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Nanomembranes for Sustainable Fresh Water Production

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ABSTRACT

The scarcity of pure drinking water has been one of the major humanitarian challenges in the globe. The world population growth, urbanization, and depleting water resources are deteriorating the water quality and global climate change has also intensified this crisis especially in countries with arid and semi-arid regions. The concern is drastically increasing and therefore scientists and engineers are challenged with urgently developing viable solutions of this problem in the near future. The development of a sustainable, cost-effective, reliable, efficient and stable water collection materials and methods for continuous fresh water production is crucial for many regions of the world. Among many other options, nanoscale membranes seem to be quite attractive and very promising option to solve the global water problem due to their low energy cost and simple operational processes to produce clean water. Most natural sources of water contain high salt concentration and other contaminants. Nanotechnology has played an important role in developing cost-effective and efficient processes for purification and use of this natural water. In addition, water can be efficiently collected from atmospheric fog and filtered using nano-membranes without using any large infrastructure. The nanotechnology-based collection systems are unique because of the fine structures of the nano-membranes with tunable properties. The produced water can be used for drinking, agriculture, gardening, medical, industrial, and other purposes. The present study investigated the availability and practical use of nanomaterials and membranes for the collection and production of pure drinking water from various natural sources. Also, some important recommendations are made based on our research results and current practices of nanotechnology applications in the water industry for pure water production.

Keywords: Nanomaterials, Water Collection, Water Purification, PAN Nanofiber, Graphene, Desalination.

1. Introduction

In recent years, the scarcity of pure drinking water has become one of the major global concern especially for the countries with arid and semi-arid regions. These areas suffer for unusually low rainfalls and therefore some of the animals, plants and human being depend on fog, mist and humid air for the source of water. Around the world, about one billion peoples are suffering from fresh drinking water [1]. Besides, industrial growth, population growth, urbanization, depleting water resources, deforestation, and many other factors ameliorate this issue. Therefore, scientists and engineers are challenged with finding the economically feasible and viable water resources to solve this problem. In some Asian, African and Latin American countries unconventional methods such as rain and groundwater harvesting, cloud seeding, and desalination are already being employed to produce pure water for drinking, agriculture, gardening, medical, industrial, and other purposes [2]. In some parts of Europe and the Middle East, desalination is the only tool for reclaiming fresh water. However, these methods are expensive with high operational cost.

In the Namib Desert, Stenocara beetle harvest water directly from the fog, mist, and drops into its mouth. This beetle's carapace has a combination of hydrophilic bumps and a hydrophobic surface that facilitate the water collection from fog [3]. When the fog droplet carried by wind comes in contact with the hydrophilic bumps, it captures the droplet and coalescence while hydrophobic surface drains the water directly to its mouth. Cribellate spiders use silks with spindle-knots and joints that provide wettability and curvature gradients to collect water from the atmosphere [4]. Besides some plants such as Cotula fallax, South Africa has 3D hierarchical structure and hydrophobic surface of its leaves, collect water from the atmosphere. Additionally, Cactaceae species and green bristle grass can effectively capture water from fog [5-6]. In the past decade, extensive research has been done on mimicking the nature to develop cleaner and efficient way for capturing atmospheric water in managing the pure water scarcity issue. For efficient fog harvesting, hydrophobicity and hydrophilicity of the collector materials for fast water capturing and easy drainage properties have a significant effect. Numerous polymeric materials such as polyacrylonitrile (PAN), polyethylene, polypropylene, and stainless steel are used as collector materials. Moreover, superhydrophobic surfaces have other advantages such as self-cleaning, stain-resisting, and drag-reducing and oil spillage separation [7-8].

The wettability of a solid surface is controlled by three factors: their chemical composition, surface geometrical structure, and homogeneity. To fabricate superhydrophobic surfaces, various methods have been proposed, including solution method, sol-gel method, solidification of alkylketene dimer, the plasma fluorination method, chemical etching, chemical vapor deposition, and electrospinning. Among these, electrospinning is the most widely used for fabricating superhydrophobic nano-fibers.

