Polysulfone membranes with CNTs/Chitosan biopolymer nanocomposite as selective layer for remarkable heavy metal ions rejection capacity

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HIGHLIGHTS
● At pH 3, the rejection of the metal ions is between 71% and 92.2%.
● Both membranes at pH 3 presents significant rejection ranged 71–92.2% for examined metal ions.
● Cu²⁺ ions are almost completely rejected by examined membranes at pH (6–8).
● At pH 10, the rejection of the metal ions is between 93.4% to 99.9%.

GRAPHICAL ABSTRACT

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ABSTRACT

Chitosan (CHIT) biopolymer has a remarkable adsorption capacity for heavy metal ions. The incorporation of multiwall carbon nanotubes (CNTs) into the CHIT matrix should enhance the water permeability and separation performance of the CHIT. The use of carboxylic acid functionalised multiwall carbon nanotubes (CNTs-COOH) as an additive is aimed at adding the COOH functional group to the CHIT matrix without blocking its adsorption sites. Therefore, two nanocomposites CNTs-COOH/CHIT and CNTs/CHIT are used as a selective layer on top of polysulfone (PS) to form CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes. To the best of our knowledge, the efficiency of the CNTs-COOH/CHIT nanocomposite as a selective layer on polysulfone sheet to enhance the membrane’s rejection for metal ions is reported for the first time. Both fabricated membranes are investigated in terms of morphology, wettability, surface charge, porosity and water permeability. CNTs-COOH/CHIT/PS membrane recorded water flux rate 64.4 L m⁻² h⁻¹ at transmembrane pressure 22 bar, where CNTs/CHIT/PS membrane recorded 57.15 L m⁻² h⁻¹ at transmembrane pressure 22 bar. Heavy metal ions rejection capabilities of both membranes are evaluated at various pHs and transmembrane pressures. Both CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes effectively reject Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺, and Co²⁺ ions from aqueous solutions. At pH 3, CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes presented significant rejection ranged 71–92.2% for examined metal ions. Where at pH range (6–8), Co²⁺ rejection reached up to 92.2% and 89.6% by CNTs /CHIT/PS and CNTs-COOH/CHIT/PS membranes, respectively. Overall, the CNTs-COOH/CHIT/PS membrane shows metal ions rejection superior to that of the CNTs/CHIT/PS membrane.

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1. Introduction

Freshwater resources are diminishing in many parts of the world [1]. This problem is expected to aggravate owing to multiple factors. Climate change, population growth, water contamination, and abuse of water resources contribute to freshwater water scarcity [1–3]. Therefore, there is a need for efficient and feasible technologies for treating waste/contaminated water. Membrane technologies provide an economical and efficient approach for water purification and desalination [4]. Conventional filtration, microfiltration, and ultrafiltration membranes work on particle size exclusion, i.e., these techniques separate contaminants based on their particle sizes. However, nanofiltration and reverse osmosis membranes are used generally for the separation of ions and salt [5].

During the past few decades, membrane technology has advanced in the direction of integrating adsorption and filtration processes [6,7]. Membrane-coated adsorbents have proven effective in water desalination and separating hazardous components, including heavy metal ions, dyes, and toxic organic compounds, from wastewater [5,8–12]. The principal mechanism of the membrane adsorption is similar to the typical adsorption process, in which substances are transferred from a fluid bulk to a solid surface. This process can work under weak physical forces and/or stronger chemical forces [13].

Chitosan (CHIT) has been getting considerable attention in the field of membranes. It is one of the most abundant biopolymers and is thus easily available and affordable [14]. It is an eco-friendly material because it is biodegradable and non-toxic. It is considered a highly useful material for adsorbent membranes in the field of water treatment [15–17]. It is hydrophilic owing to the large number of hydroxyl groups in its glucose units [18]. It has unique perm selectivity for water [19,20], and can be easily modified and casted into films [21]. In addition, the significant amount of -NH2 and -OH groups on the CHIT chain act as coordination sites. Therefore, it possesses high adsorption capacity for heavy metal ions [14]. The CHIT membrane surface bears a positive charge in an acidic medium and is negatively charged in a basic solution [15]. This change in the CHIT surface charge plays a key role in its performance as a membrane [22].

