Acid-Modified ZnO Nanoparticles Embedded Polysulfone Membranes for Separation of Copper from Industrial Wastewater

Pallavi Mahajan-Tatpate[1,2], Supriya Dhume[1], Sachin Chavan[3] and Yogesh Chendake[1,*]

[1] *Department of Chemical Engineering, Bharati Vidyapeeth (Deemed to be) University, College of Engineering, Pune, Maharashtra, India*

[2] *School of Chemical Engineering, Polymer Engineering Department, MIT-World Peace University, Pune, Maharashtra, India*

[3] *Department of Mechanical Engineering, Bharati Vidyapeeth (Deemed to be) University, College of Engineering, Pune, Maharashtra, India*

Abstract: Copper is one of the crucial materials for the biological activity of human beings and is known for antimicrobial properties during wound management. Hence its presence in the effluent is overlooked although it is reported to be detrimental at higher concentrations. Its effect on humans varies from simple dizziness, diarrhea to liver/kidney damage, etc. Various techniques are reported for separation of these toxic pollutants from effluent. This article focuses on development of polysulfone-based membranes with use of additives: polyethylene glycol (PEG) and ZnO nanoparticles (NPs) (nascent and modified with HCl) for separation of copper from effluent by Donnan Exclusion principle. The incorporation of acid treated ZnO NPs in membrane matrix provides surface charge to membrane. This results in repulsive interaction with copper salts from process which retained in retentate as per Donnan exclusion principle. The membrane formed with 40% PSF- 0.8% ZnO NPs shows the rejection of copper up to 40%, which raises to 61% when instead of nascent NPs, HCl treated NPs were used. The rejection efficiency of the membrane raises up to 90% when PEG was used along with PSF and ZnO NPs (acid treated). The use of modified NPs in membrane matrix has strong impact on membrane morphology and rejection efficiency. The modification of surface charge properties and morphological distribution of NPs is supported by FTIR and EDX. Further the separation works upon physical distribution of NPs, which would help to maintain the stability properties of PSF based membrane enhancing its applicability in actual process conditions.

Keywords: Copper, Wastewater, Recovery, Membrane, ZnO Nano powder, Acid modification, Donnan exclusion.

1. INTRODUCTION

Heavy metal contaminated water treatment is still a big challenge today. Industry effluent, solid waste, and natural calamities discharge a large amount of heavy metals into the surface and underground water bodies [1,2]. Most observed heavy metals in wastewater are chromium, arsenic, lead, mercury, copper, iron, cadmium, manganese, zinc, nickel, etc. [3-7] Recently in India, water in Kabini river-Karnataka and Kolleru lake, Machilipatnam Coast in Andhra Pradesh were found to be contaminated with metal ion pollutants *viz.*, Cr, Cu, Cd, Fe, Mn, Ni, Pb and Zn [8-10]. Among these pollutants, copper was one of the major metal ions in wastewater. The presence of copper in wastewater is due to the use of copper in various industrial applications *viz.* metal processing, semiconductor, metallurgy, smelting, electroplating, plastic, etching, polishing, paint, printing operations, etc. [4, 11]. Apart from this, leaching from water pipes, algae treatment, and wood preservatives leads to the loss of copper to water bodies [11]. Most of these processes can discharge 10-150 ppm copper in the effluent [12]. InBalanagar, Hyderabad, India sediment samples contain copper in the range of 90.6 to 810.1mg/kg with an average content being 256.06 mg/kg [13]. Similar high soil contamination of copper much above the maximum permissible limit was reported in Italy and Mexico [14]. This copper can cause toxic effects such as vomiting, diarrhea, headache, cramps, tremors, hair loss, dizziness, epigastric pain, anemia, and kidney damage; while its accumulation in the liver, brain, and pancreas can cause death [12, 15]. It is also harmful to the aquatic ecosystem due to accumulation in the gills of fish [16]. This forced the WHO-2018 to define the median permissible limit of copper in water should not be more than 1.5 ppm. The norms are made even more stringent in the USA and European countries, where the recommended dietary tolerance of copper for adults and children between ages 1 to 18 years is 0.9 and 0.34 to 1.3 mg/day, respectively [17]. This underlines the need for the removal of this copper from effluent and other water resources to avoid its entry into the digestion system.

Though the presence of copper in water at concentrations above the permissible limit is detrimental, it has various applications and large importance. It is one of the vital elements supporting

---

[*] Address correspondence to this author at the Department of Chemical Engineering, Bharati Vidyapeeth (Deemed to be) University, College of Engineering, Pune, Maharashtra, India; Tel: +91 20 24107390. Ext. 319; Email: yjchendake@bvucoep.edu.in

E-ISSN: 2410-1869/22 © 2022 Cosmos Scholars Publishing House

biological activities in living organisms [6, 12, 16, 18], whereas it is essential for the normal growth and metabolism of plants [19]. Copper-based compounds can be used as enzymes for redox reactions [20]. Moreover, it is used in construction, power transmission, electronic item / industrial machines, vehicle production, coin production, electrical wiring, and nanoparticles for different applications like catalysis, etc. [11, 21]. Thus, it necessitates not only the separation but recovery of copper for further applications in industrial and medicinal purposes.