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The present study investigated the availability and practical use of nanomaterials and membranes for the collection and production of pure drinking water from various natural sources. The superhydrophilic electrospun polymer nanofibers were fabricated and water collection capacity was measured. Besides, the practical use of superhydrophilic nanofibers for filtration of water from various sources (e.g., surface, groundwater, and industrial water) was investigated in detail. Also, use of graphene thin film for removal of bacteria, viruses, heavy metals and ions, complex organic and inorganic compounds, and other pathogens and pollutants present in various water sources was analyzed.

2. Nanotechnology for Efficient Water Production from Atmosphere

Very few studies focused on the production of pure water from fog using nanotechnology. Almasian et al. [9] fabricated the fluorinated super-hydrophobic PAN nanofibers for investigating their harvesting properties. They synthesized fluroamine compound to modify the surface properties of PAN nanofibers. The superhydrophobic PAN nanofibers synthesis process was optimized by varying the temperature, time and the amount of fluoroamine compound. The synthesized PAN nanofibers have a water contact angle (WCA) of 159° and low surface energy of 17.1 *mN/m*. The water collection efficiency of 335 $mg/cm^2/h$ was achieved by the fluorinated PAN nanofibers whereas untreated PAN fibers have a capacity of 31 $mg/cm^2/h$. Besides the water collection efficiency can be improved by increasing the distance of the nanofibers mat from humidifier and tilting angle because of increasing the water mobility. Wang et al. [10] fabricated cotton fabric with light-induced super-hydrophilic bumps. The superhydrophobic bumps were created by the spray coating of TiO_2 nano-suspension with a unique raised structure as the result of interfacial tension of the TiO_2 nano-suspension. These bumps provide both the wettability gradient and shape gradient ameliorating the water coalescence and water production. Another research group fabricated bioinspired hydrophilic–superhydrophobic patterned hybrid surface that is facile, low cost and easy to operate for efficient fog collection [11]. They placed a superhydrophobic metal-based gauze onto hydrophilic polystyrene by the thermal pressing method. The hybrid surfaces have polystyrene patches within the holes of the metal gauzes. This process offers easy optimization of the collection process by controlling the pattern's dimensions, such as the size of the gauze mesh. The process has the potential for scaling-up because of availability of polystyrene and the metal gauze. The copper gauze was calcined in an oven at 400°C for 3h to form copper oxide nanostructures coating on the surface of the gauze. Then the oxide gauze was treated with 1H, 1H, 2H, 2H perfluorodecanethiol (PFDT, 97%) to convert it to hydrophobic followed by thermal pressing of the modified gauze with polystyrene to form the hybrid surface with patterned wettability. The fog collection efficiency of about 159 mg cm^2 h^{-1} is achieved by hydrophilic-superhydrophobic patterned hybrid surface. Bai et al. [12] investigated the water collection efficiency of the surfaces having star-shaped wettability patterns. The surface with star-shape wettability patterns integrates both the *surface energy gradient and Laplace pressure gradient* that facilitate quick coalescence of water droplets. This surface is more efficient in terms of water collection than uniform superhydrophilic or uniform superhydrophobic surfaces. Besides, surface with smaller pattern size is more efficient than the larger, having the similar pattern shape because of the Laplace pressure gradient. This result reveals that water collection with pattern surfaces, the pattern shape and size play an important role to improve the water collection efficiency. Lalia et al. [13] fabricated hydrophobic PVDF-HFP nanowebs by electrospinning process and impregnated this nanoweb with lubricants (total quartz oil and Krytox 1506) to investigate the fog collection efficiency. The lubricant impregnated nanomats reduce the contact angle hysteresis and improve the water collection efficiency. In addition, lubricant impregnated nanomats have less drainage of oil from the surface along with shedding water. Table 1 compares the water collection efficiency of nanofibers using various materials.

Table 1 Comparison of fog collection capacity using different collector materials.

