

SEPARATION MEMBRANE FOR WATER TREATMENT, METHOD FOR MANUFACTURING THE SAME, AND CONTAINER COMPRISING THE SAME**FIELD OF INVENTION**

The present invention relates to a separation membrane for water treatment, a method of manufacturing the separation membrane, and a portable liquid container comprising the separation membrane as a filter.

BACKGROUND

Worldwide, 1 in 9 people has no access to clean and safe drinking water. According to the World Health Organization (WHO), water contamination is currently one of the world's leading causes of death and it is expected to worsen with climate change. Around 159 million people are still dependent on surface water (such as water from lakes, ponds, rivers, and streams) and 423 million people take water from unprotected wells and springs. Unlike other water contaminants such as colloidal particles, volatile organic compounds (VOC), odour and pathogens etc., heavy metals such as cadmium (Cd), lead (Pb), arsenic (As), and copper (Cu) are highly soluble in water and can easily contaminate aquatic ecological environments. Heavy metal ions at a very low concentration (ppm) in the human body can result in abnormal physiological activities. Therefore, these toxic heavy metal ions have become a worldwide problem and have drawn increasing efforts for their effective removal from the environment.

Moreover, rapid economic development brings new challenges and creates new environmental exposures to toxic substances. Industrial activities, especially electroplating, mineral processing, metallurgy, pipe manufactures, batteries smelting, automotive surface coating, semiconductor industry, chemical industries and manufacturing processes may directly or indirectly discharge toxic heavy metal contaminants into natural waters and aquatic environments. Further, municipal drinking water in many countries is still being delivered through lead pipes, brass fittings, or pipes joined with lead solder, which are all susceptible to corrosion and hence, leading to leaching of both soluble and particulate lead (Pb) heavy metals into the drinking water. Unfortunately, exposure is even worse in underdeveloped countries where a lack of resources and awareness limits the use of expensive industrial wastewater treatment processes.

In recent years, selective adsorption and separation of metal ions from wastewater has received more attention. Conventional methods such as physicochemical treatment (including chemical precipitations, coagulation-flocculation, ion-exchange resins, adsorption, evaporation, and biosorption) and hybrid processes comprising high pressure driven reverse osmosis (RO) in combination with adsorption (using ion exchange resins/activated carbon) are commonly adopted to remove toxic heavy metal ions from wastewater. In particular, metal oxides, such as iron oxide and aluminium oxide, and other nanomaterials have been already applied as pollutant sorbents due to their high surface/volume ratio, high reactivity, and ion-exchange capacity. However, these methods generate large volumes of sludge, involve corrosive chemicals, are highly sensitive to the pH of the

solution, have slow reaction kinetics, cannot handle highly-concentrated metals, are time-consuming and high in operational cost and energy consumption.

In particular, two main problems of existing UF (ultrafiltration) membranes used in such wastewater treatment process are that (a) it cannot remove any dissolved metal ions due to their relatively large membrane pore size (100nm) and (b) exhibits high fouling due to accumulation of organics and biological pollutant in the wastewater which cause deterioration of the membrane performance (such as flux reduction, rejection impairment and membrane breakage). The resulting effects of membrane fouling are high operational costs due to the frequent cleaning process (physical or chemical) and short membrane lifespan.

Similarly, the main problems of using NF (nanofiltration) membranes are that (a) they can only remove selective heavy metal ions (b) they require either a very high working pressures (3-30bar)/high feed concentration (500-1000ppm) or high alkaline condition (pH12) to reject heavy metal ions in the wastewater and (c) they exhibit a very low anti-fouling properties.

SUMMARY

According to an example of the present disclosure, there are provided a separation membrane, a method of manufacturing the same, and a portable liquid container as claimed in the independent claims. Some optional features are defined in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of a bipolar separation membrane with triple configuration according to an example of the present disclosure.

Figure 2 is a flowchart illustrating a step-by-step surface charge coating process onto a polymeric support membrane.

Figure 3A shows a Scanning Electron Microscope (SEM) image of a flat sheet polyacrylonitrile (PAN) membrane made with 7 weight percentage (wt%) PAN precursor concentration.

Figure 3B shows an image illustrating a result of a wettability analysis of a flat sheet PAN membrane made with 7 wt% PAN precursor concentration.

Figure 3C shows a graph illustrating results of a wettability analysis of a flat sheet hydrolysed PAN membrane (i.e. H-PAN), hydrolysed for different time intervals: 30mins, 1hr, 2hrs, 3hrs and 4 hrs.

Figure 3D shows a SEM image of a cross-section of a hollow fiber PAN membrane.

Figure 3E shows a SEM image under high magnification illustrating a result of a surface morphology analysis of a hollow fiber PAN membrane.

Figure 4 is a flowchart illustrating a layer-by-layer successive ionic layer adsorption and reaction (SILAR) process for coating a polycationic layer, a zwitterionic layer and a polyanionic layer onto a hydrolysed PAN membrane.

Figure 5 shows SEM images of a polyethylenimine (PEI) coated H-PAN membrane (PEI/H-PAN) at different precursor concentrations: 5mg/ml, 25mg/ml, and 50mg/ml, and at different dipping cycles: single layer, bilayer and triple layer.

Figure 6A shows a Fourier-transform infrared spectroscopy (FTIR) spectrum of a PEI coated H-PAN membrane (PEI/H-PAN), a hydrolysed PAN membrane (H-PAN), and an unhydrolysed PAN membrane (PAN).

Figure 6B shows the graph of Zeta potential vs pH of a PEI coated H-PAN membrane (PEI/H-PAN).

Figure 7A shows a FTIR spectrum of a synthesized polyether (sulfobetaine methacrylate) PSBMA powder.

Figure 7B to 7E show X-ray photoelectron spectroscopy (XPS) spectra of a synthesized PSBMA powder including the wide spectrum (Figure 7B), the C_{1s} individual spectrum (Figure 7C), the N_{1s} individual spectrum (Figure 7D) and, the S_{2p} individual spectrum (Figure 7E).

Figure 7F to 7H show Atomic Force Microscopy (AFM) images of a neutral charged PSBMA coated PEI/H-PAN membrane (PSBMA/PEI/H-PAN). Figure 7F is a two dimensional (2D) image in low magnification while Figure 7G is a 2D image in high magnification. Figure 7H is a three dimensional (3D) image of the PSBMA/PEI/H-PAN membrane.

Figure 8A is a graph illustrating a result of a wettability analysis of a neutral charged PSBMA coated H-PAN membrane (PSBMA/H-PAN) at different PSBMA precursor concentrations: 0.05 wt%, 2 wt% and 4 wt%.

Figure 8B is a graph of Zeta potential vs pH of a neutral charged PSBMA coated H-PAN membrane (PSBMA/H-PAN) at different PSBMA concentrations: 0.05 wt%, 2 wt% and 4 wt%.

Figure 9 is a FTIR spectrum of a control unhydrolysed PAN membrane and surface modified PAN membranes including H-PAN, PEI/H-PAN, PSBMA/PEI/H-PAN and PSS/PSBMA/PEI/H-PAN membranes.

Figure 10 shows a graph illustrating results of a adsorption study conducted on a control unhydrolysed PAN membrane and surface modified membranes including H-PAN, PEI/H-PAN, PSBMA/PEI/H-PAN and PSS/PSBMA/PEI/H-PAN for Pb^{2+} metal ion with respect to time (in hours).

Figure 11 is a graph illustrating a result of a rejection (%) study conducted on a bipolar triple layer membrane (PSS/PSBMA/PEI/H-PAN) with Cu^{2+} metal ions at pH 5, pH 7 and pH 9.

Figure 12A is a graph showing the results of a pure water flux study conducted on a control unhydrolysed PAN membrane (PAN), a bilayer membrane (PSS/PEI/H-PAN) and a triple layer membrane (PSS/PSBMA/PEI/H-PAN).

Figure 12B shows the results of a rejection (%) study of a bilayer membrane (PSS/PEI/H-PAN) and a triple layer membrane (PSS/PSBMA/PEI/H-PAN) using $CuCl_2$ at pH 5.2 and working pressure 2 bar.

Figure 12C shows the results of a rejection (%) study of a bilayer membrane (PSS/PEI/H-PAN) and a triple layer membrane (PSS/PSBMA/PEI/H-PAN) using $CdCl_2$ at pH 5.2 and working pressure 2 bar.

Figure 12D shows the results of a rejection (%) study of a bilayer membrane (PSS/PEI/H-PAN) and a triple layer membrane (PSS/PSBMA/PEI/H-PAN) using $PbCl_2$ at pH 5.2 and working pressure 2 bar.

Figure 13 shows the results of an antifouling study, comparing the pure water flux of a triple layer membrane (PSS/PSBMA/PEI/H-PAN) with that of a control unhydrolysed PAN membrane and a bilayer membrane (PSS/PEI/H-PAN).

Figure 14A shows a result of a membrane pore size distribution study of a control unhydrolysed PAN membrane.

Figure 14B shows a result of a membrane pore size distribution study of a PSS/PSBMA/PEI/H-PAN membrane.

Figure 15A shows a cross-sectional front view of a first example of a fully assembled portable liquid container according to an example of the present disclosure.

Figure 15B shows a cross-sectional front view of a bottom portion of the portable liquid container of Figure 15A.

Figure 15C shows a cross-sectional front view of a top portion of the portable liquid container of Figure 15A.

