

**NANOFIBER MEMBRANE-BASED WATER
TREATMENT SYSTEMS FOR DESALINATION AND
HEAVY METALS REMOVAL**

POOJA YADAV



**CENTRE FOR RURAL DEVELOPMENT AND
TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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FOR DESALINATION AND HEAVY METALS REMOVAL**

by

Pooja Yadav

CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY

submitted

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CERTIFICATE

This is to certify that the thesis entitled “**Nanofiber Membrane-based Water Treatment Systems for Desalination and Heavy Metals Removal**”, being submitted by **Ms. Pooja Yadav** to the Indian Institute of Technology Delhi for the award of “**Doctor of Philosophy**” is a record of bonafide research work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

Dr. Vivek Kumar

Professor

Centre for Rural Development and Technology

Indian Institute of Technology Delhi

New Delhi-110016

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ABSTRACT

The global water demand is increasing dramatically with expanding population, urbanization and agricultural practices. Additional factors like descending monsoon levels, inefficient water network and management, unrestricted groundwater extraction, overexploitation all add to the water stress situation, especially in underdeveloped and developing nations. Considering the speedily exhausting fresh water sources, the demand for alternatives such as desalination of saline/seawater, treatment of polluted water sources has arisen. In the present research work, two membrane-based technologies have been employed for desalination and heavy metals removal application.

Among various processes used for water desalination, membrane distillation is a promising desalination technology providing additional advantages such as, lower operating temperature, lower operating pressure which requires less demand for mechanical strength of the membrane, lower fouling, high rejection of non-volatile impurities, possibility of implementing low grade heat source (geothermal/solar/waste energy). The membrane properties like hydrophobicity and permeability plays crucial role in MD process performance. In present study, superhydrophobic (water contact angle $> 150^\circ$) composite nanofibrous membranes were prepared using polyvinylidene fluoride (PVDF) and silica nanoparticles via electrospinning process followed by modification. The resultant modified membranes exhibited high water contact angle of $154.6 \pm 2.2^\circ$, high liquid entry pressure of 143 ± 4 kPa and smaller mean pore size of 0.27 ± 0.3 μm . The water contact angle or hydrophobicity of any surface is directly proportional to its surface roughness. Loading of silica nanoparticles creates hierarchical roughness and numerous tiny air pockets are formed on the surface to roll off water droplets easily and prevent pore wetting. The modified membranes (6 wt% silica) were used in continuous vacuum membrane distillation (VMD) test with 3.5 wt% NaCl feed solution, a stable flux (> 11.5 $\text{kg}/\text{m}^2/\text{h}$) and high salt rejection (99.9 %) was obtained after 22 hours of operation. On the other hand, the pristine membrane (0 wt% silica) produced slightly higher flux during initial hours of VMD test, the flux gradually decreased after 8 hours of operation and dropped sharply after 16 hours with drastic drop in permeate quality. The high initial flux in case of pristine membrane is due to larger pore size and lower liquid entry pressure (LEP), however, large pores are prone to wetting and eventually result in poor salt rejection. Moreover, the modified membranes showed high stability with negligible leaching of silica nanoparticles. The fouling tendency of these membranes was assessed through elemental analysis of membrane surface after completion of VMD test, no fouling was recorded in case of modified

membranes. The modified membranes were also tested for heavy metals (arsenic and iron) removal potential in VMD system, the removal performance was compared to that of pristine and commercial membranes. The modified membrane produced stable flux with high rejection rates for both the metals, the permeate flux and permeate quality of pristine membrane started declining after few hours of operation. On the other hand, the commercial membrane produced slightly higher flux accompanied with lower rejection. In conclusion, the novel modified membranes fabricated in this study holds robust anti-wetting properties, high permeability and have great potential in desalination and heavy metal removal applications.

The second part of this research work include synthesis and immobilization of hydrous manganese oxide (HMO) nanoparticles within polyacrylonitrile (PAN) nanofibers using electrospinning technique. The synthesized HMO nanoparticles and HMO-PAN nanocomposite were characterized and studied for adsorption of heavy metal ions of lead and arsenic in batch setup. The initial pH of solution played important role during metal ions removal and maximum adsorption capacities for Pb(II) and As(V) were achieved at pH values 7.0 and 5.0, respectively. The adsorption isotherm data of lead and arsenic was best represented by Langmuir and Freundlich models, respectively. The maximum adsorption capacities obtained from Langmuir isotherm for Pb(II) and As(V) were 194.4 mg/g and 95.7 mg/g, respectively. The nanocomposite adsorbent was efficiently reused for multiple adsorption-desorption cycles retaining about 88% (for Pb) and 83% (for As) of the total adsorption capacity after five cycles of usage. Hence, the synthesized nanocomposite proved to be remarkable adsorbent for lead and arsenic with merits of easy fabrication, stability and regeneration ability.

