(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 December 2014 (04.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/194228 A1

(51) International Patent Classification:
B01D 63/02 (2006.01)

(21) International Application Number:
PCT/US2014/040289

(22) International Filing Date:
30 May 2014 (30.05.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/829,838 31 May 2013 (31.05.2013) US

(71) Applicant: THE JOHNS HOPKINS UNIVERSITY [US/US]; 3400 N. Charles Street, Baltimore, MD 21218 (US).

(72) Inventors: SCHWAB, Kellogg, J.; 503 Adelaide Lane, Bel Air, MD 21015 (US). **HUANG, Haiou**; 16 Nightingale Way, Apt. A4, Lutherville, MD 21093 (US). **TYCHENE, Benoit**; 1 Rue Marcel Dore, Batiment 16, F-86022 Poitiers Cedex (FR). **FAIRBROTHER, David, Howard**; 3410 1/2 University Place, Baltimore, MD 21218 (US). **JACANGELO, Joseph, G.**; 40814 Stoneburner Mill Lane, Lovettsville, MD 20180 (US). **AJMANI, Gaurav**; 108 W. 39th Street, Apt. 6, Baltimore, MD 21210 (US). **LAHR, Miranda**; 2726 Maryland Avenue, Apt. 3, Baltimore, MD 21218 (US).

(74) Agent: CHILDERS, Jeffrey, W.; Ward and Smith, P.A., 1001 College Court, P.O. Box 867, New Bern, NC 28563 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

[Continued on next page]

(54) Title: APPLICATION OF CARBON NANOTUBES OR CARBON PARTICLES ONTO HOLLOW FIBER POLYMERIC MATERIALS

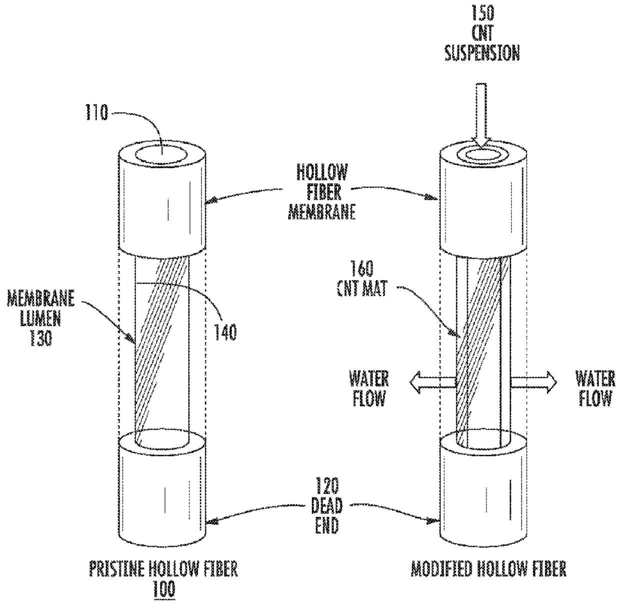

FIG. 1

(57) Abstract: Methods for generating carbon mats on the inner surface of hollow fiber membranes are disclosed, along with such modified fiber membranes, and methods of use thereof. A method comprises: providing a plurality of carbon nanotubes and/or carbon particles suspended in a solution to form a suspension; providing one or more polymeric hollow fiber membranes, wherein the one or more polymeric hollow fiber membranes have at least one open end in fluid communication with a lumen, and wherein the lumen defines an inner surface of the one or more polymeric hollow fiber membranes; dispensing the suspension in the at least one open end of the one or more polymeric hollow fiber membranes; and filtering the suspension of carbon nanotubes and/or carbon particles through the one or more polymeric hollow fiber membranes.

WO 2014/194228 A1

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

APPLICATION OF CARBON NANOTUBES OR CARBON PARTICLES ONTO HOLLOW FIBER POLYMERIC MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 61/829,838, filed May 31, 2013, the content of which is herein incorporated by reference in its entirety.

BACKGROUND

In the past decade, the unique physicochemical properties of nanomaterials, such as nanosilver, nano-scale metal oxides, and carbon nanotubes (CNTs), have allowed for significant breakthroughs to be realized in numerous fields, including commercial products, analytical tools, water purification, and medicine. J.M. Schnorr, T.M. Swager, Chem. Mater. (2010); M. Paradise, T. Goswami, Materials and Design (2007); S. R. Corrie, et al., J. Mater. Chem. (2008); N. Savage, M.S. Diallo, J. Nanopart. Res. (2005); and M.R. Wiesner. Water Sci. Technol. (2006). Among the various types of nanomaterials, CNTs are particularly well suited to positively impact water treatment as transformative components in the design of new nano-enabled environmental technologies based on separation processes (adsorption, filtration, and the like). X. Ren, et al., Chem. Eng. J. (2011); and A.V. Herrera-Herrera et al., Anal. Chim. Acta (2012).

In part, this interest in CNTs is driven by their extremely high surface area-to-volume ratios, which makes them attractive candidates as a new class of carbon-based sorbents for chemical and microbial removal from water. B. Karn, et al., Environ. Health Perspect. (2009); T.C. Zhang, et al., Nanotechnologies for water environment applications. American Society of Civil Engineers (2009); and N. Savage, M.S. Diallo. J. Nanopart. Res. (2005).

CNT surfaces also can be selectively functionalized to enhance sorption properties by introducing specific functional groups. C. Lu, H. Chiu, Chem. Eng. Sci. (2006); Y.-H. Li, et al., Carbon (2003); C. Chen, X. Wang, Ind. Eng. Chem. Res. (2006); H.H. Cho, et al., Environ. Sci. and Technol. (2008); and H.H. Cho, et al., Langmuir (2010). Thus, CNTs are effective at removing hydrophobic organic chemicals, H. Li, et al., Chem. Commun. (2010); J. Heo, et al., Water Sci. Technol. (2011); and C.D. Vecitis, et al., J. Phys. Chem. C (2011), heavy metals, T.

Mohammadi, M.A. Tofighy, J. Hazard. Mater. (2011); O. Moradi, Chem. Biochem. Eng. Q. (2011); D.S. Su, et al., New Carbon Mater. (2011); O. Moradi, et al., Carbon Nanostruct. (2010); and X.K. Wang, et al., J. Hazard. Mater. (2009), natural organic matter, J. Heo, et al., Water Sci.Technol. (2011), as well as viruses and bacteria. A.S. Brady-Estévez, et al., Water Res. (2010); S.T. Mostafavi, et al., Desalination (2009); and S. Kang, et al., Environ. Sci. Technol. (2009).

The high surface area and conductivity also enables CNT mats to function as three-dimensional porous electrodes. This characteristic has opened up the possibility of using redox reactions to destroy contaminants when they adsorb onto CNT mats, augmenting sorption as a means for contaminant removal. C.D. Vecitis, et al., Environ. Sci. Technol. (2011); C.D. Vecitis, et al., J. Phys. Chem. C (2001); A. Tiraferri, et al., ACS Appl. Mater. Interfaces (2011); M.S. Rahaman, et al, Environ. Sci.Technol. (2012); H. Liu, C.D. Vecitis, J. Phys. Chem. C (2012); G.D. Gao, C.D. Vecitis, ACS Appl. Mater. Interfaces (2012); and G. Gao, C.D. Vecitis, Environ. Sci. Technol. (2011).

For example, concomitant electrolysis during filtration through CNT mats was found to remove *E. coli* bacteria and MS2 viruses by more than 6-$\log_{10}$. C.D. Vecitis, et al., Environ. Sci. Technol. (2011). In addition to contaminant removal, previous studies have shown that microporous CNT mats, when attached to flat sheet membranes enhance fouling resistance, tripling the time for the transmembrane pressure (TMP) to increase with minimal reduction in the membrane's clean water permeability. G.S. Ajmani, et al., Water Res, (2012). This enhanced resistance to fouling has been ascribed to the ability of the CNT mat to trap species responsible for fouling. X. Yang, et al., Carbon. (2013).

The potential for CNTs to enhance a membrane’s fouling resistance is further aided by their chemical stability towards harsh chemicals, such as sodium hypochlorite, used to control organic fouling and prevent biofilm formation on membrane surfaces during water purification. J.S. Baker, L.Y. Dudley, Desalination (1998); and A. Subramani, E.M.V. Hoek, Desalination (2010). Membranes modified by CNT mats clearly hold significant promise for improving the energy efficiency and sustainability of next-generation membranes for water purification.

Moreover, the commercial and economic viability of integrating CNTs into membranes has been made possible by increased demand and production. The Project on Emerging Nanotechnologies; Woodrow Wilson International Center for

Scholars. Kilogram quantities of CNTs can now be purchased for less than $1,000. Thus, at the present time, the most significant obstacles to successful integration of CNTs within hybrid membranes for full-scale water purification are technical limitations, including: (i) incorporation of CNTs into the membrane in such a way that the full benefits of the CNTs are preserved; and, (ii) creation of a hybrid structure that remains stable during water purification.

CNTs have been used to create membranes by growing vertically aligned CNTs, J.K. Holt, et al., Science (2006), and by forming CNT-polymer composites, where the CNTs are incorporated within a porous polymeric matrix. E. Celik, et al., Water Res. (2011); X. Chen, et al., ACS Appl. Mater. Interfaces (2012); and H.A. Shawky, et al., Desalination (2011). Since vertically aligned CNTs are difficult to scale-up, most research has focused on creating CNT-polymer composites. Depending on the preparation processes and CNT characteristics, however, CNT-composite membranes show no major improvement, in terms of water flux and separation characteristics, compared to available commercial membranes. H. Wu, et al., J. Membr. Sci. (2010); and E. Celik, et al., Water Res. (2011). Mechanically stable CNTs also have recently been successfully grafted onto the surface of cellulose nitrate membranes as a minor (20% maximum) component of a matrix containing poly(vinyl) alcohol and succinic acid. C.F. DeLannoy, et al., J. Membr. Sci. (2012). For CNTs to exert their full benefit in a hybrid membrane, however, they should be present on the membrane's surface to the exclusion of any polymer, as shown by the high contaminant removal efficiency and improved fouling resistance of pure CNT mat filters. A.S. Brady-Estévez, et al., Water Res. (2010); and G.S. Ajmani, et al., Water Res, (2012).

Unfortunately mats created from pure CNTs on flat sheet membranes exhibit poor hydraulic stability and cannot be easily handled or integrated into real world membrane systems. A. Deneuve, et al., Appl. Catal., A (2011). A major limitation caused by this hydraulic instability is that the CNT mats cannot be cleaned by backwashing or exposure to cross-flow because large quantities of the CNTs are immediately released from the membrane's surface and into the permeate during backwashing. This limitation due to the release of CNTs from the membrane not only greatly restricts their practical value, but also raises important health and safety concerns associated with the potential presence of CNTs in the filtrate, e.g., treated water. Synthetic strategies have recently been used to chemically graft CNTs onto the surface of cellulose nitrate membranes, although only as a minor component (20%) maximum) of a matrix containing poly(vinyl) alcohol and succinic acid. C.F. DeLannoy, et al., J. Membr. Sci. (2012).

Further, membrane processes for full-scale water treatment, excepting desalination, mainly operate with hollow fiber membranes made out of materials, such as polyvinylidene fluoride (PVDF) and polyether sulfone (PES), D. Furukawa, A Global Perspective of Low Pressure Membranes, National Water Research Institute, Fountain Valley, California, 2008, studies of hybrid CNT membranes have concentrated on flat sheet membrane configurations. S. Steiner, et al., Carbon (2012). Hollow fiber, low pressure membranes (LPMs) may be operated in either an inside-out (active layer on the inner surface) or outside-in (active layer on the outer surface) configuration. LPMs are a physical barrier for contaminant removal, G.P. Westerhoff, et al., Water Supply (1996), removing aquatic constituents larger than membrane pores, such as algae, bacteria, and parasites. The removal of human enteric viruses (20 nm to 90 nm in diameter) by LPMs, however, is often incomplete as these small diameter viruses can pass through the larger diameter pores in LPMs. Additionally, LPMs cannot remove most dissolved substances with the exception of limited adsorption of some organic chemicals. K. Majewska-Nowak, et al., Desalination (2006); H. Huang, et al., Environ. Sci. Technol. (2009); C. Jucker, M.M. Clark, J. Membr. Sci. (1994); and G. Amy, J. Cho, Water Sci. Technol. (1999).

SUMMARY

In some aspects, the presently disclosed subject matter provides a method for preparing a carbon mat on an inner surface of a polymeric hollow fiber membrane, the method comprising: (a) providing a plurality of carbon nanotubes and/or carbon particles; (b) suspending the plurality of carbon nanotubes and/or carbon particles in a solution to form a suspension of carbon nanotubes and/or carbon particles; (c) providing one or more polymeric hollow fiber membranes, wherein the one or more polymeric hollow fiber membranes have at least one open end in fluid communication with a lumen, and wherein the lumen defines an inner surface of the one or more polymeric hollow fiber membranes; (d) dispensing the suspension of carbon nanotubes and/or carbon particles in the at least one open end of the one or more polymeric hollow fiber membranes; and (e) filtering the suspension of carbon nanotubes and/or carbon particles through the one or more polymeric hollow fiber membranes operating in dead-end mode from the inside-out to deposit a carbon mat on an inner surface of the polymeric hollow fiber membrane.

In other aspects, the presently disclosed subject matter provides a polymeric hollow fiber membrane prepared by the presently disclosed methods, wherein the polymeric hollow fiber membrane has a carbon mat deposited on an inner surface thereof.

In yet other aspects, the presently disclosed subject matter provides a method for filtering an effluent, the method comprising passing the effluent through a polymeric hollow fiber membrane having a carbon mat deposited on an inner surface thereof.

Certain aspects of the presently disclosed subject matter having been stated hereinabove, which are addressed in whole or in part by the presently disclosed subject matter, other aspects will become evident as the description proceeds when taken in connection with the accompanying Examples and Figures as best described herein below.

BRIEF DESCRIPTION OF THE FIGURES

Having thus described the presently disclosed subject matter in general terms, reference will now be made to the accompanying Figures, which are not necessarily drawn to scale, and wherein:

FIG. 1 depicts preparation of a CNT mat by filtering a CNT suspension through a hollow fiber membrane from the "inside out." Membrane before loading (Left). Modified membrane (Right);

FIGS. 2A and 2B show variation in TMP (bar) vs. Filtration time (min) during the preparation of MWCNT mats on the inner surface of HF-PVDF (A) and HF-PES (B) hollow fiber membranes. Stage 1: Filtration of the MWCNT suspension through the membrane from the "inside out". Stage 2: Filtration of Milli-Q water through the membrane following MWCNT loading;

FIGS. 3A and 3B are SEM images of CNT mats created on the inner surface of (A) PVDF and (B) PES hollow fiber membranes. The white arrows show the mat depth on each membrane (depth corresponding to 11 g m^{-2} mass loading);

FIGS. 4A and 4B show mass of MWCNTs released from HF-PVDF-CNT (A) and HF-PES-CNT (B) membranes during a sequence of backwashing steps where the flow direction was reversed (i.e., from the "outside in"). Results are shown for experiments performed on three different HF-PVDF-CNT and HF-PES-CNT membranes. The backwashing steps consisted of (in order) prolonged backwashing with Milli-Q water, hydraulic stress with Milli-Q water and finally chemical cleaning. During each step the mass of CNTs released was determined by UV-vis analysis of the backwash;

FIGS. 5A and 5B are SEM pictures of MWCNT mats on the inner surface of PVDF (A1 and A2) and PES (B1 and B2) hollow fiber membranes after the membranes were backwashed. A1 and B2 are zoomed out SEM images that show the cross section of the modified hollow fibers. A2 and B2 SEM images show the detailed nature of the membrane/MWCNT interface;

FIGS. 6A and 6B show TMP increase (*P-P0*) during the filtration of a 5 ppm alginate suspension through (A) PVDF and (B) PES virgin and MWCNT modified hollow fiber membranes. The flux of alginate was held constant at 67 L h^{-1} m^{-2}. The vertical arrows indicate times at which the membrane was backwashed with the permeate at 134 L h^{-1} m^{-2}. Data are shown for four cycles of 80 min filtration followed by 6 min backwashes;

FIG. 7 shows a representative loading procedure used to create a CNT mat on the inner surface of HF-PVDF membrane (HF-PVDF-CNT);

FIG. 8 is UV-Vis spectra showing that in the region between 800 nm to 900 nm there is no absorbance from the surfactant (Triton-X), but absorbance from CNTs is still observed in this region;

FIG. 9 is a calibration curve showing how the absorbance in the 800-nm to 900-nm range is related to MWCNT mass concentration;

FIG. 10 is UV-Vis spectra showing that in the region between 800 nm to 900 nm there is no absorbance from SRNOM;

FIG. 11 shows backwashing of CNT mats created on the outer surface of a HF-PVDF membrane with Milli-Q water. The darkening of the solution and the appearance of 'white' regions on the membrane's surface during backwashing highlight the mat's hydraulic instability;

FIG. 12 is a graph showing the variation in transmembrane pressure (TMP) during SRNOM filtration;

FIG. 13 is a visual analysis of CNTs released from the least stable HF-PES-CNT membrane studied during several different backwashing steps. For comparison an example of a CNT feed solution used to create the mats also is shown;

FIG. 14 shows and high resolution SEM images of Powder Activated Carbon (PAC) mats created on the inner surface of PVDF hollow fiber membranes. In the higher resolution SEM images (lower image) the PAC mat is clearly visible as a discrete structure on the inner surface of the PVDF membrane.

DETAILED DESCRIPTION

The presently disclosed subject matter now will be described more fully hereinafter with reference to the accompanying Figures, in which some, but not all embodiments of the presently disclosed subject matter are shown. Like numbers refer to like elements throughout. The presently disclosed subject matter may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Indeed, many modifications and other embodiments of the presently disclosed subject matter set forth herein will come to mind to one skilled in the art to which the presently disclosed subject matter pertains having the benefit of the teachings presented in the foregoing descriptions and the associated Figures. Therefore, it is to be understood that the presently disclosed subject matter is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims.

I. CARBON MATS ON THE INNER SURFACE OF POLYMERIC HOLLOW FIBER MEMBRANES

Novel membrane technologies for water purification are urgently needed to meet the increasing demand for clean industrial water and safe drinking water. Toward this goal, porous carbon nanotube (CNT) mats adsorbed on flat sheet membranes have been shown to significantly improve fouling resistance and contaminant removal capabilities. Unfortunately, these CNT mats are easily removed by backwashing, which severely limits their practical value in commercial membranes.

A significant challenge originates from the low mechanical stability of CNTs deposited on polymeric materials, which prevents their effective sustained use. To overcome this limitation, the presently disclosed subject matter provides carbon mats, comprising single-walled and/or multi-walled CNT (SWCNTs and MWCNTs) hollow tube structures and/or carbon particles, built inside polymeric hollow fiber membranes (HFMs). The carbon mat structure is established by filtering a SWCNT and/or MWCNT and/or carbon particle suspension through the lumen of hollow polymeric fibers using an inside-out process. The CNTs and carbon particles are rejected by the porous polymer and accumulate at the inner surface of the HFMs, thereby creating a stable, highly porous carbon mat structure.

The presently disclosed carbon-coated HFMs exhibit, depending on the CNT and/or carbon particle and HFM properties, high fouling resistance and high separation capacities for both chemical and biological contaminants. The confined volume inside each fiber lumen and the symmetric geometry of the hollow tube restricts CNT or carbon particle resuspension and improves the stability of the carbon mat structure without the need of additional process or chemical addition. As such, the carbon mat structure inside a HFM shows superb hydraulic and chemical stability and remains stable following backwashing and chemical cleaning.

The stability of the presently disclosed carbon mats can be determined, for example, from scanning electron microscopy images of the hybrid membranes and by quantifying the mass of carbon lost during prolonged backwashing, hydraulic stress, and exposure to harsh chemical cleaning agents. Compared to virgin membranes, the presently disclosed carbon-modified membranes exhibited improved fouling resistance during filtration of alginate which was sustained through multiple backwashing cycles, further demonstrating the stability of the carbon mats. Separate experiments determined that no measureable quantities of carbon entered the permeate when natural organic matter was filtered through a carbon-modified membrane. Collectively, these results demonstrate that the presently disclosed carbon-modified membranes could positively impact the sustainability and performance of existing hollow fiber membranes being used in water purification. In addition, the presently disclosed integrated CNT-HFM composites contain electrical conductive properties conducive to charge-associated contaminant removal and membrane cleaning processes.

By integrating CNTs and/or carbon particles and HFMs, the presently disclosed methods provide filters with high fouling resistance and high contaminant (both chemical and biological) removal efficiency that remain stable following backwashing and chemical cleaning. These capabilities will improve the capacity of impurity removal, as well as decrease power requirements for filtration separation, and offer the potential to provide considerable cost savings to the end users when applying treatment. Accordingly, the development of stable carbon mat structures onto polymeric materials provides a sustainable, scalable technique to dramatically improve the capacity and sustainability of filtration separation.

Further, the use of functionalized CNTs and/or carbon particles enables a carbon-HFM to be customized for removal of targeted impurities. This characteristic dramatically increases applications for which carbon-HFMs can be used including, but not limited to, water and wastewater treatment, water reuse, medical procedures and treatments (e.g., kidney dialysis), industrial processes (e.g., microchip processing, food production, and the like), and analytical processes (e.g., solid phase microextraction, electrical sensors, and the like). The presently disclosed subject matter also provides a non-metallic electrical conductance material for use in separation processes and power transfer.

Accordingly, referring now to FIG. 1, in some embodiments, the presently disclosed subject matter provides a method for preparing a carbon mat on an inner surface of a polymeric hollow fiber membrane, the method comprising: (a) providing a plurality of carbon nanotubes and/or carbon particles; (b) suspending the plurality of carbon nanotubes and/or carbon particles in a solution to form a suspension of carbon nanotubes and/or carbon particles; (c) providing one or more polymeric hollow fiber membranes **100**, wherein the one or more polymeric hollow fiber membranes **100** have at least one open end **110** in fluid communication with a lumen **120** and at least one dead end **130**, and wherein the lumen **120** defines an inner surface **140** of the one or more polymeric hollow fiber membranes **100**; (d) dispensing the suspension **150** of carbon nanotubes and/or carbon particles in the at least one open end **110** of the one or more polymeric hollow fiber membranes **100**; and (e) filtering the suspension **150** of carbon nanotubes and/or carbon particles through the one or more polymeric hollow fiber membranes **100** operating in dead-end mode from the inside-out to deposit a carbon mat **160** on an inner surface **140** of a polymeric hollow fiber membrane **100**.

In particular embodiments, the plurality of carbon nanotubes comprise multi-walled carbon nanotubes. Multi-walled nanotubes (MWNT) comprise, in some embodiments, multiple rolled layers of concentric tubes of graphene or a single sheet of graphite is rolled in around itself, for example, like a scroll of parchment or a rolled newspaper.

In yet other embodiments, the plurality of carbon nanotubes comprise single-walled carbon nanotubes. For example, a single-walled carbon nanotube can include a one-atom thick layer of graphite, e.g., graphene, that can be wrapped into a seamless cylinder.

In some embodiments, the plurality of carbon nanotubes have a diameter from about 50 nm to about 80 nm. In other embodiments, the plurality of carbon nanotubes have a length from about 10 μm to about 20 μm. In still other embodiments, the plurality of carbon nanotubes have a specific surface area of about 60 $m^2 g^{-1}$. In further embodiments, the plurality of carbon nanotubes comprise unfunctionalized carbon nanotubes.

In some embodiments, the carbon particles comprise powdered activated carbon particles.

Many polymeric hollow fiber membranes known in the art aresuitable for use with the presently disclosed methods and compositions. Common polymeric hollow fiber membranes include, but are not limited to, polymers or copolymers selected from the group consisting of cellulose acetate (CA), nitrocellulose (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone (PES), polyacrilonitrile (PAN), polyamide, polyimide, polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyvinylchloride (PVC).

Criteria for selecting polymeric hollow fiber membranes suitable for use with the presently disclosed methods and compositions can include, but are not limited to, a desired binding affinity for compounds to be separated, an ability to withstand the required cleaning conditions, rigidity, stereoregularity, crystallinity, glass transition temperature, polarity of its functional groups, hydrophilicity or hydrophobicity (e.g., related to surface free energy), presence of ionic charge, chemical or thermal resistance, density, porosity, and an ability to bind the carbon nanofiber mat deposited therein, in addition to practical considerations, such as cost and availability.

In some embodiments, the one or polymeric hollow fiber membranes are hydrophilic. In such embodiments, the one or more hydrophilic polymeric hollow fiber membranes comprise polyether sulfone (PES). In some embodiments, the one or more polymeric hollow fiber membranes have a nominal pore size of about 0.03 μm. In other embodiments, the one or more polymeric hollow fiber membranes are capable of sustaining a maximum flux of pure water flux of about 1200 ± 120 L h^{-1} m^{-2} bar^{-1}.

In other embodiments, the one or more polymeric hollow fiber membranes are hydrophobic. In such embodiments, the one or more polymeric hollow fiber membranes comprise polyvinylidene fluoride (PVDF). In such embodiments, the one or more polymeric hollow fiber membranes have a nominal pore size of about 0.1 μm. In some embodiments, the one or more polymeric hollow fiber membranes are capable of sustaining a maximum flux of pure water of about 655 ± 85 L h^{-1} m^{-2} bar^{-1}.

In some embodiments, the carbon mat comprises powdered activated carbon (PAC). Activated carbon is a form of carbon comprising small, low-volume pores that result in an increase in surface area available for adsorption. Due to its high degree of microporosity, one gram of activated carbon can have a surface area in excess of 500 m^2. An activation level sufficient for useful application may be attained solely from high surface area; however, further chemical treatment can enhance its adsorption properties.

Active carbons can be made in particulate form as powders or fine granules less than about 1.0 mm in size. Powdered active carbon (PAC) is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve. Particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller are designated as PAC.

In some embodiments of the presently disclosed methods, the solution in which the carbon mat is prepared comprises an aqueous solution. In other embodiments, the aqueous solution comprises a non-ionic surfactant. In still other embodiments, the method comprises sonicating the solution of carbon nanotubes for a period of time.

Accordingly, in some embodiments, the presently disclosed subject matter provides a polymeric hollow fiber membrane having a carbon nanotube mat deposited on an inner surface thereof. In some embodiments, the polymeric hollow fiber membrane comprises a polymer selected from the group consisting of a hydrophilic polymer and a hydrophobic polymer. In still other embodiments, the polymeric hollow fiber membrane comprises a polymer selected from the group consisting of polyether sulfone (PES) and polyvinylidene fluoride (PVDF).

In some embodiments, the polymeric hollow fiber membrane comprises a total mass of carbon nanotubes deposited on the inner surface thereof of about 11 g m^{-2}. In other embodiments, the polymeric hollow fiber membrane comprises an electrical conductance material.

In yet other embodiments, the presently disclosed subject matter provides a method for filtering an effluent, the method comprising passing the effluent through a polymeric hollow fiber membrane having a carbon mat deposited on an inner surface thereof. In certain embodiments, the effluent is selected from the group consisting of water, wastewater, and a biological fluid. In particular embodiments, the biological fluid comprises blood.

In other embodiments, the method further comprises an industrial process. In such embodiments, the industrial method comprises a process selected from the group consisting of microchip processing and food processing.

In yet other embodiments, the presently disclose method further comprises removing anthropogenic and/or naturally occurring substances, e.g., arsenic, from groundwater and the like. Generally, the presently disclosed methods can be used to remove contaminants from a source of water.

In further embodiments, the method further comprises an analytical process. In such embodiments, the analytical process comprises solid phase microextraction.

Following long-standing patent law convention, the terms “a,” “an,” and “the” refer to “one or more” when used in this application, including the claims. Thus, for example, reference to “a subject” includes a plurality of subjects, unless the context clearly is to the contrary (e.g., a plurality of subjects), and so forth.

Throughout this specification and the claims, the terms “comprise,” “comprises,” and “comprising” are used in a non-exclusive sense, except where the context requires otherwise. Likewise, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing amounts, sizes, dimensions, proportions, shapes, formulations, parameters, percentages, quantities, characteristics, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about” even though the term “about” may not expressly appear with the value, amount or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are not and need not be exact, but may be approximate and/or larger or smaller as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art depending on the desired properties sought to be obtained by the presently disclosed subject matter. For example, the term "about," when referring to a value can be meant to encompass variations of, in some embodiments, ± 100% in some embodiments ± 50%, in some embodiments ± 20%, in some embodiments ± 10%, in some embodiments ± 5%, in some embodiments ±1%, in some embodiments ± 0.5%, and in some embodiments ± 0.1% from the specified amount, as such variations are appropriate to perform the disclosed methods or employ the disclosed compositions.

Further, the term "about" when used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range and modifies that range by extending the boundaries above and below the numerical values set forth. The recitation of numerical ranges by endpoints includes all numbers, e.g., whole integers, including fractions thereof, subsumed within that range (for example, the recitation of 1 to 5 includes 1, 2, 3, 4, and 5, as well as fractions thereof, e.g., 1.5, 2.25, 3.75, 4.1, and the like) and any range within that range.

EXAMPLES

The following Examples have been included to provide guidance to one of ordinary skill in the art for practicing representative embodiments of the presently disclosed subject matter. In light of the present disclosure and the general level of skill in the art, those of skill can appreciate that the following Examples are intended to be exemplary only and that numerous changes, modifications, and alterations can be employed without departing from the scope of the presently disclosed subject matter. The descriptions and specific examples that follow are only intended for the purposes of illustration, and are not to be construed as limiting in any manner to make compounds of the disclosure by other methods.

EXAMPLE 1

Materials and Methods

Carbon Nanotubes: Commercially available pristine (unfunctionalized) multiwalled CNTs (MWCNTs) were purchased from Cheap Tubes, Inc. (Vermont, USA). According to the manufacturer's specifications, the MWCNTs exhibit diameters ranging from 50 nm to 80 nm and lengths between 10 μm to 20 μm and a specific surface area of 60 m^2 g^{-1}. Prior to loading, MWCNT suspensions were prepared at a concentration of approximately 750 mg L^{-1} in Milli-Q water (18 MΩ cm^{-1}) with 0.9 % v/v H_2O of non-ionic surfactant (Triton X100). To disperse the CNTs, all MWCNT suspensions were sonicated in a water bath sonicator for 30 min (Aquasonic 250HT).

Hollow Fiber Membranes: Two types of commercially available hollow fiber (HF) membranes were used; PES and PVDF. The PES membranes were hydrophilic with a nominal pore size of 0.03 μm and are capable of sustaining a maximum pure water flux of approximately 1200 ± 120 L h^{-1} m^{-2} bar^{-1}. The PVDF membranes are hydrophobic with a nominal pore size of 0.1 μm and are able to sustain a maximum flux of pure water of approximately 655 ± 85 L h^{-1} m^{-2} bar^{-1}.

Creating Membrane Modules: All filtration experiments were performed using the bench-scale filtration system described in Huang et al., Water Res. (2007). Virgin hollow fiber PES (HF-PES) and PVDF (HF-PVDF) membranes, 9.5 cm in length, were potted in epoxy at each end with one end cut open to allow inside out, dead end filtration. The inner surface area of approximately 9 cm^2 was kept consistent across different modules by modifying the number of fibers per module: four fibers for HF-PES and six fibers for HF-PVDF modules.

Once prepared, the HF-PVDF and HF-PES membrane modules were soaked overnight in a 25 %v/v H_2O isopropanol solution and then attached to the filtration system. Prior to each experiment the module was flushed with Milli-Q water and the pure water flux measured by the flux step method. E. Filloux, et al., Water Res. (2012). A new membrane module was used for each experiment.

FIG. 1 summarizes the approach used to create CNT mats on the inner surface virgin HF-PES and HF PVDF membranes. PES and PVDF hollow fiber membranes modified by the addition of CNT mats to their inner surfaces are referred to herein as HF-PES CNT and HF-PVDF-CNT membranes, respectively.

CNT mats were created by filtering 13 mL of a 750 mg L^{-1} CNT suspension through each hollow fiber in the module (6 fibers for HF-PVDF and 4 for HF-PES) in an inside-out mode at a constant filtration flux of 134 L h^{-1} m^{-2} using a peristaltic pump (Masterflex L/S, Cole-Palmer, USA). The CNT loading was maintained at approximately 11 g m^{-2}.

During the CNT loading process, the TMP was recorded every 10 seconds with a pressure transducer (A-68075-32, Cole Parmer) connected to an electronic board (PersonalDaq 55, Measurement Computing Corporation, USA). The mat was created during the filtration process at CNTs were trapped on the inner surface of the hollow fibers. Once the CNTs had been loaded, the residual surfactant was flushed from the module with Milli-Q water until the TMP reached a constant value. Once created, the pure water flux passing through the HF-PES-CNT and HF-PVDF-CNT membranes was determined using Milli-Q water and the flux step method. E. Filloux, et al., Water Res. (2012). Referring now to FIG. 7, is a photograph of a module during the formation of a HF-PVDF-CNT membrane.

The CNT loading (mg MWCNT m^{-2}) was determined by multiplying the MWCNT concentration (mg L^{-1}) by the total volume of MWCNT-containing solution filtered through the hollow fibers. This allowed the total mass of MWCNTs (mg) used during the loading process to be calculated. This value was then divided by the inner surface area of the HF-PVDF or HF-PES modules (m^2) to obtain the CNT loading (mg MWCNT m^{-2}).

EXAMPLE 2

Evaluating the Hydraulic Stability of CNT Mats

Once the CNT mats were created, mat stability was evaluated by reversing the flow of water through HF-PES-CNT and HF-PVDF-CNT membranes using hydraulic backwashing, i.e., outside-in filtration. These backwashing studies tested CNT mat stability over a range of hydraulic conditions and solution chemistries. Three different backwash conditions were applied in sequence: (i) long term stress that involved two hours of backwashing with Milli-Q water at 85 L h^{-1} m^{-2}; (ii) hydraulic stress where four shorter (three minute) backwashing steps with Milli-Q water at increasing fluxes ranging from 85 L h^{-1} m^{-2} to 420 L h^{-1} m^{-2} were performed; each step was performed by flux pulsation (the flux was increased instantaneously and not incrementally) to simulate the effect of hydraulic stress; and (iii) chemical stress where three sequential (three minute) backwashing steps at 85 L h^{-1} m^{-2} were performed with three different chemicals in Milli-Q water: (a) synthetic surface water (49 ppm $NaHCO_3$, 28 ppm $CaSO_4$, 25 ppm $MgSO_4$ and 1.9 ppm KCl); (b) 5 ppm and 500 ppm sodium hypochlorite solution; and (c) a non-ionic surfactant suspension (0.9 % v/v H_2O Triton-X).

The (i), (ii), (iii) sequence of backwashing steps was performed in triplicate, i.e., on three HF-PES-CNT and three HF-PVDF-CNT modules. In general, the backwashing conditions used to test the hydraulic stability of the CNT mats represent worst case scenarios in terms of duration, flux and chemical reagents compared to those used in normal filtration operation. The mass of CNTs dislodged from the mats was determined by analyzing the backwashed water using UV-Vis Spectroscopy (UV-Vis). For the long backwash step, an aliquot of backwashed water was collected every 10 minutes. For each of the steps described in stress tests (ii) and (iii), a 3 mL aliquot of the backwashed water sample was collected.