Figure 16A shows a cross-sectional front view of a second example of a fully assembled portable liquid container with a bottle cap according to an example of the present disclosure.

Figure 16B shows a cross-sectional front view of the portable liquid container of Figure 16A without a bottle cap.

Figure 16C shows a cross-sectional front view of the bottle cap of the portable liquid container of Figure 16A.

Figure 17A shows a cross-sectional front view of a third example of a fully assembled portable liquid container according to an example of the present disclosure.

Figure 17B shows a cross-sectional front view of the components of the portable liquid container of Figure 17A.

Figure 17C shows a first use scenario of the portable liquid container of Figure 17A.

Figure 17D shows a second use scenario of the portable liquid container of Figure 17A.

DETAILED DESCRIPTION

Examples of the present disclosure relate to a bipolar separation membrane with a triple layer configuration, a method of producing said separation membrane, and use of the separation membrane (e.g. in a portable drinking bottle). A novel surface modified membrane is proposed. An example of such membrane can effectively remove majority of charged ion pollutants at very low operating pressure (less than 1.5 bar), and low feed concentration (20ppm to 100ppm) with enhanced anti-fouling functionality.

A. Separation Membrane with Triple Layer Configuration

Figure 1 shows a schematic diagram of an example of a separation membrane with triple layer configuration 100. It comprises (a) a first polycationic layer as a base layer 104 deposited onto a support membrane 102, (b) a second zwitterionic layer as a selective layer 106 deposited on the base layer 104, and (c) a third polyanionic layer as a protective layer 108 deposited on the selective layer 106. In the present example, the separation membrane 100 is bipolar, and comprises a triple layer

configuration. In specific examples as follows, the separation membrane 100 is also known by other terms such as bipolar triple layer membrane or triple layer membrane in the present disclosure. A PSS/PSBMA/PEI/H-PAN membrane consisting of the layers PSS/PSBMA/PEI/H-PAN described later in the present disclosure is a specific example of the separation membrane 100. It should be appreciated that although one sequential arrangement (i.e. the first polycationic layer over the support membrane 102, the second polyzwitterionic layer over the first polycationic layer and the third polyanionic layer over second polyzwitterionic layer) of the triple layer configuration is described herein, the order of layering of the first polycationic layer, the second polyzwitterionic layer and the third polyanionic layer can be re-arranged based on the surface charge of the support membrane and acceptable performance can still be expected.

In one example, a nitrile polymer is used as the support membrane 102. One option is to use polyacrylonitrile (PAN) as the support membrane 102. The support membrane 102 may contain inorganic composite additives such as TiO_2 and ZnO and carbon nanofiber (CNF) to enhance adsorption and for antibacterial functionality of the bipolar triple layer membrane 100. In addition, the support membrane 102 may be a nanoporous layer that effectively removes small particulates/microbes due to size exclusion.

In the present example, a polycationic polymer is used as the base layer 104 in the triple layer configuration. The polycationic polymer may be selected from polyethylenimine (PEI), poly(allylamine hydrochloride) (PAH), poly(2-methacryloxyethyltrimethylammonium bromide) (PMOTAB) and chitosan..

In relation to the selective layer 106, a zwitterionic polymer is used in the present example. The zwitterionic polymer may be polyether (sulfobetaine methacrylate) (PSBMA). Using a zwitterionic polymer as the selective layer 106 confers high adsorption and rejection properties to the bipolar triple layer membrane 100 that effectively removes both anion and cationic ions and in particular, heavy metal ions and also antifouling properties.

In relation to the protective layer 108, a polyanionic polymer is used in the present example. The polyanionic polymer may be selected from poly sodium 4-styrene sulfonate (PSS) and polyacrylic acid (PAA). The polyanionic polymer has high affinity and adsorption properties towards divalent and trivalent heavy metal ions such as Pb^{2+} , Cd^{2+} and Cr^{3+} .

One of the advantages of the present bipolar separation membrane 100 with triple layer configuration is that it is able to remove dissolved heavy metal ions in wastewater through the adsorption and rejection mechanism. Specifically, the bipolar triple layer membrane 100 can remove the majority of charged pollutant (i.e. cation and anion) at each individual layer i.e. (1) Base layer: polycationic (+), (2) Selective layer: polyzwitterionic (z), and (3) Protective layer: polyanionic (-). The polyanionic and polycationic layers can effectively reject the charged pollutants due to electrostatic repulsion (Donnan exclusion). It can also separate all uncharged solutes due to nanopore size effects (size exclusion) provided by the nanoporous feature of the membrane. In addition, the present bipolar triple layer membrane 100 has antifouling properties conferred by the polyzwitterionic layer.

A proposed portable liquid container is designed to integrate the bipolar triple layer membrane 100 of Figure 1 as a filter to remove charged contaminants, including dissolved heavy metals,

instantly at a very low concentration (preferably less than 100ppm) in surface water. The proposed portable liquid container with the filter comprising the separation membrane 100 of Figure 1 exhibits rejection greater than 95% for divalent and trivalent heavy metal ions such as Arsenic (As), Copper (Cu^{2+}), Cadmium (Cd^{2+}), Lead (Pb^{2+}), and Chromium (Cr^{3+}) at very low working pressure (preferably less than 1.5bar). The compact cost-effective, separation membrane 100 filter can be applied to provide clean, fresh and safe drinking water for outdoor travellers, disaster recovery/poor sanitation areas and households in third world countries.

B. Method of Producing the Separation Membrane 100

Conventionally, interfacial polymerization was adopted for the preparation of a thin-film composite (TFC) membrane with a selective surface charge layer. However, the scaling up of the selective surface charge layer for larger surface area membrane remains a challenge due to its non-uniformity, low coating density, and environmental issues.

The bipolar separation membrane 100 of Figure 1 with triple layer configuration is developed via an easily scalable room temperature dip coating method (layer by layer) at optimum conditions i.e. at an optimum number of dipping cycles, polymer concentration and dipping time.

Figure 2 shows a step-by-step surface charge coating process for coating charged polymeric layers layer by layer onto a polymeric support membrane to form the bipolar separation membrane 100 of Figure 1 with triple layer configuration. There are 4 steps in total and they will be described herein below.

With reference to Figures 1 and 2, generally, the support membrane 102 is hydrolysed in a step 1 illustrated by 120 in Figure 2. A polycationic (i.e. positively charged) layer is coated on the hydrolysed support membrane 102 in a step 2 illustrated by 122 in Figure 2 via, for example, a room temperature dip coating method. A polyzwitterionic (neutral charge) layer is coated over the earlier polycationic coating in a step 3 illustrated by 124 in Figure 2 via, for example, a further room temperature dip coating method. A polyanionic (i.e. negatively charged) layer is coated on over the earlier polyzwitterionic coating in a step 4 illustrated by 126 in Figure 2 via, for example, a further room temperature dip coating method. The room temperature dip coating method may be a successive ionic layer adsorption and reaction (SILAR) process. The details of the aforementioned steps are described as follows.

(a) Formation of the Support Membrane 102

In the present disclosure, the terms "flat sheet" and "hollow fiber" refer to two different conformations that the bipolar triple layer membrane 100 may take. Specifically, a flat sheet membrane refers to a flat piece of membrane wherein wastewater is to pass through to be filtered while hollow fiber membrane refers to typically a tubular membrane with a lumen wherein wastewater is to pass through from the outside the tubular membrane into the lumen, or vice versa, to be filtered. The hollow fiber membranes may be bundled together to filter large volume of wastewater.

A nitrile group polymer is chosen as a material for the support membrane 102, which can be in the form of either a flat sheet membrane or a hollow fiber membrane. The polymer is dissolved in a

solvent (such as dimethylformamide (DMF)), containing inorganic composite additives comprising TiO_2 and carbon nanofiber (CNF) to form a homogenous polymer solution. The support membrane 102 in the form of either flat sheet membrane or hollow fiber membrane is then formed from the homogenous polymer solution through an electrospinning technique or a conventional dry-wet spinning technique at room temperature.

In the present example, polyacrylonitrile (PAN) polymer is chosen as the nitrile group polymer for the support membrane 102 due to its high solvent resistance, thermal stability, chemical stability and the enrichment of nitrile group (CN) for hydrolysis.

Electrospinning is used to obtain the support membrane 102 in the form of a flat sheet. Electrospinning is a commercially viable fabrication technique that enables large-scale production of nanofiber mats with macroscale interstitial spaces and porosity. During the electrospinning process to form the support membrane 102 of the present example, a sol-gel polymer solution synthesized from the polyacrylonitrile (PAN) polymer and inorganic composite additives (such as TiO_2 and Carbon nanofiber (CNF)), with Dimethylformamide (DMF) as the solvent, is used.

In one example, PAN is first dissolved in 20 mL of DMF solvent to form a clear white polymer solution with 7 weight percentage (wt%) PAN without agglomeration. This clear white polymer solution (PAN/DMF) is then stirred in a hotplate at 55°C for 6 hrs to form a yellow colour sol-gel solution. Solution viscosity can be modified by changing PAN polymer concentration (i.e. PAN wt%). The prepared sol-gel solution is allowed to cool down at room temperature (e.g. 28°C) and subsequently transferred into a 10 ml clean syringe for electrospinning.