सार

जनसंख्या, शहरीकरण और कृषि पद्धतियों के विस्तार के साथ वैश्विक जल की मांग नाटकीय रूप से बढ़ रही है। अतिरिक्त कारक जैसे मानसून का गिरता स्तर, अप्रभावी जल तंत्र और प्रबंधन, अप्रतिबंधित भूजल दोहन, अत्यधिक दोहन सभी जल तनाव की स्थिति को बढ़ाते हैं, विशेष रूप से अविकसित और विकासशील देशों में। तेजी से समाप्त हो रहे ताजे जल स्रोतों को ध्यान में रखते हुए, खारे/समुद्री जल के अलवणीकरण, प्रदूषित जल स्रोतों के उपचार जैसे विकल्पों की मांग उठी है। वर्तमान शोध कार्य में, अलवणीकरण और भारी धातुओं को हटाने के अनुप्रयोग के लिए दो झिल्ली-आधारित प्रौद्योगिकियों को नियोजित किया गया है।

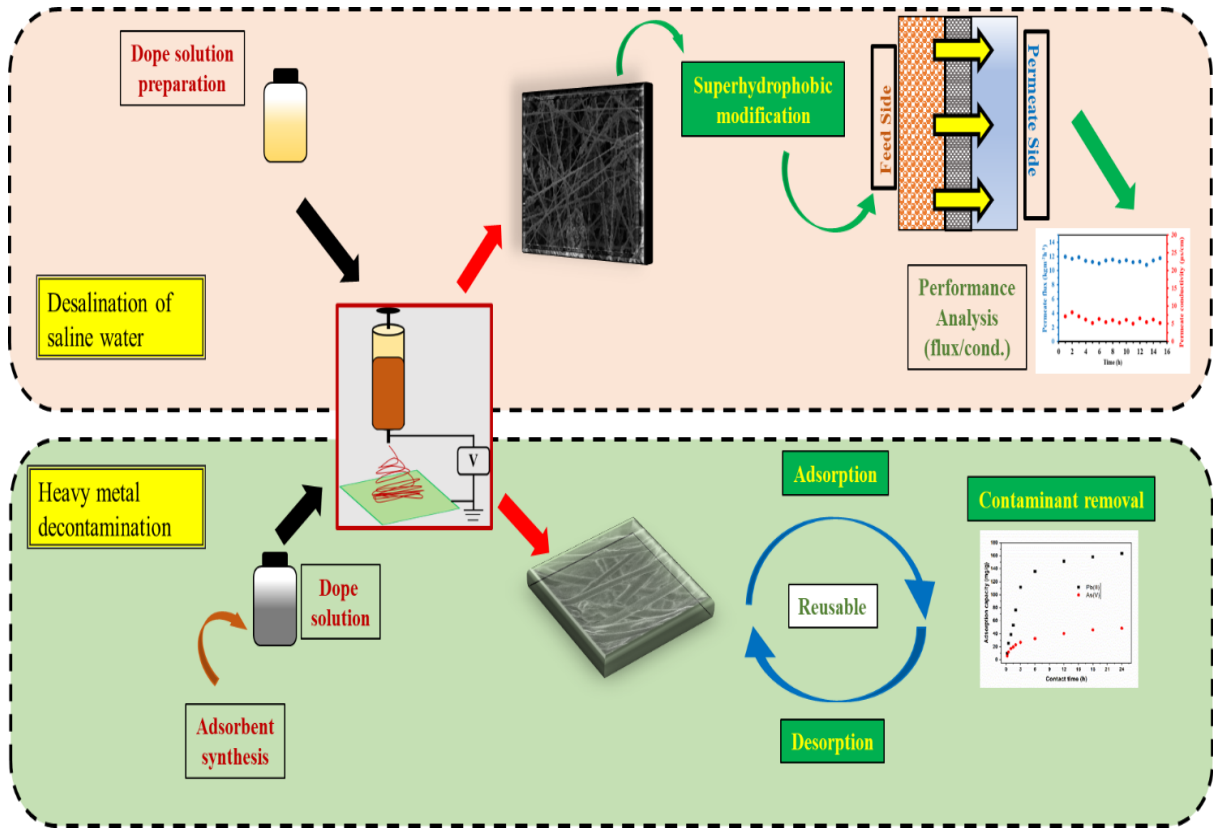
जल अलवणीकरण के लिए उपयोग की जाने वाली विभिन्न प्रक्रियाओं में, झिल्ली आसवन एक आशाजनक अलवणीकरण तकनीक है जो कम ऑपरेटिंग तापमान, कम परिचालन दबाव जैसे अतिरिक्त लाभ प्रदान करती है, जिसके लिए झिल्ली की यांत्रिक शक्ति की कम मांग, कम दूषण, गैर-वाष्पशील अशुद्धियों की उच्च अस्वीकृति की आवश्यकता होती है। निम्न श्रेणी के ताप स्रोत (भूतापीय/सौर/अपशिष्ट ऊर्जा) को लागू करने की भी संभावना रहती है। हाइड्रोफोबिसिटी और पारगम्यता जैसे झिल्ली के गुण एमडी प्रक्रिया प्रदर्शन में महत्वपूर्ण भूमिका निभाते हैं। वर्तमान अध्ययन में, सुपरहाइड्रोफोबिक (जल संपर्क कोण $>150^\circ$) मिश्रित नैनोफाइबर झिल्ली को इलेक्ट्रोस्पिनिंग प्रक्रिया के माध्यम से पॉलीविनाइलिडीन फ्लोराइड (पीवीडीएफ) और सिलिका नैनोकणों का उपयोग करके संशोधन के बाद तैयार किया गया था। परिणामी संशोधित झिल्लियों ने $154.6 \pm 2.2^\circ$ का उच्च जल संपर्क कोण, 143 ± 4 केपीए का उच्च तरल प्रवेश दबाव और $0.27 \pm 0.3 \mu\text{m}$ का छोटा औसत छिद्र आकार प्रदर्शित किया। किसी भी सतह का जल संपर्क कोण या हाइड्रोफोबिसिटी उसकी सतह की खुरदरापन के सीधे आनुपातिक है। सिलिका नैनोकणों को भारित करने से पदानुक्रमित खुरदरापन पैदा होता है और पानी की बूंदों को आसानी से लुढ़काने और छिद्रों को गीला होने से रोकने के लिए सतह पर कई छोटे वायु पॉकेट बन जाते हैं।