The main disadvantages of CHIT membranes include their substandard mechanical properties [20], poor acid stability, and low surface area, and porosity [5]. To overcome these disadvantages, both physical and chemical modifications can be utilised. Chemical modifications can significantly enhance the flexibility and chemical stability of CHIT; however, these improvements come at the expense of its adsorption capability. Chemical modifications take place in the functional groups of CHIT, mainly on amino groups. In contrast, physical modifications such as multilayer casting and addition of inorganic reenforcements enhance its porosity, surface area, and mechanical properties without blocking its active adsorption sites [5]. Multilayer casting can optimise the membrane structure, mechanical stability, and performance of CHIT without blocking its active sites.

Using inorganic fillers in polymeric membranes enhances membrane features and performance [23]. Zeolites, metal/metal-oxide nanoparticles, dendrimers, and carbon nanomaterials have invited significant attention in the field of membrane science [24–27]. Carbon nanotubes are known for their unique mechanical, thermal, electrical, and chemical properties [28]. Their smooth inner cavity hydrophobic surfaces support fast water transport through them [29]. Furthermore, the significantly small diameters of the tubes aid their ability to separate low-molecular-weight materials and ions [30]. In addition, the surfaces of carbon nanotubes can be chemically modified without altering their structures. Consequently, the addition of carbon nanotubes to the polymer matrix provides an opportunity to design nanocomposite membranes with better transport efficiencies and rejection properties. Shawky et al. synthesised a multiwall carbon nanotubes/polyamide nanocomposite membrane with a threefold rejection capability for NaCl, higher than that of the pristine polyamide membrane [31]. Additionally, it was found that the flux rate of the polysulfone (PS) membrane increased as the loading percentage of the multiwall carbon nanotubes increased [32].

In this study two nanocomposite membranes (CNTs-COOH/CHIT/PS, CNTs/CHIT/PS) are investigated for the rejection of metal ions such as Cu$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Co$^{2+}$. PS sheet is used as a porous support layer. As far as we know, CNTs-COOH/CHIT nanocomposite is investigated as selective layer for heavy metal ions rejection for the first time. A thin layer of nanocomposite is cast on the top of the PS sheet by the evaporation casting method as illustrated in the graphical abstract. Different characterisation techniques are used to inspect the hydrophilicity, morphology, porosity, and surface charge of each membrane. Furthermore, the membranes rejection capabilities for metal ions at different pH are explored.

2. Materials and methods

2.1. Materials

The PS support layer (PS-20) was obtained from Sepro, USA. CHIT, with medium molecular weight, was obtained from Sigma-Aldrich Chemicals. Multi-walled carbon nanotubes (CNTs) (KNT-M31) were obtained from Grafen Chemical Industries. The COOH functionalised carbon nanotubes (CNTs-COOH) (PD15L1-5-COOH) were purchased from Nanolab Incorporation. Acetic acid glacial was bought from Scharlau Chemie, Spain. Hydrochloric acid (HCl) 32% was bought from Scharlau Chemie, Spain. Certified analytical grade sodium hydroxide (NaOH) was purchased from Merck Millipore, Germany. Metal pure standard (1000 ㎍/mL, 2% HNO₃) of Cu, Ni, Pb, Cd, Ba, and Co were purchased from PerkinElmer. In this study, all solutions were prepared using Milli-Q® water (resistivity of 18.2 MΩ.cm).

2.2. Membrane preparation

Membrane preparation involved two steps, as represented in the graphical abstract. The first step was the preparation of the dispersion as follows. A CHIT solution (0.5% w/v) was prepared by dissolving 0.5 g of CHIT in 100 mL of Milli-Q water containing 1% (v/v) acetic-acid solution. The solution was heated for 3 h at 80 °C with continuous stirring and then filtered using filter paper to remove any undissolved particles. Next, CNTs (15 mg) were added to the CHIT solution (15 mL of the filtered solution) and sonicated for 24 min to obtain CNTs/CHIT dispersion. Similarly, the CNTs-COOH/CHIT dispersion was prepared by dispersing 15 mg of CNTs-COOH in 15 mL of the filtered solution (CHIT). The second step was the casting of the prepared dispersion via evaporation-induced phase separation method as detailed next. The CNTs/CHIT dispersion (5 mL) was spread over the PS sheet (40 cm²) using a Gardco Automatic Drawdown Machine II (DP-8301) to form a thin film (top layer). The Microm II Film Applicator slot height was adjusted to 0.1 mm to control the membrane thickness. The nanocomposite membrane was left to air dry. Next, the fabricated CNTs/CHIT/PS membrane was immersed in a 1% aqueous solution of sodium hydroxide for 30 min. After washing the membrane several times with DI water, it was stored in DI water until examined. Similarly, CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes were prepared from the CNTs-COOH/CHIT dispersion and CHIT solution, respectively.

2.3. Scanning electron microscopy

The surface morphologies and cross sections of the membranes were examined using a Schottky field emission scanning electron microscope (SFSEM) (JSM-7610F JEOL Ltd., Tokyo, Japan). Each membrane was fixed on a stub with carbon dots and sputter coated twice for 30 s using a JEOL JEC-3000FC fine coater (JEOL Ltd., Tokyo, Japan). The coated samples were examined at different magnifications using acceleration voltages ranging from 5 to 15 kV.
2.4. Contact-angle measurement

Static contact-angle method was employed to determine the wetting ability of all membranes using Milli-Q water. A flat membrane surface (4 mm × 35 mm) was clamped flat on a microscope slide. Using a microsyringe, a 2-μL water droplet was dropped on the membrane surface. The images of the droplet were taken by a U3 Series digital camera. Then the contact angle between the droplet and membrane surface was measured by the Ramé-hart DROPimage Advanced software. This procedure was repeated on randomly selected parts on the surface of each membrane.

2.5. Nitrogen adsorption/desorption isotherm

The nitrogen adsorption/desorption isotherms for all membranes were measured by a gas sorption instrument (Micromeritics ASAP 2020) at 50 K. The samples were cut into small pieces (2 × 2 mm) and then de-gassed at 50 °C for 16 h under vacuum before being tested. Surface areas were estimated using the Brunauer-Emmett-Teller (BET) method. Pore sizes of all membranes were calculated using the Barret-Joyner-Halenda method [33]. The specific surface areas, cumulative pore volumes (Pvol), and pore sizes (Pdiam) of the investigated membranes were obtained.

2.6. Zeta potential

The membrane surface charges were investigated using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria) as detailed in [34]. Measurements of streaming potentials were performed in a tangential mode. The sample dimensions were 10 × 20 mm. The experiments were run at 25 °C temperature and a pressure ramp in the range of 0–300 mbar. The electrolyte solution was 1 mM potassium chloride. The pH was automatically titrated from 2.5 to 10 using a 0.05 M HCl solution and 0.05 M NaOH. The zeta potential values were plotted as a function of pH, and the isoelectric point of each sample was determined. The surface zeta potential was calculated using the Attract® software and Fairbrother–Mastin relationship [35,36].

2.7. Membrane performance

The performance of the fabricated membranes was evaluated using a cross-flow filtration system (Sterlitech™ CF042 Membrane Test Skid, Sterlitech Corp., USA). The Effective Membrane Area is 42 cm². The Feed Flow Rate was adjusted at ≈4 L/min. All membranes are evaluated over a single filtration cycle. The feed water contained 10 ppm concentration of a mixture of heavy metals ions, namely, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Ba²⁺, and Co²⁺. To achieve a steady-state operation, all results of the water permeability and metals rejection were taken after 30 min of water filtration experiments. The rejection tests were executed at pH 3, 7, and 10. The results were recorded at transmembrane pressures of 6, 10, 14, 18, and 22 bar. All permeability and salt-rejection experiments for membranes were performed at approximately 20 ± 2 °C.