The mat's stability during each backwashing step was assessed by determining the mass of CNTs dislodged from the mats. This assessment was done by analyzing the concentration of MWCNTs in the backwashed water using UV-Vis spectroscopy (UV-Vis). To determine the concentration (and thereby the mass), of CNTs released during each backwash step by UV-Vis, it is necessary to ensure that all of the CNTs are dispersed. CNT dispersion of any aggregates was accomplished by first adjusting the pH of the backwash solution to 10, as it has been shown previously that high pH improves CNT dispersion. B. Smith, et al., Environ. Sci. Technol. (2009). Following this step, 0.5 % v/v H_2O of the surfactant Triton X100 was added to the solution and sonicated at 70 W (Branson 1510) for approximately 15 min. The CNT concentration was then determined by measuring the average UV absorbance (Cary 50 UV-Vis Spectrophotometer, Varian Medical Systems, Palo Alto, CA, USA) in the 800-nm to 900-nm range, where control studies (see FIG. 8) showed that Triton X100 does not absorb, but MWCNTs absorb/scatter light. The sensitivity of these measurements was enhanced by using a 5-cm path length UV-Vis cell (Starna Cells, Inc., Atascadero, CA, USA).

The correlation between UV absorbance in the 800-nm to 900-nm range and MWCNT mass concentration (mg L^{-1}) was determined by conducting separate control studies where known masses of MWCNTs powders were dispersed in Milli-Q with 0.5% Triton X100 v/v H_2O (see FIG. 9). The CNT mass released from the mat in any backwash experiment was determined by multiplying the CNT mass concentration determined by UV-Vis by the total volume collected during the backwash. The limit of MWCNT detection was determined by discerning the lowest UV-Vis absorbance value that could be discerned from the baseline (0.011 absorbance units). A range of uncertainty in the MWCNT detection limit was then calculated from the uncertainty in the calibration curve shown in FIG. 9. Based on this analysis, the limit of MWCNT detection was estimated to be between $2.5 - 6.6\times10^{-5}$ mg MWCNT.

EXAMPLE 3

SEM Imaging of the CNT Mats

The inner surfaces of HF-PVDF-CNT and HF-PES-CNT hollow fiber membranes were imaged using a cold cathode field emission scanning electron microscope (JEOL 6700F, FESEM) with 1.0 nm resolution at 15 keV. Hollow fiber membrane surfaces were imaged after CNT loading and then again after the backwashing steps described in Example 2. Prior to analysis, each membrane sample was dried for 48 hours at room temperature. Cross-sectional images were taken by first cryo-snapping the CNT modified membranes in the presence of liquid nitrogen and then sputter-coating them with platinum to prevent charging during SEM. Samples were then mounted vertically onto the side of a sample stub and imaged at various magnifications.

EXAMPLE 4

Evaluation of CNT Release into the Permeate During NOM Filtration

During membrane operation, there is a potential for organic matter to remobilize CNTs from the mats and transport these CNTs through the hollow fiber membranes into the permeate. To evaluate this possibility, Suwannee River Natural Organic Matter (SRNOM) was used; a type of NOM that has been used extensively in previous membrane studies. N. Her, et al., Water Res. (2004); and W.-Y. Ahn, et al., J. Membr. Sci. (2008). The SRNOM suspension was prepared at a concentration of 5 mg L^{-1} SRNOM diluted in 49 ppm $NaHCO_3$, 28 ppm $CaSO_4$, 25 ppm $MgSO_4$ and 1.9 ppm KCl and was filtered through a HF-PVDF-CNT module at 67 L h^{-1} m^{-2} in two, 60 minute cycles. In between these two cycles, the HF-PVDF-CNT membrane was backwashed with the permeate at 85 L $h^{-1}m^{-2}$. The concentration of CNTs in the permeate and the backwash solutions was determined by the method described in Example 2, also taking advantage of the fact that NOM does not adsorb in the 800-nm to 900-nm region (see FIG. 10). Data from the UV-Vis analysis of the permeate are provided in Table 1.

Table 1: UV-Vis analysis of the permeate and the backwash during SRNOM filtration through a HF-PVDF-MWCNT membrane.

Filtration time (mins)	UV-Vis Absorbance (800 - 900nm)	MWCNT mass (μg)
10	0.00589476	0. 110
20	0.00393495	0. 073
60	0.00606117	0. 113
70	0.00653772	0.122
80	0.00207881	0. 039
120	0.00366814	0. 068
Backwash	0.14075784	2. 623

EXAMPLE 5

Effect of CNT Mats on Membrane Antifouling Properties

The fouling behavior of HF-PVDF-CNT and HF-PES-CNT membranes, including the effect of backwashing, was compared to virgin HF-PVDF and HF-PES membranes by measuring the change in TMP during the filtration of sodium alginate. In these studies, sodium alginate was chosen as a fouling surrogate for NOM rather than SRNOM because it has higher fouling potential, N. Her, et al., Water Res. (2004); Y. Ye, et al., Desalination (2005); and K. Katsoufidou, et al., J. Membr. Sci. (2007), due to the presence of larger concentrations of higher weight macromolecules. Consequently, the filtration of alginate leads to membrane fouling on an accessible experimental timescale.

Further, in these studies, an alginate suspension (5 ppm sodium alginate diluted in 47 ppm $NaHCO_3$ and 380 ppm KCl) was prepared at pH 7 and exhibited a conductivity of approximately 750 μScm^{-1} at 20°C. This alginate suspension was filtered through HF PVDF, HF-PES and HF-PVDF-CNT, HF-PES-CNT membranes in dead-end mode, at a constant flux of 67 L $h^{-1}m^{-2}$ through four cycles of 80 min, with each filtration cycle followed by 6 minutes of backwashing with the permeate at

85 $Lh^{-1}m^{-2}$. Thus, the net permeate volume was equal to 90% of the feed water volume.

Membrane fouling was evaluated by measuring the rate of TMP increase ($d(P_t - P_0)/dt$) versus time during each filtration cycle, where P_0 is the initial TMP prior to the filtration of the alginate solution and P_t is the TMP at time, t. The irreversible fouling was determined after each backwashing step by the pressure increase (ΔP) measured at the onset of the subsequent filtration cycle.

EXAMPLE 6

Results and Discussion

6.1 Preparation and Characterization of CNT Mats

FIG. 2 illustrates the change in transmembrane pressure (TMP) observed during the creation of three representative HF-PVDF-CNT (FIG.2–A, left) and three representative HF-PES-CNT (FIG.2-B, right) membranes. For each type of membrane, results are shown for three separate experiments; based on the volume and concentration of the MWCNT-containing solution used the total mass of MWCNTs deposited on the inner surface of each membrane was approximately 11 g m^{-2}. As the MWCNT suspension was being filtered through the membranes (Stage 1), the TMP increased rapidly, reaching a maximum after approximately 6 min of filtration time, which corresponds to approximately 12 mL.

During Stage 1, the average TMP increase is higher for the HF-PVDF membranes (approximately 0.9 bars) than for the HF-PES membranes (approximately 0.5 bars). This difference in behavior between the two types of hollow fiber membranes is consistent with the hypothesis that the TMP increase during Stage 1 is predominantly a result of physical interactions, specifically hydrophobic interactions, between the base membrane and the surfactant present in the feed solution. A.-S. Jönsson, B. Jönsson, J. Membr. Sci. (1991). As reported by Jönsson and Jönsson, stronger interactions (and thus greater changes in the TMP) would be expected between the hydrophobic segments of the surfactant and the hydrophobic HF-PVDF membranes, as compared to the more hydrophilic HF-PES membranes.

Once the volume of the MWCNT suspension filtered through the membrane corresponded to the desired MWCNT mass loading (approximately 13 mL based on the MWCNT concentration), the MWCNTs suspension was replaced by Milli-Q water (Stage 2). At this point, FIG. 2 shows that for both HF-PVDF-CNT (FIG. 2-A) and HF-PES-CNT (FIG. 2-B) membranes, the TMP decreased rapidly as the surfactant left the membrane and entered the permeate. After approximately 40 minutes of washing with Milli-Q water, the TMP across all of the membranes remained roughly constant at values that were either comparable to, or slightly higher than those of the virgin hollow fiber membranes.

In terms of permeability, for the HF-PVDF-CNT and HF PES-CNT membranes, the values were 500 ± 68 L $h^{-1}m^{-2}bar^{-1}$ and 1080 ± 200 L $h^{-1}m^{-2}bar^{-1}$, respectively. In contrast, the permeability of the virgin HF-PVDF and HF-PES membranes was 655 ± 85 L $h^{-1}m^{-2}bar^{-1}$ and 1200 ± 120 $Lh^{-1}m^{-2}bar^{-1}$, respectively. Thus, the generation of CNT mats inside the hollow fibers reduces the membranes' permeability by approximately 22 % for HF-PVDF-CNT and 10 % for HF-PES-CNT membranes, respectively. These relatively small changes in the hybrid membrane's characteristics suggest that the CNT mats exhibit a large porosity and thus a low hydraulic resistance as compared to the base membrane.

SEM analysis of both HF-PVDF-CNT and HF-PES-CNT membranes (FIG. 3) confirms that the loading procedure creates a hybrid membrane structure with micron thick CNT mats adsorbed on the inner surface of the hollow fiber. Furthermore, SEM images reveal that the interface between the CNT mat and the base membrane is relatively sharp and well-defined with little or no evidence of CNTs within the pores of either the HF-PVDF or HF-PES membranes. Based on the membrane's pore size (0.1 μm and 0.03 μm for the HF-PVDF and HF-PES, respectively), compared to the CNT geometry (O.D > 50 nm, Length: 10 μm -20 μm), a total rejection of CNTs by the membrane during loading is expected, leading to their adsorption at the inner membrane surface and the creation of a MWCNT mat.

This characteristic is in contrast to previous studies, where MWCNTs (O.D: 10 nm - 20 nm, Length: 10 μm to 20 μm) dispersed by Triton-X100 were observed to permeate through flat sheet PVDF membranes which exhibited significantly higher pore size (membrane pore size approximately 0.45μm) and where filtration occurred under quite different preparative conditions (vacuum filtration). G.S. Ajmani, et al., Water Res, (2012). The properties of the base membrane and details of the loading procedure would therefore both seem to be important parameters in determining if a discrete CNT mat is formed.

6.2 Stability of MWCNT mats during backwashing

The stability of the HF-PVDF-CNT and HF-PES-CNT membranes under different backwashing and cleaning conditions were analyzed using UV-Vis (see FIG. 4). The extent to which the hydraulic stability of the CNT mats created on both HF-PVDF and HF-PES membranes was reproducible was investigated by conducting experiments in triplicate on separate HF-PVDF CNT and HF-PES-CNT membranes. During long-term backwashing with Milli-Q water, the only measureable quantity of CNTs removed from the membrane occurred during the beginning of the backwash (< 10 min).

Referring now to FIG. 4, this trend was observed for all of the HF PVDF-CNT and HF-PES-CNT membranes, and suggests that CNTs displaced at the onset of the backwashing correspond to loosely bound aggregates of CNT particles that were only weakly adhered to the CNT mats. Without wishing to be bound to any one particular theory, it is thought that this observation is a consequence of the high CNT concentrations in the suspensions used to create the mats (750 mg L^{-1}), which will result in some CNT aggregates/bundles that are likely to be less tightly bound within the mat. For backwashing times in excess of approximately 10 minutes, however, the quantity of CNTs removed by backwashing with Milli-Q water decreased for all of the HF-PVDF-CNT and HF-PES-CNT membranes examined to values that were at or below the detection limit (> 6.6 10^{-5} mg MWCNT), indicating that the remaining CNTs in the mats were stable under these backwashing conditions. Indeed, except for the very beginning of the backwash (< 10 mins), the entire volume collected during the 2 hours of backwashing exhibited no UV absorbance in the 800-nm to 900-nm range, confirming that the quantity of CNTs released during this step is extremely low (FIG. 4).

For all of the HF-PVDF-CNT and HF-PES-CNT membranes studied, the total mass of MWCNTs lost from the CNT mats during long-term backwashing with Milli-Q water was < 50 µg as compared to the approximately 10 mg MWCNTs used to create them. Thus, the total amount of MWCNTs removed during this two-hour period of backwashing (samples taken every 10 min) represents< 0.5 % of the total MWCNT mass loaded. After this long-term backwash, all of HF-PVDF-CNT and HF-PES-CNT membranes were hydraulically stressed by rapidly increasing the hydraulic flux. For the majority of the membranes tested, the quantity of MWCNTs released during these hydraulic stress steps was below the detection limit even at really high water fluxes (i.e., 420 L $h^{-1}m^{-2}$), although one of the HF-PES-CNT membranes did lose measureable quantities of MWCNTs for each of the hydraulic steps (see FIG. 4).

The last backwash step was chemically cleaning the CNT modified hollow fiber membranes using different solution chemistries. In general, the quantity of CNTs removed during each one of the different chemical treatment steps was small (e.g., less than about 0.05 mg); the most disruptive treatment was the backwash with the synthetic water solution at a flux of 85 L h^{-1} m^{-2}. Based on the total mass of MWCNTs lost during the entire sequence of backwashing steps, it is evident that the MWCNT mats formed on the HF-PVDF-CNT and HF-PES-CNT membranes are hydraulically stable, i.e., they are baskwashable. For five of the six HF-PVDF-CNT and HF-PES-CNT membranes tested, the fraction of MWCNTs lost is less than 1% of the initial MWCNT mass used to create the mats. In general, the HF-PVDF-CNT and HF-PES-CNT membranes exhibited comparable stabilities, which suggest that MWCNT stability is more a function of their structure than specific interactions with the membrane surface.

Cross-sectional SEM images of the HF-PVDF-CNT (FIG. 5A; HF-PVDF) and HF-PES CNT (FIG. 5B; HF-PES) membranes acquired after the backwashing steps confirm the hydraulic stability of the CNT mats. In addition, to the retention of the CNTs, the lower magnification SEM images (FIG. 5, A1 and B1) also reveal that the CNT mats are formed continuously around the inner surface of the hollow fiber membranes with a relatively uniform thickness. The higher resolution electron micrographs (FIG. 5, A2 and B2) highlight the intact nature of the CNT mat after backwashing, the similar thickness compared to the mat before backwashing (compare FIG.s 3A and 3B) and the abrupt nature of the interface that still exists between the CNT mat and the base membrane (HF-PVDF or HF-PES). The UV-Vis and SEM measurements both demonstrate the ability of the simple preparative approach described herein to produce CNT mats on the inner surface of hollow fiber membranes.

The robustness of the HF-PVDF-CNT and HF-PES-CNT mats created on the inner surface of the membranes after backwashing contrasts with the instability of CNTs mats when they were deposited on the outer surface of the same membrane. A darkening of the solution in the membrane module (FIG. 11) demonstrates that even simple backwashing from the inside out removed large quantities of CNTs deposited on the outer surface of a HF-PVDF membrane. This observation is consistent with previous studies on the instability of CNT mats adsorbed on flat sheet membranes after simple backwashing with Milli-Q water. G.S. Ajmani, et al., Water Res (2012). In contrast, backwashed samples collected when the CNT mats were deposited on the inner surfaces of the hollow fiber membranes were colorless to the naked eye, indicative of a dramatically greater stability.

6.3 Stability of CNT Mats during filtration of organic matter (humic substances)

The experiments conducted hereinabove reveal how CNT mats prepared on the inside surface of hollow fiber membranes remain intact during aggressive membrane cleaning (i.e., backwashing). Therefore, the HF-PVDF-CNT and HF-PES-CNT membranes can be expected to remain functional in practical, real world applications without the need to continuously regenerate the CNT mats. This constant regeneration would severely compromise their practical utility. It also is important to confirm, however, that CNTs do not breakthrough the membrane and enter the permeate during normal inside out water filtration. This requirement is important because any breakthrough of CNTs during filtration would raise important safety issues, as CNTs could enter the treated water where their environmental health and safety effects remain unresolved and are the topic of intense scientific debate. J. M. Wörle-Knirsch, et al., Nano Lett. (2006).

To test the stability of CNTs during normal operation (i.e., inside out filtration) a humic substance (SRNOM; 5 mg C L^{-1}) was filtered through a HF-PVDF-CNT membrane at 67 L h^{-1} m^{-2} over a two hour period. At selected times during SRNOM filtration, 3 mL aliquots of the permeate were analyzed by measuring the UV-Vis in the 800-nm to 900-nm region, for any evidence of CNTs. Humic substances exhibit a strong propensity for facilitated transport and for stabilizing CNTs as suspended particles, M.A. Chappell, et al., Environ. Pollut. (2009), and SRNOM filtration is thus a stringent test for CNT stability.

To test the stability of the CNTs under conditions most likely to facilitate their transport through the membrane, (1) the membrane pore size should be relatively large; and (2) the SRNOM should not induce fouling, which would decrease the membrane's effective pore size and the propensity for CNT transport.

To address the first issue, the HF-PVDF membrane was investigated because of its larger pore size (0.1 μm for HF-PVDF vs. 0.03 μm for HF-PES), as compared to the CNT dimensions (lengths of 10 μm - 20 μm with outer diameters of 50 nm to 80 nm). To address the second issue, SRNOM (< 800 Da determined by HPLC-SEC with DOC detection) was chosen because the molecular weight of SRNOM is small enough so that no fouling would be expected during SRNOM filtration through the HF-PVDF membrane. During SRNOM filtration the UV absorbance of all permeate samples was below the MWCNT detection limit (0.011 absorbance units in the 800-nm to 900-nm range). The TMP also remained constant, indicating a lack of organic fouling, as expected (FIG. 12). UV analysis of the backwash conducted at the end of the SRNOM filtration cycle using the permeate (85 L $h^{-1}m^{-2}$) revealed the presence of approximately 10 μg MWCNTs. Thus, the presently disclosed results demonstrate that, within the observed detection limits, no facilitated CNT transport occurred through the HF-PVDF-CNT membrane during inside out SRNOM filtration, although a small quantity of MWCNTs was removed during backwashing as expected from the results on hydraulic stability (section 6.2. hereinabove).

In sum, the presently disclosed results with SRNOM support the idea that CNT mats can be used in hollow fiber membranes (even for larger pore sized ultrafiltration membranes) without introducing unwanted CNTs in the treated water.

6.4 Effectiveness and stability of MWCNT mats during alginate filtration

As previously reported, G.S. Ajmani, et al., Water Res, (2012), CNT mats created on flat sheet PVDF membranes can reduce membrane fouling. The fouling resistance of HF-PVDF-CNT and HF-PES-CNT membranes was tested by monitoring the change in TMP during the filtration of sodium alginate, atypical fouling surrogate used in membrane studies. It should be noted that this example is distinct from the one previously described in Section 6.3 immediately hereinabove, which was designed specifically to evaluate the potential for any CNT remobilization during filtration of organic matter.

In contrast, the filtration of sodium alginate represents far more aggressive fouling conditions, allowing the benefits that CNT mats have on fouling resistance to be evaluated, as well as their ability to sustain any improvements in performance through several backwashing steps. FIG.6-A shows that during each cycle of alginate filtration the rate of TMP increase for the HF-PVDF-CNT membranes decreased considerably compared to the HF-PVDF membranes. For example, the fouling rate in the first cycle, as determined by the slope of the pressure increase vs. time in the linear part of the curve, was equal to 2 and 0.8 mbar min^{-1} for the HF PVDF and HF-PVDF-CNT membranes, respectively. Thus, the presence of the CNT mat reduced the fouling rate by about 60% during the first cycle.

Improvements in the anti-fouling properties of the HF-PVDF-CNT membranes were sustained through all four filtration cycles, with the final TMP after approximately 5 hours equal to 0.3 and 0.1 bars for the HF-PVDF and HF-PVDF20 CNT membranes, respectively. The improved fouling resistance of the HF-PVDF-CNT membranes was sustained through repeated backwashing steps, shown in FIG. 6-A, supporting the idea that the presently disclosed CNT mats are hydraulically stable, i.e., are backwashable.

In addition to the improvements in fouling resistance, the presently CNT mats decreased the extent of irreversible fouling. After the last backwash, the permeability of the HF-PVDF and HF-PVDF-CNT membranes was 468 $Lh^{-1}m^{-2}bar^{-1}$ and 395 $Lh^{-1}m^{-2}bar^{-1}$, respectively. Before fouling, the permeability of the HF-PVDF and HF-PVDF CNT membranes was 655 ± 85 $Lh^{-1}m^{-2}bar^{-1}$ and 434 $Lh^{-1}m^{-2}bar^{-1}$. Thus, the irreversible fouling reduced the permeability of the HF-PVDF membranes by 29%, but the HF-PVDF-CNT membrane by only 9%.

The CNT mats were, however, less effective at reducing alginate fouling when adsorbed on the inner surface of PES membranes. During the first cycle, the fouling rate was 2 mbar min^{-1} and 1.3 mbar min^{-1} for the HF-PES and HF-PES-CNT membranes, respectively. Furthermore, after each filtration cycle, the relative improvement of the HF-PES-CNT membrane compared to the HF-PES membrane decreased such that the performance of the HF-PES-CNT and the HF-PES membrane were virtually indistinguishable from one another after three backwash cycles.

The extent of irreversible fouling was negligible for either the HF-PES-CNT membrane or the HF-PES membrane. Without wishing to be bound to any one particular theory, it is thought that the CNT mats have a greater effect on the performance of the HF-PVDF membranes can be ascribed to the difference in pore-size between the hollow fiber membranes and the CNT mats. The HF-PVDF and HF-PES membranes have pore sizes of approximately about 0.1 μm and less than about 0.03 μm, respectively; the CNT mats have a pore size distribution predominantly in the range of about 0.01 μm to about 0.1 μm, based on previous findings using flat sheet membranes. G.S. Ajmani, et al., Water Res, (2012). Thus, for the HF-PVDF membrane the CNT mat introduces a new, finer filter that helps to trap particles responsible for clogging/blocking membrane pores. In contrast, the pore size in the HF-PES membrane is comparable to that in the CNT mat and consequently the CNT mat produced far less of a change in the antifouling properties of the hybrid membrane.

6.5 Rationalizing the CNT Mat Stability

One finding of the presently disclosed subject matter is that backwashable CNT mats can be generated on the inner surfaces of hollow fiber membranes using a simple preparative method. Without wishing to be bound to any one particular theory, it is thought is that the detailed nature of membrane-CNT interactions is not playing a major role in determining the mat's stability due to the ability to create stable CNT mats on two membranes (HF-PVDF and HF-PES) with very different physicochemical properties (different hydrophilic properties, pore size, chemical composition, and the like).

To explore the generalizability of a mat's stability on the inner surface of a hollow fiber membrane a limited number of experiments were conducted using powder activated carbon (PAC) (200-400 mesh; 75-35 micron), rather than CNTs. In these studies, surfactant stabilized particles of powder activated carbon (PAC) were filtered through a HF-PVDF membrane from the inside-out using an experimental approach analogous to the one used for CNTs. During the loading procedure a qualitatively similar variation in TMP was observed. Thus, at the end of the PAC loading step and subsequent flushing of the surfactant with Milli-Q water the measured TMP was similar to that of the virgin membrane. Two HF-PVDF-PAC membrane modules were created in this way, with loadings of about 19 g cm^{-2} and about 28 g cm^{-2}. Both membranes were then subjected to prolonged backwashing with Milli-Q water and hydraulic stress as described in Example 2.2 (i) and (ii). Visual analysis of the backwashed water showed that the vast majority of the PAC had been retained within the membranes. This observation was confirmed by SEM analysis, which showed that PAC mats remained on the inner surface of the HF-PVDF (see FIG. 13). This result indicates that the stability of the CNT mats, which are the focus of this disclosure, is not a consequence of the unique physicochemical properties of CNTs but is a more generalizable phenomenon that can likely be extended to a range of other materials.

Thus, a key question is why are the mats created on the inner surface of the hollow fiber membranes stable to aggressive backwashing, while mats deposited either on flat sheet membranes or on the outer surface of hollow fiber membranes are easily removed by the most simple backwashing steps. As a first step toward rationalizing this phenomenon it is constructive to consider the stresses that mats experience during backwashing as a result of the water pressure. Based on the SEM images shown in FIG. 5 the CNT mats can be considered as a thin walled cylinder since their thickness is less than 1/20 of their diameter. As stated previously by Brinket *et al.* hollow fibers, and therefore by inference the CNTs mats, will be mainly subjected to radial and circumferential stresses during filtration, although longitudinal stress can be neglected as the fiber is open on one end. During backwashing the greatest stress experienced by a mat loaded on the outer surface of fiber is tensile hoop stress which exerts a force that tries to expand the material. In contrast, a mat created on inner surface of a fiber is subjected to compressive hoop stresses. Thus, the presently disclosed results suggest that the difference in mat stability is related principally to the nature and directionality of stresses that they experience during backwashing (compressive or tensile) with mats being more resistant to compressive as opposed to tensile forces. Indeed, for a given material its compressive strength is generally higher than its tensile strength. Moreover, the magnitude of the stresses experienced by the mat during backwashing depend on the diameter of the mat; CNT mats created on the outer surface will be subjected to higher stress because they exhibit larger diameters than ones created on the inner surface. Thus, both the nature and magnitude of the forces both point towards a greater stability for CNT mats created on the inner surface of hollow fibers and subjected to outside-in backwashing. Further theoretical studies and computational modeling will be necessary to fully explore the reasons for the mat's stability.

6 Implications for Future Research and Membrane Applications

The presently disclosed subject matter demonstrates that hydraulically stable CNT mats, i.e., CNT mats that are backwashable, can be generated using a simple preparative method on the inner surfaces of hollow fiber membranes, in sharp contrast to the instability of CNT mats deposited either on flat sheet membranes or on the outer surface of the hollow fiber membranes. C.F. DeLannoy, et al., J. Membr. Sci. (2012). Again, without wishing to be bound to any one particular theory, it is thought that the detailed nature of membrane-CNT interactions is not playing a major role in determining the mat's stability, due to an ability to create stable CNT mats on two membranes (HF-PVDF and HF-PES) with very different physicochemical properties (different hydrophilic properties, pore size, chemical composition, and the like).

Instead, it is thought that the hydraulic stability of the CNT mats created on both HF-PVDF and HF-PES membranes is a consequence of the directionality of the forces they are subjected to during backwashing. Thus, for CNT mats adsorbed on the inner surface of a cylindrical HF membrane, the net force exerted on the CNTs by outside-in water flow through the membrane from all directions during backwashing could well be counterbalanced with forces converging to the center of the hollow fiber.

In contrast, mats created on the outer surface of a hollow fiber or on a flat sheet will experience a net pull from the water during backwashing, explaining why the mats become unstable and detach from the membrane surface. To test this hypothesis, the stability of the mats on hollow fiber membranes that possess larger inner diameters can be explored, with the expectation that above a certain critical membrane diameter the mats will become unstable.

The stability of different HF membrane-CNT combinations (e.g., single walled and oxidized multiwalled CNTs) also can be investigated to the extent which the creation of stable CNT mats on the inner surfaces of HFs represents a generalizable phenomenon. In addition to identifying the fundamental physical and chemical reasons for mat stability, the ability of these CNT mats to improve membrane performance can be explored, for example, by comparing longer term antifouling properties, as well as virus and contaminant removal properties of virgin and CNT modified hollow fibers. Related studies can explore the effect of the mat's characteristics including, but not limited to, thickness, type and concentration of CNT, on both hydraulic stability and water purification properties.

The discovery that stable CNT mats can be created on the inner surface of hollow fiber membranes means that other unique properties of CNT mats potentially also can be exploited during routine membrane operation.

Further, the unique ability to pass current through the presently disclosed CNT mats, an attribute which has recently been exploited to destroy viruses and contaminants by redox processes occurring within the mats, also can be explored. C.D. Vecitis, et al., Environ. Sci. Technol. (2011). The presence of a conductive CNT-containing layer at the membrane surface also has been shown to be capable of mitigating the effects of biofouling. K.H. Schoenbach, et al., IEEE Trans. Plasma Sci. (1997).

Indeed, applications for the presently disclosed stable CNT mats can be envisioned in a wide number of applications, ranging from medical devices to power transfer situations. By measuring changes in conductance during operation, CNT mats also could be used to remotely monitor a membrane's integrity and performance in the field, something that is otherwise difficult to do. It should be noted, however, that these advances and potential applications only apply to hollow fiber membranes being operated in an inside-out mode.

In sum, the presently disclosed subject matter provides a method to generate hydraulically stable, i.e., backwashable, CNT mats on the inner surface of polymeric hollow fiber membranes. The presently disclosed methods involve filtering a CNT suspension through a hollow fiber membrane operating in dead-end mode from the inside-out. The CNT mats do not significantly change the base membranes' permeability, although one attribute is their ability to withstand backwashing, including long term backwashing and hydraulic stress with Milli-Q water and chemical cleaning. On average, the CNT mats lost < 1% of their initial mass during these backwashing steps as measured by UV-Vis, while the mat's stability was confirmed visually by cross-sectional SEM images taken before and after backwashing.

The surprising stability of the presently disclosed CNT mats is in marked contrast to the hydraulic instability of CNT mats created on the outer surface of hollow fiber membranes or on flat sheet membranes toward even the simplest and least aggressive backwash steps. The potential for the presently disclosed CNT mats to enhance hollow fiber membrane performance characteristics is highlighted by their ability to sustainably improve the anti-fouling resistance of HF-PVDF membranes, through several filtration/cleaning steps. The presently disclosed results open the door to the practical implementation of CNT mats into real world membrane applications, with the potential to improve anti-fouling resistance, as well as contaminant and virus removal capabilities of hollow fiber membranes.

REFERENCES

All publications, patent applications, patents, and other references mentioned in the specification are indicative of the level of those skilled in the art to which the presently disclosed subject matter pertains. All publications, patent applications, patents, and other references are herein incorporated by reference to the same extent as if each individual publication, patent application, patent, and other reference was specifically and individually indicated to be incorporated by reference. It will be understood that, although a number of patent applications, patents, and other references are referred to herein, such reference does not constitute an admission that any of these documents forms part of the common general knowledge in the art.

J.M. Schnorr, T.M. Swager, Emerging Applications of Carbon Nanotubes. Chem. Mater. 23 (2010) 646–657.

M. Paradise, T. Goswami, Carbon nanotubes – Production and industrial applications. Materials and Design 28 (2007) 1477–1489.

S. R. Corrie, R. Vogel, I. Keen, K. Jack, D. Kozak, G. Lawrie, B.J. Battersby, P. Fredericks, M. Trau. A Structural Study of Hybrid Organosilica Materials for Colloid-based DNA Biosensors. Journal of Materials Chemistry 18 (2008) 523-529.

N. Savage, M.S. Diallo. Nanomaterials and Water Purification: Opportunities and Challenges. Journal of Nanoparticle Research 7 (2005) 331-342.

M.R. Wiesner. Responsible Development of Nanotechnologies for Water and Wastewater Treatment. Water Sci. Technol. 53 (2006) 45-51.

X. Ren, C. Chen, M. Nagatsu, X. Wang. Carbon nanotubes as adsorbents in environmental pollution management: A review. Chemical Engineering Journal 170 (2011) 395–410.

A.V. Herrera-Herrera, M.Á. González-Curbelo, J. Hernández-Borges, M.Á. Rodríguez-Delgado. Carbon nanotubes applications in separation science: A review. Analytica Chimica Acta 734 (2012) 1–30.

B. Karn, T. Kuiken, M. Otto. "Nanotechnology and In Situ Remediation: A review of the benefits and potential risks". Environmental Health Perspectives 117 (2009) 1823-1831.

T.C. Zhang, R.Y. Surampalli, K.C.K. Lai, Z. Hu, R.D. Tyagi, I.M.C. Lo. Nanotechnologies for water environment applications. American Society of Civil Engineers: Reston, VA, (2009).

N. Savage, M.S. Diallo. "Nanomaterials and Water Purification: Opportunities and Challenges". Journal of Nanoparticle Research 7 (2005), 331-342.

C. Lu, H. Chiu. "Adsorption of Zinc(II) from Water with Purified Carbon Nanotubes". Chem. Eng. Sci. 61 (2006) 1138-1145.

Y.-H. Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu. "Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes". Carbon 41 (2003) 1057-1062.

C. Chen, X. Wang, "Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes". Ind. Eng. Chem. Res. 45 (2006) 9144-9149.

H.H. Cho, B.A. Smith, J.D. Wnuk, D.H. Fairbrother, W. P. Ball. "Influence of Surface Oxides on the Adsorption of Naphthalene onto Multiwalled Carbon Nanotubes". Environmental Science and Technology 42 (2008), 2899-2905.

H.H. Cho, K. Wepasnick, B.A. Smith, F.K. Bangash, D.H. Fairbrother, W.P. Ball. "Sorption of Aqueous Zn[II] and Cd[II] by Multiwall Carbon Nanotubes: The Relative Roles of Oxygen-Containing Functional Groups and Graphenic Carbon". Langmuir 26 (2010) 967-981.

H. Li, X. Gui, L. Zhang, S. Wang, C. Ji, J. Wei, K. Wang, H. Zhu, D. Wu, A. Cao, Carbon nanotube sponge filters for trapping nanoparticles and dye molecules from water, Chem. Commun. (Cambridge, U.K.) 46 (2010) 7966–7968.

J. Heo, L. Joseph, Y. Yoon, Y.G. Park, N. Her, J. Sohn, S.H. Yoon, Removal of micropollutants and NOM in carbon nanotube-UF membrane system from seawater, Water Sci.Technol. 63 (2011) 2737–2744.

C.D. Vecitis, G. Gao, H. Liu, Electrochemical Carbon Nanotube Filter for Adsorption, Desorption, and Oxidation of Aqueous Dyes and Anions, J. Phys. Chem. C 115 (2011) 3621–3629.

T. Mohammadi, M.A. Tofighy, Adsorption of divalent heavy metal ions from water using carbon nanotube sheets, J. Hazard. Mater. 185 (2011) 140–147.

O. Moradi, The Removal of Ions by Functionalized Carbon Nanotube: Equilibrium, Isotherms and Thermodynamic Studies, Chem. Biochem. Eng. Q. 25 (2011) 229–240.

D.S. Su, Y.J. Xu, R. Arrigo, X. Liu, Characterization and use of functionalized carbon nanotubes for the adsorption of heavy metal anions, New Carbon Mater. 26 (2011) 57–62.

O. Moradi, K. Zare, M. Monajjemi, M. Yari, H. Aghaie, The Studies of Equilibrium and Thermodynamic Adsorption of Pb(II), Cd(II) and Cu(II) Ions from Aqueous Solution onto SWCNTs and SWCNT-COOH Surfaces, Fullerenes, Nanotubes, Carbon Nanostruct. 18 (2010) 285–302.

X.K. Wang, C.L. Chen, J. Hu, D.D. Shao, J.X. Li, Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II), J. Hazard.Mater. 164 (2009) 923–928.

A.S. Brady-Estévez, T.H. Nguyen, L. Gutierrez, M. Elimelech, Impact of solution chemistry on viral removal by a single-walled carbon nanotube filter, Water Res. 44 (2010) 3773–3780.

S.T. Mostafavi, M.R. Mehrnia, A.M. Rashidi, Preparation of nanofilter from carbon nanotubes for application in virus removal from water, Desalination 238 (2009) 271–280.

S. Kang, M.S. Mauter, M. Elimelech, Single walled carbon nanotubes exhibit strong antimicrobial activity, Environ. Sci. Technol. 43 (2009) 2648–2653.