संशोधित झिल्ली (6 wt% सिलिका) का उपयोग 3.5 wt% NaCl फीड समाधान के साथ निरंतर वैक्यूम झिल्ली आसवन (VMD) परीक्षण में किया गया था एवं 22 घंटे के ऑपरेशन के बाद एक स्थिर प्रवाह ($> 11.5 \text{ kg/m}^2/\text{h}$) और उच्च नमक अस्वीकृति (99.9%) प्राप्त किया गया था. दूसरी ओर, वीएमडी परीक्षण के शुरुआती घंटों के दौरान प्रिस्टीन झिल्ली (0 wt% सिलिका) ने थोड़ा अधिक फ्लक्स उत्पन्न किया, 8 घंटे के ऑपरेशन के बाद फ्लक्स धीरे-धीरे कम हो गया और 16 घंटों के बाद परमिट गुणवत्ता में भारी गिरावट के साथ तेजी से गिरा। प्रिस्टाइन झिल्ली के मामले में उच्च प्रारंभिक प्रवाह बड़े छिद्र आकार और कम तरल प्रवेश दबाव (एलईपी) के कारण होता है, हालांकि बड़े छिद्रों में गीलापन होने का खतरा होता है और अंततः खराब नमक अस्वीकृति होती है। इसके अलावा, संशोधित झिल्लियों ने सिलिका नैनोकणों की नगण्य लीचिंग के साथ उच्च स्थिरता दिखाई। वीएमडी परीक्षण के पूरा होने के बाद झिल्ली की सतह के मौलिक विश्लेषण के माध्यम से इन झिल्लियों की दूषण प्रवृत्ति का आकलन किया गया था, संशोधित झिल्लियों के मामले में कोई दूषण दर्ज नहीं किया गया था। संशोधित झिल्लियों का वीएमडी प्रणाली में भारी धातुओं (आर्सेनिक और लौह) को हटाने की क्षमता के लिए भी परीक्षण किया गया था, हटाने के प्रदर्शन की तुलना प्रिस्टाइन और वाणिज्यिक झिल्लियों से की गई थी। संशोधित झिल्ली ने दोनों धातुओं के लिए उच्च अस्वीकृति दर के साथ स्थिर प्रवाह का उत्पादन किया, ऑपरेशन के कुछ घंटों के बाद प्राचीन झिल्ली के परमिट फ्लक्स और परमिट गुणवत्ता में गिरावट शुरू हो गई। दूसरी ओर, वाणिज्यिक झिल्ली कम अस्वीकृति के साथ थोड़ा अधिक प्रवाह उत्पन्न करती है। निष्कर्ष में, इस अध्ययन में निर्मित नवीन संशोधित झिल्लियों में मजबूत गीला-रोधी गुण, उच्च पारगम्यता है और अलवणीकरण और भारी धातु हटाने के अनुप्रयोगों में काफी संभावनाएं हैं।