Several conventional methods *viz.*, chemical precipitation, coagulation, flocculation, flotation, ion-exchange, adsorption, electrochemical, and advanced membrane methods have been reported for the separation of these metal ions [7, 22-25]. They have limitations of chemical usage resulting in sludge generation which poses a concern of discarding, and dumping (secondary pollution). This limits the applicability of conventional processes [7, 26, 27]. On the other hand, the processes like reverse osmosis and nanofiltration membranes remove essential univalent (Na^+) and bivalent (Ca^{+2}, Mg^{+2}) [28] ions, required for biological and other applications. The electrodialysis method has fouling, and concentration polarization issues hence need pretreatment of feed and regular cleaning to remove the deposited metal ions [29]. All these methods also have issues with high energy requirements and operational limitations [27]. The micellar and polymer enhanced ultrafiltration (UF) methods require the addition of modifiers, and surfactants before feed passes through the membrane. It affects the purity of recovered metals and necessitates further treatment for their recovery. The adsorptive ultrafiltration membranes are recently reported for metal separation. They have limitation of saturation of membrane's active surface area, which will affect the separation efficiency of membrane [30]. Thus, a careful selection and design of the method are necessary to overcome these limitations. The chosen method should be environment friendly, economic, sustainable, and should have industrial applicability.

Among these methods, the ultrafiltration membrane process consumes comparatively less energy [7] while retaining the desired essential elements in water without compromising separation efficiency for heavy metals. Also, it is cost comparable with conventional processes considering secondary treatment process and recovery issues. Thus, the present work is targeted toward modification and optimization of the UF membrane for the efficient separation and recovery of copper from effluent along with excellent transport characteristics.

This study is designed to enhance polysulfone (PSF) membrane properties by use of porogen agent-polyethylene glycol (PEG) and surface modifier- ZnO nanoparticles (with or without acid treatment). The ZnO nanoparticles anchoring in the membrane and their impact on Donnan exclusion-based separation of copper are studied. Formed membranes showed substantial enhancement in copper removal property up to 90%, without the use of any micelles or other complexing agents. It resolves not only the issue of water purification but also recovers a natural entity-copper which is reutilized for further applications.

2. MATERIAL AND METHODS

2.1. Material

PSF of Molecular weight (M.W.) 35000 was obtained from Otto Chemie Pvt. Ltd. N, N'-Dimethyl acetamide (DMAc), and PEG with M.W. 200 (PEG-200) were bought from High Purity Lab. Pvt. Ltd. India. Zinc oxide nano powder of 80-100 nm size was procured from Nanoshel LLC. HCl and cupric chloride were purchased from Merck Ltd. India and Loba Chemie Pvt. Ltd. respectively. From Ahlstrom Hollytex, non-woven polyester backing 3324 was obtained.

2.2. Membrane Preparation

The membrane was prepared using a dope solution containing 40 to 43% PSF, 8% PEG, 0 to 1% ZnO nano powder, and DMAc solvent. The solution was continuously stirred to ensure complete dissolution. Further, the membrane was cast using an automatic casting system 'Shivohm' containing a doctor knife to spread the dope solution on a glass sheet. The membrane was prepared by the phase separation method. The formed membranes were well stored for further application. The pictorial view of membrane preparation and metal ion separation process is shown in Figure **1**.

2.3. Membrane Analysis

2.3.1. Pure Water Flux

Water flux plays a significant role to define the transport property of porous membranes. Amicon type dead-end cell was used to measure water flux at room temperature using distilled water. Water flux was measured using equation 1:

$$J = \frac{V}{A \times \Delta t} \tag{1}$$

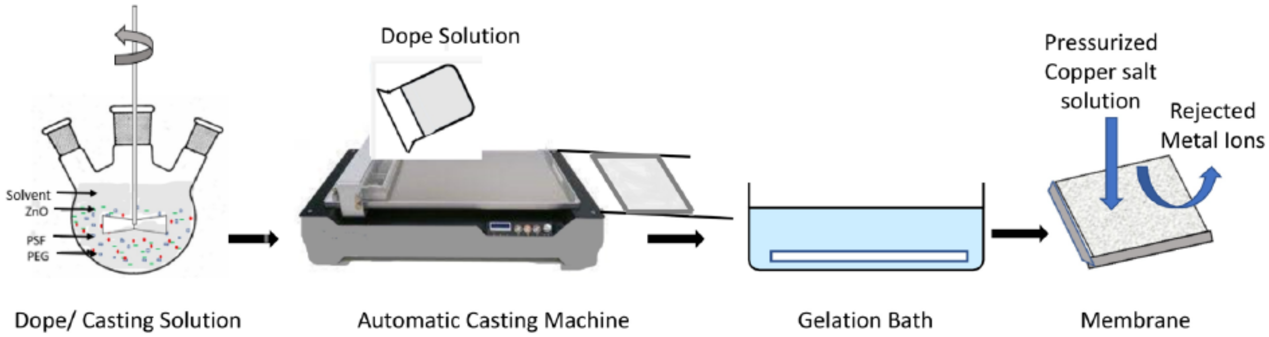

Figure 1: Membrane preparation and application stepwise process.

where 'J' is pure water flux in liters per meter square hour (LMH), 'V' is a volume of water collected in liters, 'A' is an active area of membrane in square meters and 'Δt' is the time difference in an hour [25, 31-35].

2.3.2. Bubble Point Analysis

The bubble point analysis method is used to measure the maximum pore size of the membrane. In this method, wet membrane is placed in the analysis cell and gradually the pressure is increased till the bubble point is reached. At this pressure, the continuous flow rate of air is obtained. The maximum pore size is calculated by using Cantor's equation.

$$r_{Pi} = \frac{2.\sigma.cos\theta}{Pi} \quad (2)$$

where r_{pi} is pore radius, σ is surface tension, θ is contact angle and Pi is the bubble point pressure [35].