Collector Materials	Production Capacity ($mg/cm^2.h$)	References
PVDF-HFP nano-webs	110	13
Patterned superhydrophobic Glass	61.8	14
Electrospun PVDF-HFP-FPOSS	81	15
Bioinspired surfaces with star-shaped wettability patterns	278	12
Fluorinated PAN nanofiber	335	8

3. Nano-membranes for Waste Water Treatment and Desalination

Freshwater and energy are fundamental needs for the enhancement of modern human life and civilization. Using an accelerated and cost-effective process for the desalination of seawater can be an encouraging solution to the water problem. In the past, fossil fuels have been used as a dominant source of energy, but their detrimental impact on the environment and increased cost have made renewable energy resources more important. The reverse osmosis is the most widely used method for water desalination and about half of the world's installed desalination capacity is based on this process. In this process highly pressurized water pass through a semi-permeable membrane which allows the water molecule to pass but not salt ions. However, water transport in this process is slow and fouling is also another issue. Therefore, new membrane materials needed to be developed to solve this issue. Integrating nanotechnology into water treatment and desalination have great potential in this sector. Most of the nano-filter based multifunctional filtration systems do not require large infrastructures or centralized system and can be portable to the remote regions for efficient water treatment.

Graphene was discovered as a single-layer of isolated graphite atoms arranged in 2D hexagonal shape, making it the thinnest and strongest material that is known to date. The graphene thin films have the potential for removal of bacteria, viruses, heavy metals and ions, complex organic and inorganic compounds, and other pathogens and pollutants present in various water sources (e.g., surface, groundwater, and industrial water). The graphene nano-membranes can also be used for desalination of the salt water for continuous fresh water production. The graphene for thin film fabrication can be fabricated by the modified chemical method and the synthesis process as described elsewhere [16-17]. The vacuum filtration is the facile method for the fabrication of graphene thin film from aqueous graphene oxide (GO) dispersions through a filter membrane and then drying and peeling it off from the filter paper [18-19]. By controlling the volume of aqueous graphene, the thickness of the film can be controlled. The facile synthesis of GO thin film opens up the door for an ideal next-generation membrane as the cost-effective, mechanically robust and sustainable alternative for water purification and desalination. Joshi et al. [20] investigated the permeation phenomena of GO thin film prepared by vacuum filtration method. The GO thin film is vacuum tight when it is dry but act as a molecular sieve at wet state. It blocks all solutes having a radius larger than 4.5 angstrom. However, comparatively smaller ions permeate through the GO thin film at a faster rate. The single layer GO is a porous sheet-like material and when it forms a thin film, a network of nano-porous structure forms. At hydrated state, these nano-capillaries open up and pass the species that fit in. Wang et al. [21] studied the water transport phenomenon of functionalized GO thin film by molecular dynamics simulation. Their simulation results reveal that transport of water up to 66 L/cm^2/day/MPa with greater than 99% salt rejection can be achieved by using nano-porous graphene membrane whereas the conventional osmosis process can transport only 0.01–0.05 L/cm^2/day/MPa with similar salt rejection. Comparing to the commercialized membranes, the graphene nano-porous membranes offer 2–3 orders of magnitude higher salt rejection and water permeability. The fast transport of water molecules through the graphene sheets are attributed by the atomic thickness of the graphene sheets. They also find that if the graphene nano-pores are chemically functionalized with hydrogen, it can better reject the salts ions but lower the flow rate. These results showed that graphene nano-membrane has the potential to be used for high-permeability desalination membrane. The water permeability of polyimide/GO thin film was also investigated [22]. The polyimide/GO thin film has a multilayer structure with an interlayer spacing of around 0.83 nm. The concentration of GO is 0 to 0.02 wt. % and increasing GO ameliorate the hydrophilicity of the film. In addition, the permeate water flux under 300 psi increased from 39.0 ± 1.6 to 59.4 ± 0.4 L/m^2 h, while rejections of NaCl and Na_2SO_4 decreased only slightly from 95.7 ± 0.6% to 93.8 ±0.6% and 98.1±0.4% to 97.3±0.3%, respectively. The interlayer spacing of GO nano-sheets served as a water channel and greatly influence the water permeability.

4.0 Super-Hydrophilic Nanofibers for Fog Collection

4.1 Fabrication of Super-Hydrophilic Nanofibers

Polyacrylonitrile (PAN) and Polyvinylchloride (PVC) nanofibers were fabricated by the electrospinning process. In a typical fabrication process, the PAN and PVC powders were separately mixed with Poly vinylpyrrolidone (PVP), Polyethylene glycol (PEG), and chitosan (0, 4, 8, 16, and 32 wt %) and dissolved in dimethylformamide (DMF). The solution was then stirred at 300 rpm for 30 minutes at 70°C. Then the polymeric solutions were electro-spun with a DC voltage of 25 kV, a feed rate of 3 mL/hr, and a spinneret-to-collector distance of 25 cm. All experiments were conducted at room temperature under ambient conditions.