इस शोध कार्य के दूसरे भाग में इलेक्ट्रोस्पिनिंग तकनीक का उपयोग करके पॉलीएक्रिलोनिट्राइल (पैन) नैनोफाइबर के भीतर हाइड्रस मैंगनीज ऑक्साइड (एचएमओ) नैनोकणों का संश्लेषण और स्थिरीकरण शामिल है। बैच सेटअप में सीसा और आर्सेनिक के भारी धातु आयनों के सोखने

के लिए संश्लेषित एचएमओ नैनोकणों और एचएमओ-पैन नैनोकम्पोजिट की विशेषता और अध्ययन किया गया था। धातु आयनों को हटाने के दौरान घोल के प्रारंभिक pH ने महत्वपूर्ण भूमिका निभाई और Pb(II) एवं As(V) के लिए अधिकतम सोखने की क्षमता क्रमशः pH 7.0 और 5.0 पर हासिल की गई। सीसा और आर्सेनिक के सोखने के इज़ोटेर्म डेटा को क्रमशः लैंगमुइर और फ्रायंडलिच मॉडल द्वारा सबसे अच्छा दर्शाया गया था। Pb(II) और As(V) के लिए लैंगमुइर इज़ोटेर्म से प्राप्त अधिकतम सोखना क्षमता क्रमशः 194.4 mg/g और 95.7 mg/g थी। उपयोग के पांच चक्रों के बाद कुल सोखने की क्षमता का लगभग 88% (पीबी के लिए) और 83% (एएस के लिए) बरकरार रखते हुए, नैनोकम्पोजिट अधिशोषक को कई अधिशोषण-विशोषण चक्रों के लिए कुशलतापूर्वक पुनः उपयोग किया गया। इसलिए, संश्लेषित नैनोकम्पोजिट आसान निर्माण, स्थिरता और पुनर्जनन क्षमता के गुणों के साथ सीसा और आर्सेनिक के लिए उल्लेखनीय अवशोषक साबित हुआ।

GRAPHICAL ABSTRACT



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LIST OF ABBREVIATIONS

AFM: Atomic force microscopy

AGMD: Air gap membrane distillation

CNT: Carbon nanotubes

DCMD: Direct contact membrane distillation

EDS: Energy-dispersive analysis of X-ray spectroscopy

ENMs: Electrospun nanofiber membranes

FAS: Fluoroalkylsilane

FESEM: Field emission scanning electron microscopy

FTES: 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane

FTIR: Fourier transform infrared spectroscopy

HMO: Hydrous manganese oxide

HRTEM: High resolution transmission electron microscopy

ICP-MS: Inductively coupled plasma mass spectroscopy

ICP-OES: Inductively coupled plasma optical emission spectroscopy

LEP: Liquid entry pressure

MD: Membrane distillation

MOFs: Metal organic frameworks

NPs: Nanoparticles

PAN: Polyacrylonitrile

PDMS: Polydimethylsiloxane

PE: Polyethylene

PFO: Pseudo first order

PH: Polyvinylidene fluoride-co-hexafluoropropylene

PP: Polypropylene

PSO: Pseudo second order

PTFE: Polytetrafluoroethylene

PVDF: Polyvinylidene fluoride

SAED: Selected area electron diffraction

SGMD: Sweeping gas membrane distillation

TCD: Tip-collector distance

VMD: Vacuum membrane distillation

WCA: Water contact angle

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction