Performance evaluation of modified fabricated cotton membrane for oil/water separation and heavy metal ions removal

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Abstract
Preparation of effective membrane with special surface treatment for oil/water separation having promising future and low manufacturing cost. The suggested membrane was fabricated by a simple treatment via increasing the hydrophilicity of the cotton fabric surface. The cotton fabric was impregnated in poly(acrylic acid-co-N-methylol acrylamide), poly(AA-co-NMA), where NMA acts as bonding agent. Sodium hypophosphite (SHP) was added to the modification solution to enhance the bonding between the cotton fabric and the PAA. The modified fabric was thermally dried and cured at different temperatures. It was found that, the presence of 3.5% NMA and addition of 5% SHP to the modification solution then curing at 190°C gave the highest amount of bonded PAA to the cotton fabric. The success of the modification process was confirmed by scanning electron microscope, Fourier transformer infrared and the increase in the contact angle of the cotton fabric after modification. Furthermore, the prepared membrane was evaluated for oil (n-hexane, toluene, and petroleum ether)/water separation and also for heavy metal ions removal (Cd2+ and Co2+). Neutralization of the produced membrane with ammonium hydroxide resulting in a higher contact angle and consequently higher separation efficiency for oil/water mixtures and higher performance for heavy metal ions removal compared to the unneutralized one.

KEYWORDS
heavy metal ions removal, membranes, modification, oil/water separation

1 | INTRODUCTION

Water contamination is one of the most serious environmental challenges worldwide due to the increased anthropogenic activity and inadequate long-term remediation techniques. Oil wastewater and heavy metal ions pollution have become hot research topics because of the rapid expansion in global industrial activities, since many accidental oil spills and industrial wastewater have caused considerable harm to the individuals and to the environment.1–4 Heavy metal ions and oily water kill animals and harm people’s health in a variety of ways. Furthermore, due to oily wastewater and polluting using heavy metal ions, difficulties with safe freshwater have aggravaed and are expected to grow worse in the next decades.5–7 Separating oil from oily water and efficiently
removing heavy metal ions are well regarded as long-term techniques. As a result, natural or artificial materials that can efficiently separate oil/water mixtures and remove heavy metal ions, are in high demand and remain a difficult task. It is noted that a significant variety of traditional technologies have been adopted for the removal of waste oil. For example, gravity separation, hydrocyclone centrifugal separation, chemical pretreatment (coagulation–floculation), coalescing media, gas flotation, biological treatment, and media filtration. Compared to the above methods, membrane filtration is recognized as one of the most promising methods for the separation of oil from oil/water mixtures due to its advantages including the absence of chemical additives, high flux, environmental friendliness, energy efficiency, easy processing, and low maintenance cost, stable effluent quality, and small area requirement. The recent development of super-hydrophobic–superoleophilic materials such as sponges, foams and textiles, as well as superhydrophilic–underwater-superoleophobic membranes and meshes created by combining surface chemical compositions and surface roughness provides an encouraging opportunity for scientists to deal with oily water by adsorbing oils or by separating oil/water mixtures.

Many studies have developed a novel method to improve separation efficiency in the field of oil/water separation. For example, grafting of acrylic acid (AA) and acrylamide (AM) onto eucalyptus pulp cellulose, using one-step electrospinning procedure to create a smart poly(vinylidene fluoride)-graft-poly(AA) and using alkaline-induced phase-inversion process to prepare a polyionized hydrogel polymer (sodium polyacrylate-acrylamide (AM) onto eucalyptus pulp cellulose, using modified poly(AA) with benzoic acid functionality including N-methylol AM (NAM) percentage, sodium hypophosphite (SHP) percentage, and curing temperature, were studied to optimize the amount of poly(AA-co-NMA) bonded to the cotton fabric. The designated membrane was evaluated in the acid and ammonium salt forms as a multifunction membrane for oil (n-hexane, toluene and petroleum ether)/water separation and heavy metal ions removal (Cd2+ and Co2+). The contact angle at different pH (1, 7, and 11) of various oils on the surface of the prepared membrane was measured. In addition, the removal efficiency (R) and adsorption capacity (Q) of the acid and ammonium salt forms of the prepared membrane for the heavy metal ions (Cd2+ and Co2+) were estimated.