4.2 Morphology, WCA and Fog Collection Efficiency of Super-Hydrophilic Nanofibers

A scanning electron microscope (FEI Nova Nano SEM 450) was used to study the morphology of the fabricated PAN and PVC electro-spun nanofibers. Fig. 1 presents the SEM images of PAN nanofibers with different inclusions. The average diameter of the fiber without any inclusions are approximately 450 nm and the surface of the fibers are smooth (Fig. 1a). However adding inclusions produce small asperities and bumps, which may affect the surface hydrophobicity of the nanofiber mats (Fig. 1 b, c, d).

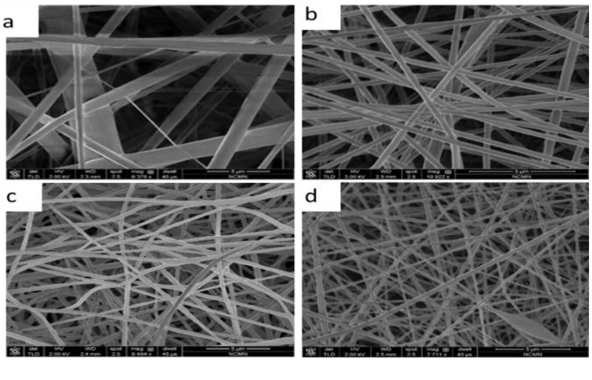

Fig. 1 SEM photographs of PAN nanofibers (a) no inclusion; (b) 16 wt% PVP; (c) 16 wt% PEG and (d) 16 wt% chitosan [23].

The WCA of the fabricated nanofibers were measured by a water contact angle goniometer (KSV Instruments Ltd., Model #CAM 100). The inclusions PVP, PEG, and chitosan were used in this study because of their hydrophilic nature and higher dissolution rate in most solvents. The WCA of the PAN and PVC nanofibers with various inclusions are summarized in Table 2 [23]. As can be seen, without any inclusions the PAN and PVC nanofibers exhibit a WCA of 14° and 22° respectively. However, incorporation of various inclusions especially 16, and 32 wt% of PVP, PEG and chitosan drastically reduced the WCA, making super-hydrophilic nanofibers which is a suitable material for fog harvesting from the atmosphere.

Table 2 WCA of nanofibers with various inclusions.

	Nano fibers	Inclusion	Inclusion wt (%)				
			0	4	8	16	32
WCA (°)	PAN	PVP	14	11	4	<5°	<5°
		PEG	14	13	8	<5°	<5°
		Chitosan	14	12	6	<5°	<5°
	PVC	PVP	22	13	7	<5°	<5°
		PEG	22	16	8	5	<5°
		Chitosan	22	16	9	5	<5°

The WCA of PAN fibers incorporated with 16wt % of PVP at 0 and 2 seconds interval is presented in Fig. 2. It was difficult to monitor the WCA of the hydrophilic nanofibers and especially the super-hydrophilic nanofibers. Within 2 seconds, the water bubble flattened on the nanofiber surface and was absorbed completely by the nanofibers mats. Most of the fibers showed water contact angles below 5° within a few seconds.

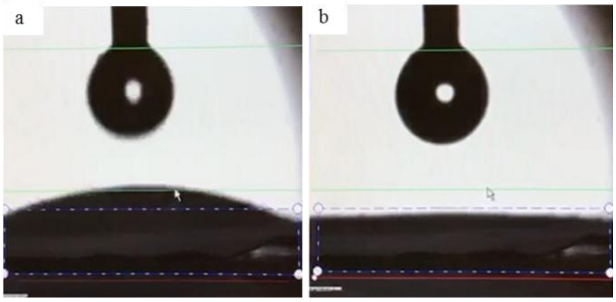

Fig. 2 WCA of PAN fibers incorporated with 16 wt% PVP at (a) 0 second, and (b) 2-second interval.