The optimized spinning parameters for forming the support membrane 102 in the form of a flat sheet of the present example are for example, polymer concentration of 7 wt% PAN, applied voltage of 21 kV, flow rate of 1.0 ml/h, drum speed of 300 rpm, and collector-to-needle distance of 10 cm. The carbonized carbon nanofiber (CNF) is incorporated into the support membrane 102 with inorganic nanomaterials (such as TiO_2 and ZnO nanoparticles) at different compositions. CNF and the nanomaterials will enhance the adsorption and antibacterial functionality of the support membrane 102 formed. Finally, the developed support membrane 102 in the form of a flat sheet is hot pressed onto a polyethylene terephthalate (PET) backing layer at 100°C for 10 mins to remove residual water and impure solvents. The surface morphology of the hot pressed support membrane 102 reveals presence of denser and interlinked fibers.

Figure 3A shows a SEM micrograph of a developed PAN support membrane 102 in the form of a flat sheet made using the aforementioned electrospinning method with 7 wt% PAN precursor concentration. The SEM micrograph confirms an interconnected pore structure with average fiber diameter that ranges around 80 nm to 200 nm. Figure 3B illustrates a result of a wettability analysis of the PAN support membrane 102 in the form of a flat sheet, exhibiting a static water contact angle of about 40° .

Alternatively, to make the support membrane 102 in the form of a hollow fiber, specifically, a hollow fiber PAN ultrafiltration (UF) membrane, a conventional dry-wet spinning technique is used. In one example, a polymer solution, containing 15 wt% PAN in DMF is first prepared by stirring the solution for 5 hours and allowing it to be degassed for 24 hours. Pure water can be used as a bore

liquid in the dry-wet spinning technique. Then, after leaving the spinneret and traveling a 50 cm air gap, the polymer solution enters into a water/solvent bath and the hollow fibers formed are collected. The hollow fibers are kept in pure water for 48 hours in order to withdraw residual solvents. The support membrane 102 in the form of the hollow fiber membrane is fabricated at 25 °C and at around 65% relative humidity.

Figure 3D shows a cross-sectional SEM image of the PAN hollow fiber support membrane 102 made using the conventional dry-wet spinning technique. External and internal diameters of the PAN hollow fiber support membrane 102 are around 1.63 mm and 0.932 μm respectively. Figure 3E shows another SEM image under high magnification illustrating the result of a surface morphology analysis of the PAN hollow fiber support membrane 102. The SEM image of the PAN hollow fiber support membrane 102 under high magnification shows uniform distribution of membrane pores with sizes ranging around 0.1 μm to 0.05 μm .

(b) Hydrolysis of the Support Membrane 102

The support membrane 102 is further hydrolysed with NaOH solution in a step 120 in Figure 2 to enhance hydrophilic properties of the support membrane 102. In the present example, the hydrolysed support membrane 102 is a hydrolysed PAN membrane (H-PAN).

Figure 3C is a graph of water contact angle (in degrees) vs time illustrating the result of a surface wettability analysis of a hydrolysed PAN membrane (H-PAN) exhibiting enhanced hydrophilic properties when compared to a control PAN membrane. The control PAN membrane in this case is a non-hydrolysed PAN membrane. Static water contact angle of the non-hydrolysed control PAN membrane is about 40° while that of the hydrolysed PAN membrane is about 21°. The static water contact angle further decreases from about 21° to about 11° when the hydrolysis reaction time for hydrolysis increases from 30 mins to 4 hours.

With reference to Figure 2, the hydrolysed support membrane 102 in the form of the H-PAN membrane (in a form of a flat sheet membrane or hollow fiber membrane) can be further cross-linked with selective surface charged polymers to form a triple layer configuration. Such selective surface charged polymers can be a base polycationic (i.e. positively charged) polymer coated in the step 2 illustrated by 122 of Figure 2, a selective polyzwitterionic (neutral charge) polymer coated in the step 3 illustrated by 124 of Figure 2, and a protective polyanionic (i.e. negatively charged) polymer coated in the step 4 illustrated by 126 of Figure 2. In the present example, the base polycationic layer, selective polyzwitterionic layer and the protective polyanionic layer may be coated using successive ionic layer adsorption and reaction (SILAR).

(c) Crosslinking the hydrolysed support membrane 102 with a polycationic polymer as the base layer 104

The hydrolysed support membrane 112 from step 1 illustrated by 120 of Figure 2 can be cross-linked with a polycationic polymer to form the base layer 104. The polycationic base layer 104 shows a high affinity (adsorption) towards oppositely charged matters and exhibits strong repulsion towards divalent cations through Donnan exclusion (electrostatic repulsion). As an example,

polyethylenimine (PEI) is selected as the material of the base layer 104. PEI has large positive charge density, which can be deposited on the support membrane surface with negative charges through a supramolecular assembly. The presence of many primary and secondary amino groups on the long carbon chains in PEI allows it to be cross-linked to form a dense active layer. The H-PAN support membrane 102 can be cross-linked with a PEI solution at concentrations such as 5mg/ml, 25mg/ml, and 50mg/ml through room temperature successive ionic layer adsorption and reaction (SILAR).

An example of the SILAR steps for coating the polycationic PEI base layer 104 on a H-PAN support membrane 200 (H-PAN) is illustrated in Figure 4. In a step 210, the hydrolysed PAN support membrane 200, is dipped into a precursor solution 218, containing PEI. The positively charged PEI is adsorbed onto the negatively charged surface of the H-PAN support membrane 200. In a step 212, the excess PEI that is loosely adsorbed is removed by washing the PEI coated H-PAN membrane 202, in deionised (DI) water 220. The washed PEI coated hydrolysed PAN membrane 204 (PEI/H-PAN) is then dried at 40°C for 30 mins. Remaining steps 214 and 230 are described later.

Optimal low concentrations of polycationic PEI polymer solution can be coated onto the H-PAN support membrane 200 of Figure 4 (which can be in a form of a flat sheet membrane or a hollow fiber membrane) using successive ionic layer adsorption and reaction (SILAR) at different dipping cycles such as single layer, two layers, or three layers.

Figure 5 shows multiple SEM images of PEI coated H-PAN support membrane (i.e. example of base layer 104 coated on support membrane 102) at different concentrations. A first SEM image 502 shows PEI with concentration of 5mg/ml coated on H-PAN support membrane. A second SEM image 504 shows PEI with concentration of 25mg/ml coated on H-PAN support membrane. A third SEM image 506 shows PEI with concentration of 50mg/ml coated on H-PAN support membrane. A fourth SEM image 508 shows a single layer of PEI coated on H-PAN support membrane. A fifth SEM image 510 shows two layers of PEI coated on H-PAN support membrane. A sixth SEM image 512 shows three layers of PEI coated on H-PAN support membrane. The 6 SEM images 502 to 512 show the coating of PEI onto H-PAN support membrane without any surface agglomeration.

The monolayer PEI coated onto the H-PAN support membrane shown in the fourth SEM image 508 exhibits high hydrophilicity with a water contact angle of 16.5° when compared with a control non-hydrolysed PAN membrane with a water contact angle of 40° and a control non-PEI coated H-PAN membrane with water contact angle of 24.62°. A further increase in polycationic layers i.e. two and three layers of PEI illustrated by the fifth SEM image 510 and the sixth SEM image 512 leads to decrease in hydrophilicity. The two layers PEI coated hydrolysed PAN membrane of the fifth SEM image 510 exhibits a water contact angle of 18° and the three layers PEI coated hydrolysed PAN membrane of the sixth SEM image 512 exhibits a water contact angle of 26°. The decrease in hydrophilicity as shown by the increase in water contact angle postulates that an increase in PEI coating thickness from monolayer of SEM image 508 to two layers of SEM image 510 to three layers of SEM image 512 is attributable to water moisture trapped in between PEI layers. Specifically, as shown in Figure 5, the average thickness of the PEI/H-PAN membrane in the SEM images 508, 510 and 512 is around 0.0357mm, 0.0430mm and 0.0483mm for single, two and three layers PEI respectively.

Figure 6A shows a FTIR spectrum of a PEI coated H-PAN membrane (PEI/H-PAN; also known herein as “PEI/H-PAN membrane”), a H-PAN membrane and an unhydrolysed PAN membrane. The FTIR spectrum of the PAN membrane shows a dominant peak at 2240 cm^{-1} , attributed to stretching vibration of the nitrile group ($\text{C}\equiv\text{N}$), and 2930 cm^{-1} and 1470 cm^{-1} , which are due to the respective stretching and bending vibrations of methylene group (CH_2). The spectrum of the H-PAN membrane shows the presence of the functional group of COO^- around the peak of 1562 cm^{-1} (strong asymmetrical stretching band) and 1402 cm^{-1} (weak symmetrical stretching band). In addition, there are appearances of peaks at 3402 cm^{-1} which corresponds to the hydroxyl group ($-\text{OH}$) and at $1699\text{--}1711\text{ cm}^{-1}$ which corresponds to the carbonyl group ($\text{C}=\text{O}$). The spectrum of the PEI/H-PAN membrane exhibit two additional absorption peaks at 1600 cm^{-1} which is the stretching and bending vibration of amine group (N-H), and 1122 cm^{-1} which is the stretching vibration of C-N group. Both N-H and C-N groups belong to the amine groups in PEI. Hence, the presence of these peaks in the FTIR spectrum indicates the successful coating of PEI (i.e. base layer 104) onto the H-PAN membrane (i.e. support membrane 102).