2 | EXPERIMENTAL

2.1 | Materials

Cotton fabric was supplied by Alexandria Company for General Supplies (Egypt) with mass per unit area of 161.55 gm/m2. AA (99.0%) was purchased from SDFCL, India. NMA (48 wt %) was purchased from Sigma-Aldrich. Hydrogen peroxide (H2O2) (50%) was supplied by Egyptian British Company, Egypt. Ammonium ferrous sulfate hexahydrate (AFSH) (98.5%) was obtained from Loba Chemie Pvt. Ltd., India. SHP was supplied by Sigma-Aldrich. Ammonium hydroxide (25%) was obtained from BDH Limited Poole England. Toluene (99.99%) (HPLC grade) and petroleum ether (boiling range = 60–80°C) were obtained from Fisher Scientific, UK and n-hexane (95%) was obtained from TEDIA Company. Cadmium chloride (CdCl2·2H2O, 99%) was supplied by CDH (Central Drug
House [P] Ltd., India). Cobalt(II) acetate tetrahydrate ((CH₃COO)₂-Co·4H₂O, 99%) was supplied by BDH Laboratory Supplies, England) and hexamethylenetetramine (HMTA) (C₆H₁₂N₄, >99%) was supplied by MERCK Schuchardt, Germany). Xylenol orange was used as indicator and ethylenediaminetetraacetic acid (EDTA) was used as chelating agent in complexometric titration of heavy metals. They were purchased from Sigma-Aldrich.

## 2.2 Synthesis of PAA

Five different poly(AA-co-NMA) with different contents of NMA (0, 1, 2, 3.5, and 5% based on the total monomer weight) were synthesized in 2 L with three-necked flask equipped with magnetic hotplate stirrer, condenser, and thermometer using solution polymerization technique. The ratios of the components of the five copolymers are reported in Table 1. The mixture of monomers (30% based on the weight of the total batch) was prepared by mixing the monomers (AA and NMA) with 15% of water. The initiator solution was prepared by mixing 10.51% of H₂O₂ (50%) with 10.51% of distilled water. The flasks contents were 0.0042% of AFSH and 33.93% of distilled water. The flasks content’s temperature was adjusted at reflux temperature (100°C) and the stirring rate was adjusted at 300 rpm. The monomers and initiator solutions were added continuously and simultaneously over 3 h. After complete addition of all reactants, the flasks contents were maintained at 100°C for 2 h to ensure complete monomer conversion, then were cooled down to 30°C. After that, the solid content of the prepared polymers was measured. Where small amount (about 1 g) of the prepared polymers was weighed (W₁) in Petri dish and placed in the oven at 105°C for 2 h. The weight (W₂) of the samples after cooling in desiccator for 30 min was determined and the solid content was determined as follows:

\[
\text{Solid content (\%) } = 100 \times \frac{W₂ - W₁}{W₁} \ldots \quad (1)
\]

## 2.3 Modification of cotton fabric with PAA

Samples of the cotton fabric with dimension of 10 × 10 cm were washed by impregnation in 300 ml of water which contains 10 g soap at 90°C for 15 min to remove any impurities sticking on the fabric. After that, the cotton fabric samples were removed, squeezed, dried in an air oven at 120°C for 30 min and weighed (W₁). Modification of the cotton fabric samples was performed by impregnation of the fabric for 5 min in solution of the previously prepared poly(AA-co-NMA) with solid content of 10%. After that, the modified samples were removed from modification solution, squeezed, and dried in air oven at 120°C for 30 min and cured at 150°C. The effect of curing temperature on the amount of bonded copolymer PAA3 was studied at different temperatures (150°C–170°C–190°C–210°C) for 7 min. The effect of addition of SHP on the bonding of copolymer PAA3 to the cotton fabric was investigated by adding different concentrations (2.5%–5%–7.5%–10%) of SHP to PAA3 solution (10%) and impregnating of cotton samples for 5 min in them. The curing temperature was 190°C in case of modification of cotton fabric with PAA3 in the presence of SHP. After curing, the modified cotton samples were immersed in 300 ml deionized water at 90°C to remove unbonded copolymer, dried in an oven at 120°C for 30 min and left to cool in desiccator for 30 min. After cooling, the fabric samples were weighed (Wᶠ) and the amount of bonded copolymer to cotton fabric was calculated using the following equation:

\[
\text{Bonded copolymer (\%) } = 100 \times \frac{Wᶠ - W₁}{W₁} \ldots \quad (2)
\]

### Table 1 Ratios of the different components

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>PAA0</th>
<th>PAA1</th>
<th>PAA2</th>
<th>PAA3</th>
<th>PAA4</th>
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<td>Monomers mixture</td>
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<td></td>
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<tr>
<td>AA</td>
<td>30</td>
<td>29.70</td>
<td>29.40</td>
<td>28.95</td>
<td>28.50</td>
</tr>
<tr>
<td>NMA</td>
<td>0 (0%)b</td>
<td>0.30 (1%)b</td>
<td>0.60 (2%)b</td>
<td>1.05 (3.5%)b</td>
<td>1.50 (5%)b</td>
</tr>
<tr>
<td>H₂O</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initiator solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>10.51</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>10.51</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Flask contents</td>
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<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>33.98</td>
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<tr>
<td>H₂O</td>
<td>10.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFSH</td>
<td>0.0042</td>
<td></td>
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</tr>
</tbody>
</table>

Abbreviation: AFSH, ammonium ferrous sulfate hexahydrate.

a All the weights are expressed in percentage based on the total batch weight.

b The percentage is based on the total monomers weight.
2.4 | Characterization and analysis

Fourier transformer infrared (FTIR) spectroscopy of poly(AA-co-NMA), modified, and unmodified cotton fabric was carried out using a Nicolet 380 spectrophotometer (Thermo Fischer Scientific) in the range of 4000–400 cm⁻¹. The polymerization of AA and NMA was confirmed through determination of poly(AA-co-NMA) molecular weight. The molecular weight was measured by Alliance e2695, Waters at 25°C using Agilent PAA sodium salt as calibration standard, flow rate: 1 ml/min and the sample concentration was 1 mg/ml. The mobile phase was a distilled water containing 100 mM NaCl, 10 mM NaH₂PO₄, and 0.02% NaN₃. The column used was PL aquagel-OH 40 and the detector used was RI. The surface morphology of the unmodified and modified cotton fabric was observed using optical microscope (Compact Video Microscope) (AC24OV, Japan) in the wet state and scanning electron microscope (SEM) Model VEGA3 (TESCAN, France). The underwater oil contact angle (OCA) of the different oils (toluene, petroleum ether, and n-hexane) on unmodified and modified cotton fabric surface at different pH values (1, 7, and 11) was observed by Compact Video Microscope. To study the underwater OCA, the samples were placed underwater and the oil dyed with plasticolors (DTP-709 Red122) was injected into water. The oil droplet contacted the undersurface of the textile and the OCA was measured.

2.5 | Oil/water mixture separation

The separation was carried out by the suggested oil/water separation system shown in Figure 1 which includes a cylinder of 5.53 cm diameter, while the prepared membrane was fixed on its bottom and a beaker was placed under the membrane as a container. The separation was achieved by gravity after 500 ml of oil/water mixture was poured into the cylinder. Three types of oil phase namely: toluene, petroleum ether, and n-hexane were used for the separation experiments. 100 ml oil and 400 ml water were mixed to form the oil/water mixture. The membrane was first wetted by neutral water without subsequent drying for the separation of oil/water mixtures in the acidic form. While in the neutralized form, the membrane was immersed in an ammonia solution (10 ml ammonia and 200 ml water) for 5 min before the separation. The prepared membranes were used to separate the same oil/water mixture several times to determine the reusing efficiency across 10 cycles. After that, the oil/water separation ability was estimated by volume measurements. A pipette was used to measure the volume of the collected oil. The separation efficiency (Kₛ) was calculated according to the following equation:

\[
Kₛ(\%) = 100 \times \frac{V_{col}}{V_o}
\]  

where \(V_{col}\) and \(V_o\) are the collected and initial volumes of oil, respectively. The gravity-driven separation flux of mixture was obtained across 10 cycles for the unmodified and modified cotton fabric by the following equation:

\[
\text{Flux} (F) = \frac{V}{St}
\]

where \(V\) is the volume of filtrate in liter (L), \(S\) is the surface area of separation material (m²), and \(t\) is the separation time (h).

2.6 | Heavy metal ions removal

A definite weight (0.5 g) of modified cotton fabric was cut into small pieces and immersed in 100 ml (concentration = 500 mg/L) of heavy metal ions solutions (cadmium chloride or cobalt acetate) at pH 7. These solutions were shaken for 2 h at 300 rpm at room
temperature. The modified cotton fabric pieces were removed by filtration and the filtrate which contains the metal ions was estimated by complexometric titration using EDTA solution (0.0005 molar) as titrant and xylene orange solution (0.1 g/100 ml H₂O) as indicator. Accurately, 10 ml of metal ions solution was introduced in 100 ml flask containing 10 ml of distilled water, 0.25 g of HMTA (as buffer), and five drops of xylene orange. The end point was obtained when the color changed from violet to yellow.

The amount of adsorbed Cd (II) and Co(II) ions on modified cotton fabric at equilibrium, \( q_e \) (mg/g) was obtained according to the following equation:

\[
q_e = \frac{(C_0 - C_e) x V}{W} \quad (5)
\]

where \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( C_0 \) is the initial concentration of the heavy metal ions solution (mg/L), \( C_e \) is the equilibrium concentration of the heavy metal ions solution (mg/L), \( V \) is the volume of heavy metal ions solution (L), and \( W \) is the weight of adsorbent modified cotton fabric (g).

The removal ratio \( (R\%) \) was calculated by the following equation:

\[
R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (6)
\]

where \( C_f \) and \( C_p \) are the concentrations of the heavy metal ions solution in the initial solution and the filtrate in rapid adsorption experiment (mg/L), respectively.

3 | RESULTS AND DISCUSSION

3.1 | Effect of modification conditions on the amount of PAA bonded

All the prepared polymers gave a solid content values in the range of 28.9–29.2. Before using in the modification, the solid content of the prepared polymers was adjusted at 10%. Three factors were studied namely, the effect of NMA concentration, SHP concentration, and the curing temperature.

3.1.1 | Effect of NMA concentration

The obtained results in Figure 2(A) showed that the amount of PAA bonded to the cotton fabric was very low (0.5%) in the absence of NMA, which may be attributed to esterification reaction between the carboxylic groups of PAA and hydroxyl groups of cotton fabric or the hydrogen bonds formation. The increase in NMA amount within PAA increased the amount of copolymer bonded to the cotton fabric up to 3.5% NMA. In addition, no significant increment in the bonded copolymer was observed in the presence of 5% NMA. The NMA monomer acts as bonding agent, where it can make ether linkages with hydroxyl groups of the cotton fabric through condensation reaction and consequently bonds the PAA to the cotton fabric as indicated in Scheme 1. As can be clearly seen, the amount of PAA bonded to the cotton fabric increased, after addition of 3.5% NMA to PAA, by 9.54% compared to PAA without NMA.