The fog harvesting capacity of the PAN and PVC nanofibers was evaluated by the humidifier unit (Vicks Warm Steam Vaporizer Humidifier). The humidifier produces fog at different rates based on the requirements. The nanofibers were placed 15 cm away from the top of the humidifier to capture, and the experiment was carried out for 60–130 minutes. The 4×4 cm nanofibers were used to measure the harvesting capacity. Fig. 3 depicted the harvesting capacity of PAN nanofibers with 16wt % PVP. The weight of the dry PAN nanofibers (without inclusion) that placed in the test chamber was 2.7 gm and after 110 minutes of moisture absorption, the weight increased to 3.21 gm corresponding to 18% moisture/fog absorption. Moreover PAN with 16 wt% PVP nanofibers, the moisture absorption increased considerably for the first 70 minutes and then slowed down (Fig. 3b). The weight of the dry sample was 2.50 gm and after 110 minutes of moisture absorption, the weight of the specimen was 3.96 gm, corresponding to a 57.6% moisture absorption. However, PVC nanofibers without any inclusions exhibit 20% moisture absorption and the fibers with 16 wt% PVP have 33.8%. These results reveal that surface hydrophilicity significantly affect the fog harvesting capacity of the nanofibers. It was observed that nanofibers were soaked with considerable moisture from the humidifier, form droplet and filled the pores of the nanofiber and finally due to gravity, the water droplet drained off.

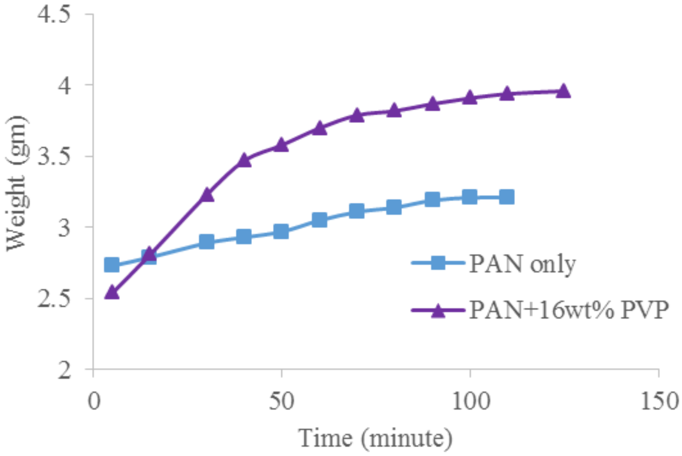

Fig. 3 Fog harvesting capacity of electro-spun nanofibers (a) PAN only and (b) PAN with 16wt % PVP [23].

5. Nanofibers for Water Filtration

5.1 Fabrication of Electro-spun Nanofibers

PVC with various proportion (2, 3, 4, and 5 wt %) of PVP inclusion nanofibers were fabricated by electrospinning process to filter the micro and nano-size particles from water. The fabrication process includes dissolving PVC into dimethyl acetamide (DMA$_C$) by stirring at 65°C for four hours. Now the electrospinning of the prepared solution was conducted similarly as explain before. The WCA of the fabricated nanofibers were measured and observed that all the nanofibers studied here exhibit hydrophilic nature (WCA less than

90^o). In order to overcome the fouling property of the membrane, coagulation is used as a pre-treatment process, which enhances the efficiency of the nanofibers for the removal of colloids. Two coagulants namely Tanfloc and Alum were used in this study. Then the water samples from three different sources (lake water, industrial jet water, and magnetite nanoparticles solution) were collected and the required amount of coagulants were added into the water and allowed for 24 hours for sedimentation. Therefore, the fabricated nanofibers were used to filter the water samples. The filtration capacity was measured in terms of turbidity, pH and total dissolved solid (TDS).