C.D. Vecitis, M.H. Schnoor, M.S. Rahaman, J.D. Schiffman, M. Elimelech, Electrochemical Multiwalled Carbon Nanotube Filter for Viral and Bacterial Removal and Inactivation, Environ. Sci. Technol. 45 (2011) 3672–3679.

C.D. Vecitis, G.D. Gao, H. Liu, Electrochemical Carbon Nanotube Filter for Adsorption, Desorption, and Oxidation of Aqueous Dyes and Anions, J. Phys. Chem. C 115 (2001) 3621–3629.

A. Tiraferri, C.D. Vecitis, M. Elimelech, Covalent Binding of Single-Walled Carbon Nanotubes to Polyamide Membranes for Antimicrobial Surface Properties, ACS Appl. Mater. Interfaces 3 (2011) 2869–2877.

M.S. Rahaman, C.D. Vecitis, M. Elimelech, Electrochemical Carbon-Nanotube Filter Performance toward Virus Removal and Inactivation in the Presence of Natural Organic Matter, Environ. Sci.Technol. 46 (2012) 1556–1564.

H. Liu, C.D. Vecitis, Reactive Transport Mechanism for Organic Oxidation during Electrochemical Filtration: Mass-Transfer, Physical Adsorption, and Electron-Transfer, J. Phys. Chem. C 116 (2012) 374–383.

G.D. Gao, C.D. Vecitis, Doped Carbon Nanotube Networks for Electrochemical Filtration of Aqueous Phenol: Electrolyte Precipitation and Phenol Polymerization, ACS Appl. Mater. Interfaces 4 (2012) 1478–1489.

G. Gao, C.D. Vecitis, Electrochemical Carbon Nanotube Filter Oxidative Performance as a Function of Surface Chemistry, Environ. Sci. Technol. 45 (2011) 9726–9734.

G.S. Ajmani, D. Goodwin, K. Marsh, D.H. Fairbrother, K.J. Schwab, J.G. Jacangelo, H. Huang, Modification of low pressure membranes with carbon nanotube layers for fouling control, Water Res, 46 (2012) 5645–5654.

J.S. Baker, L.Y. Dudley, Biofouling in membrane systems - A review, Desalination 118 (1998) 81–90.

A. Subramani, E.M.V. Hoek, Biofilm formation, cleaning, re-formation on polyamide composite membranes, Desalination 257 (2010) 73–79.

"The Project on Emerging Nanotechnologies; Woodrow Wilson International Center for Scholars."

J.K. Holt, H.G. Park, Y.M. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, Science 312 (2006) 1034–1037.

E. Celik, H. Park, H. Choi, H. Choi, Carbon nanotube blended polyethersulfonemembranes for fouling control in water treatment, Water Res. 45 (2011) 274–282.

X. Chen, L. Hong, Y. Xu, Z.W. Ong, Ceramic Pore Channels with Inducted Carbon Nanotubes for Removing Oil from Water, ACS Appl. Mater. Interfaces 4 (2012) 1909–1918.

H.A. Shawky, S.R. Chae, S.H. Lin, M. Wiesner, Synthesis and characterization of a carbon nanotube/polymer nanocomposite membrane for water treatment, Desalination 272 (2011) 46–50.

H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multi-walled carbon nanotubes/polymer composite, J. Membr. Sci. 362 (2010) 374–383.

E. Celik, L. Liu, H. Choi, Protein fouling behavior of carbon nanotube/polyethersulfone composite membranes during water filtration, Water Res. 45 (2011) 5287–5294.

C.F. DeLannoy, D. Jassby, D.D. David, M. Wiesner, A highly electrically conductive polymer-multiwalled carbon nanotube nanocomposite membrane, J. Membr. Sci. 415–516 (2012) 718–724.

A. Deneuve, K. Wang, I. Janowska, K. Chizari, D. Edouard, O. Ersen, M.-J. Ledoux, C. Pham-Huu, Bucky paper with improved mechanical stability made from vertically aligned carbon nanotubes for desulfurization process, Appl. Catal., A 400 (2011) 230–237.

D. Furukawa, A Global Perspective of Low Pressure Membranes, National Water Research Institute, Fountain Valley, California, 2008.

S. Steiner, S. Busato, P. Ermanni, Mechanical properties and morphology of papers prepared from single-walled carbon nanotubes functionalized with aromatic amides, Carbon 50 (2012) 1713–1719.

G.P. Westerhoff, M.A. Thompson, J.C. Vickers, Experiences in the application of microfiltration and ultrafiltration membrane technology in drinking-water treatment, Water Supply 14 (1996) 482–486.

K. Majewska-Nowak, I. Kowalska, M. Kabsch-Korbutowicz, Ultrafiltration of aqueous solutions containing a mixture of dye and surfactant, Desalination 198 (2006) 149–157.

H. Huang, K. Schwab, J.G. Jacangelo, Pretreatment for Low Pressure Membranes in Water Treatment: A Review, Environ. Sci. Technol. 43 (2009) 3011–3019.

C. Jucker, M.M. Clark, Adsorption of Aquatic Humic Substances on Hydrophobic Ultrafiltration Membranes, J. Membr. Sci.97 (1994) 37–52.

G. Amy, J. Cho, Interactions between natural organic matter (NOM) and membranes: Rejection and fouling, Water Sci. Technol. 40 (1999) 131–139.

H. Huang, N. Lee, T. Young, G. Amy, J.C. Lozier, J.G. Jacangelo, Natural organic matter fouling of low-pressure, hollow-fiber membranes: Effects of NOM source and hydrodynamic conditions, Water Res. 41 (2007) 3823–3832.

E. Filloux, H. Gallard, J.-P. Croue, Identification of effluent organic matter fractions responsible for low-pressure membrane fouling, Water Res. 46 (2012) 5531–5540.

B. Smith, K. Wepasnick, K.E. Schrote, A.R. Bertele, W.P. Ball, C. O'Melia, D.H. Fairbrother, Colloidal Properties of Aqueous Suspensions of Acid-Treated, Multi-Walled Carbon Nanotubes, Environ. Sci. Technol. 43 (2009) 819–825.

N. Her, G. Amy, H.-R. Park, M. Song, Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling, Water Res. 38 (2004) 1427–1438.

W.-Y. Ahn, A.G. Kalinichev, M.M. Clark, Effects of background cations on the fouling of polyethersulfone membranes by natural organic matter: Experimental and molecular modeling study, J. Membr. Sci. (2008) 128–140.

Y. Ye, P. Le Clech, V. Chen, A.G. Fane, B. Jefferson, Fouling mechanisms of alginate solutions as model extracellular polymeric substances, Desalination 175 (2005) 7–20.

K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, Experimental study of ultrafiltration membrane fouling by sodium alginate and flux recovery by backwashing, J. Membr. Sci. 300 (2007) 137–146.

A.-S. Jönsson, B. Jönsson, The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes, J. Membr. Sci. 56 (1991) 49–76.

J. M. Wörle-Knirsch, K. Pulskamp, H.F. Krug, Oops They Did It Again! Carbon Nanotubes Hoax Scientists in Viability Assays, Nano Lett. 6 (2006) 1261–1268.

M.A. Chappell, , A.J. George, K.M. Dontsova, B.E. Porter, C.L. Price, P. Zhou, E. Morikawa, A.J. Kennedy, J.A. Steevens, Surfactive stabilization of multi-walled carbon nanotube dispersions with dissolved humic substances, Environ. Pollut. (Oxford, U.K.) 157 (2009) 1081–1087.

K.H. Schoenbach, F.E. Peterkin, R.W. Alden, S.J. Beebe III, The effect of pulsed electric fields on biological cells: experiments and applications, IEEE Trans. Plasma Sci. 25 (1997) 284–292.

X. Yang, J.Lee, L.Yuan,S.-R.Chae,V.K.Peterson,A.I.Minett, Removal of natural organic matter in water using functionalized carbon nanotube buckypaper, Carbon. 59(2013)160–166.

Although the foregoing subject matter has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be understood by those skilled in the art that certain changes and modifications can be practiced within the scope of the appended claims.

THAT WHICH IS CLAIMED:

1. A method for preparing a carbon mat on an inner surface of a polymeric hollow fiber membrane, the method comprising:

(a) providing a plurality of carbon nanotubes and/or carbon particles;

(b) suspending the plurality of carbon nanotubes and/or carbon particles in a solution to form a suspension of carbon nanotubes and/or carbon particles;

(c) providing one or more polymeric hollow fiber membranes, wherein the one or more polymeric hollow fiber membranes have at least one open end in fluid communication with a lumen, and wherein the lumen defines an inner surface of the one or more polymeric hollow fiber membranes;

(d) dispensing the suspension of carbon nanotubes and/or carbon particles in the at least one open end of the one or more polymeric hollow fiber membranes; and

(e) filtering the suspension of carbon nanotubes and/or carbon particles through the one or more polymeric hollow fiber membranes operating in dead-end mode from the inside-out to deposit a carbon mat on an inner surface of a polymeric hollow fiber membrane.

2. The method of claim 1, wherein the carbon particles comprise powdered activated carbon particles.

3. The method of claim 1, wherein the plurality of carbon nanotubes comprise multi-walled carbon nanotubes.

4. The method of claim 1, wherein the plurality of carbon nanotubes comprise single-walled carbon nanotubes.

5. The method of claim 1, wherein the plurality of carbon nanotubes have a diameter from about 50 nm to about 80 nm.

6. The method of claim 1, wherein the plurality of carbon nanotubes have a length from about 10 μm to about 20 μm.

7. The method of claim 1, wherein the plurality of carbon nanotubes have a specific surface area of about 60 m^2 g^{-1}.

8. The method of claim 1, wherein the plurality of carbon nanotubes comprise unfunctionalized carbon nanotubes.

9. The method of claim 1, wherein the solution comprises an aqueous solution.

10. The method of claim 9, wherein the aqueous solution comprises a non-ionic surfactant.

11. The method of claim 1, further comprising sonicating the solution of carbon nanotubes for a period of time.

12. The method of claim 1, wherein the one or polymeric hollow fiber membranes are hydrophilic.

13. The method of claim 1, wherein the one or more hydrophilic polymeric hollow fiber membranes comprise polyether sulfone (PES).

14. The method of claim 13, wherein the one or more polymeric hollow fiber membranes have a nominal pore size of about 0.03 μm.

15. The method of claim 13, wherein the one or more polymeric hollow fiber membranes are capable of sustaining a maximum flux of pure water flux of about 1200 ± 120 L h^{-1} m^{-2} bar^{-1}.

16. The method of claim 1, wherein the one or more polymeric hollow fiber membranes are hydrophobic.

17. The method of claim 14, wherein the one or more polymeric hollow fiber membranes comprise polyvinylidene fluoride (PVDF).

18. The method of claim 17, wherein the one or more polymeric hollow fiber membranes have a nominal pore size of about 0.1 μm.

19. The method of claim 17, wherein the one or more polymeric hollow fiber membranes are capable of sustaining a maximum flux of pure water of about 655 ± 85 L h^{-1} m^{-2} bar^{-1}.

20. A carbon nanotube mat on an inner surface of a polymeric hollow fiber membrane prepared by the method of claim 1.

21. A polymeric hollow fiber membrane having a carbon nanotube mat deposited on an inner surface thereof.

22. The polymeric hollow fiber membrane of claim 21, wherein the polymeric hollow fiber membrane comprises a polymer selected from the group consisting of a hydrophilic polymer and a hydrophobic polymer.

23. The polymeric hollow fiber membrane of claim 21, wherein the polymeric hollow fiber membrane comprises a polymer selected from the group consisting of polyether sulfone (PES) and polyvinylidene fluoride (PVDF).

24. The polymeric hollow fiber membrane of claim 21, wherein the carbon nanotube mat comprises a plurality of single-walled carbon nanotubes.

25. The polymeric hollow fiber membrane of claim 21, wherein the carbon nanotube mat comprises a plurality of multi-walled carbon nanotubes.

26. The polymeric hollow fiber membrane of claim 21, comprising a total mass of carbon nanotubes deposited on the inner surface thereof of about 11 g m^{-2}.

27. The polymeric hollow fiber membrane of claim 21, comprising an electrical conductance material.

28. A method for filtering an effluent, the method comprising passing the effluent through a polymeric hollow fiber membrane having a carbon nanotube mat deposited on an inner surface thereof.

29. The method of claim 28, wherein the effluent is selected from the group consisting of water, wastewater, and a biological fluid.

30. The method of claim 29, wherein the biological fluid comprises blood.

31. The method of claim 28, wherein the method further comprises an industrial process.

32. The method of claim 31, wherein the industrial method comprises a process selected from the group consisting of microchip processing and food processing.

33. The method of claim 28, wherein the method further comprises an analytical process.

34. The method of claim 33, wherein the analytical process comprises solid phase microextraction.

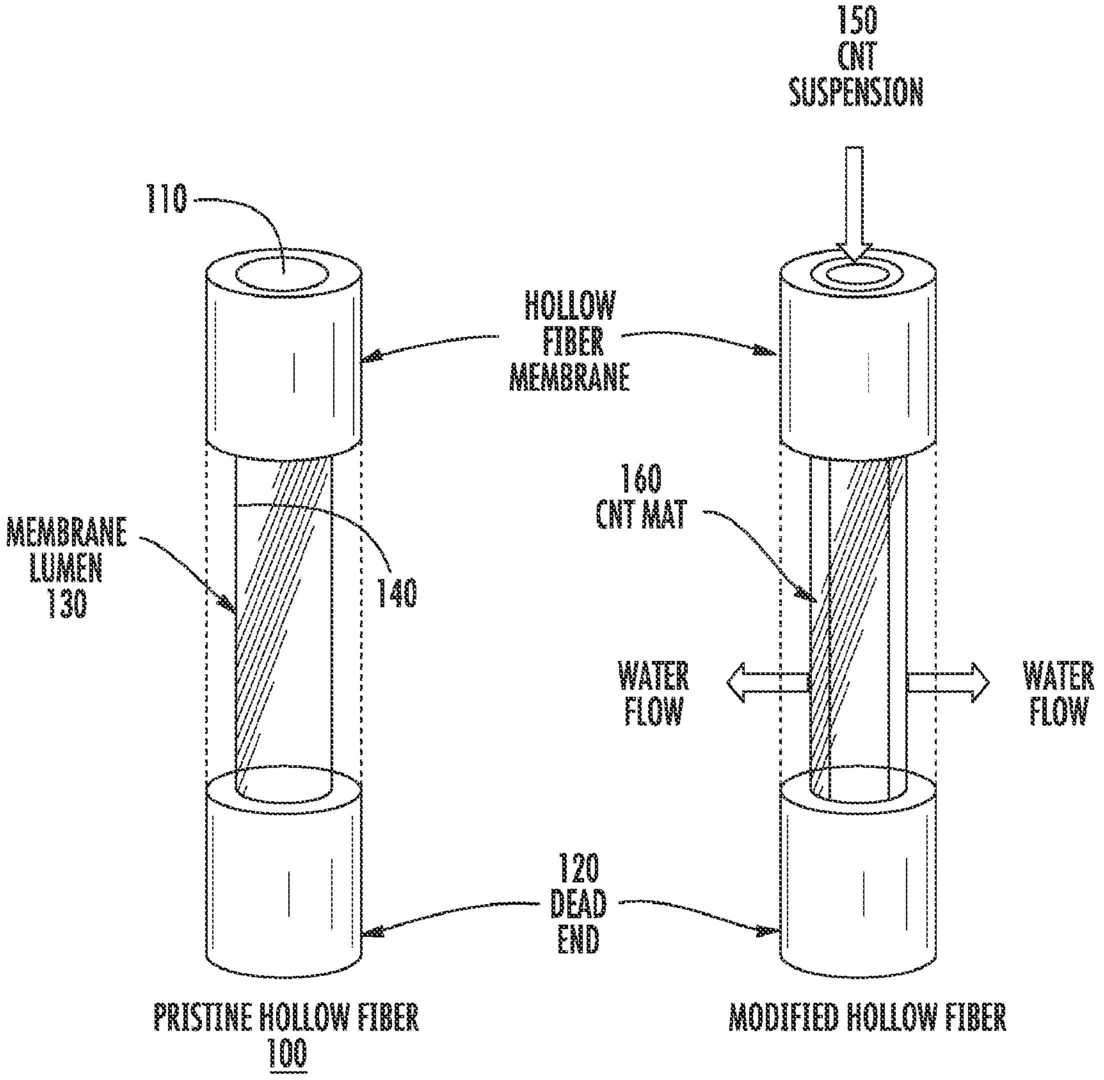
150
CNT
SUSPENSION
110
HOLLOW
FIBER
MEMBRANE
160
CNT MAT
MEMBRANE
LUMEN
130
140
WATER
FLOW
WATER
FLOW
120
DEAD
END
PRISTINE HOLLOW FIBER
100
MODIFIED HOLLOW FIBER

FIG. 1

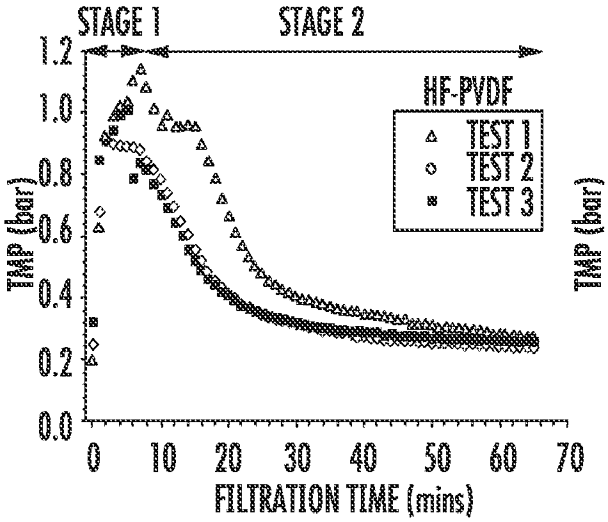
STAGE 1
STAGE 2
HF-PVDF
△ TEST 1
○ TEST 2
▪ TEST 3
TMP (bar)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
10
20
30
40
50
60
70
FILTRATION TIME (mins)