3.1.2 | Effect of curing temperature

Figure 2(B) shows the effect of curing temperatures (150, 170, 190, and 210°C) on the amount of poly(AA-co-NMA), with 3.5% NMA, bonded to the cotton fabric. Peng
et al.\textsuperscript{49} studied the effect of curing temperature on the total amount of maleic acid (MA) bonded to the cotton fabric in the presence and absence of SHP, where the results showed significant effect of curing temperature on the esterification reaction between MA and cotton fabric. Similar results were obtained, where the amount of copolymer bonded to cotton fabric increased from 5.27 to 6.51\% when the curing temperature was raised from 150 to 170\^\circ\textdegree C. The increment in the amount of copolymer bonded to cotton fabric continued up to curing temperature 190\^\circ\textdegree C reaching 11.32\% then decreased to 9.05\% as the curing temperature was raised to 210\^\circ\textdegree C.

3.1.3  |  Effect of SHP concentration

The data represented in Figure 2(C) indicated that the use of NaH\textsubscript{2}PO\textsubscript{4} as a catalyst increased the amount of poly(AA-co-NMA) bonded to cotton fabric.\textsuperscript{50} Without NaH\textsubscript{2}PO\textsubscript{4}, the amount of copolymer bonded to cotton fabric was increased from 5.27 to 11.32\% as the curing temperature was raised from 150 to 190\^\circ\textdegree C. When NaH\textsubscript{2}PO\textsubscript{4} was used as a catalyst at low concentration (2.5\%), it became 12.87\% at curing temperature 190\^\circ\textdegree C, which was higher than that of the copolymer-treated cotton without NaH\textsubscript{2}PO\textsubscript{4} by 13.7\%. Also, the amount of bonded copolymer increased from 12.87 to 14.26\% when the concentration of NaH\textsubscript{2}PO\textsubscript{4} was increased from 2.5 to 5\%. Thus, the data presented here clearly demonstrated that NaH\textsubscript{2}PO\textsubscript{4} acted as a catalyst to accelerate the reaction between the polymer and the cotton fabric and consequently increased the amount of PAA bonded to the fabric. Thus, the highest amount of copolymer bonded to cotton fabric was achieved at 5\% SHP. Hence, it was concluded that, the highest amount of the copolymer bonded to cotton fabric was achieved at 3.5\% NMA, in the presence of 5\% SHP and at curing temperature 190\^\circ\textdegree C as can be seen from Figure 2(A–C).

3.2  |  Characterization of poly(AA-co-NMA)-treated cotton fabric

3.2.1  |  FTIR spectroscopy

FTIR is one of the most widely used techniques for characterization of the organic and inorganic materials. The spectra of poly(AA-co-NMA), untreated cotton and poly(AA-co-NMA)-treated cotton are displayed in Figure 3. The spectrum (A) confirmed the formation of poly(AA-co-NMA) as indicated from the presence of the broad
peak in the range of 3100–3700 cm\(^{-1}\) which characterizes —OH groups. The peaks at 2920 and 2960 cm\(^{-1}\) are assigned to stretching vibrations of asymmetric and symmetric —CH\(_2\) groups.\(^{51}\) Also, the peak at 2850 cm\(^{-1}\) is due to the stretching vibration of —CH groups.\(^{52}\) The peaks at 1710 and 1650 cm\(^{-1}\) are assigned to the carbonyl group of —COOH and —CONH—, respectively.\(^{53}\) The characteristic peaks of NMA appeared at 1045 and 1280 cm\(^{-1}\) due to the stretching vibration of C—O—H, as reported by Kim et al.\(^{54}\) The broad peak at 3325 cm\(^{-1}\) in spectrum (B) is due to hydrogen bonded —OH groups in cotton fabric. The peak at 1635 cm\(^{-1}\) is due to absorbed water molecules. The vibrations characteristics peaks of —CH appeared at 2894, 1424, and 1370 cm\(^{-1}\). The —OH in plane bending is characterized by the peaks at 1315 and 1200 cm\(^{-1}\). The peak at 1156 and 1034 cm\(^{-1}\) are due to asymmetric bridge C—O—C and asymmetric stretching of C—O.\(^{55}\) The presence of the characteristic peaks of poly(AA-co-NMA) in the spectrum (C) of treated cotton fabric such as the peak at 1714 cm\(^{-1}\) confirms the bonding between the PAA and cotton fabric. In addition, the polymerization of PAA was confirmed using molecular