2.3.3. Membrane Metal Ion Rejection Analysis

A 1000 ppm cupric chloride salt solution was prepared in distilled water and used for rejection analysis. This solution is fed to a dead-end cell mounted with a membrane. This system was pressurized and permeate was collected. The double beam UV Vis Spectrophotometer (UV 3000+ of Lab India) was used to measure the concentration of metal ions in the feed and permeate sample. The copper ion rejection was studied by measuring absorbance at 216 nm wavelength. Based upon the concentration analysis percent rejection (% R) was calculated by:

$$\%R = \left[1 - \frac{C_p}{C_f}\right] \times 100 \quad (3)$$

where C_p and C_f are the concentration of permeate and feed, respectively [32, 34].

2.3.4. FTIR Spectrum

The Fourier transform infrared (FTIR) spectra was recorded by the spectrometer (ALFA-Bruker) in the range of 4000–500 cm^{-1}. In FTIR infrared radiations were passed through the sample, where some of the radiations will be absorbed by the sample and the rest will pass through it. Based on transmittance, the graph was plotted between wavenumber and transmittance [36-38].

2.3.5. Energy Dispersive X-Ray (EDX) Analysis

The analysis of surface properties, chemical composition, and distribution of components was investigated using EDX analysis. The Bruker XFlash 6130 was used for EDX analysis with excellent resolution, 123eV at Mn Kα and 45eV at C Kα with an element detection range from Be to Am. The samples were gold coated by a sputter coater to make them conductive.

In EDX analysis, a very small part of the membrane is deeply studied for the surface elemental chemical composition distribution [39-41]. Here highly charged electrons or protons are bombarded on membrane samples. EDX spectrum shows the peaks corresponding to element composition [36].

3. RESULTS AND DISCUSSION

3.1. Material Selection

Polysulfone is well known for its chemical, mechanical, and thermal properties [42, 43]. The main limitation of PSF membranes is their hydrophobic nature which leads to a decrease in permeability property and increases membrane fouling [38, 44] resulting in a decrease in membrane lifespan. To overcome this limitation, hydrophilicity was imparted to the membrane using PEG as an additive [38, 44]. It is easily leachable in a water-non-solvent bath and improves membrane porosity and pore density. It is used as a pore-forming agent, which avoids the formation of macro voids and improves the wettability of the membrane. Also, it improves membrane selectivity and transport rate [45]. Dimethyl acetamide was used as a solvent as it forms a stable dope solution at high PSF concentrations [35]. The increase in PSF concentration will help to improve membrane selectivity. Water was used as a non-solvent bath as DMAc and PEG are easily soluble in water [39, 46] and helps to add porosity to the membrane. The increase in PSF concentration and use of PEG changes gelation kinetics. It leads to form a denser structure with smooth thin selective porous top layer. It helps to increase the rejection property of the membrane. ZnO nano powder was further used to impart charge to the membrane. Thus, according to the Donnan exclusion principle, similarly charged particles repel each other, which will help to increase in rejection property of the membrane. Also, ZnO nano powder is low cost, easy to process, and imparts hydrophilicity to the membrane, hence improves permeability, transport, and selectivity of the membrane [33, 47-50]. Also, the use of ZnO nanoparticles in membrane preparation is increasing due to their photocatalytic self-cleaning property, which helps to reduce membrane fouling, and concentration polarization which improves membrane lifespan [50].

3.2. Effect of PSF Concentration and ZnO Nano Powder Modification by Acid Treatment on Copper Rejection

The rejection of copper ions is mainly concerned with size and charge exclusion. The implementation of the Donnan exclusion principle for membrane anchored with ZnO nano powder with and without acid modification was studied. The use of ZnO nano powder in the membrane was also studied by Alabi A. *et al*. 2018. ZnO nano embedded membrane shows good selectivity and transport rate as compared to pristine polymer membrane [51]. Copper rejection for membranes prepared with different PSF concentrations, and ZnO nano powder with or without HCl treatment is shown in Figure **1**. It was observed that the copper rejection was 40% for membranes prepared from 40% PSF and ZnO NPs. The rejection was increased from 40 to 61% when the membrane was prepared from HCl modified ZnO NPs instead of nascent NPs. It attributes to the reaction between ZnO and HCl forms $ZnCl_2$ and interaction between $ZnCl_2$ and PSF imparts a partial charge to the membrane. The formed membrane acts like an electrolyte with denser morphology and thin, porous structure, a similar observation was reported by Panda S. R. *et al*. 2014. According to the Donnan exclusion principle, the similar charge of a copper solution and that of membrane experiences repulsion which increases the copper rejection property of the membrane. Similar behavior of increase in chromium rejection property for membrane prepared with ZnO nano powder (HCl treated) was reported by Mahajan-Tatpate P. *et al*. 2021. Apart from this, the formed $ZnCl_2$ increases membrane smoothness and forms a thin selective top layer with excellent pore geometry [42, 52]. Thus, HCl treated ZnO nano powder embedded membranes give better performance than pristine ZnO nano powder embedded membranes.

Similarly, the effect of PSF concentration was studied for copper rejection. An increase in base polymer and dope solution concentration modifies the gelation condition for the membrane prepared by sol-gel method. This reduction in solvent content and enhanced solid content help to reduce the membrane pore size. This reduction in membrane pore size helps to improve their rejection properties [35]. The similar properties were observed for concentration up to 40 %. Beyond this condition, when PSF concentration was increased from 40 to 43%, a decrease in rejection properties have been observed. It can be attributed to variation in gelation kinetics at higher concentration (43%). There is possibility of large agglomerate formation enhancing the pore size and uneven distribution of ZnO nano powder. Both these conditions in combination results in decreasing rejection as shown in Figure **2**.