FIG. 2A

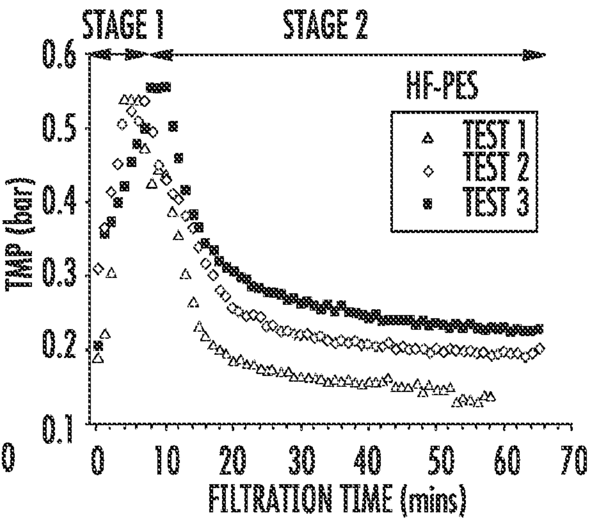
STAGE 1
STAGE 2
HF-PES
△ TEST 1
◇ TEST 2
▪ TEST 3
TMP (bar)
0.1
0.2
0.3
0.4
0.5
0.6
0
10
20
30
40
50
60
70
FILTRATION TIME (mins)

FIG. 2B

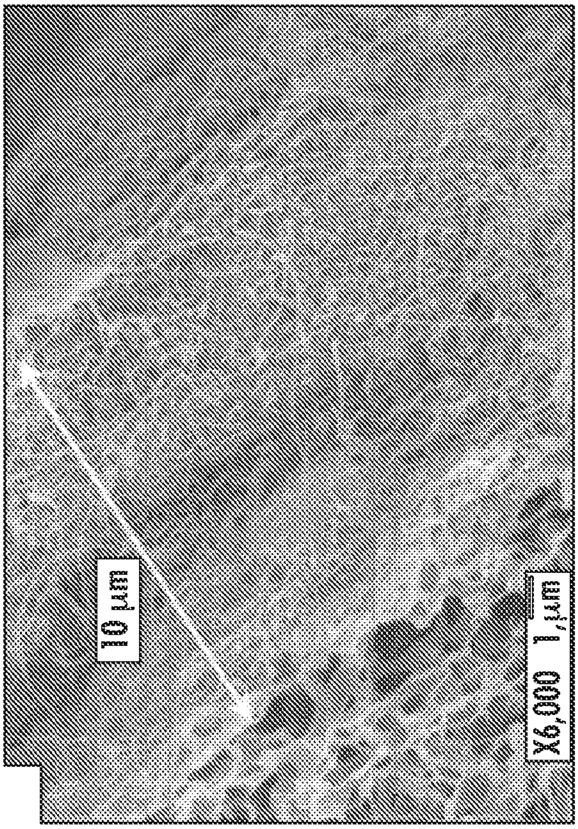

FIG. 3A

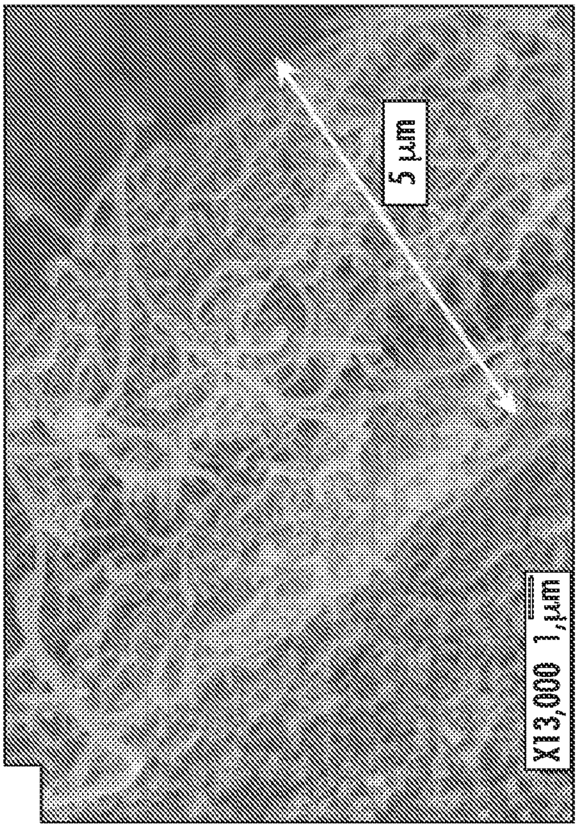

FIG. 3B

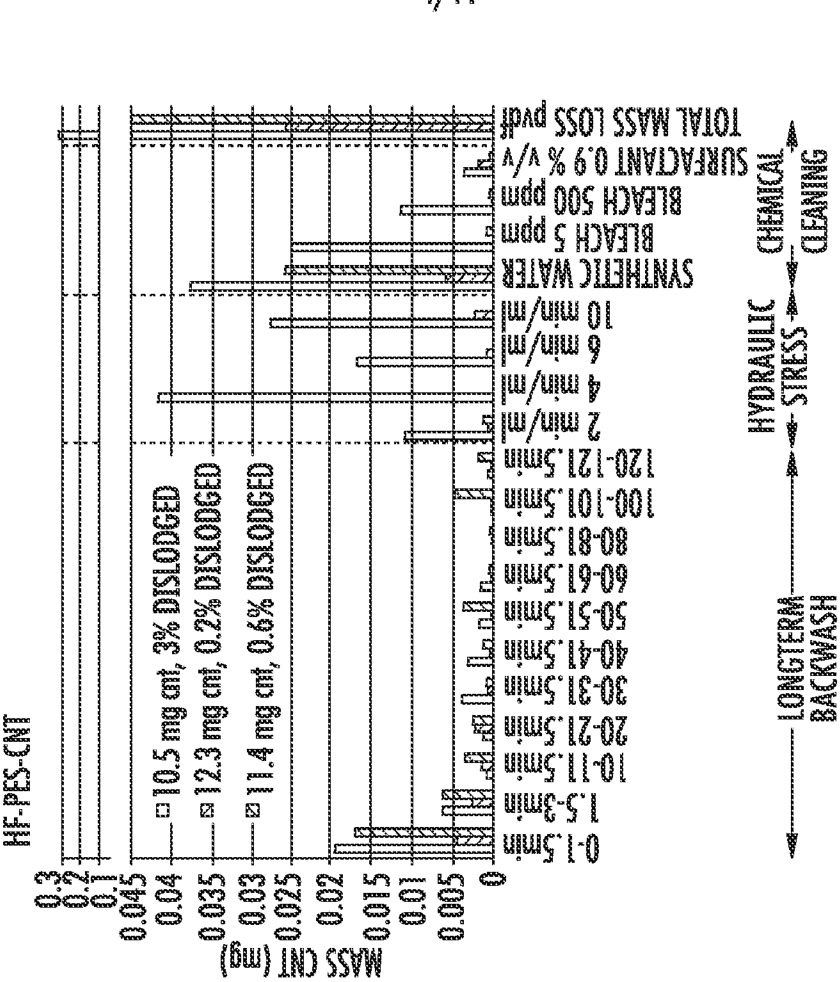
HF-PES-CNT
MASS CNT (mg)
0.3
0.2
0.1
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
□ 10.5 mg cnt, 3% DISLODGED
▨ 12.3 mg cnt, 0.2% DISLODGED
▨ 11.4 mg cnt, 0.6% DISLODGED
0-1.5min
1.5-3min
10-11.5min
20-21.5min
30-31.5min
40-41.5min
50-51.5min
60-61.5min
80-81.5min
100-101.5min
120-121.5min
2 min/ml
4 min/ml
6 min/ml
10 min/ml
SYNTHETIC WATER
BLEACH 5 ppm
BLEACH 500 ppm
SURFACTANT 0.9 % v/v
TOTAL MASS LOSS pvdf
LONGTERM BACKWASH
HYDRAULIC STRESS
CHEMICAL CLEANING

FIG. 4B

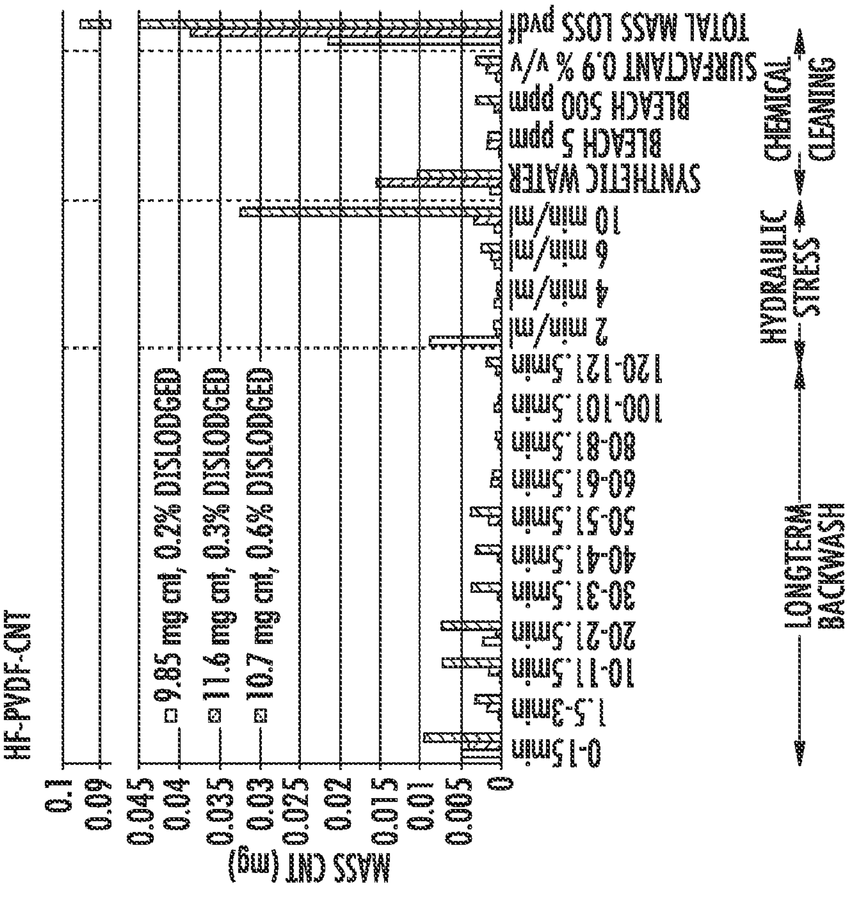
HF-PVDF-CNT
MASS CNT (mg)
0.1
0.09
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
□ 9.85 mg cnt, 0.2% DISLODGED
▨ 11.6 mg cnt, 0.3% DISLODGED
▨ 10.7 mg cnt, 0.6% DISLODGED
0-15min
1.5-3min
10-11.5min
20-21.5min
30-31.5min
40-41.5min
50-51.5min
60-61.5min
80-81.5min
100-101.5min
120-121.5min
2 min/ml
4 min/ml
6 min/ml
10 min/ml
SYNTHETIC WATER
BLEACH 5 ppm
BLEACH 500 ppm
SURFACTANT 0.9 % v/v
TOTAL MASS LOSS pvdf
LONGTERM BACKWASH
HYDRAULIC STRESS
CHEMICAL CLEANING

FIG. 4A

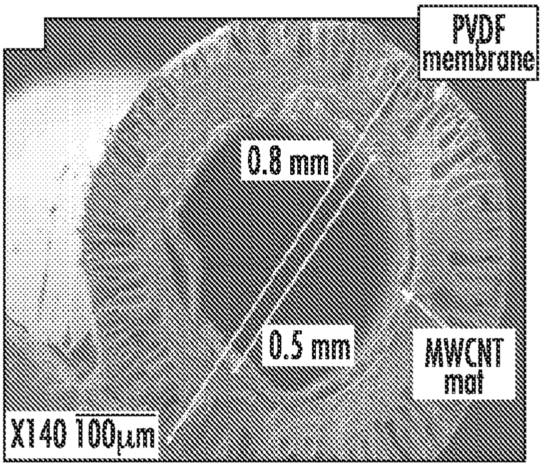

FIG. 5A

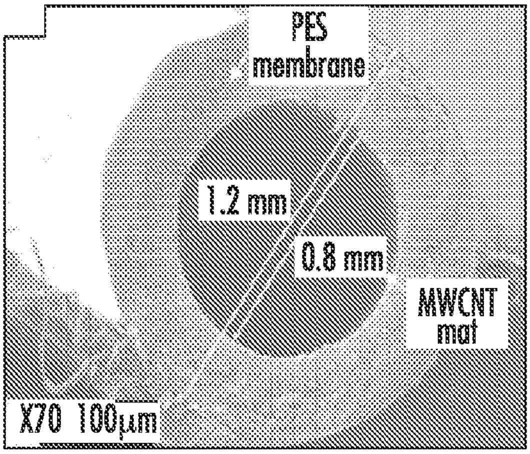

FIG. 5B

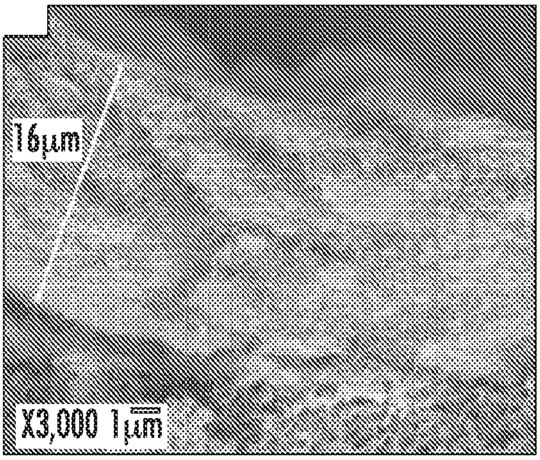

FIG. 5C

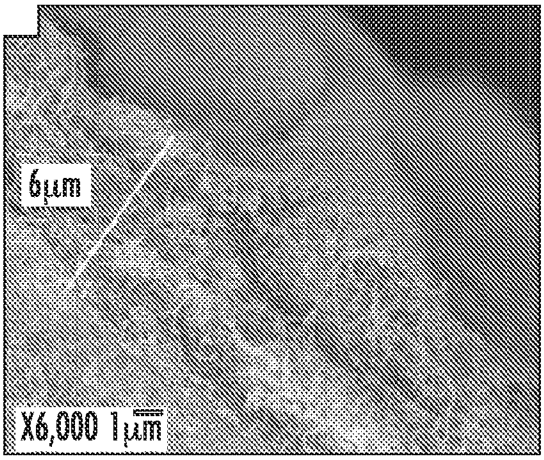

FIG. 5D

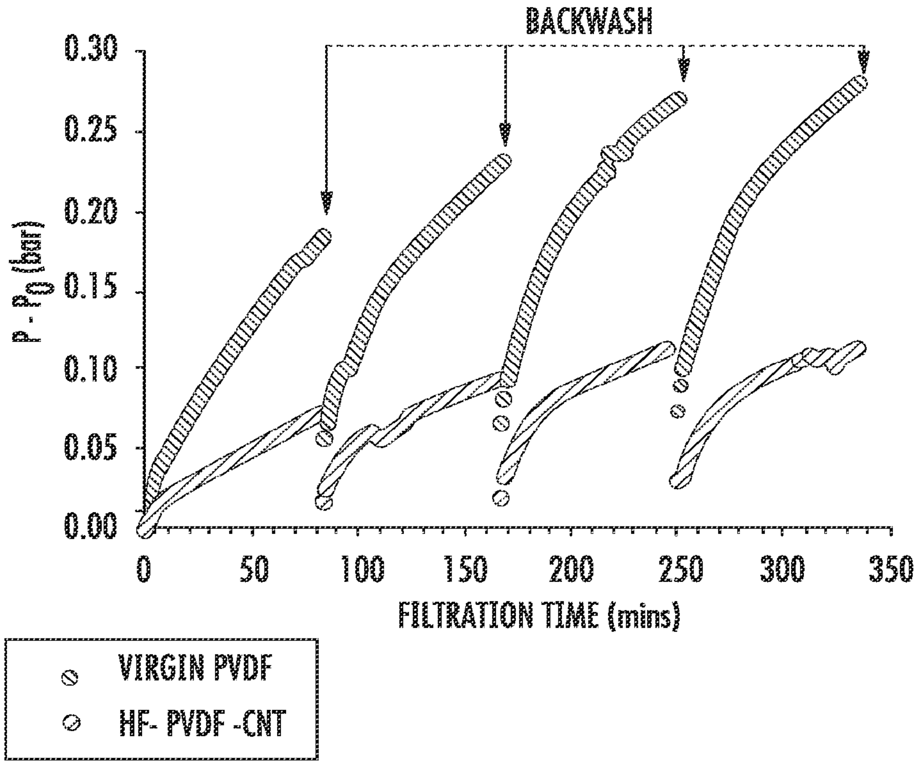
BACKWASH
0.30
0.25
0.20
0.15
0.10
0.05
0.00
P - P0 (bar)
0
50
100
150
200
250
300
350
FILTRATION TIME (mins)
VIRGIN PVDF
HF- PVDF -CNT