![Optical images of: (a) wet unmodified cotton fabric, (b) wet of unneutralized modified cotton fabric, and (c) wet neutralized modified cotton fabric and scanning electron microscope (SEM) images of: (d) unmodified cotton fabric (150×), (e) modified cotton fabric (150×), (f) unmodified cotton fabric (500×), and (g) modified cotton fabric (500×)]
3.3 | Surface morphology

The surface morphology of the unmodified and modified cotton fabrics was observed using optical microscope (Figure 4(A–C)) and SEM (Figure 4(D–G)). Figure 4(A–C) shows the optical images of the wet unmodified and modified cotton fabrics, where it can be clearly seen that, the pores of the modified cotton fabrics are smaller than those of unmodified cotton fabric. The reduction in the pore size of cotton fabric may be attributed to the swelling of the bonded poly(AA-co-NMA) resulting from the bonding to water molecules. The neutralization of the bonded copolymer increased its hydrodynamic volume as a result of mutual electrostatic repulsion between the negative ammonium carboxylate groups which reduced the pore size of cotton fabric to more extent.56,57 Figure 4(D–G) shows the SEM micrographs of unmodified and modified cotton fabrics at 150× and 500×. It could be observed that, the SEM micrographs of unmodified cotton fabric displayed smooth and clean surface compared to that of modified cotton fabric. The differences of the surface morphology could be easily observed on the modified cotton fabric which displayed rough surface and where a dense layer of poly(AA-co-NMA) film was formed on it.58

3.4 | Performance of modified cotton fabric membrane in oil/water separation

The underwater OCA of the different oils namely; toluene, n-hexane, and petroleum ether, on the surface of modified cotton fabric at different pH values (1, 7, and 11) of water was used as an indicator for the surface wettability. In general, the modified cotton fabric exhibited contact angle higher than 125° which indicated that, the modification of cotton fabric by the copolymer improved the hydrophilicity even at low pH = 1. It was observed that, the OCA of the different oils used was increased as the pH of the water was increased over than 140° at neutral pH = 7, which indicated the increase of the hydrophilicity of the modified cotton fabric. With increasing the pH value to 11, the surface of modified cotton fabric became underwater superoleophobic, where modified cotton fabric recorded OCA values 153, 150, and 155° with toluene, n-hexane, and petroleum ether, respectively.

As the pH was raised, the fabric became superhydrophilic, due to the variation of ionization state of

<table>
<thead>
<tr>
<th>pH</th>
<th>Toluene contact angle</th>
<th>n-Hexane contact angle</th>
<th>Petroleum ether contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 1</td>
<td>(130°)</td>
<td>(128°)</td>
<td>(127°)</td>
</tr>
<tr>
<td>PH = 7</td>
<td>(143°)</td>
<td>(145°)</td>
<td>(144°)</td>
</tr>
<tr>
<td>pH = 11</td>
<td>(153°)</td>
<td>(150°)</td>
<td>(155°)</td>
</tr>
</tbody>
</table>

Abbreviation: OCA, oil contact angle.
the copolymer. The copolymer chains were deprotonated and shifted from a globule to an extended conformation, allowing them to make strong bonds with water molecules and creating a more hydrophilic surface.\textsuperscript{44,59} The deprotonation of the poly(AA-co-NMA) happened with the increase of the pH value making mutual repulsion between the carboxylate groups and consequently higher swelling ratio and higher hydrodynamic volume. At high pH value, the surface was superhydrophilic and underwater superoleophobic, allowing passage of the water through oil phase. The swelling of copolymer layer in water and high repellency to oil achieved the underwater superoleophobic. On the fabric surface, a hydrogel-like membrane could be observed as indicated from optical images in Figure 4(A–C) representing the wet unmodified, unneutralized and neutralized modified cotton fabric, respectively. When the fabric was modified with acidic water (pH = 1), the OCA decreased to 127°:130° according to the oil type as shown in Table 2 indicating that the coated fabric membrane became less hydrophilic. The protonated polymers with collapsed structure prevented water from wetting the fabric and attained high affinity to the oil.\textsuperscript{44} It was concluded that the modification of cotton fabric with poly(AA-co-NMA) improved the hydrophilicity of membrane, which increased to more extent with the increase in pH value as shown from contact angle results in Table 2.

![Figure 5](image_url)

**Figure 5** Separation efficiency of different types of oil for: (a) acidic and (b) neutralized form of modified cotton fabric membrane
3.5 | Oil/water separation

The oil/water separation experiment was utilized to demonstrate the superhydrophilicity and underwater superoleophobicity of the modified cotton fabric. When oil/water mixture was poured into the suggested system, the water easily flowed through the modified cotton fabric while the oil clogged up, suggesting that the oil/water mixture was successfully separated with great efficiency. The separation efficiency for different examined types of oil phase, namely toluene, petroleum ether, and \( n \)-hexane was calculated using Equation (3). As indicated from Figure 5(A,B), the separation efficiency was estimated for PAA modified cotton fabric membrane over 10 cycles of oil/water mixture separation. It can be seen from Figure 5(A), the separation efficiency of acid form membrane ranged from 90 to 92%. In addition, the separation efficiency for neutralized form was higher, as indicated from Figure 5(B), where it ranged from 98 to 99%. The unmodified cotton fabric did not show any separation efficiency where all oil phases passed from the cotton fabric. The separation efficiency in the neutralized form was higher than that in acidic form. This may be attributed to that, the OCA increased with the increase in the pH values as indicated above, which enhanced the superhydrophilicity and underwater superoleophobicity of the modified cotton fabric surface, allowing water uptake in oil.\(^5,60\) In addition, the swelling of poly(AA-co-NMA) layer bonded to modified cotton fabric formed a hydrogel-like membrane on the fabric surface which imparted a high repellency to oils.\(^44,61\) Further investigation of the cycling performance of the neutralized and unneutralized modified cotton fabric showed that, both modified cotton fabric membranes maintained their high separation efficiency after 10 separation cycles. The flux of modified cotton fabric membranes with different oil/water systems across 10 cycles was determined according to Equation (4). As shown in Table 3, the flux rate decreased as the pH value of the water was increased, where the bonded PAA swells, clogs the pores of the fabric and retarded the flow of the water as shown in the optical images of the wet membranes. These results indicated that the designed modified cotton fabric membrane achieved high separation efficiency, large permeation flux, and excellent stability for many separation cycles with many types of oil/water systems.

3.6 | Heavy metal ions removal

A high contact area and a strong interaction between adsorbents and metal ions are required for effective adsorption of adsorbents for the removal of metal ions. The hydrogel copolymer chains in this study contain functional groups such as COOH and COO\(^-\) in unneutralized and neutralized form, respectively. These functional groups served as active sites for adsorption of metal ions. The proposed adsorption mechanism was attributed to the metal ions chelating to the functional groups via the electrostatic interactions at pH = 7. The results of the current study are shown in Table 4 investigated the adsorption performance of modified cotton fabric in both acidic and neutralized form. The modified cotton fabric was used to adsorb and remove various traces of metal ions (Cd\(^{2+}\) and Co\(^{2+}\). The removal ratios of unneutralized modified cotton fabric reached 35.27% for Cd\(^{2+}\) \( (q_e = 36.95 \text{ mg/g}) \) and 30.21% for

### Table 3
Flux of modified cotton fabric membranes for the different examined oil/water systems in acidic and neutralized form after (1–10) cycles