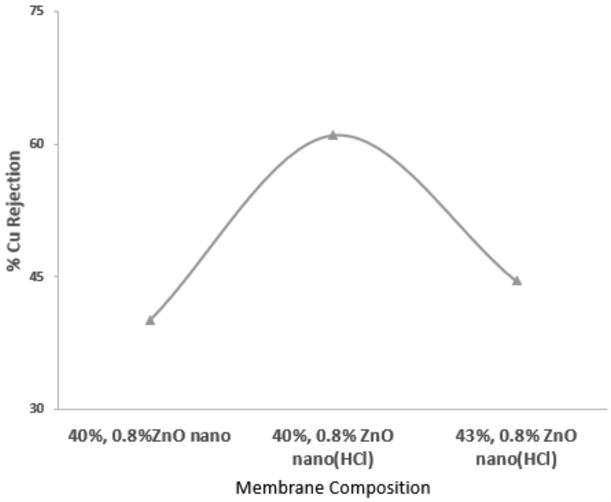

Figure 2: Effect of PSF concentration and ZnO NPs chemical modification on Copper Rejection for PSF-ZnO NPs membrane.

3.3. Effect of ZnO Nano Powder (Acid Treated) Concentration on Copper Rejection

A rejection study of copper was observed for membranes prepared from 40% PSF, 8% PEG (M.W. 200), and 0.2 to 1 % HCl treated ZnO nano powder. Optimization of PEG concentration for PSF membrane was studied by Dhume S. *et al*. 2020, it was observed that at 8 % PEG concentration there is a good equilibrium among selectivity and transport property of membrane. Membrane obtained have smaller pore size and hence will increase rejection property of membrane without much affecting pure water flux. Acid (HCl) treated ZnO form $ZnCl_2$, which has a good interaction with PSF. It changes the gelation kinetics of the membrane, resulting in good rejection properties [42, 52].

Also, the interaction between PSF and PEG imparts hydrophilicity to the membrane which helps to overcome the membrane's major limitation of fouling and hence will help to increase membrane life. Similarly, M.W. of PEG also plays a crucial role to determine membrane properties. The use of low M.W. PEG reduces membrane flux [53] which features the pore size reduction of the membrane which is desired property of the present work to enhance copper rejection.

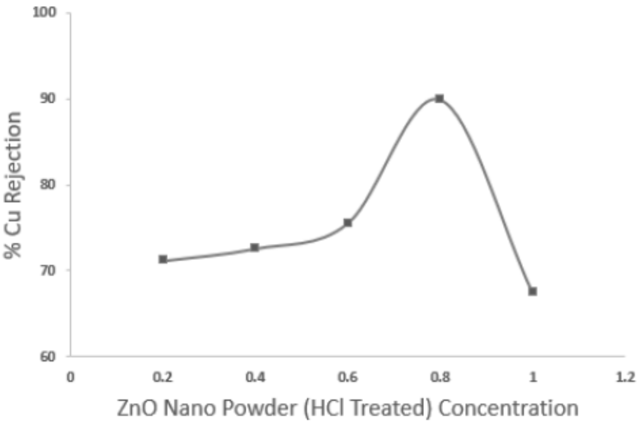

Figure 3: Effect of concentration of HCl treated ZnO nano powder on Copper Rejection for 40%PSF-8%PEG membrane.

From Figure **3** it is observed that as the concentration of ZnO nano powder is increased from 0.2 to 0.8%, copper rejection has increased from 71 to 90%. It attributes that up to 0.8% concentration ZnO nano powder was homogeneously dispersed in dope solution and charge intensity of membrane is maximum. Thus, maximum rejection was observed at 0.8% concentration. Whereas with further increase in ZnO concentration up to 1%, copper rejection has decreased to 68%. These attributes at 1% concentration ZnO nano powder clusters may be formed resulting in uneven distribution and forming a comparatively weak charged membrane.

3.4. Water Flux and Pore Size

The dope solution concentration is significant to define the membrane transport properties as shown in Figure **4**. The HCl treated ZnO nano powder was used to optimize the performance of PSF-PEG membrane [42, 51]. The use of ZnO nano powder up to 0.8 % causes an increase in pure water flux denotes the pore size of membrane will be more. But there is a decrease in the pore size of the membrane up to 0.8% and after that, at 1% flux has decreased and pore size has increased. An increase in water flux, though the decrease in pore size attributes that there is an increase in a pore density or number of pores of the membrane. The membrane with good transport and good selectivity for rejection is the desired property of current work.

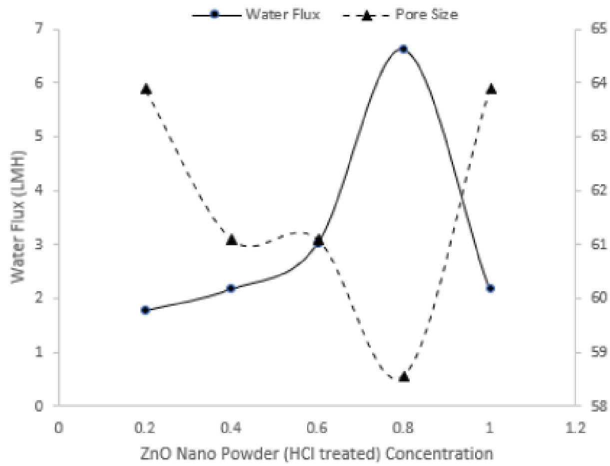

Figure 4: Effect of concentration of HCl treated ZnO nano powder on membrane water flux and pore size.

It shows up to 0.8% ZnO concentration improved interaction of PSF/PEG and proper uniform distribution of ZnO nano powder, and equal charge distribution in membrane matrix. This we have even observed in Figure **3** and confirmed with improved rejection property of membrane up to 0.8% nano powder concentration. At 1% ZnO nano powder concentration, a decrease in water flux and rejection property of membrane attributes to accumulation and improper distribution of nano powder, its charge, and weak interaction with polymer.

3.5. FTIR Analysis

The FTIR spectra indicate the type of bond, stretching, or components present [36-38]. The membrane shows a slight variation in the absorption band for different compositions as shown in Figure **5**.

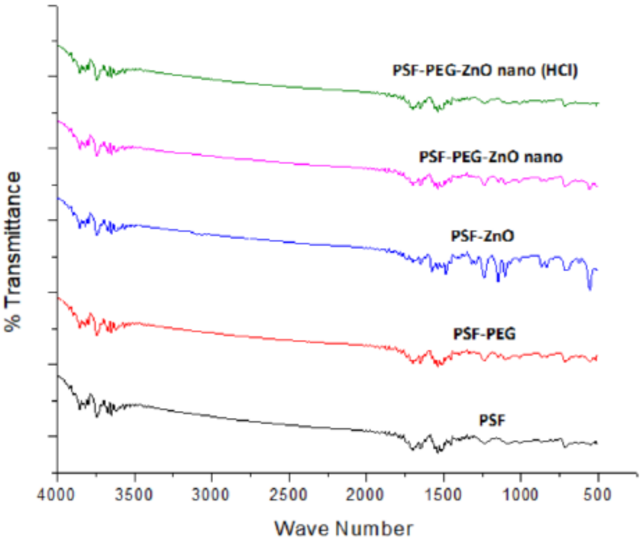

Figure 5: FTIR spectra of PSF, PSF-PEG, PSF-ZnO, PSF-PEG-ZnO nano powder, and PSF-PEG-ZnO nano powder (HCl) membrane.

From Figure **5**, it was observed that, after the addition of PEG, and ZnO in PSF membrane, there is little or no change in the FTIR pattern as a very small amount of additives was used during membrane fabrication. Similar results were reported by Leo C.P. *et al*. 2012. It was observed that the absorption band at 1083 cm^{-1} is an ether (-C-O-C-) group of PSF [37], and it gets shifted to 1104 for PSF embedded with PEG, ZnO, and PEG-ZnO together. While ZnO nanoparticles when interacting with HCl, the surface modification of the membrane was observed, and its ether group band shifted to a new position at 1083 cm^{-1} for PSF-PEG-ZnO (HCl) membrane. This shows the stronger interaction and variation in molecule surface property, and surface charge. Thus, when the secondary molecule (metal ion) comes in contact with surface-charged material, due to the repulsion between similarly charged ZnO nanoparticles and metal ions, there will be a surface double layer formation of heavy metal ions on the surface of the membrane. It leads to a concentration gradient, which causes the repulsion and rejection of heavy metal ions. Similarly at 1235 cm^{-1} stretching vibration of aryl ether was observed for PSF [38] which shifted to 1239-1241 for PSF membrane prepared with the use of PEG, ZnO, and PEG-ZnO combination, and further, it shifted to 1236 for PEG-ZnO modified with HCl. The phenyl (C-H) peak was observed at 719 and shifted to 714 cm^{-1} for membrane embedded with ZnO. ZnO generally shows absorption below 1000 cm^{-1} in the fingerprint area. The peak at 556 of PSF shifted to 553 cm^{-1} due to ZnO stretching. No additional peaks were formed due to PEG additive due to overlapping of PSF ether and C-H group. This stretching and bending attribute that when HCl interacts with ZnO, modifies the membrane, and changes the electronic environment which is stable. This contributes to an increase in interactive repulsion between the similar charges of membrane and metal ions according to the Donnan exclusion principle. It leads to enhancement in the rejection property of copper.

3.6. EDX

Surface chemistry and composition have a large effect on the transport and rejection properties of the membrane. The membranes with similar composition, pore size, and porosity can possess variations in rejection properties for different components based upon interaction with surface molecules. Hence the analysis of surface properties, chemical composition, and distribution of components is investigated using EDX analysis.

Table **1** shows the elements present in the membrane by energy dispersive X-ray. EDX data from Table **1** underlines the importance of interaction and possible variation in Cu rejection properties. When the membrane was composed of PSF and pristine ZnO

Table 1: EDX Data of Membrane with Different Compositions (wt%)

Membrane Composition	C	O	S	Zn	Cl
40%PSF, 0.8%ZnO	72.05	21,83	5.98	0.14	
40% PSF, 0.8%ZnO (HCl)	70.64	23.21	5.94	0.05	0.16
43% PSF, 0.8%ZnO (HCl)	72.81	21.03	5.72	0.09	0.35

nanoparticles, it can show the absence of Cl in the membrane matrix. Whereas when it was treated with HCl, the presence of Cl was observed. The data in Table **1** supports the interaction of ZnO nanoparticles with HCl by the presence of Cl in the membrane matrix. Also, the increase in the amount of ZnO for 43% is supported by a high amount of Zn and Cl present is shown in EDX data.

4. CONCLUSIONS

The harmful effects of copper on the environment and living organisms demanded its removal from water. Further, its recovery is important as this natural entity-metal ion has large applicability. The separation is dependent on parameters such as feed condition (pH, concentration), method efficiency, operational cost (economics), environmental impact, etc. Limitations of conventional and membrane-based methods impose the need to develop a new design that overcomes the separation method issues. Thus, in this study, PSF-based membranes prepared with PEG as an additive and HCl treated ZnO nano powder as a surface modifier were used for the same. Some of the major outcomes can be pointed out as:

A. The use of ZnO nano powder resulted in surface charge modification of membranes while maintaining transport properties. Such incorporation of the charge in the membrane by pre-synthesis preparation process developed mechanical and chemical stable membranes without altering PSF properties.

B. These membranes showed a reduction in fouling and the similar charge of membrane surface and metal ion solution improves separation efficiency of membrane using the Donnan exclusion principle.

C. It was observed that copper rejection efficiency of the membrane has increased from 40% to 90% for pristine to acid (HCl) treated ZnO nano powder along with the use of PEG.

This method has industrial applicability due to its easy fabrication process, sustainability, and techno-commercial impact. Further membrane optimization study is required to opt for maximum rejection efficiency and to maintain copper ion level in water within its permissible limit. Also, the membrane properties can be tuned as per the transport property requirements and for multi-metal ions separation.

ABBREVIATIONS

DMAc:	Dimethyl acetamide
EDX:	Energy Dispersive X-ray
FTIR:	Fourier Transform Infrared
LMH:	Liters per meter square hour
M.W.:	Molecular weight
NPs:	Nanoparticles
PEG:	Polyethylene glycol
PSF:	Polysulfone
UF:	Ultrafiltration
USA:	United States of America
UV vis:	Ultraviolet-visible
WHO:	World health organization

STATEMENTS AND DECLARATIONS

Acknowledgments

We thank Bharati Vidyapeeth (Deemed to be) University College of Engineering, Pune, and MIT-World Peace University, Pune for providing us the useful resources. We also thank for the financial support from DST- Nano Mission (Sanction No. SR/MN/NT/-1029/2015).

Funding

We thank for the financial support from DST- Nano Mission (Sanction No. SR/MN/NT/-1029/2015).

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Pallavi Mahajan-Tatpate, Supriya Dhume, Sachin Chavan, Yogesh Chendake.

Ethical Approval and Consent to Participate

This study is related to the separation and recovery of waste generated. It is not related to animal and health studies/trials. Hence ethical approval is not required on this topic. However, the institution committee has gone through the work plan and approved the same.

Consent for Publication

Consent is given for publication in the 'International Journal of Membrane Science and Technology'.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability and Materials

All the research work is original and belongs to the authors. Data of the same is available with authors and not being considered anywhere for publication.

REFERENCES

[1] Kapahi M, Sachdeva S. Bioremediation Options for Heavy Metal Pollution. Journal of Health & Pollution. 2019; 9(24). https://doi.org/10.5696/2156-9614-9.24.191203

[2] Paul D. Research on heavy metal pollution of river Ganga: A review. Annals of Agrarian Science [Internet]. 2017; 15(2): 278-86. https://doi.org/10.1016/j.aasci.2017.04.001

[3] Xu X, Cao X, Zhao L, Wang H, Yu H, Gao B. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. Environmental Science and Pollution Research. 2013; 20(1): 358-68. https://doi.org/10.1007/s11356-012-0873-5

[4] Ihsanullah, Abbas A, Al-Amer AM, Laoui T, Al-Marri MJ, Nasser MS, *et al*. Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. Separation and Purification Technology. 2016; 157: 141-61. https://doi.org/10.1016/j.seppur.2015.11.039

[5] Briffa J, Sinagra E, Blundell R. Heavy metal pollution in the environment and their toxicological effects on humans. Heliyon [Internet]. 2020; 6(9): e04691. https://doi.org/10.1016/j.heliyon.2020.e04691

[6] Ngoc NTM, Chuyen N Van, Thao NTT, Duc NQ, Trang NTT, Binh NTT, *et al*. Chromium, Cadmium, Lead, and Arsenic Concentrations in Water, Vegetables, and Seafood Consumed in a Coastal Area in Northern Vietnam. Environmental Health Insights. 2020; 14. https://doi.org/10.1177/1178630220921410

[7] Mahajan-Tatpate P, Dhume S, Chendake Y. Removal of Heavy Metals from Water: Technological Advances and Today's Lookout Through Membrane Applications. International Journal of Membrane Science and Technology. 2021; 8: 1-21. https://doi.org/10.15379/2410-1869.2021.08.01.01

[8] Taghinia Hejabi A, Basavarajappa HT, Karbassi AR, Monavari SM. Heavy metal pollution in water and sediments in the Kabini River, Karnataka, India. Environmental Monitoring and Assessment. 2011; 182(1-4): 1-13. https://doi.org/10.1007/s10661-010-1854-0

[9] Sharma S Das. Risk assessment via oral and dermal pathways from heavy metal polluted water of Kolleru lake - A Ramsar wetland in Andhra Pradesh, India. Environmental Analysis Health and Toxicology. 2020; 35(3): e2020019. https://doi.org/10.5620/eaht.2020019

[10] Sharma R, Singh NS, Singh DK. Impact of heavy metal contamination and seasonal variations on enzyme's activity of Yamuna river soil in Delhi and NCR. Applied Water Science [Internet]. 2020; 10(3): 1-8. https://doi.org/10.1007/s13201-020-1166-7

[11] Al-Saydeh SA, El-Naas MH, Zaidi SJ. Copper removal from industrial wastewater: A comprehensive review. Journal of Industrial and Engineering Chemistry [Internet]. 2017; 56: 35-44. https://doi.org/10.1016/j.jiec.2017.07.026

[12] Abdullah N, Yusof N, Lau WJ, Jaafar J, Ismail AF. Recent trends of heavy metal removal from water/wastewater by membrane technologies. Journal of Industrial and Engineering Chemistry [Internet]. 2019; 76: 17-38. https://doi.org/10.1016/j.jiec.2019.03.029

[13] Machender G, Dhakate R, Rao STM, Rao BM, Prasanna L. Heavy metal contamination in sediments of Balanagar industrial area, Hyderabad, Andra Pradesh, India. Arabian Journal of Geosciences. 2014; 7(2): 513-25. https://doi.org/10.1007/s12517-012-0759-3

[14] Tang SY, Qiu YR. Selective separation of copper and zinc and regeneration of polymer from electroplating effluent using shear induced dissociation coupling with ultrafiltration. Korean Journal of Chemical Engineering. 2019; 36(8): 1321-7. https://doi.org/10.1007/s11814-019-0310-2