Figure 6B shows the surface charge properties of the PEI/H-PAN membrane. The zeta potential which reveals the surface charge properties of a membrane is examined at different pH values by measuring the streaming potential using electrolyte solutions. Figure 6B shows a mostly positive surface charge for the PEI coated H-PAN membrane (i.e. PEI/H-PAN). The surface charge of the PEI/H-PAN membrane decreases with increase in pH up to an isoelectric point (pH 9.5), above which, negative surface charge is observed. The PEI crosslinking not only decreases membrane pore size but also deposits adequate amine groups on the membrane surface. These amine groups will increase the positive surface charge of the PEI cross-linked membranes.

(d) Layering a zwitterionic polymer as the selective layer 106

Zwitterion-based polymers are promising antifouling materials due to their high hydrophilicity, long-term durability, and environmental stability. Zwitterionic polymers have both cationic and anionic groups with overall neutral charge resulting in significant hydration via electrostatic interactions. In one example, polyether (sulfobetaine methacrylate) (PSBMA) is chosen as the neutral surface charged zwitterionic polymer to be used as the selective layer 106 in the triple layer configuration of the bipolar triple layer membrane 100 of Figure 1. PSBMA is synthesized through a polymerization process using sulfobetaine methacrylate (SBMA) monomer as starting material and then coated over the polycationic layer of the PEI/H-PAN membrane. The PEI/H-PAN membrane may be in a form of a flat sheet membrane or a hollow fiber membrane. The zwitterionic selective layer 106 can be coated onto the PEI/H-PAN membrane through successive ionic layer adsorption and reaction (SILAR). Figure 4 illustrates the SILAR steps, which continues from step 212 described earlier. In a step 214, the washed and dried PEI coated hydrolysed PAN membrane (i.e. PEI/H-PAN membrane) 204 is dipped into a precursor solution 222, containing PSBMA. The zwitterionic charged PSBMA is adsorbed onto the positively charged PEI surface of the PEI/H-PAN membrane 204. In a step 216, the excess PSBMA that is loosely adsorbed is removed by washing the PSBMA coated PEI/H-PAN membrane 206, in deionised (DI) water 220. Thereafter, the washed PSBMA coated PEI/H-PAN

membrane (PSBMA/PEI/H-PAN also known herein as "PSBMA/PEI/H-PAN membrane") 208, is dried at room temperature. The dip coating of the PSBMA is performed with different wt% of PSBMA solution such as 0.05%, 2%, and 4% at optimum dipping conditions such as 10 deposition cycles, 100mm/sec dipping speed and 30 seconds dipping time interval.

Figure 7A shows a FTIR spectrum of the PSBMA powder used in step 214 of Figure 4. In the FTIR spectrum, the presence of PSBMA can be ascertained from the sulfonate groups and the ester carbonyl groups observed from the bands of the -S=O stretch at 1044 cm^{-1} and 1193 cm^{-1} , the -C-S stretch at 606 cm^{-1} , and the O-C=O stretch at 1727 cm^{-1} . Figure 7B shows a XPS spectrum of PSBMA powder which also confirms the presence of PSBMA from predominant S_{2p} (167eV) and N_{1s} (402eV) peaks. The individual spectrum of S_{2p} (Figure 7E) further confirms the presence of sulfonate group (O=S=O) in PSBMA. Atomic compositions of the synthesized PSBMA were around 67.37 % for C_{1s} , 5.34% for N_{1s} , 22.19% for O_{1s} and 4.9% for S_{2p} .

Surface roughness is an important structural parameter because it is used to study the permeate flux and fouling behaviour in the membrane. Figures 7F to 7G illustrate a surface roughness study of a PSBMA/PEI/H-PAN membrane. The average surface roughness (R_a) and root mean square surface roughness (RMS or R_q) is determined in the surface roughness study. Figure 7F and 7G show two dimensional (2D) Atomic Force Microscopy (AFM) images in low and high magnifications respectively and Figure 7H shows a three dimensional (3D) AFM image of a scan area of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ of a PSBMA/PEI/H-PAN membrane. In this case, the control PAN membrane used for comparison is non-hydrolysed and not coated with any layers. A change in surface roughness is observed from $R_q\text{ }429\text{nm}/R_a\text{ }342\text{nm}$ for the control PAN membrane to $R_q\text{ }515\text{nm}/R_a\text{ }412\text{nm}$ for PSBMA/PEI/H-PAN membrane.

Surface wettability of the PSBMA/PEI/H-PAN membrane can be studied at different PSBMA polymer weight percentage (wt%). Figure 8A shows the results of such study. With an increase in weight percentage (wt%) of the PSBMA polymer from 0.05 wt% to 4 wt%, the surface wettability of the PSBMA/PEI/H-PAN membrane increases with a decreases in water contact angle from 30° to 17° when compared to a control unhydrolysed PAN membrane water contact angle of 41° . Hence, modification of the PEI/H-PAN membrane by adding the PSBMA selective layer (i.e. an example of the selective layer 106) further increases the surface hydrophilicity of the resultant PSBMA/PEI/H-PAN membrane due to the strong hydration capacity of zwitterionic polymers.

Surface charges play a crucial role in nanofiltration according to the Donnan effects of rejection of charged solutes. The surface charge of the PSBMA/PEI/H-PAN membrane in the pH range from 3 – 10 was measured by a surface zeta potential analyser. Figure 8B shows the zeta potential vs pH graph of the PSBMA/PEI/H-PAN membrane. It can be seen from Figure 8B that a control H-PAN membrane has a strong negative charge in the range of -88mV to -132 mV in the pH range from 3 to 10, which is favourable for the coating of selective surface charge coatings as described. In this case, the control H-PAN membrane used for comparison is a PAN membrane that is hydrolysed but not coated with any layers. The addition of PSBMA to a PEI/H-PAN membrane (i.e. PSBMA/PEI/H-PAN) in weight percentage of 0.05 wt% and 2 wt% slightly alters the surface charge to -60 mV and -40 mV at lower pH 3. However, at 4wt% PSBMA, the resultant PSBMA/PEI/H-PAN

membrane shows a drastic swift in surface charge between pH 3 - 5.8 (e.g. +20 mV) and showed negative surface charge (e.g. -50 mV) beyond pH 5.8 and above. Hence, 4wt% PSBMA is desirable, in particular for coating of a polyanionic layer in the next step.

(e) Layering of a polyanionic coating as the protective layer 108

In a last step 126, as illustrated in Figure 2, a polyanionic layer 108 is coated over the bilayer membrane 116. As an example, polystyrene sodium sulfonate (PSS) is selected as the material of the polyanionic layer 108. PSS is coated onto the PSBMA/PEI/H-PAN membrane through successive ionic layer adsorption and reaction (SILAR). Figure 4 illustrates the SILAR steps, which continues from step 216 described earlier. In a step 228, the washed and dried PSBMA coated PEI/H-PAN membrane (i.e. PSBMA/PEI/H-PAN membrane) 208 is dipped into a precursor solution 232, containing PSS. The negatively charged PSS is adsorbed onto the zwitterionic PSBMA surface of the PSBMA/PEI/H-PAN membrane 208. In a step 230, the excess PSS that is loosely adsorbed is removed by washing the PSS coated PSBMA/PEI/H-PAN membrane in deionised (DI) water 220. Thereafter, the washed PSS coated PSBMA/PEI/H-PAN membrane (PSS/PSBMA/PEI/H-PAN; also known herein as "PSS/PSBMA/PEI/H-PAN membrane") 226, is dried at room temperature.

After the triple-layer (PSS/PSBMA/PEI/H-PAN) membrane is completed. The membrane is then crosslinked with glutaraldehyde (GA) by immersing the membrane in GA aqueous solution at 30°C for 12 hrs. Finally, the crosslinked membrane is rinsed with deionized (DI) water and dried to produce the covalent crosslinked (PSS/PSBMA/PEI/H-PAN) membrane.

Figure 9 shows FTIR spectra of a control PAN membrane (non-hydrolysed and not coated) and several surface modified PAN membranes including H-PAN, PEI/H-PAN, PSBMA/PEI/H-PAN and PSS/PSBMA/PEI/H-PAN membranes. Figure 9 illustrates the confirmation results of the PSS/PSBMA/PEI/H-PAN membrane manufactured using the methods described earlier. The FTIR spectra of all the membranes shows a dominant peak at 2240 cm^{-1} which is attributed to the stretching vibration of the nitrile group ($\text{C}\equiv\text{N}$), and at 2930 cm^{-1} and 1470 cm^{-1} which are due to the respective stretching and bending vibrations of methylene group (CH_2). The spectrum of all the H-PAN membranes i.e. H-PEI, PEI/H-PAN, PSBMA/PEI/H-PAN and PSS/PSBMA/PEI/H-PAN membranes show the presence of the functional group of COO^- around the peak of 1562 cm^{-1} (strong asymmetrical stretching band) and 1402 cm^{-1} (weak symmetrical stretching band). In addition, there are appearances of peaks at 3402 cm^{-1} which corresponds to the hydroxyl group ($-\text{OH}$) and at $1699\text{--}1711\text{ cm}^{-1}$ which corresponds to the carbonyl group ($\text{C}=\text{O}$). The spectrum of all PEI coated H-PAN membranes i.e. PEI/H-PAN, PSBMA/PEI/H-PAN and PSS/PSBMA/PEI/H-PAN exhibits two additional absorption peaks at 1600 cm^{-1} which is the stretching and bending vibration of amine group (N-H), and 1122 cm^{-1} which is the stretching vibration of C-N group. Both N-H and C-N groups belong to the amine groups in PEI. Hence, the presence of these peaks in the FTIR spectra of the PEI coated H-PAN membranes indicate the successful coating of PEI onto the H-PAN membrane. The FTIR peaks in the spectrum of the PSS/PSBMA/PEI/H-PAN membrane confirm the successful coating of the PSS/PSBMA/PEI/H-PAN membrane due to the predominant peaks at 1187 cm^{-1} and 1176 cm^{-1} for $\text{O}=\text{S}=\text{O}$ group.