FIG. 6A

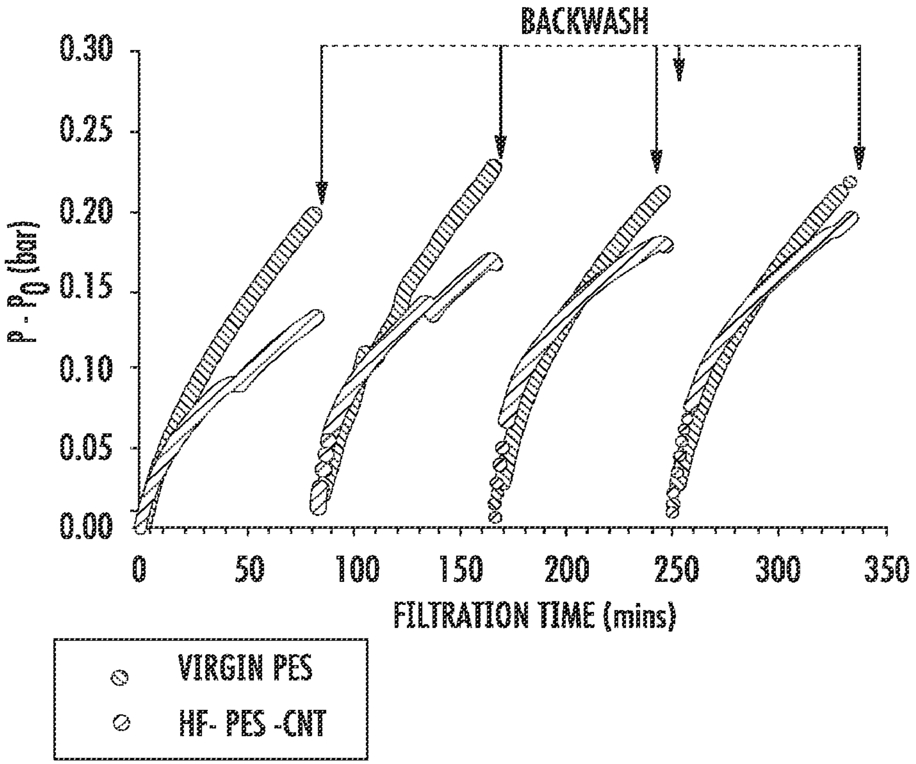
BACKWASH
0.30
0.25
0.20
0.15
0.10
0.05
0.00
P - P0 (bar)
0
50
100
150
200
250
300
350
FILTRATION TIME (mins)
VIRGIN PES
HF- PES -CNT

FIG. 6B

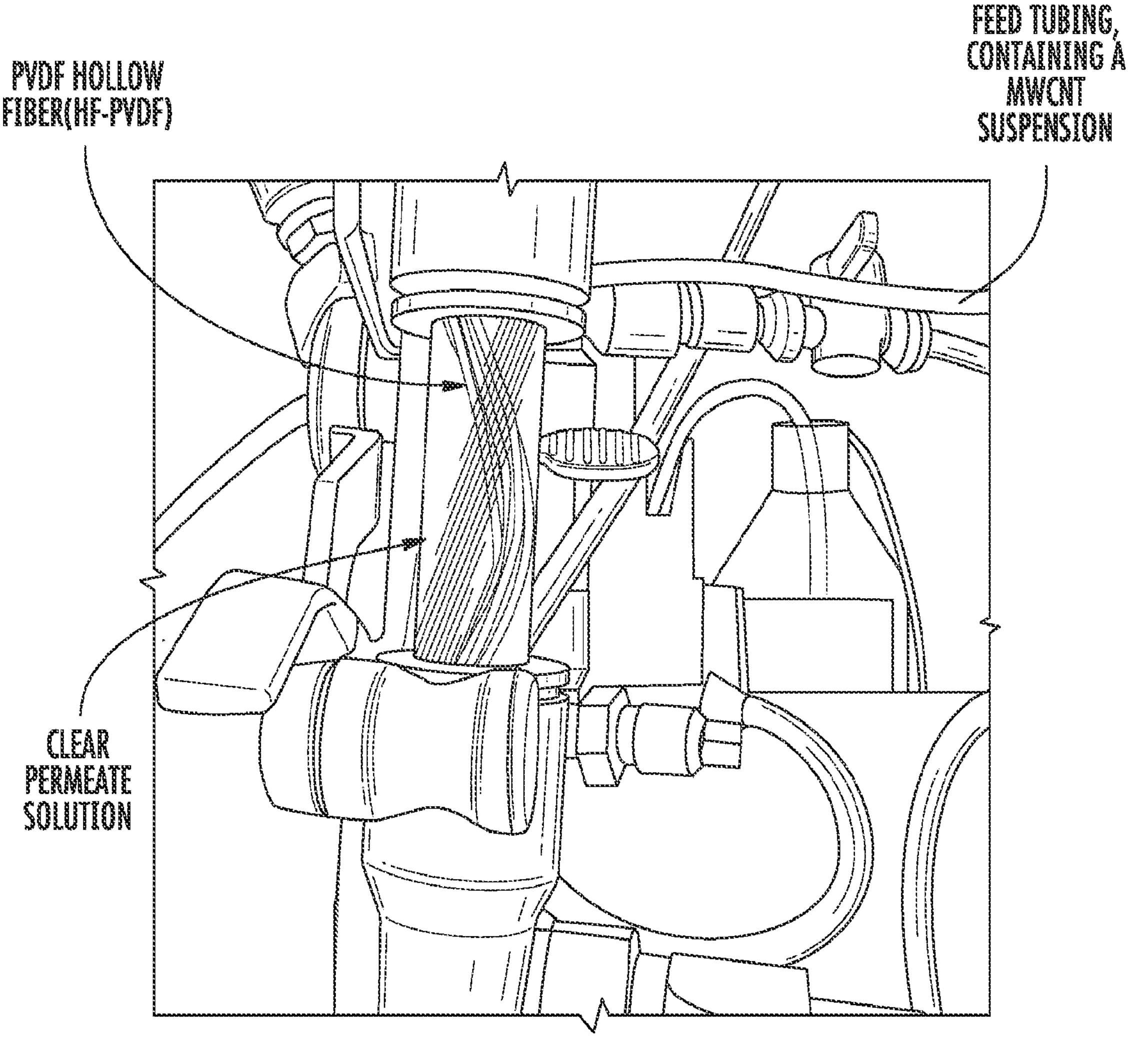
PVDF HOLLOW FIBER(HF-PVDF)
FEED TUBING, CONTAINING A MWCNT SUSPENSION
CLEAR PERMEATE SOLUTION

FIG. 7

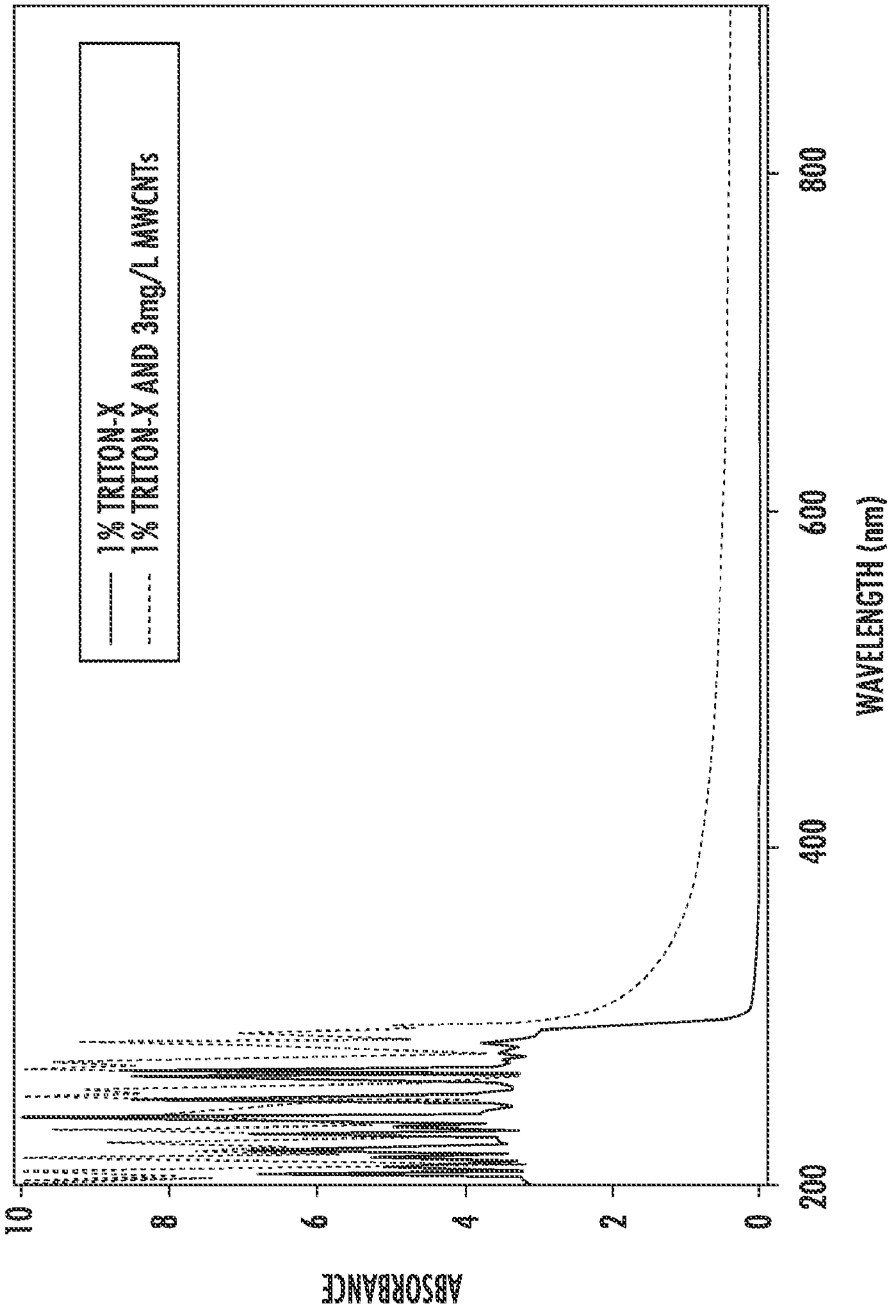
1% TRITON-X
1% TRITON-X AND 3mg/L MWCNTs
ABSORBANCE
0
2
4
6
8
10
WAVELENGTH (nm)
200
400
600
800

FIG. 8

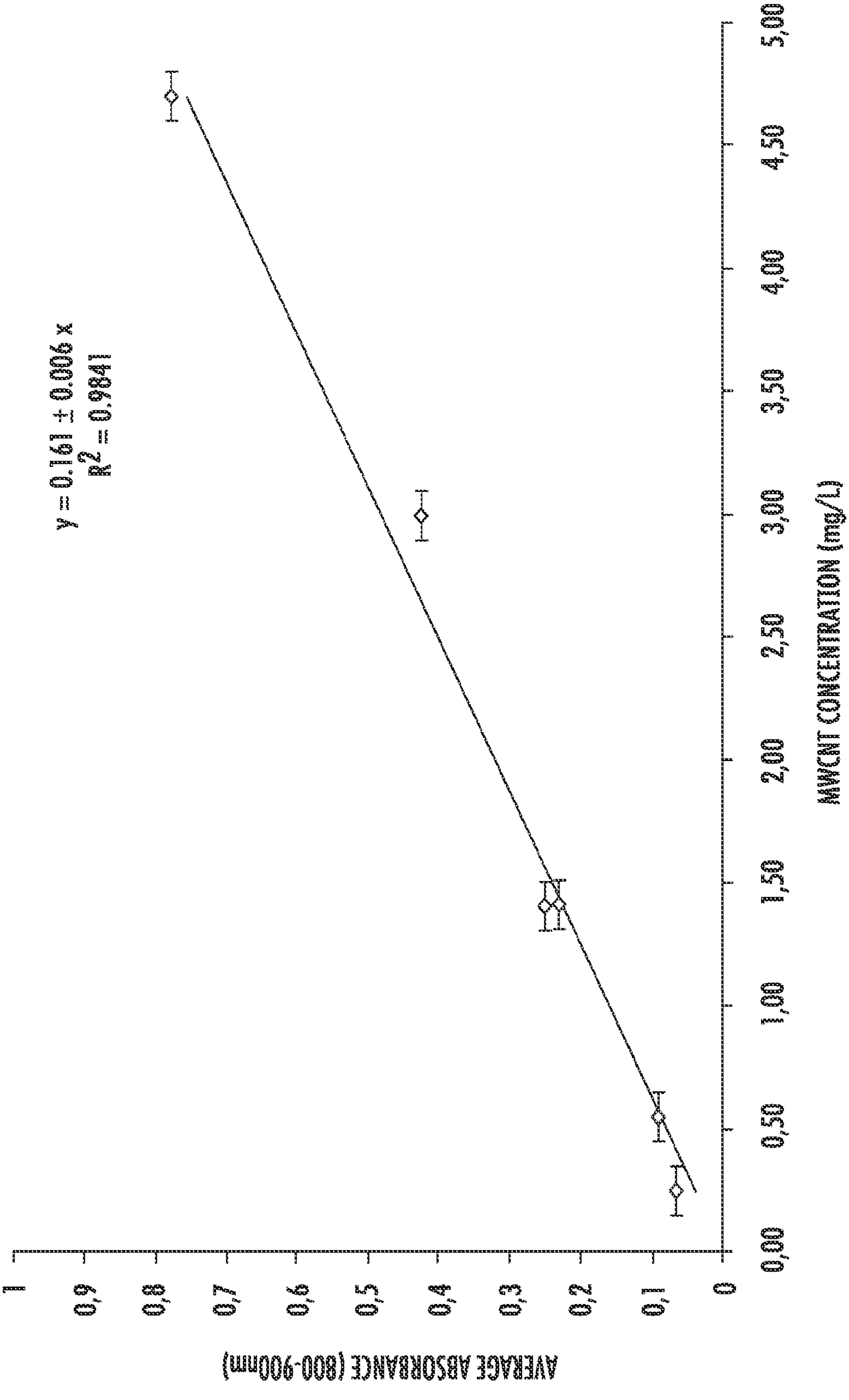
y = 0.161 ± 0.006 x
R2 = 0.9841
AVERAGE ABSORBANCE (800-900nm)
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
MWCNT CONCENTRATION (mg/L)
0,00
0,50
1,00
1,50
2,00
2,50
3,00
3,50
4,00
4,50
5,00

FIG. 9

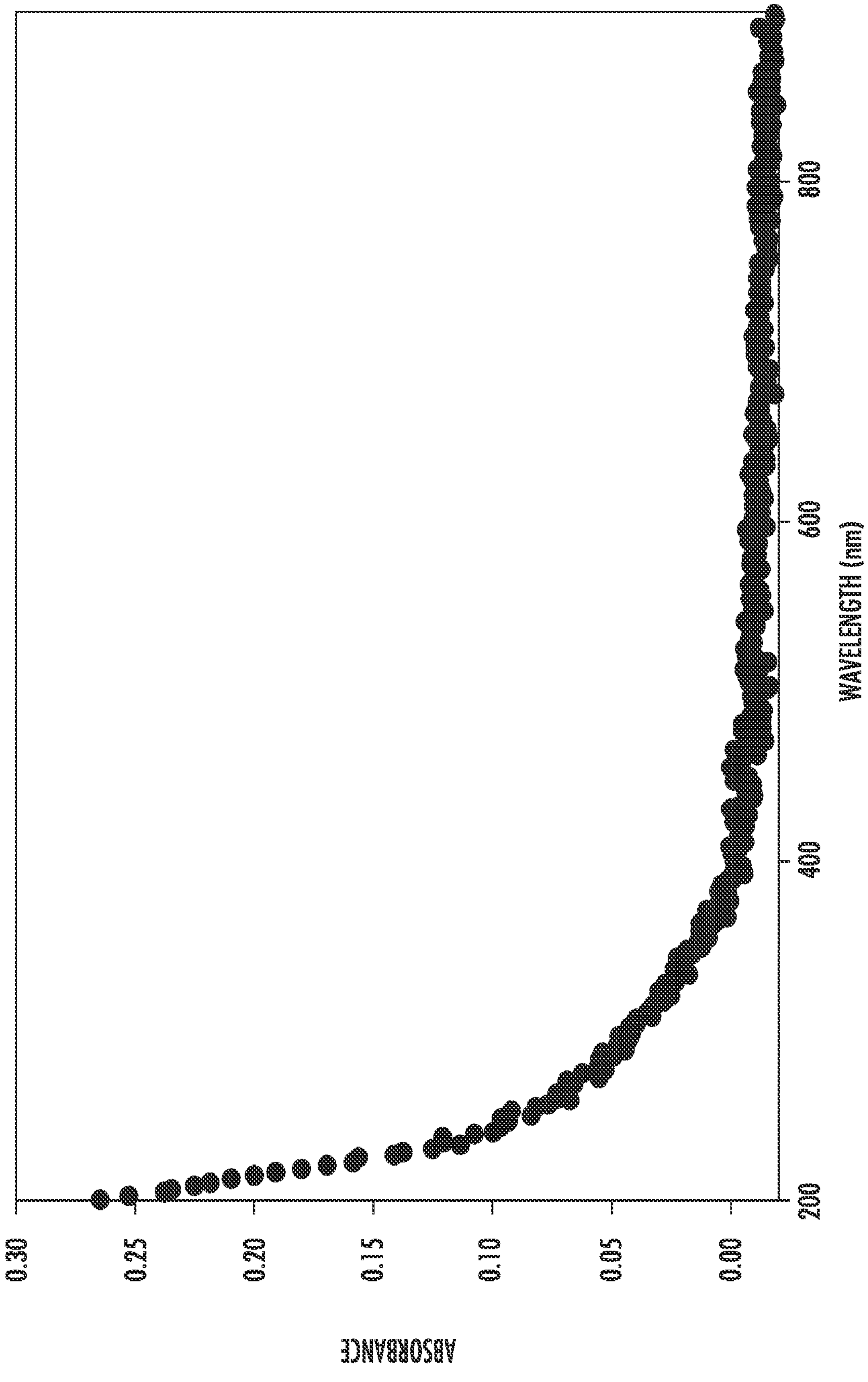
ABSORBANCE
0.30
0.25
0.20
0.15
0.10
0.05
0.00
200
400
600
800
WAVELENGTH (nm)