2.7.1. Permeability

The water flux was calculated using Eq. (1) [37,38]:

\[
J = \left( \frac{1}{A} \right) \left( \frac{dV_p}{dt} \right) = \left( \frac{C_p}{C_f} \right) \cdot 100
\]

where \( J \), \( V_p \), and \( t \) are, respectively, the water flux (in L m⁻² h⁻¹), permeate volume (in L), membrane area (in m²), and treatment time (in h).

2.7.2. Heavy metal ions rejection

The metal ions rejection, \( R \), is calculated using Eq. (2) [37,38]:

\[
R = \left( \frac{C_p}{C_f} \right) \cdot 100
\]

where \( C_p \) and \( C_f \) are the metal ion concentrations in the permeate and feed streams, respectively. A quantitative determination of metal ions is made by the inductively coupled plasma atomic emission spectrometry using the Perkin-Elmer Plasma 400 equipment.

3. Results and discussion

3.1. Morphology of membrane

The morphology of the membrane is mainly affected by the manufacturing technique and materials used. The membrane morphology gives a good insight into the flux, pore size, pore geometry, and pore distribution of the membrane [39]. In this study, surface and cross-section SEM images of each membrane were taken (Figs. 1–4). The SEM image of the PS surface reveals a smooth, homogeneous, and flat surface with an irregular pore structure. The cross-section image of PS displays a random and irregular sponge-like pore structure (Fig. 1). Although, the CHIT membrane surface and cross section (Fig. 2) exhibit a morphology different from that observed in PS images. The SEM images show that CHIT has a highly porous structure (Fig. 1). The porous structure appears to have a high degree of interconnectivity (Fig. 2(b)).

SEM images of CNTs-COOH /CHIT/PS membrane are represented in Fig. 3. The CNTs-COOH diameter appear to be larger than expected ≈ 64 nm (see Fig. 3(b)). This is due to the wrapping of CHIT chain around CNTs-COOH. This wrapping is a result of the interaction between COOH group on CNT wall and the -OH and -NH2 groups of the CHIT chain [40]. This indicates a quite compatibility between CHIT and CNTs-COOH, which is in agreement with the previous literature [40].

On the contrary, CNTs/CHIT/PS membrane SEM images demonstrate that the diameters of CNTs is as expected ≈ 20 nm (see Fig. 4(b, d)). This indicates that the dispersion of CNTs in chitosan is probably lower than the dispersion of CNTs-COOH. This is apparently due to the
weak molecular interaction between CNTs and CHIT in addition to the hydrophobic nature of CNTs [40,41]. Therefore, CNTs tends to form agglomerates within the CHIT matrix. Thus, we can assume that CNTs-COOH are better dispersed into CHIT matrix than CNTs.

3.2. Hydrophilicity/hydrophobicity of membranes

The chemistry of the membrane surface affects its performance significantly [42,43]. Hydrophilicity/hydrophobicity of the membrane surface is one significant criterion that affects the membrane performance [42–44]. It directly affects the interaction of the membrane surface with water, organic, and inorganic colloidal substances [45–47]. The static contact-angle method is considered one of the standard measurements for hydrophilicity/hydrophobicity of solid surfaces [48]. Generally, when the contact angle of the examined surface is decreased, it indicates that its hydrophilic character has increased. In this study, the contact angles of the CHIT/PS, CNTs/CHIT/PS, and CNTs-COOH/CHIT/PS membranes were record as 73°, 63.5°, and 53.4°, respectively (see Table 1 and Supplementary Information Appendix Fig. S1). These values show that the hydrophilicity of the fabricated membranes decreases in the following order: CNTs-COOH/CHIT/PS > CNTs/CHIT/PS > CHIT/PS. Therefore, it is apparent that the dispersion of both CNTs and CNTs-COOH in the CHIT matrix enhanced its hydrophilicity. This result is in agreement with previous studies [44]. Moreover, it is found that the CNTs-COOH/CHIT/PS membrane is more hydrophilic than the CNTs/CHIT/PS membrane because of the presence of the carboxylic group on the wall of CNTs. This, in turn, increases the hydrophilicity of the membrane and improves the dispersion of CNTs in the aqueous solution and polymers [42].