[15] Bandehali S, Parvizian F, Moghadassi AR, Hosseini SM. Copper and lead ions removal from water by new PEI based NF membrane modified by functionalized POSS nanoparticles. Journal of Polymer Research. 2019; 26(9). https://doi.org/10.1007/s10965-019-1865-7

[16] Vardi Venkateswarlu CV. GSC Biological and Pharmaceutical Sciences Bioaccumulation of heavy metals in edible marine fish from coastal areas of Nellore 2020; 10(01): 18-24. https://doi.org/10.30574/gscbps.2020.10.1.0244

[17] Taylor AA, Tsuji JS, Garry MR, McArdle ME, Goodfellow WL, Adams WJ, *et al*. Critical Review of Exposure and Effects: Implications for Setting Regulatory Health Criteria for Ingested Copper. Environmental Management [Internet]. 2020; 65(1): 131-59. https://doi.org/10.1007/s00267-019-01234-y

[18] Abd Hamid S, Shahadat M, Ballinger B, Farhan Azha S, Ismail S, Wazed Ali S, *et al*. Role of clay-based membrane for removal of copper from aqueous solution. Journal of Saudi Chemical Society [Internet]. 2020; 24(10): 785-98. https://doi.org/10.1016/j.jscs.2020.08.007

[19] Yruela I. Copper in plants. Brazilian Journal of Plant Physiology. 2005; 17(1): 145-56. https://doi.org/10.1590/S1677-04202005000100012

[20] Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Molecular, clinical and environmental toxicicology Volume 3: Environmental Toxicology [Internet]. Vol. 101, Molecular, Clinical and Environmental Toxicology. 2012. 133-164 p. https://doi.org/10.1007/978-3-7643-8340-4_6

[21] Gawande MB, Goswami A, Felpin FX, Asefa T, Huang X, Silva R, *et al*. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. Chemical Reviews. 2016; 116(6): 3722-811. https://doi.org/10.1021/acs.chemrev.5b00482

[22] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management [Internet]. 2011; 92(3): 407-18. https://doi.org/10.1016/j.jenvman.2010.11.011

[23] Al-Saydeh SA, El-Naas MH, Zaidi SJ. Copper removal from industrial wastewater: A comprehensive review. Journal of Industrial and Engineering Chemistry [Internet]. 2017; 56(July): 35-44. https://doi.org/10.1016/j.jiec.2017.07.026

[24] Azimi A, Azari A, Rezakazemi M, Ansarpour M. Removal of Heavy Metals from Industrial Wastewaters: A Review. Chem Bio Eng Reviews. 2017; 4(1): 37-59. https://doi.org/10.1002/cben.201600010

[25] Ates N, Uzal N. Removal of heavy metals from aluminum anodic oxidation wastewaters by membrane filtration. Environmental Science and Pollution Research. 2018; 25(22): 22259-72.
https://doi.org/10.1007/s11356-018-2345-z

[26] Muthumareeswaran MR, Alhoshan M, Agarwal GP. Ultrafiltration membrane for effective removal of chromium ions from potable water. Scientific Reports [Internet]. 2017; 7(January): 1-12.
https://doi.org/10.1038/srep41423

[27] Qasem NAA, Mohammed RH, Lawal DU. Removal of heavy metal ions from wastewater: a comprehensive and critical review. npj Clean Water. 2021; 4(1).
https://doi.org/10.1038/s41545-021-00127-0

[28] Emamjomeh MM, Torabi H, Mousazadeh M, Alijani MH, Gohari F. Impact of independent and non-independent parameters on various elements' rejection by nanofiltration employed in groundwater treatment. Applied Water Science [Internet]. 2019; 9(4): 1-10.
https://doi.org/10.1007/s13201-019-0949-1

[29] Khan SUD, Khan SUD, Danish SN, Orfi J, Rana UA, Haider S. Nuclear Energy Powered Seawater Desalination [Internet]. Renewable Energy Powered Desalination Handbook: Application and Thermodynamics. Elsevier Inc.; 2018. 225-264 p.
https://doi.org/10.1016/B978-0-12-815244-7.00006-4

[30] Mondal S, Kumar Majumder S. Fabrication of the polysulfone-based composite ultrafiltration membranes for the adsorptive removal of heavy metal ions from their contaminated aqueous solutions. Chemical Engineering Journal [Internet]. 2020; 401(June): 126036.
https://doi.org/10.1016/j.cej.2020.126036

[31] Mulder M. Basic principles of membrane technology. 1991.
https://doi.org/10.1007/978-94-017-0835-7

[32] Lohokare HR, Bhole YS, Kharul UK. Effect of support material on ultrafiltration membrane performance. Journal of Applied Polymer Science. 2006; 99(6): 3389-95.
https://doi.org/10.1002/app.23039

[33] Javdaneh S, Mehrnia MR, Homayoonfal M. Fabrication of polysulfone/zinc oxide nanocomposite membrane: Investigation of pore forming agent on fouling behavior. Korean Journal of Chemical Engineering. 2016; 33(11): 3184-93.
https://doi.org/10.1007/s11814-016-0178-3

[34] Hebbar RS, Isloor AM, Prabhu B, Inamuddin, Asiri AM, Ismail AF. Removal of metal ions and humic acids through polyetherimide membrane with grafted bentonite clay. Scientific Reports [Internet]. 2018; 8(1).
https://doi.org/10.1038/s41598-018-22837-1

[35] Dhume SS, Mahajan-Tatpate P, Chendake YJ. Optimization of PSF Membrane Transport Properties with the Use of Porogenic Additive. Journal of Applied Membrane Science & Technology. 2020; 24(3): 57-73.
https://doi.org/10.11113/amst.v24n3.193