Table 1 below shows detailed surface atomic content of a hydrolysed PAN membrane (H-PAN) and different surface modified PAN membranes i.e. PEI/H-PAN membrane, PSS/H-PAN membrane, PSBMA/PEI/H-PAN membrane, and PSS/PSBMA/PEI/H-PAN membrane. The membranes were analysed using X-ray Photoelectron Spectroscopy (XPS). The degree of PEI modification in the hydrolysed PAN membranes was indicated by XPS through the N_{1s} to O_{1s} ratio (N_{1s}/O_{1s}). From Table 1, it is noted that there is increment in N_{1s}/O_{1s} between the H-PAN membrane before PEI modification i.e. 1.67 and the PEI/PAN membrane after PEI modification i.e. 2.26. This confirms the successful modification of the polycationic (PEI) coating on the H-PAN membrane. The PSS/PSBMA/PEI/H-PAN membrane exhibits additional S_{2p} peaks at 166 eV with the atomic percentage varying from 1% to 4.63%. The presence of the sulfonate group (S_{2p}) also confirms the successful deposition of PSBMA and PSS polymer onto the membrane surface.

Table 1: Surface atomic content of the different membrane types by XPS

Membrane Type	Atomic Content (%)			
	O1s	N1s	S2p	C1s
H-PAN	7.76	13.02	-	78.08
PEI/H-PAN	7.23	16.35	-	75.61
PSS/H-PAN	21.79	9.02	3.59	65.15
PSBMA/PEI/H-PAN	15.19	5.06	1.09	78.65
PSS/PSBMA/PEI/H-PAN	17.56	8.99	4.63	68.51

Capillary flow porometry (CFP) also known as gas-liquid porometry is used to measure pore size and pore size distribution of the manufactured membrane before and after the coating of the triple layer. Figures 14A and 14B show the pore size distributions of a control PAN membrane (non-hydrolysed and not coated with any layers) and a PSS/PSBMA/PEI/H-PAN membrane respectively. The pore size of a control PAN membrane (non-hydrolysed and not coated with any layers) is around 106.2 nm and the developed bipolar triple layer membrane (PSS/PSBMA/PEI/H-PAN) exhibits an average pore size of around 3.92 nm. The membrane pore size decreases significantly during the triple layer surface charge coating process. Hence, the selective surface charge layers (specifically, the PEI, PSBMA and PSS layers) effectively reduce the pore size of the membrane with respect to the number of coated layers.

C. Performance analysis of the Separation Membrane 100 in the form of a flat sheet membrane

(a) Metal ion adsorption study

A metal ion adsorption study was conducted to analyse the performance of the PSS/PSBMA/PEI/H-PAN membrane in the form of a flat sheet membrane.

Conventional composite membranes with surface modification (e.g. thio-functionalized, bis(2-pyridylmethyl) amino groups, diazoresin ethylenediaminetetraacetic acid (DR-EDTA) layer) and other selective adsorbents (e.g. MWCNT, graphene oxide, graphene oxide-chitosan aerogel, sulfonated multi-walled carbon nanotubes) were tested in the metal ion adsorption study. These conventional

composite membranes could absorb the metal ions to some degree. However, the adsorption capacity of these membranes is limited to the number of grafted functional groups in the polymer chain of the composite membrane.

PAN-based membranes have been applied in many applications, such as microfiltration, ultrafiltration, and desalination. However, none of them shows the promising results of the proposed bipolar membrane 100 of Figure 1 with triple layer configuration.

A specific example of the proposed bipolar triple layer membrane 100, which is the PSS/PSBMA/PEI/H-PAN membrane, was evaluated using Pb^{2+} metal ion at a fixed pH of 6 and a concentration of 300ppm. In addition, a control PAN membrane (non-hydrolysed and not coated with any layers), a H-PAN membrane, a PEI/H-PAN membrane and a PSBMA/PEI/H-PAN membrane were evaluated under the same conditions as that of the PSS/PSBMA/PEI/H-PAN membrane. Figure 10 is a graph of adsorption capacity Q_e (mg/g) vs Time (in hours), illustrating the metal ion adsorption performance of the evaluated membranes.

The PEI/H-PAN and PSBMA/PEI/H-PAN membranes displayed maximum adsorption capacities for Pb^{2+} metal ion at 180.1 mg/g and 119.07 mg/g respectively at a reaction time of about 4 hours. Such initial spikes in Q_e could be due to Pb^{2+} ions being attracted to the surface of the PEI/H-PAN and PSBMA/PEI/H-PAN membranes. However, the Pb^{2+} ions will then slowly be trapped in the membranes resulting in adsorption capacity of about 100 mg/g with respect to a time of 48 hours. However, the control PAN, H-PAN and PSS/PSBMA/PEI/H-PAN membranes showed average adsorption capacities of around 12.77mg/g, 29.28mg/g and 60 mg/g respectively after 4 hours reaction time and finally saturated after 8 hours with an average adsorption capacity of around 17 mg/g, 21mg/g and 60mg/g respectively. From these results, it is clear that the control PAN membrane cannot absorb metal ions effectively, thereby restricting its application in water treatment application. The adsorption capacity increases after implementing the triple layer selective surface charge coating over PAN membrane and this is mainly due to the presence of the amine group.

(b) Rejection study

Figure 11 illustrates rejection (%) performance of the bipolar separation membrane 100 of Figure 1 with triple layer configuration using cross-flow filtration with feed flow rate of about 250ml/min, pressure of 0.5 bar, 300ppm Cu^{2+} concentration, and different pH conditions such as acidic (pH 5), neutral (pH 7) and base (pH 9). Specifically, the PSS/PSBMA/PEI/H-PAN membrane tested is in the form of a flat sheet membrane.

From Figure 11, it is noted that the bipolar separation membrane 100 with triple layer configuration shows about 50% rejection for the divalent Cu^{2+} metal ion in acidic condition (pH 5). High rejection (~99%) was observed for Cu^{2+} at pH 7 and 9. It can be observed that the increase in pH results in higher rejection because at higher pH, the tendency of metal salts to precipitate is higher, thus the bigger solid particles can be easily filtered out via size exclusion method.

The bipolar separation membrane 100 with triple layer configuration was similarly tested with Cd^{2+} and Pb^{2+} metal ions at pH 5 (acidic condition)(not shown in Figure 11). It is noted that there is a significant rejection observed for Cd^{2+} at 33.0% despite the smaller molecular size as compared to the

divalent Pb^{2+} metal ion at 6.53%. This is due to the fact that both Cu^{2+} and Cd^{2+} metals prefer to form hydrates even in solution form, leading to bigger molecular size, thus becoming easier to be removed by the membrane.

D. Performance analysis of the Separation Membrane 100 in the form of a hollow fiber membrane

Figure 12A shows the result of a pure water flux study on a bilayer membrane (i.e. PSS/PEI/H-PAN membrane) and a triple layer membrane (i.e. PSS/PSBMA/PEI/H-PAN membrane) using a laboratory scale filtration setup. A control PAN membrane that is not hydrolysed and not coated with any layers was included in the study for comparison purposes.

From Figure 12A, the water flux of the control PAN membrane was around $115 \text{ L.m}^{-2}.\text{h}^{-1}$. In comparison, the water flux of the bilayer (PSS/PEI/H-PAN) membrane was around $77 \text{ L.m}^{-2}.\text{h}^{-1}$ and the water flux of the bipolar triple layer (PSS/PSBMA/PEI/H-PAN) membrane was around $61 \text{ L.m}^{-2}.\text{h}^{-1}$. The difference in water flux in the modified membranes evidently shows the change in membrane pore size at the nanoscale with the additional surface charge coatings such as the PEI, PSBMA and PSS layers.

The rejection (%) efficiency of the bilayer membrane (i.e. PSS/PEI/H-PAN) and the bipolar triple layer membrane (i.e. PSS/PSBMA/PEI/H-PAN) were tested using different heavy metal ions such as Cu^{2+} , Cd^{2+} and Pb^{2+} at a fixed concentration of 300ppm, a working pressure of 2 bars, a working temperature of 28°C and pH at 5.2. As shown in Figures 12B, 12C and 12D, the average percentage rejection of the bilayer (PSS/PEI/H-PAN) membrane was around 69.8%, 40%, 34.5% and the percentage rejection of the bipolar triple layer membrane was around 95%, 70.6%, 74% for Cu^{2+} , Cd^{2+} and Pb^{2+} metal ions respectively. Evidently, the bipolar triple layer (PSS/PSBMA/PEI/H-PAN) membrane shows a superior rejection efficiency compared to the bilayer (i.e. PSS/PEI/H-PAN) membrane.

The PSS/PSBMA/PEI/H-PAN membrane shows high metal ion rejection towards heavy metal ions mainly due to the selective surface charge layers coated on the H-PAN membrane using the polycationic (PEI), polyanionic (PSS) and zwitterionic (PSBMA) polymers. The zwitterionic polymer bearing equivalent amount of cationic amine and anionic sulfonate groups confers high charge capacity and nearly neutral charges to the membrane and thus, the bipolar triple layer membrane can easily either adsorb or repel divalent metal ions. The successive ionic layer adsorption and reaction (SILAR) applied in the manufacture of the bipolar triple layer membrane can significantly alter the pore size and enhance the membrane surface charge (polyanionic/neutral charge/polycationic) for effective removal of heavy metal ion in wastewater.