3.3. Surface areas and average pore diameters of membranes

The results of the nitrogen adsorption/desorption measurements are
summarised in Table 2. The adsorption/desorption isotherms on CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes are given in (Supplementary Information Figs. S1 and S2), respectively. These isotherms were obtained by plotting the volume of nitrogen adsorbed ($V_{ads}$) against the relative pressure ($P/P_0$). The samples show a stepwise adsorption and desorption isotherm. Based on the IUPAC classification of adsorption isotherms, the isotherms for both membranes represent a combination between type II and III isotherms with a type H4 hysteresis loop. This indicates that the samples have a cylindrical mesoporous structure [49]. Furthermore, the pore size distribution results, studied based on the Barrett-Joyner-Halenda process, record that the average pore diameter ranged from 58 to 59 nm. The BET surface areas of the CNTs/CHIT/PS and CNTs-COOH/CHIT/PS membranes were 7.03 and 6.81 m$^2$/g, respectively. These values are higher than those determined by using the CNTs/CHIT buckypaper (Table 2) [33,50,51]. It can be assumed that the method used to prepare these membranes is better for producing membranes with large internal pore diameters and high surface areas, which, in turn, play an important role in increasing permeability. As shown in Table 2, the surface area of the CNTs-COOH/CHIT/PS membrane is slightly smaller than the surface area of the CNTs/CHIT/PS membrane. This is apparently due to the denser morphology of the CNTs-COOH/CHIT/PS membrane, which results in blocking some pores (see Figs. 3 and 4).

3.4. Zeta potential

The charge on a membrane surface is the key factor in predicting and understanding the filtration performance of a membrane [36]. The zeta potential has an impact on the wettability of the membrane surface [4]. A higher charge density on a membrane surface is accompanied with a higher hydrophilicity of the membrane [37]. Moreover, it governs the interaction between the membrane surface and solutes in the feed.

Fig. 5 shows the zeta potential ($\zeta$) as a function of the pH for CNTs/CHIT/PS and CNTs-COOH/CHIT/PS membranes. CNTs/CHIT/PS membrane showed similar pattern to previously reported chitosan composites at acidic medium [52–55]. At $pH < 5$, the observed variation in $\zeta$ is probably due to the change in chitosan viscosity which in turn causes the expansion of chitosan chains [56]. The isoelectric point

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$A_{BET}$ (m$^2$/g)</th>
<th>$d_{BET}$ (nm)</th>
<th>$P_{vol}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs/CHIT/PS</td>
<td>7.03 ± 0.06</td>
<td>58</td>
<td>0.1025</td>
</tr>
<tr>
<td>CNTs-COOH/CHIT/PS</td>
<td>6.81 ± 0.05</td>
<td>59</td>
<td>0.0997</td>
</tr>
<tr>
<td>CNTs/CHIT buckypaper</td>
<td>–</td>
<td>3.7 [33]</td>
<td>–</td>
</tr>
<tr>
<td>CNTs-COOH/CHIT buckypaper</td>
<td>–</td>
<td>19 [51]</td>
<td>–</td>
</tr>
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</table>
of the CNTs/CHIT/PS membrane surface is observed at pH 6.7, where the membrane surface possesses a positive charge at pH > 6.7 and a negative charge at pH < 6.7. Likewise, the CNTs-COOH/CHIT/PS membrane surface isoelectric point is recorded at pH 5.98, with a positive charge at pH > 5.98 and a negative charge at pH < 5.98. The CHIT membrane surface bears a positive charge in the acidic medium because of the protonation of -NH2 groups on its chain. In contrast, it is negatively charged in the basic solution as a result of the dissociation of CH2OH groups or the adsorption of OH⁻ from the solution [15]. This change in the CHIT surface charge significantly affects the mass transfer and interfacial properties of its surface as a membrane.