[36] Jhaveri JH, Murthy ZVP. A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. Desalination [Internet]. 2016; 379: 137-54.
https://doi.org/10.1016/j.desal.2015.11.009

[37] Fahmey MS, El-Aassar AHM, M.Abo-Elfadel M, Orabi AS, Das R. Comparative performance evaluations of nanomaterials mixed polysulfone: A scale-up approach through vacuum enhanced direct contact membrane distillation for water desalination. Desalination [Internet]. 2019; (August): 111-6.
https://doi.org/10.1016/j.desal.2017.08.020

[38] Shahlol OMA, Isawi H, El-Malky MG, Al-Aassar AEHM, zwai A El. Performance evaluation of the different nano-enhanced polysulfone membranes via membrane distillation for produced water desalination in Sert Basin-Libya. Arabian Journal of Chemistry [Internet]. 2020; 13(4): 5118-36. 1
https://doi.org/10.1016/j.arabjc.2020.02.011

[39] Nawi NIM, Chean HM, Shamsuddin N, Bilad MR, Narkkun T, Faungnawakij K, *et al*. Development of hydrophilic PVDF membrane using vapour induced phase separation method for produced water treatment. Membranes. 2020; 10(6): 1-17.
https://doi.org/10.3390/membranes10060121

[40] Zuo X, Wang L, He J, Li Z, Yu S. SEM-EDX studies of SiO2/PVDF membranes fouling in electrodialysis of polymer-flooding produced wastewater: Diatomite, APAM and crude oil. Desalination [Internet]. 2014; 347: 43-51.
https://doi.org/10.1016/j.desal.2014.05.020

[41] Zuo DY, Xu YY, Xu WL, Zou HT. The influence of PEG molecular weight on morphologies and properties of PVDf asymmetric membranes. Chinese Journal of Polymer Science (English Edition). 2008; 26(4): 405-14.
https://doi.org/10.1142/S0256767908003072

[42] Panda SR, De S. Preparation, characterization and performance of ZnCl2 incorporated polysulfone (PSF)/polyethylene glycol (PEG) blend low pressure nanofiltration membranes. Desalination [Internet]. 2014; 347: 52-65.
https://doi.org/10.1016/j.desal.2014.05.030

[43] Kheirieh S, Asghari M, Afsari M. Application and modification of polysulfone membranes. Reviews in Chemical Engineering. 2018; 34(5): 657-93.
https://doi.org/10.1515/revce-2017-0011

[44] Aroua MK, Zuki FM, Sulaiman NM. Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration. Journal of Hazardous Materials. 2007; 147(3): 752-8.
https://doi.org/10.1016/j.jhazmat.2007.01.120

[45] Garcia-Ivars J, Alcaina-Miranda MI, Iborra-Clar MI, Mendoza-Roca JA, Pastor-Alcañiz L. Enhancement in hydrophilicity of different polymer phase-inversion ultrafiltration membranes by introducing PEG/Al2O3 nanoparticles. Separation and Purification Technology [Internet]. 2014; 128: 45-57.
https://doi.org/10.1016/j.seppur.2014.03.012

[46] Padilha LF, Borges CP. PVC membranes prepared via non-solvent induced phase separation process. Brazilian Journal of Chemical Engineering. 2019; 36(1): 497-509.
https://doi.org/10.1590/0104-6632.20190361s20170132

[47] Alhoshan M, Alam J, Dass LA, Al-Homaidi N. Fabrication of polysulfone/ZnO membrane: Influence of ZnO nanoparticles on membrane characteristics. Advances in Polymer Technology. 2013; 32(4): 1-7.
https://doi.org/10.1002/adv.21369

[48] Chung YT, Ba-Abbad MM, Mohammad AW, Benamor A. Functionalization of zinc oxide (ZnO) nanoparticles and its effects on polysulfone-ZnO membranes. Desalination and Water Treatment [Internet]. 2016; 57(17): 7801-11.
https://doi.org/10.1080/19443994.2015.1067168

[49] Pintilie SC, Tiron LG, Birsan IG, Balta S. Influence of ZnO nanoparticle size and concentration on the polysulfone membrane performance. Materiale Plastice. 2017; 54(2): 257-61.
https://doi.org/10.37358/MP.17.2.4828

[50] Shen L, Huang Z, Liu Y, Li R, Xu Y, Jakaj G, *et al*. Polymeric Membranes Incorporated With ZnO Nanoparticles for Membrane Fouling Mitigation: A Brief Review. Frontiers in Chemistry. 2020; 8.
https://doi.org/10.3389/fchem.2020.00224

[51] Alabi A, AlHajaj A, Cseri L, Szekely G, Budd P, Zou L. Review of nanomaterials-assisted ion exchange membranes for electromembrane desalination. npj Clean Water [Internet]. 2018; 1(1).
https://doi.org/10.1038/s41545-018-0009-7

[52] Kim JH, Lee KH. Effect of PEG additive on membrane formation by phase inversion. Journal of Membrane Science. 1998; 138(2): 153-63. https://doi.org/10.1016/S0376-7388(97)00224-X

[53] Mahajan-Tatpate P, Dhume S, Chendake Y. Recovery of chromium using membrane containing charged material. IOP Conference Series: Materials Science and Engineering. 2021; 1146(1): 012022. https://doi.org/10.1088/1757-899X/1146/1/012022

Received on 29-08-2022 Accepted on 28-09-2022 Published on 09-10-2022

DOI: https://doi.org/10.15379/2410-1869.2022.07

© 2022 Mahajan-Tatpate *et al.*; Licensee Cosmos Scholars Publishing House.
This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/), which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.