Generally, membrane fouling causes a significant decrease in water flux which leads to the increase of production costs, energy consumption and cleaning frequencies. An antifouling study was conducted using a control PAN membrane (not hydrolysed and not coated with any layers), a PSS/PEI/H-PAN membrane and a PSS/PSBMA/PEI/H-PAN membrane for two cycles of BSA solution filtration in the time period of 3 hrs 30mins. Figure 13 shows the result of the antifouling study. The pure water flux of the PSS/PSBMA/PEI/H-PAN membrane remained the highest at greater than 80%

after two cycles of filtration, compared to that of the control PAN membrane and the PSS/PEI/H-PAN membrane. The high flux recovery of the PSS/PSBMA/PEI/H-PAN membranes was mainly due to the presence of zwitterionic PSBMA polymer layer which exhibits good anti-fouling functionality.

E. Portable Water Container with the Separation Membrane 100

A portable liquid container comprising a filter that comprises the bipolar separation membrane 100 of Figure 1 with triple layer configuration is proposed. The liquid contained in the portable liquid container can be water or liquid containing water. Being portable, the portable liquid container can be conveniently moved between locations without much effort. The portable liquid container can be in a form of a portable drinking container.

An example of such portable drinking container can comprise a filter comprising the bipolar triple layer membrane 100 for filtering liquid to be treated, and a permeate liquid collector for holding treated liquid. A pump assembly may be supplied separately or integrated with the portable drinking container for applying pressure to drive liquid to be treated through the bipolar triple layer membrane 100. The pump assembly may be of a low-pressure type and may be hand operated. Water, or liquid containing water, can be pumped through the bipolar triple layer membrane 100 using the pump assembly and the filtered water or liquid can be collected in the permeate liquid collector.

Figures 15A to 15C, 16A to 16C and 17A to 17D show schematic drawings of cross-sectional views of three examples of proposed portable drinking bottles 300, 400 and 500 respectively.

Figure 15A shows a bottle 300 with a bottom portion 302 and a top portion 304 assembled to form the bottle 300. The top portion 304 comprises a filter 301 for filtering untreated liquid. In the present example, the bottle 300 is substantially cylindrical in shape.

Figure 15B shows the bottom portion 302 of the bottle 300. The bottom portion 302 can be detachably attached to the top portion 304 of the bottle 300. The bottom portion 302 can be used as a permeate liquid collector to collect permeate water that passes through the filter 301. The bottom portion 302 is substantially cylindrical and comprises a body 306 with a particular volume for holding liquid, a neck 308 and a first finish 310 (or rim) disposed at a top end. The first finish 310 provides a first wide opening 311 having substantially the diameter of the bottom portion 302. An outer circumference of the first finish 310 comprises a threaded surface 312 configured to mesh with the top portion 304 of the bottle 300.

Figure 15C shows the top portion 304 of the bottle 300, which comprises the filter 301. The top portion 304 also comprises an upper half and a lower half that are each shaped like a cylinder. However, the diameter of the upper half is smaller than the diameter of the lower half.

The upper half of the top portion 304 is made up of a second finish 330 (or mouthpiece or liquid outlet) with a diameter smaller than that of the first finish 310. The second finish 330 extends from a shoulder 333 of the top portion 304. An outer circumference of the second finish 330 comprises a threaded surface 331 for meshing with a corresponding threaded surface of the bottle cap 332. Such threaded surfaces 331 allow the bottle cap 332 to be screwed onto the second finish 330.

In the lower half of the top portion 304, there is a recess 313 for receiving the first finish 310 of the bottom portion 302. An inner wall of the recess 313 is configured with a corresponding threaded surface 314 to mesh with the threaded surface 312 of the first finish 310 of the bottom portion 302. The threaded surfaces 312 and 314 allow the lower half of the top portion 304 to be screwed to the first finish 310 of the bottom portion 302.

The lower half of the top portion 304 further comprises the filter 301. The filter 301 comprises a membrane module 326 that comprises a circular membrane housing 328 for holding the separation membrane 100 of Figure 1 in the form of a flat sheet membrane. The separation membrane 100 is also circular in shape and appears like a circular disc. The membrane housing 328 holds the circumference edge of the separation membrane 100. The circumference edge of the separation membrane 100 is slotted in an inner radial groove of the membrane housing 328 and the membrane housing 328 holds the separation membrane 100 between radial extensions of the membrane housing 328 that form the inner radial groove. An outer circumference of the membrane housing 328 can be detachably fitted to, attached to (e.g. by adhesive), or integrated with an inner surface of the top portion 304 at a position below the shoulder 333 of the top portion 304. In the case that the membrane housing 328 is detachably fitted to the top portion 304, the membrane housing 328 is removable for cleaning and/or changing the separation membrane 100 and/or the membrane housing 328. The membrane housing 328 can be made of flexible material that is rubber and/or plastic based. Optionally, the membrane housing 328 can be made with diameter slightly larger than the diameter of the recess 313. With slightly larger diameter, the membrane housing 328 can stay in the position at which the membrane housing 328 is fitted to the top portion 304 due to friction and expansion pressure of the membrane housing 328 acting on the inner surfaces of the top portion 304. In the present example, the inner surface of the top portion 304 below the shoulder 333 is formed with a step to receive the membrane housing 328.

The filter 301 further comprises an adsorbent 320 for enhanced filtration. The adsorbent 320 may be commercially available activated carbon or clays for adsorbing, for example, natural organic compounds, taste and odour compounds, and synthetic organic chemicals. The adsorbent 320 is disposed below the membrane module 326, specifically between the membrane module 326 and the recess 313. In another example, the membrane module 326 may be disposed between the adsorbent 320 and the recess 313. The adsorbent 320 is held by two ring shaped extensions 322 and 324 disposed to extend from an inner wall of the top portion 304. The ring shaped extensions 322 and 324 can be attached to (e.g. by adhesive), integrated with the top portion 304 or are two separate ring gaskets that are put in place in the following manner. In the case that the membrane housing 328 is the type that is removable and detachably fitted to the inner surface of the top portion 304 below the shoulder, the membrane housing 328 is first fitted in place, followed by the first ring gasket 324, followed by the adsorbent 320 and then the second ring gasket 322. In the case that the membrane housing 328 is attached to or integrated with the top portion 304, the first ring gasket 324 will be first fitted to contact the membrane housing 328, followed by the adsorbent 320 and followed by the second ring gasket 322. Similarly, the ring gaskets 322 and 324 can be made of flexible material that is rubber and/or plastic based. Each of the ring gaskets 322 and 324 can also be made with diameter

slightly larger than the diameter of the inner circumference of the lower half of the top portion 304. With slightly larger diameter, each ring gasket 322 or 324 can stay in the position at which the ring gasket 322 or 324 is fitted to the top portion 304 due to friction and expansion pressure of the ring gasket 322 or 324 acting on the inner surfaces of the top portion 304.

In one use scenario of the bottle 300, the second finish 330 or the recess 313 is attached to the pump assembly to pump liquid through the filter 301 and the filtered liquid will flow out of the other end of the top portion 304 that is not attached to the pump assembly. The filtered liquid can be collected by the bottom portion 302 of the bottle 300. The bottle 300 may be fully assembled with the top portion 304 attached to the bottom portion 302 and in this case, it will be the second finish 330 being attached to the pump assembly and the bottom portion 302 will collect the filtered liquid. In this case, the user may drink the treated liquid contained in the bottom portion 302 of the bottle 300 by unscrewing the top portion 304 and then drink straight from the wide opening 311 provided by the first finish 310. Alternatively, the user may drink treated liquid through the second finish 330 when the bottle 300 is fully assembled by squeezing the bottle 300 to force the liquid to go through the filter 301 and out through the second finish 330. In this case, the bottle 300 has to be made of flexible and resilient material, which can be rubber, plastic, composite material, and the like. In another example, a user may filter untreated liquid twice by first using the pump assembly and collect the first treated liquid filtered by the filter 301 in the bottom portion 302. Thereafter, the user squeezes the first treated liquid through the filter 301 to filter a second time and the user then drinks the second time filtered liquid.

Figure 16A shows a bottle 400 fully assembled with a bottle cap 404. The bottle cap 404 comprises a filter 401 for filtering untreated liquid. The bottle cap 404 is detachably attached to a liquid outlet 410 of the bottle 400.

Figure 16B shows a configuration 402 of the bottle 400 without the bottle cap 404. In the present example, the bottle 400 is substantially cylindrical in shape. The configuration 402 further comprises a body 406 for containing a particular volume of liquid, a neck 408 and a finish 410 (i.e. the liquid outlet) disposed at a top end. The finish 410 has a diameter smaller than the diameter of the body 406. An outer circumference of the finish 410 comprises a threaded surface 412 configured to mesh with the bottle cap 404.

Figure 16C shows the bottle cap 404 of the bottle 400, which comprises the filter 401. The bottle cap 404 comprises a first portion and a second portion. The second portion is to be fitted into the first portion.