3.5. Membrane performance

3.5.1. Water permeability

The chemical composition, hydrophilicity, and surface charge of the membrane significantly impact the water flux rate [57] because these aspects affect the interaction between the membrane surface and solution. This interaction might involve different secondary forces, such as, dipole-dipole, van der Waals, electrostatic interaction, and hydrogen bonding. In this study, the flux rate was plotted against the transmembrane pressure for both CNTs-COOH/CHIT/PS and CNTs/CHIT/PS membranes (Fig. 5). Water permeability for each membrane was obtained from the slope, and the data are recorded in Table 1. Although raising the pressure typically increases the water flow velocity through the membrane pores, the tangential forces acting on the membrane are increased as well. Consequently, these forces cause deformation of membrane pores. This membrane compaction can cause a decrease in the flux rate of the membrane. This can explain the deviation from linearity of flux rate at 14 bar transmembrane pressure. CNTs-COOH/CHIT/PS offers higher water permeabilities (3.92 ± 0.50 L m⁻² h⁻¹ bar⁻¹) and significantly higher flux rates (see Fig. 6) when compared to those of CNTs/CHIT/PS (1.57 ± 0.13 L m⁻² h⁻¹ bar⁻¹). Generally, both the investigated membranes demonstrated improvements in water permeabilities when compared with previous studies [33,51]. This indicates that the membrane preparation method demonstrated in this study did enhance the water permeability of the membranes.

3.5.2. Heavy metals-rejection capability

Using a cross-flow cross-flow filtration system, CNTs-COOH/CHIT/PS and CNTs-COOH/CHIT/PS membranes were tested for the rejection of metal ions, namely, Co⁺², Ni⁺², Cu⁺², Cd⁺², and Pb⁺². The membranes’ rejection abilities for heavy metal ions at different pH and transmembrane pressure values are presented in Figs. 7–12. It is found that the pH of the solution impacts the surface charge of the CHIT modified membranes (see Section 3.4) as well as the ionisation degree of the materials in the solution [58]. Consequently, the pH of the solution affects the overall ability of the membrane to adsorb or remove metal ions from an aqueous solution as shown in this study [18].

For polyelectrolytes, such as CHIT, adsorption may occur from various aspects: van der Waals interactions, hydrophobic bonding, electrostatic attraction, hydrogen bonding, and the chemical reaction with surface functional groups. If the membrane surface and ions in the
feed are similarly charged, adsorption occurs when non-electrostatic attraction is greater than the electrostatic repulsion [7,15,59–61]. This is probably the case with the CNTs-COOH/CHIT/PS membrane at pH < 5.98 and with the CNTs/CHIT/PS membrane at pH < 6.70.

The metal ions rejection results follow an approximately similar pattern in both the investigated membranes. At pH = 3, the CNTs/CHIT/PS membrane rejection for all investigated metal ions was in the 71–92% range at various transmembrane pressures, with Co²⁺ (92.2% rejection at 10 bar transmembrane pressure) and Pb²⁺ (71.3% rejection at 6 bar transmembrane pressure) being the most and least rejected metal ions, respectively. The CNTs/CHIT/PS membrane rejection for metal ions followed the trend Co²⁺ > Cd²⁺ = Ni²⁺ > Cu²⁺ > Pb²⁺. The CNTs-COOH/CHIT/PS membrane showed a different affinity for metal ions, following the trend Cu²⁺ ≈ Co²⁺ ≈ Ni²⁺ > Cd²⁺ > Pb²⁺. In this case, Co²⁺ (99.6% rejection at 18 bar transmembrane pressure) and Pb²⁺ (71.3% rejection at 6 bar transmembrane pressure) were the most and least rejected ions, respectively.

