. Figure 7(a) shows the uniform morphology of NPM fibers, which were covered totally by MWCNTs. The composite structure of NPM fibers were confirmed clearly in Figure 7(b) with the matrix of NPM fibers and large bundles of MWCNTs. In the structure of NPM–SiG/EG–TFC, MWCNTs bundles build MWCNTs bridges with larger diameter compared to in of NPM–SiG/H₂O–TFC, increasing strength of connection between NP fibers. Figure 6(b, c) shows the length of MWCNTs bridges up to about 1 μm, indicating that amide bonds are formed between –NH₂ groups of NP fibers and –COOH groups on the side wall of long MWCNTs. In this reaction period, MWCNTs connected together helping the bundles...
grown long and large in EG media. The pairing connection of MWCNTs were confirmed clearly in structure of NPM–SiG/H2O–TFC (Figure 4(c)), where the reaction media of distilled water allowed small amount of MWCNTs grafted on NP fibers. Amidation reaction in EtOH media allowed MWCNTs grafted to the side wall of NP fiber (Figure 7(b, c)), showing that MWCNT-COOH dispersed in EtOH is easy to participate in the reaction to create large MWCNTs bundles on NP fibers and connect together into a dense network. Simultaneously, MWCNTs surround NP skeleton structure, creating a distinctly rough side wall of NPM fibers. Therefore, it can be seen that low polarity solvents can easily release long MWCNT-COOH dispersed in it for amidation reaction with support of SiG particles. As the lowest polarity solvents of all used, hydrogen bonds between EtOH and MWCNT-COOH are easily broken down to release –COOH groups. As a results, the NPM–SiG/EtOH–TFC form with large amount of MWCNTs that grafted on each fiber.

Figure 8 shows the Ca^{2+} rejection efficiency from CaCl2 solution of original nylon 66 membrane and NPM–SiG/EtOH–TFC. After 5, 10, 15 and 20 filtration cycles, NPM–SiG/EtOH–TFC shows a much higher rejection efficiency than the original nylon 66 membrane. The nylon 66 membrane with average pore size of 0.45 μm is usually used to remove micro-organism and large scale particles such as organic molecules and nucleases, while they are almost incapable of removing metal ions. However, the efficiency of NPM–SiG/EtOH–TFC is superior to that of nylon 66, corresponding to 9.14% compared with 0.85% after 20 cycles, respectively. It shows that Ca^{2+} ions are significantly captured by MWCNTs bundles due to their formation is very dense and almost fulfill the void in the skeletal structure of nylon 66 membrane (Figure 7(a)). Figure 7(b) confirms that the original pore size (0.45 μm) of nylon 66 membrane is reduced to a range equivalent to the diameter of MWCNTs (about 20–30 nm). This drastic reduction in pore size of NPM–SiG/EtOH–TFC increased its ability to trap Ca^{2+}. In addition, the –COOH groups on side wall of MWCNT easily combine with Ca^{2+} to hold them when the salt fluid flows through NPM–SiG/EtOH–TFC. In the vacuum filtration test, the initial solution had Ca^{2+} concentration of about 1700 ppm, which is average compared with solutions during actual chitin or chitosan production. In the early stages of production, fluids are formed by crushing the crustaceans and dissolving them with acidic media, resulting in very high concentrations of Ca^{2+} being generated from calcium carbonate in crustacean shells. Such Ca^{2+} concentration is reduced partially or completely through many treatments process. The large pore size membranes are used in the early stages to remove residues including powder of shells, carcasses and insoluble proteins, while the novel membranes such as NPM–SiG/EtOH–TFC can be used in middle or late stages of chitin and chitosan fluid treatments. Thus, the functionalization method in this study can directly create a novel composite fiber on the skeleton structure of nylon 66 membrane, and enhance its performance for Ca^{2+} removal application.

4. Conclusion

In summary, the analytical results confirm that NPM-TFC can be successfully fabricated directly from nylon 66 membrane without changing its skeleton structure by ultrasound assisted/silica gel-catalyzed amidation with pPD and MWCNT-COOH. The first hydrolysis-amidation step decreases surface roughness of by reducing number of cavities as well as their diameter from 2–3 μm to 1–2 μm. The SiG catalyst clearly shows its important role in promoting and controlling the amidation reaction between –NH2 groups of NP fibers and –COOH groups of MWCNT-COOH, while ultrasound support can remove residual precursors and catalyst particles from such amidation reaction. Most importantly, the high quality NPM-TFCs is dedicated by the reaction media. In particular, reaction solvents with medium polarity and low boiling point, such as EtOH, help MWCNT-COOH to disperse stably and easily release them for the amidation reaction. In resulted NPM-TFCs from SiG catalyzed EtOH media, the adjacent as well as distant NP fibers are grafted and connected by large bundles of MWCNTs, which enhances the Ca^{2+} rejection efficiency of the membrane from 0.85% to 9.14% in vacuum filtration test.

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