The first portion of the bottle cap 404 comprises a recess 413 for receiving the second portion. Inner walls of the recess comprise a threaded surface 414 for meshing with the corresponding threaded surface 412 of the finish 410. Such threaded surfaces 412 and 414 allow the bottle cap 404 to be screwed onto the finish 410. On an end that is opposite to the recess 413 of the first portion of the bottle cap 404, there is provided a shoulder 433. A mouthpiece 430 for drinking extends from the shoulder 433. The mouthpiece 430 resembles a conical shape with an opening 411 at the apex location of the conical shape. The mouthpiece 430 can be enclosed by a cap 432, which covers the mouthpiece 430 to prevent the mouthpiece 430 from being exposed when it is not in use.

The second portion of the bottle cap 404 comprises the filter 401. The filter 401 comprises a membrane module 427 that comprises a circular membrane housing 420 for holding the separation membrane 100 of Figure 1 in a form of a flat sheet membrane. The separation membrane 100 is also circular in shape and appears like a circular disc. The membrane housing 420 holds the circumference edge of the separation membrane 100. The circumference edge of the separation membrane 100 is slotted in an inner radial groove of the membrane housing 420 and the membrane housing 420 holds the separation membrane 100 between radial extensions of the membrane housing 420 that form the inner radial groove. An outer circumference of the membrane housing 420 can be detachably fitted to, attached to (e.g. by adhesive), or integrated with an inner surface of the bottle cap 404 at a position below the shoulder 433. In the case that the membrane housing 420 is detachably fitted to the bottle cap 404, the membrane housing 420 is removable for cleaning and/or changing the separation membrane 100 and/or the membrane housing 420. The membrane housing 420 can be made of flexible material that is rubber and/or plastic based. Optionally, the membrane housing 420 can be made with diameter slightly larger than the diameter of the inner circumference of the recess 413. With slightly larger diameter, the membrane housing 420 can stay in the position at which the membrane housing 420 is fitted to the bottle cap 404 due to friction and expansion pressure of the membrane housing 420 acting on the inner surfaces of the bottle cap 404. In the present example, the inner surface of the bottle cap 404 below the shoulder 433 is formed with a step to receive the membrane housing 420.

The filter 401 further comprises an adsorbent 426 for enhanced filtration. The adsorbent 426 may be commercially available activated carbon or clays for adsorbing, for example, natural organic compounds, taste and odour compounds, and synthetic organic chemicals. The adsorbent 426 is to be disposed below the membrane module 427. In the case that the membrane module 427 is removable from the bottle cap 404, the adsorbent 426 is to be inserted after the membrane module 427 is first inserted to the location below the shoulder 433. The adsorbent 426 has a tubular shape with a hollow core. The hollow core is comprised of an ultrafilter 428. Hence, the adsorbent 426 forms an outer core and the ultrafilter 428 forms an inner core. Optionally, the ultrafilter 428 comprises the separation membrane 100 made into a form of a hollow fiber membrane that is cylindrical in shape. The adsorbent 426 comprises a flanged end 415, which is for contacting the membrane module 427 when the adsorbent 426 is fitted into the bottle cap 404. Optionally, the membrane module 427 can be attached to (e.g. by adhesive) or integrated with the flanged end 415 of the adsorbent 426.

In one use scenario of the bottle cap 400, the mouthpiece 430 or the recess 413 is attached to the pump assembly to pump liquid through the filter 401 and the filtered liquid will flow out of the other end of the bottle cap 404 that is not attached to the pump assembly. The filtered liquid can be collected by the body 406 of the bottle 400 and in this case, the body 406 is used as a permeate liquid collector. The bottle 400 may be fully assembled with the bottle cap 404 attached to the finish 410 and in this case, it will be the mouthpiece 430 being attached to the pump assembly and the body 406 will collect the filtered liquid. In this case, the user may drink the treated liquid contained in the body 406 of the bottle 400 by unscrewing the bottle cap 404 and then drink straight from the opening of the finish 410. Alternatively, the user may drink treated liquid through the mouthpiece 430 when the bottle

400 is fully assembled by squeezing the bottle 400 to force the liquid to go through the filter 401 and out through the mouthpiece 430. In this case, the bottle 400 has to be made of flexible and resilient material, which can be rubber, plastic, composite material, and the like. In another example, a user may double filter untreated liquid by first using the pump assembly and collect the first treated liquid filtered by the filter 401 in the body 406. Thereafter, the user squeezes the first treated liquid through the filter 401 to filter a second time and the user then drinks the second time filtered liquid.

Figure 17A shows a fully assembled bottle 500 comprising a filter module 502, a permeate water collector 504, pump assembly 508 and a bottle cap 506. Both the filter module 502 and permeate water collector 504 are substantially cylindrical in shape. The filter module is of a shorter radius and height compared to the permeate water collector 504, such that the filter module 502 may fit inside the permeate water collector 504. The filter module 502 further comprises an adsorbent 514, the separation membrane 100 described herein in flat sheet form 510 as well as another one of the separation membrane 100 described herein in hollow fibre form 512. The adsorbent 514 may be commercially available activated carbon or clays for adsorbing, for example, natural organic compounds, taste and odour compounds, and synthetic organic chemicals. The adsorbent 514 may be disposed between the separation membrane in flat sheet form 510 and the separation membrane in tubular fibre form 512, as shown in Figure 17A. The permeate water collector 504 may further comprise a mouthpiece 528, which is covered by the bottle cap 506.

Figure 17B shows the components of the bottle 500 of Figure 17A to be assembled together. Firstly, the pump assembly 508 has a first and second threaded portion 518 and 522 on an inside surface configured to couple with the filter module 502 and permeate water collector 504 respectively. More particularly, the first threaded portion 518 is of a smaller radius configured to couple with the filter module 502 and the second threaded portion 522 is of a larger radius configured to couple with the larger permeate water collector 504. Accordingly, the filter module 502 has a corresponding threaded portion 516 on an outside surface that meshes with the first threaded portion 518 of the pump assembly 508 and the permeate water collector 504 has a corresponding threaded portion 520 on an outside surface that meshes with the second threaded portion 522 of the pump assembly 508. Furthermore, the sizes of the filter module 502 and the permeate water collector 504 allow them to be coupled to the pump assembly 508 together.

With reference to Fig. 17B and 17C, the pump assembly 508 comprises a handle 536 connected to a first end of a shaft 538 movable in a tubular body 540 extending into a fluid holding space 539 in the filter module 502. The pump assembly 508 comprises an intermediate portion 537 with a first and a second through-hole 535 and 541, wherein the shaft 538 is slidable along the first through-hole 535 and air is allowed to enter freely through the second through-hole 541. A piston 542 is connected to a second end of the shaft 538 that is opposite to the handle 536. There is provided one-way air valves 544 and 546 that allow air through in one direction and not the other way round. Air valve 544 is located at the piston 542 and air valve 546 is located at a terminating end of the tubular body 540 inside the fluid holding space 539. Air valve 544 is configured to draw air into the tubular body 540 when the handle 536 is operated to slide the piston 542 via the shaft 538 from a piston position located closer to the air valve 546 at the terminating end of the tubular body 540 to a

position closer to the intermediate portion 537. Air valve 546 is configured to expel air from the tubular body 540 into the fluid holding space 539 when the piston 542 is slid from a piston position closer to the intermediate portion 537 to a piston position closer to the air valve 546 at the terminating end of the tubular body 540. When the pump assembly 508 is attached to the filter module 502 and fluid resides in the fluid holding space 539, the air expelled into the fluid holding space 539 will push the fluid through the separation membrane in the form of hollow fibre 512, the adsorbent 514 and the separation membrane in the form of flat sheet 510, thereby filtering the fluid. The handle 536 has to be operated to slide the piston 542 from the piston position closer to the air valve 546 at the terminating end of the tubular body to the piston position closer to the intermediate portion 537 to draw more air into the tubular body 540 before the air can be expelled from the tubular body 540 into the fluid holding space 539 via the air valve 546 again. In the present example, the pump assembly 508 is part of the bottle 500 and is detachably connectable to the bottle 500. The features of the pump assembly 508 described in the present example is just one way to implement a pump assembly. It should be appreciated that other suitable pump assembly designs may also be implemented. The handle 536 is also semi-rotatable in both directions (clockwise and anti-clockwise direction) to lock the handle 536 to the intermediate portion 537 and unlock the handle 536 from the intermediate portion 537 respectively.

Disposed toward the opposite end of the threaded portion 520 of the permeate water collector 502 and nearer to the mouthpiece 528 is a second threaded portion 524 that is configured to couple with the bottle cap 506. Accordingly, the bottle cap 506 has a corresponding thread portion 526 to mesh with the second threaded portion 524 of the permeate water collector 504. When fitted together, the mouthpiece 528 is entirely covered by the bottle cap 506.

Figure 17C shows a first use scenario of the bottle 500 of Figure 17A. Untreated water 530 is first filled up in the fluid holding space 539 of the filter module 502. The filter module 502 and permeate water collector 504 are then fitted to the pump assembly 508 by engaging the threaded portions 516 and 520 of the filter module 502 and permeate water collector 504 with the corresponding threaded portions 518 and 522 of the pump assembly 508. When fitted together, the pump assembly 508 is used to push the untreated water 530 through the separation membrane in the form of hollow fibre 512, the adsorbent 514 and the separation membrane in the form of flat sheet 510 thereby filtering the untreated water 530. Once filtered, the treated water 534 is collected in the permeate water collector 504. A user can drink from the bottle 500 by sucking through the mouthpiece 528.

Figure 17D shows a second use scenario of the bottle 500 of Figure 17A. Untreated water 530 is first filled up in the fluid holding space 539 the filter module 502. The filter module 502 is then fitted to the pump assembly 508 by engaging the threaded portion 516 to the corresponding threaded portion 518 of the pump assembly. When fitted together, the pump assembly 508 is used to push the untreated water 530 through the separation membrane in the form of hollow fibre 512, the adsorbent 514 and the separation membrane in the form of flat sheet 510 thereby filtering the untreated water 530. Unlike the first use scenario according to Figure 17C, the treated water 534 may be directly collected in the bottle cap 506 for instant consumption by a user.

Flux and rejection functionality of the portable liquid container in the form of a portable drinking bottle was tested at a laboratory using different divalent and trivalent heavy metal ions. Heavy metal ion water samples with about 20ppm for Arsenic (As), and about 100ppm for Copper (Cu^{2+}), Chromium (Cr^{3+}), Cadmium (Cd^{2+}) and lead (Pb^{2+}) were evaluated. The tested portable drinking bottle with the PSS/PSBMA/PEI/H-PAN membrane module exhibits heavy metal ions rejection of ~ 97.04%, 96.50%, 92.52%, 96.73% and 98.06% rejection for Cu^{2+} , Cr^{3+} , Cd^{2+} , Pb^{2+} and As heavy metal ions at very low operating pressure (0.5 bar).

Additionally, tables 2 and 3 below show a comparison of the rejection percentage of the heavy metal ions between a bilayer (PSS/PEI/H-PAN) filter and a triple layer (PSS/PSBMA/PEI/H-PAN) filter when both are applied to portable drinking bottle. It is noted that there is an overall improvement in metal ion rejection performance in the triple layer (PSS/PSBMA/PEI/H-PAN) filter compared to the bilayer (PSS/PEI/H-PAN) filter.

Table 2: Rejection percentage of a bilayer (PSS/PEI/H-PAN) filter (Polycationic/Polyanionic)

Heavy metal ions	Before filtration (ppm)	After filtration (ppm)	Rejection percentage (%)
Arsenic (As)	19.55	1.77	90.95
Cadmium (Cd)	100.8	31.96	68.29
Chromium (Cr)	101.7	29.45	71.04
Copper (Cu)	101.6	28.93	71.53
Lead (Pb)	100.1	30.19	69.84

Table 3: Rejection percentage of a triple layer (PSS/PSBMAPEI/H-PAN) filter (Polycationic/zwiterion/polyanionic)

Heavy metal ions	Before filtration (ppm)	After filtration (ppm)	Rejection percentage (%)
Arsenic (As)	21.22	0.41	98.07
Cadmium (Cd)	96.61	7.22	92.53
Chromium (Cr)	99.27	3.47	96.50
Copper (Cu)	106.4	3.14	97.05
Lead (Pb)	98.97	3.23	96.74

Based on the above findings presented in tables 2 and 3, it is concluded that the proposed bipolar triple layer membrane 100 of Figure 1 can be used as an economical water filter that can be employed in a portable water container. In the form of a portable water bottle, the bottle can be used by outdoor travellers, in disaster recovery/poor sanitation areas, and in households of third world countries. The bipolar triple layer membrane 100 itself can be used in industrial water filtration systems.

In view of the foregoing description, the proposed bipolar membrane 100 of Figure 1 with triple layer configuration is able to remove the majority of charged pollutant (i.e. cation and anion) at each individual layer i.e. (1) Base layer: polycationic (+), (2) Selective layer: polyzwitterionic (z) and (3) protective layer: polyanionic (-). The bipolar membrane layers, polyanionic and polycationic, can effectively reject the charged pollutants due to electrostatic repulsion (Donnan exclusion) and due to nanopore size effects (size exclusion). In addition, the selective layer i.e. zwitterionic polymers in the triple layer configuration will provide antifouling capabilities.

Conventionally, interfacial polymerization is used to manufacture thin-film composite (TFC) membrane with selective surface charge layer. However, the scaling up of the selective surface charge layers for larger surface area membrane remains a challenge due to non-uniform, low coating density, and environmental issues faced during the manufacture process.

In an example of the present disclosure described above, the proposed bipolar membrane 100 with triple layer configuration is developed via an easily scalable room temperature dip coating (layer by layer) at optimum conditions i.e. optimum number of dipping cycles/polymer concentration and dipping time.

The bipolar membrane 100 with triple layer configuration can be integrated into a portable water purification system, for example, a portable water drinking bottle. Such portable water purification system exhibits an enhance rejection for heavy metal ions at very low operation pressure (less than 1.5bar) and pH between 6-7.

The proposed bipolar triple layer membrane 100 offers several advantages over other conventional membranes such as low energy consumption in the manufacturing process, and efficient metal ion separation at low feed concentration. The proposed bipolar membrane 100 with triple layer configuration can act as an economical water filter which can be employed in a portable water bottle suitable for use by outdoor travellers, in disaster recovery/poor sanitation areas, in households in third world countries. Of course, the proposed bipolar membrane 100 can also be used in industrial water filtration systems.

Examples of the present disclosure may have the following features.

There is provided a separation membrane (e.g.100) for water treatment, wherein the bipolar separation membrane comprises a support membrane (e.g. 102) over which the following layers are layered: a first polycationic layer (e.g. 104); a second polyzwitterionic layer (e.g. 106); and a third polyanionic layer (e.g. 108).

The support membrane (e.g. 102) may comprise an organic polymer containing a nitrile group.

The support membrane (e.g. 102) may contain inorganic composite additives selected from a group comprising titanium (IV) dioxide, zinc oxide and carbon nanofiber (CNF).

The organic polymer containing a nitrile group may be polyacrylonitrile (PAN).

The first cationic layer (e.g. 104) may comprise one of the following: polyethylenimine (PEI) or chitosan.

The second polyzwitterionic layer (e.g. 106) may comprise polyether(sulfobetaine methacrylate) (PSBMA).

The third polyanionic layer (e.g. 108) may comprise polystyrene sodium sulfonate (PSS).

The support membrane (e.g. 102) may comprise polyacrylonitrile (PAN), the first polycationic layer (e.g. 104) may comprise polyethylenimine (PEI), the second polyzwitterionic layer (e.g. 106) may comprise polyether(sulfobetaine methacrylate) (PSBMA); and the third polyanionic layer (e.g. 108) may comprise polystyrene sodium sulfonate (PSS).

The first polycationic layer (e.g. 104) may be layered over the support membrane (e.g. 102), the second polyzwitterionic layer (e.g. 106) may be layered over the first polycationic layer (e.g. 104); and the third polyanionic layer (e.g. 108) may be layered over the second polyzwitterionic layer (e.g. 106).

There is also provided a method of manufacturing the separation membrane above, the method comprising (a) dissolving a polymer in a solvent, wherein the solvent comprises dimethylformamide (DMF); (b) forming the support membrane (e.g. 102) from the polymer solution by electrospinning technique or dry-wet spinning technique; (c) hydrolyzing the support membrane (e.g. 102); (d) crosslinking the support membrane (e.g. 102) with additional selective surface charged polymers to produce the triple layer configuration, wherein the triple layer configuration comprises: the first polycationic layer (e.g. 104); the second polyzwitterionic layer (e.g. 106); and the third polyanionic layer (e.g. 108); and (e) cross-linking with glutaraldehyde (GA) to produce the separation membrane.

The first polycationic layer (e.g. 104), second polyzwitterionic layer (e.g. 106) and third polyanionic layer (e.g. 108) may be coated over the support membrane (e.g. 102) using successive ionic layer adsorption and reaction (SILAR).

There is also provided a portable liquid container comprising a filter, wherein the filter comprises the separation membrane (e.g. 100).

The portable liquid container (e.g. 500) or a portion of the portable liquid container may be attachable to a pump assembly (e.g. 537) to pump liquid through the filter, wherein the portable liquid container (e.g. 500) or portion of the portable liquid container comprises the filter.

The pump assembly (e.g. 537) may be part of the portable liquid container (e.g. 500) and may be detachably connectable to the portable liquid container (e.g. 500).

The filter may be detachably connectable to the portable liquid container (e.g. 500).

The portable liquid container may be a portable drinking bottle.

The portable drinking bottle (e.g. 300) may comprise: (a) a top portion (e.g. 304) comprising the filter (e.g. 301); and (b) a bottom portion (e.g. 302) detachably attached to the top portion (e.g. 304), the top portion (e.g. 304) comprises a liquid outlet on which a bottle cap (e.g. 322) can be disposed.

The portable drinking bottle (e.g. 400) may comprise a bottle cap (e.g. 404) comprising the filter (e.g. 401), wherein the bottle cap (e.g. 404) is detachably attached to a liquid outlet of the portable drinking bottle (e.g. 400).

The bottle cap may comprise a mouthpiece (e.g. 430) for drinking.

In the specification and claims, unless the context clearly indicates otherwise, the term "comprising" has the non-exclusive meaning of the word, in the sense of "including at least" rather than the exclusive meaning in the sense of "consisting only of". The same applies with corresponding grammatical changes to other forms of the word such as "comprise", "comprises" and so on.

While the invention has been described in the present disclosure in connection with a number of examples and implementations, the invention is not so limited but covers various obvious modifications and equivalent arrangements, which fall within the purview of the appended claims. Although features of the invention are expressed in certain combinations among the claims, it is contemplated that these features can be arranged in any combination and order.