For pH = 6–8, variation is seen in the rejection of metal ions for both membranes. The rejection of most metal ions decreases except for those of Cu²⁺ and Pb²⁺. Cu²⁺ ions are almost completely rejected by CNTs/CHIT/PS and CNTs-COOH/CHIT/PS membranes with ≈ 99.5% and ≈ 98% rejection, respectively. This can be attributed to multiple factors: affinity of CHIT towards different metal cations (decreasing acid character of metal cation with respect to the base character of CHIT), metal ionic radius, and metal ion hydration capacity [61–64].

The observed sharp increase in Cu²⁺ rejection by both membranes is attributed to multiple aspects. One is the formation of Cu(II) hydroxide precipitates beyond pH 6.8, which can also adsorb on CHIT [14,65]. Also, CHIT has the highest binding strength for Cu²⁺ when compared with the other investigated metal ion [64]. In addition to the competition factor, since CHIT has limited free amine groups at that pH range. Although, CHIT has a significant number of reactive amine groups [66], the free amino group protonation constant (log $K_p$) equals 6.3.

$$\text{RHN}^- + H^+ \Leftrightarrow \text{RNH}_2^+; K_p$$  (3)

Therefore, on average, more than 20% of amino groups on the CHIT chain are protonated even at pH 6.9 [14,15].

When comparing the results at different pH, a significant increase in the rejection of all metal ions at pH 10 is observed. According to Eq. (3), the higher the pH, the less amount of the protonated positively charged amine groups on the CHIT chain. Moreover, under alkali conditions, the CHIT chains are "more flexible," which allow more adsorption sites to be utilised, thereby resulting in an increase in the adsorption capacity of the membrane [15]. Another possible reason is that a basic solution may cause precipitation of metal hydroxides [14].

The CNTs-COOH/CHIT/PS membrane shows remarkable rejection for Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, and Pb²⁺ when compared with the CNTs/CHIT/PS membrane. The incorporation of CNTs-COOH, which has a hydrophilic (COOH) group, causes the polymer chains to extend significantly further and exposes more adsorption sites to bind with metal ions [67]. In addition, carboxylic (–COOH) groups have a higher tendency to chelate metal ions compared with the –NH₂ group of CHIT resulting in an increase in the overall adsorption capability of the membrane [61]. Consequently, the CNTs-COOH/CHIT/PS membrane had ≈ 99% rejection for all examined metal ions.
4. Conclusions

CNTs-COOH/CHIT and CNTs/CHIT nanocomposites are investigated for the first time as a selective layer on the PS membrane for the removal of metal ions. Overall, both investigated membranes CNTs-COOH/CHIT/PS and CNTs/CHIT/PS effectively reject Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, and Co^{2+} ions from aqueous solutions at pH 3 and 10. Where at pH = 6–8, the investigated membranes exhibit remarkable rejection for Cu^{2+} and Pb^{2+}. The carboxylic group on the walls of CNTs has a strong impact on the characteristics and performance of the CNTs-COOH/CHIT/PS membrane. SEM images show that CNTs-COOH are better dispersed in CHIT than the unfunctionalised CNTs owing to the interaction between the carboxylic group on the CNTs walls and the functional groups on the CHIT chain. Furthermore, the impact of the carboxylic group on CNTs-COOH increased the hydrophilicity of CNTs-COOH/CHIT/PS membrane when compared to CNTs/CHIT/PS. In addition, it significantly improves the metal ions rejection of the membrane, allowing almost 99% rejection for all investigated metal ions at pH = 10. In conclusion, this study provides a viable method for obtaining remarkably efficient and eco-friendly membranes for the separation of heavy metal ions from aqueous solutions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2020.124268.

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A. Refaat Alawady, et al.