5.2 Turbidity, pH and TDS of Water Samples

The Tanfloc and Alum coagulated water samples from different sources were filtered using PVC nanofibers incorporated with PVP and data were recorded. Table 3 summarizes the characteristics of filtered lake water using PVC nanofibers [24]. The optimum coagulant dosage for Tanfloc and Alum is 15mg/L and 50mg/L respectively. It was observed that turbidity reduction is very effective in coagulation/filtration process when compared with the direct membrane filtration process. The turbidity of lake water samples before filtration is 21 Nephelometric Turbidity Units (NTU). However, using Tanfloc coagulant, the turbidity drops to 0.2 NTU. Moreover, Alum also reduces the turbidity of lake water samples. Besides the TDS values also reduced significantly using nanofibers as filter membranes. In addition, the pH of filtered lake water drops using both coagulants when compared to as received water samples.

Coagulant		Optimum Coagulant: Tanfloc-15mg/L Alum-50mg/L	Coagulation/ Filtration	Direct Membrane-Filtration (Before filtration/after filtration)
Tanfloc	Turbidity	1 NTU	0.20 NTU	21 NTU/0.49 NTU
	pH	8.09	8.09	8.14/8.14
	TDS	460ppm	450ppm	460ppm/440ppm
Alum	Turbidity	1.92 NTU	0.30 NTU	21 NTU/0.49 NTU
	pH	7.49	7.49	8.14
	TDS	472ppm	447ppm	460ppm/440ppm

Table 3 Characteristics of lake water samples before and after filtration.

The similar investigation was conducted for industrial jet water and magnetic nanoparticles solution samples using both types of coagulants. The turbidity, pH, and TDS of the water samples were measured before and after filtration. Fig. 4 illustrated the residual turbidity of filtered water samples using both types of coagulant. From Fig. 4, it's seen that coagulation-filtration is the most effective way to reduce the turbidity of the water. For industrial jet water samples, the optimum coagulant dosage for Tanfloc and Alum is 25mg/L and 50mg/L respectively. Before filtration, the turbidity was approximately 32 NTU, which was reduced to 2.9 NTU using Tanfloc coagulation-filtration process. Moreover, Alum coagulant added filtered water samples also exhibit a reduction of water characteristics using nanofiber as a filter membrane. The filtered magnetic nanoparticles solution samples using both types of coagulants also reveal that PVC with PVP inclusion nanofibers are very effective to filter the magnetic nanoparticles solution.

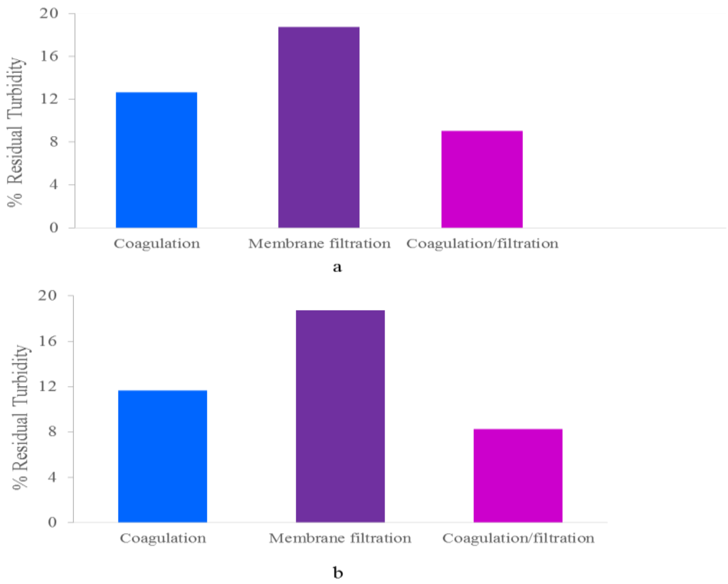

Fig. 4 The residual turbidity of filtered water using (a) Tanfloc and (b) Alum coagulant (Samples-Industrial jet water) [24].

4. Conclusions

Super-hydrophobic/super-hydrophilic nanofibers could be a potential solution to address the water scarcity crisis in the desert regions of the globe. Incorporation of hydrophilic polymer (PVP, PEG, chitosan) into PAN and PVC nanofibers ameliorate the fog harvesting capacity. The moisture absorption of about 58% was achieved by PVP treated superhydrophilic PAN nanofibers whereas untreated PAN nanofibers exhibit about 18% moisture absorption. Besides, superhydrophilic electrospun nanofibers have the potential to filter water. The coagulation and filtration by the superhydrophilic nanofibers is an effective way to filter the water.

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