FIG. 10

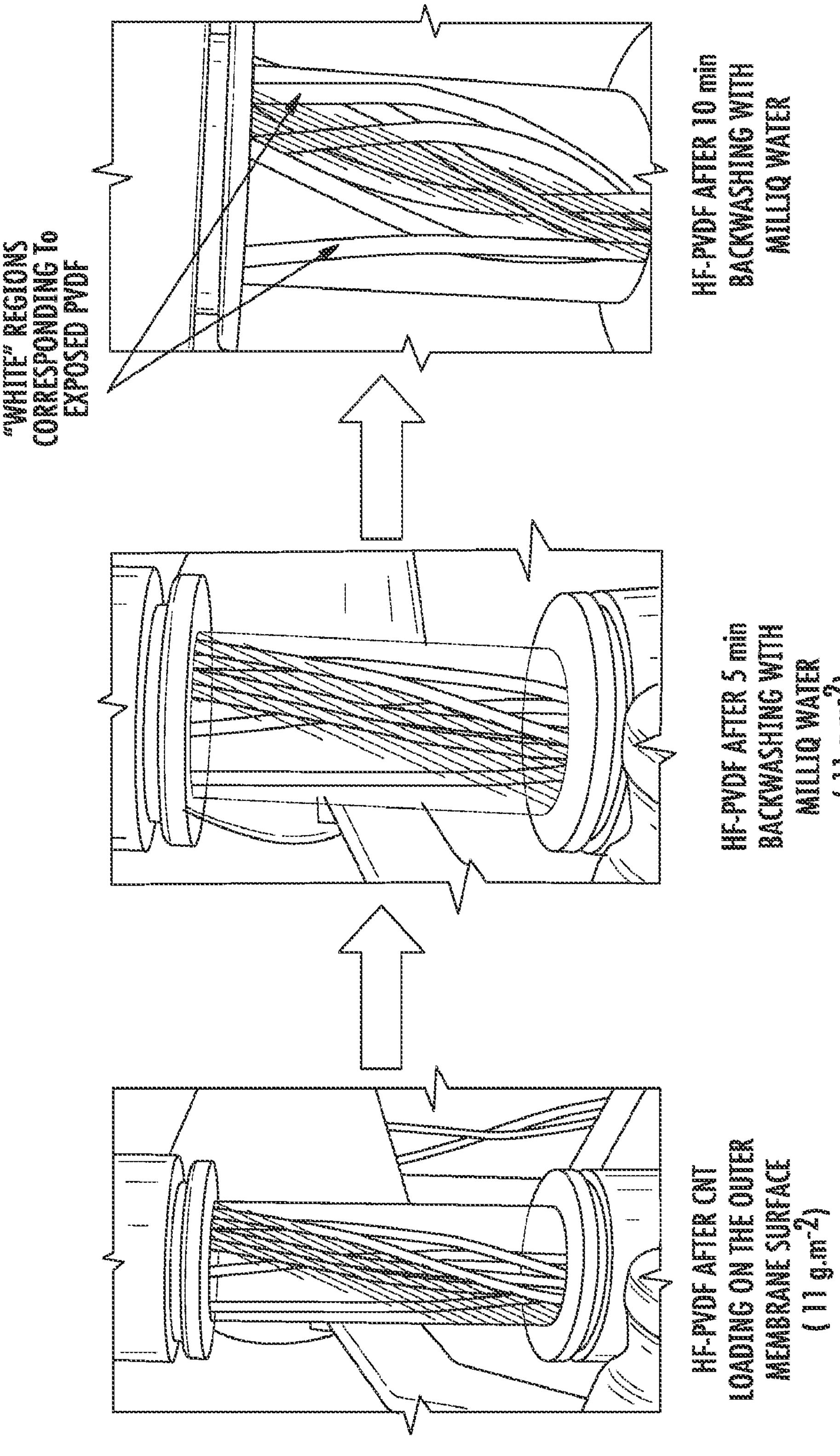
HF-PVDF AFTER CNT LOADING ON THE OUTER MEMBRANE SURFACE (11 g.m^{-2})
HF-PVDF AFTER 5 min BACKWASHING WITH MILLIQ WATER (11 g.m^{-2})
HF-PVDF AFTER 10 min BACKWASHING WITH MILLIQ WATER
"WHITE" REGIONS CORRESPONDING To EXPOSED PVDF

FIG. 11

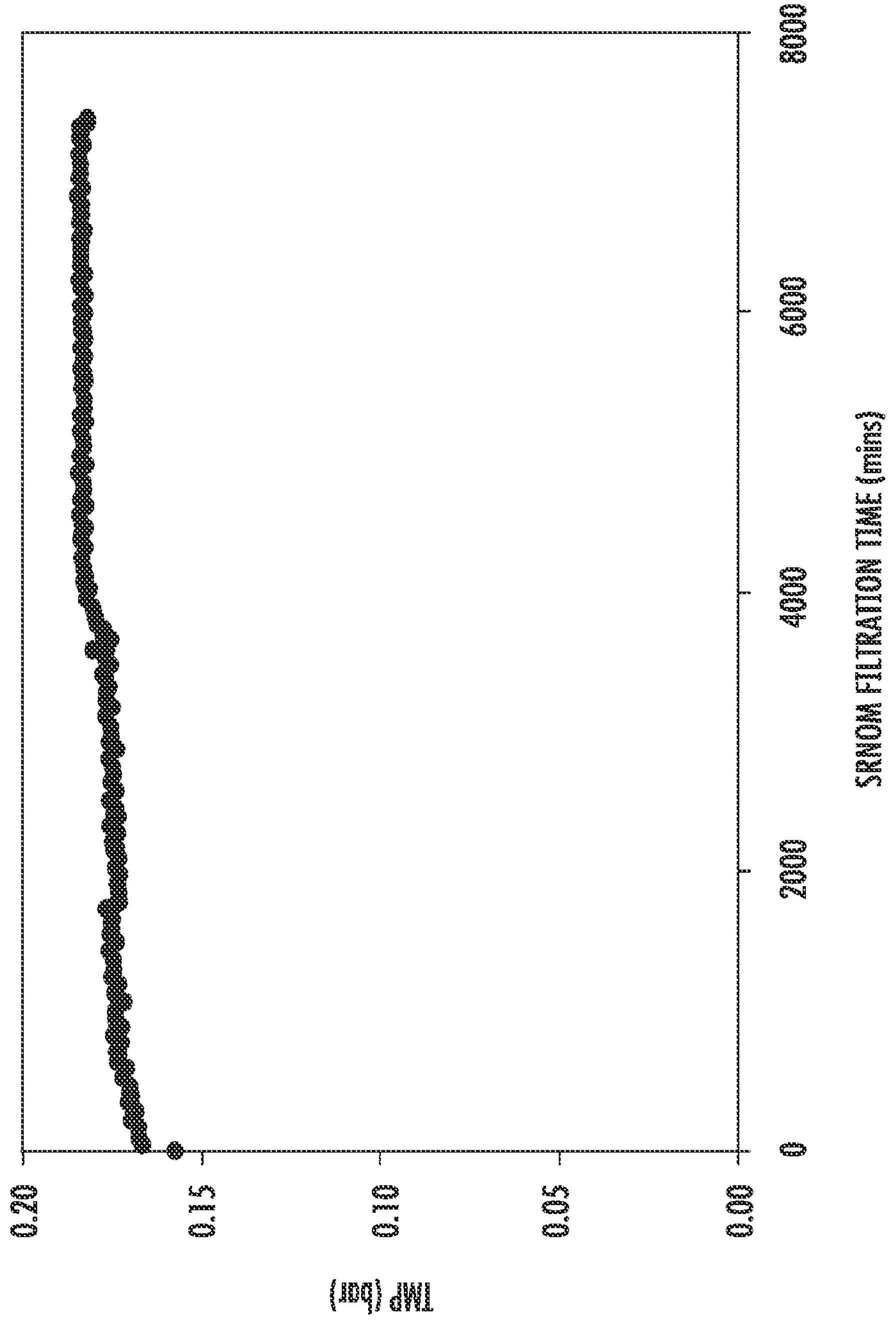
TMP (bar)
0.20
0.15
0.10
0.05
0.00
0
2000
4000
6000
8000
SRNOM FILTRATION TIME (mins)

FIG. 12

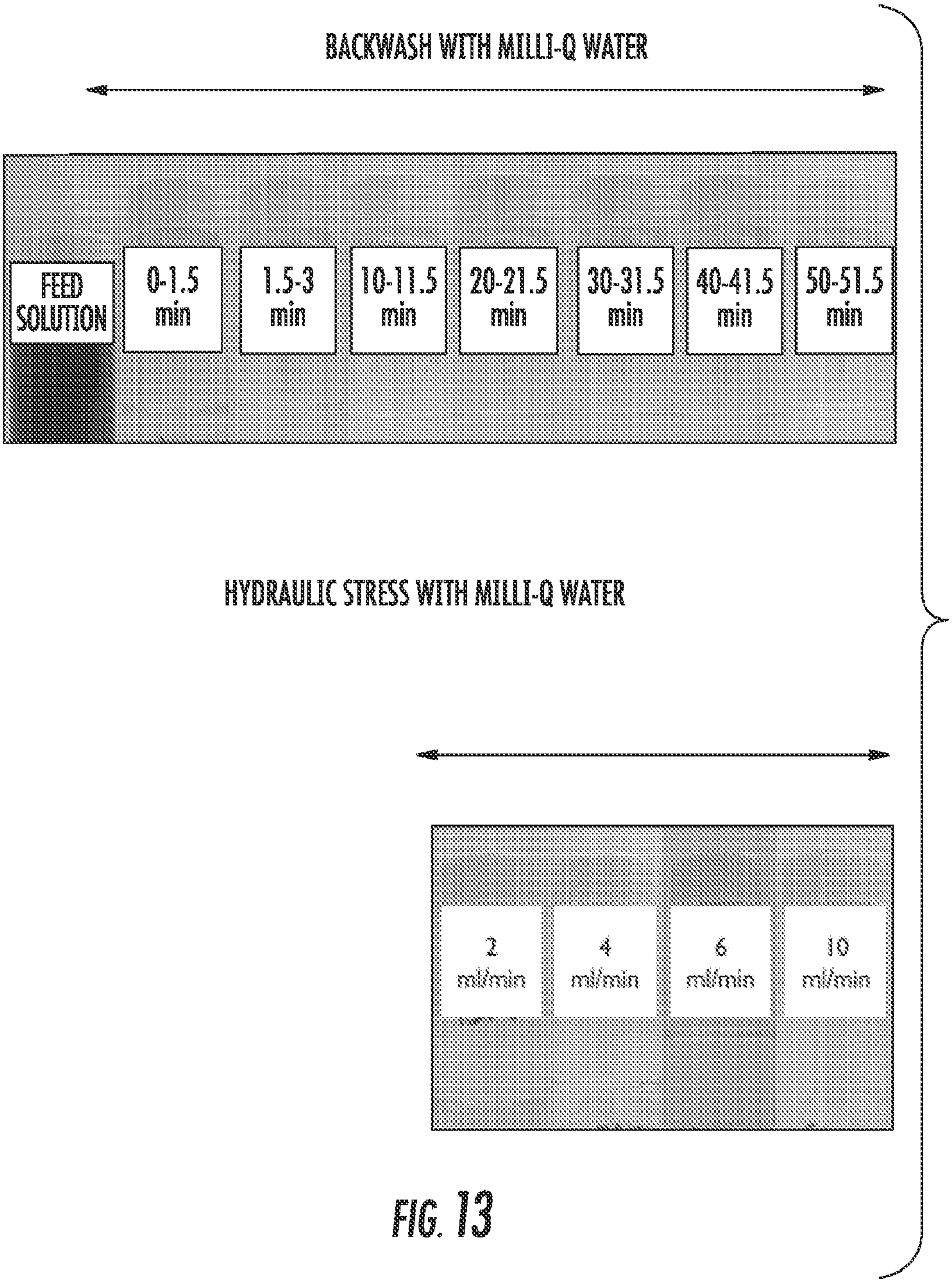
BACKWASH WITH MILLI-Q WATER
FEED SOLUTION
0-1.5 min
1.5-3 min
10-11.5 min
20-21.5 min
30-31.5 min
40-41.5 min
50-51.5 min
HYDRAULIC STRESS WITH MILLI-Q WATER
2 ml/min
4 ml/min
6 ml/min
10 ml/min

FIG. 13

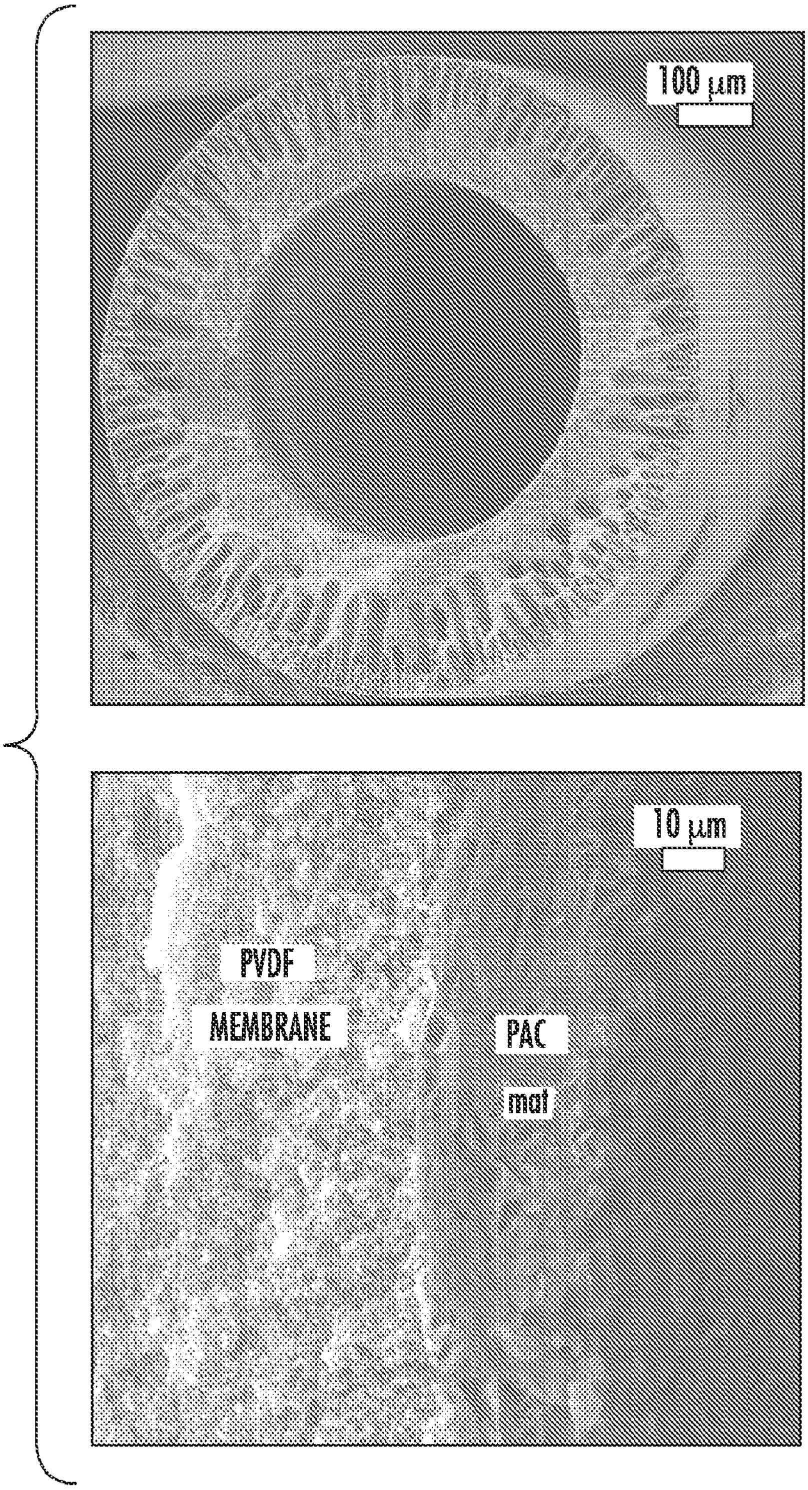

FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/040289

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 63/02 (2014.01)
CPC - B01D 69/08 (2014.09)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - B01D 61/00, 63/02; B32B 5/16 (2014.01)
CPC - B01D 63/02, 69/08, 71/68 (2014.09)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 210/650; 427/180; 977/750, 752

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0283475 A1 (HYLTON et al) 19 November 2009 (19.11.2009) entire document	1-5, 9, 11, 16, 20-22, 24, 25, 28
Y		6-8, 10, 12-15, 17-19, 23, 27, 29-34
Y	US 7,011,760 B2 (WANG et al) 14 March 2006 (14.03.2006) entire document	6, 7
Y	US 2012/0114841 A1 (O'BRYAN et al) 10 May 2012 (10.05.2012) entire document	8, 27
Y	US 2010/0320146 A1 (KRAUSE et al) 23 December 2010 (23.12.2010) entire document	10, 12-15, 17-19, 23, 33, 34
Y	US 5,762,798 A (WENTHOLD et al) 09 June 1998 (09.06.1998) entire document	14, 15, 17-19, 29, 30
Y	US 6,623,637 B1 (MONZEN et al) 23 September 2003 (23.09.2003) entire document	31, 32

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
04 September 2014

Date of mailing of the international search report
15 OCT 2014

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:
Blaine R. Copenheaver
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774