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Acetic Flux (L/m².h)</th>
<th>Neutralized Flux (L/m².h)</th>
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<tr>
<td></td>
<td>Toluene</td>
<td>Petroleum ether</td>
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<tr>
<td>1</td>
<td>21413</td>
<td>19985</td>
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<tr>
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<tr>
<td>9</td>
<td>9517</td>
<td>7312</td>
</tr>
<tr>
<td>10</td>
<td>8327</td>
<td>6813</td>
</tr>
</tbody>
</table>
Co\textsuperscript{2+} ($q_e = 38.64 \text{ mg/g}$). The neutralized form of modified cotton fabric was more efficient than that of the unneutralized one, where the removal ratios reached 59.94\% for Cd\textsuperscript{2+} ($q_e = 62.73 \text{ mg/g}$) and 43.98\% for Co\textsuperscript{2+} ($q_e = 56.31 \text{ mg/g}$). The neutralization of modified cotton fabric improved the removal ratio by 69.9\% for Cd\textsuperscript{2+} and 45.6\% for Co\textsuperscript{2+} as shown in Table 4. These results demonstrated that the pH has a significant impact on the metal ions removal efficiency. The balance between COOH and COO\textsuperscript{−} is used to discuss the high metal removal efficiency with the salt form of PAA modified cotton fabric. This balance is shifted to formation of COO\textsuperscript{−} groups after neutralization of PAA modified cotton with ammonium hydroxide. Because COO\textsuperscript{−} groups increased in the salt form of PAA modified cotton, the electrostatic attraction between Cd\textsuperscript{2+} or Co\textsuperscript{2+} and COO\textsuperscript{−} increased resulting in higher removal of heavy metal ions.\textsuperscript{1,62–64}

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Adsorbents</th>
<th>Concentration of metal ions (mg/L)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Removal ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial concentration</td>
<td>Final concentration</td>
<td></td>
</tr>
<tr>
<td>Cd\textsuperscript{2+}</td>
<td>Unmodified cotton fabric</td>
<td>525.11</td>
<td>522.43</td>
<td>0.54</td>
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<tr>
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<td>Modified cotton fabric (unneutralized)</td>
<td>339.90</td>
<td>36.95</td>
<td>35.27</td>
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<tr>
<td></td>
<td>Modified cotton fabric (neutralized)</td>
<td>210.38</td>
<td>62.73</td>
<td>59.94</td>
</tr>
<tr>
<td>Co\textsuperscript{2+}</td>
<td>Unmodified cotton fabric</td>
<td>641.80</td>
<td>635.98</td>
<td>1.16</td>
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<tr>
<td></td>
<td>Modified cotton fabric (unneutralized)</td>
<td>447.91</td>
<td>38.64</td>
<td>30.21</td>
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<tr>
<td></td>
<td>Modified cotton fabric (neutralized)</td>
<td>359.51</td>
<td>56.31</td>
<td>43.98</td>
</tr>
</tbody>
</table>

4 | CONCLUSIONS

In this study, the cotton fabric was modified with hydrophilic poly(AA-co-NMA) to improve the oil/water separation and for heavy metal ions removal efficiency. The success of the modification process was confirmed by the appearance of the characteristic peaks of the copolymer in the FTIR spectrum of the modified cotton fabric. In addition, the optical images and the SEM micrographs confirmed the bonding of the copolymer to the surface of cotton fabric. The optimum conditions which gave higher bonded copolymer to cotton fabric were achieved at 3.5\% NMA, in the presence of 5\% SHP and at curing temperature 190°C. The modified cotton fabric exhibited high separation efficiency for different oil/water systems up to 10 cycles with high flux rates. The neutralized modified cotton fabric gave higher separation efficiency (98–99\%) with all examined oils compared to the unneutralized one (90–92\%). The higher separation efficiency of the neutralized modified cotton fabric was attributed to the increase in OCA, which was higher than 150° at pH value = 11. Also, the neutralization of modified cotton fabric improved the removal ratios by 69.9\% for Cd\textsuperscript{2+} and 45.6\% for Co\textsuperscript{2+} compared to the unneutralized one.

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AUTHOR CONTRIBUTIONS

Ahmed Abdel-Hakim and Amira H. Abdella performed the experiment; analysis of the results and wrote the original draft. Ferial M. Tera contributed to methodology, the experiment; analysis of the results and wrote the original draft. Magdy W. Sabaa, Hoda Y. Gohar and Riham R. Mohamed reviewed and edited the manuscript.

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