REMOVAL OF IRON AND MANGANESE FROM GROUNDWATER BY NANOHYBRID SILVER DECORATED GRAPHENE OXIDE (Ag-GO) POLYSULFONE NANOFILTRATION MEMBRANE

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ABSTRACT

Iron (Fe) and manganese (Mn) are common metallic elements that naturally coexist in groundwater. Elevated levels of these metallic ions will result in an undesirable rusty taste and reddish hue, rendering the water unsuitable for consumption. Polymer-based membrane technology can play a significant role in removing Fe and Mn from groundwater. However, polymer-based such polysulfone (PSf) membrane possessed a hydrophobic characteristic. Thus, the objective of this study was to fabricate and characterize PSf nanofiltration membrane impregnated with silver decorated graphene oxide (Ag-GO) via wet phase inversion technique. Based on results obtained, PSf/Ag-GO exhibit enhanced properties, such as good water flux (32.47 L/m^2.h) and improved hydrophilicity (89% of porosity). The performance of fabricated membranes was studied using a bench-scale dead-end stirred cell by investigating salt (1000 mg/L) rejection and Fe & Mn removal at feed concentration of 10-100 mg/L and 1 mg/L, respectively. Results showed that the rejection of Na_2SO_4 was higher compared to NaCl. Good rejection of Fe and Mn was also achieved higher than 85%. The most substantial impact on removal efficiency was caused by adjusting the pH of feed solution (pH 3-12). The removal of Fe and Mn was found significantly higher at basic pH (between 9 and 12) compared to acidic pH. This was due to the transformation of soluble divalent Fe^{2+} and Mn^{2+} ions to insoluble Fe^{3+} and Mn^{4+}. At this condition, it is expected that the rejection mechanism by sieving effect has contributed to the improvement of Fe and Mn removal in basic pH. In conclusion, embedding Ag-GO has successfully improved the hydrophilicity of PSf membranes due to the additional of hydroxyl group and more importantly, able to achieve high removal of Fe and Mn at 10 – 100 mg/L. Above all, the rejection mechanism of Fe and Mn was found have been impacted by the adjustment of feed solution pH whereby the sieving effect and Donnan effect are resulted by the solute-membranes interaction.

ABSTRAK

Besi (Fe) dan mangan (Mn) adalah unsur logam yang biasa wujud secara bersama dalam air bawah tanah. Pada kandungan kedua-dua ion logam yang tinggi menyebabkan rasa karat dan warna air kemerahan, yang mana tidak sesuai untuk diminum. Teknologi membran berasaskan polimer boleh berperanan penting dalam menyingirkan Fe dan Mn daripada air bawah tanah. Walau bagaimanapun, membran polisulfon (PSf) mempunyai ciri hidrofobik. Oleh itu, objektif kajian ini adalah untuk menghasilkan dan mencirikan membrane PSf nano penurasan yang ditambah bersama zarahnano perak-graphene oksida (Ag-GO) melalui teknik pembalikan fasa basah. Berdasarkan keputusan yang diperoleh, PSf/Ag-GO mempunyai sifat yang dipertingkatkan, seperti aliran air yang baik (32.47 $L/m^2.h$) dan ciri hidrofilik yang dipertingkatkan (89% penyingkiran). Prestasi membran yang telah difabrikasi dikaji menggunakan sel teraduk hujung mati skala makmal dengan mengkaji penyingkiran garam (1000 mg/L) dan penyingkiran Fe & Mn pada kepekatan suapan 10-100 mg/L dan 1 mg/L, masing-masing. Hasil kajian menunjukkan penyingkiran Na_2SO_4 adalah lebih tinggi berbanding dengan NaCl. Penyingkiran yang baik terhadap Fe dan Mn juga dicapai iaitu melebihi 85%. Kesan yang paling ketara terhadap kecekapan penyingkiran adalah disebabkan oleh pelarasan pH larutan suapan (pH 3-12). Penyingkiran Fe dan Mn didapati lebih tinggi secara ketara pada pH kealkalian (antara 9 dan 12) berbanding pH keasidan. Ini disebabkan oleh perubahan ion Fe^{2+} dan Mn^{2+} dwivalen larut kepada Fe^{3+} dan Mn^{4+} yang tidak larut. Pada keadaan ini, dijangka bahawa mekanisme penyingkiran dengan kesan penyaringan telah dijangkakan menyumbang kepada peningkatan penyingkiran Fe dan Mn dalam pH keakalian. Kesimpulannya, penyisipan Ag-GO telah berjaya meningkatkan hidrofilisiti membran PSf kerana penambahan kumpulan fungsi hidroksil dan yang lebih penting, mampu mencapai penyingkiran Fe dan Mn yang tinggi iaitu pada 10 – 100 mg/L. Terutamanya, mekanisme penyingkiran Fe dan Mn didapati telah dipengaruhi oleh pelarasan pH larutan suapan yang mana kesan penurasan dan kesan Donnan adalah terhasil daripada interaksi zat terlarut dengan membran.

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APPROVAL

The Examination Committee has met on **6 October 2023** to conduct the final examination of **Nur Syahirah Binti Suhalim** on his degree thesis entitled **'Removal of Iron and Manganese from Groundwater by Nanohybrid Silver Decorated Graphene Oxide (Ag-GO) Polysulfone Nanofiltration Membrane.**

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DECLARATION OF THESIS

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Title : Removal Behaviour Study of Iron and Manganese Rejection from Groundwater by Nanohybrid Polysulfone Nanofiltration Membranes
Academic session :

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LIST OF ABBREVIATIONS

3D	- 3-Dimensional
AFM	- Atomic Force Microscopy
APHA	- American Public Health Association
ATR	- Attenuated Total Reflectance
BSA	- Bovine Serum Albumin
CFSK	- Combined Film Theory-Spiegler-Kedem
CNF	- Cellulose Nanofibers
CP	- Concentration Polarisation
CS	- Chitosan
DABSA	- Diaminobenzenesulfonic
DE	- Dielectric Exclusion
DMF	- Dimethylformamide
DMSO	- Dimethyl sulfoxide
DOSM	- Department of Statistics Malaysia
DSPM	- Donnan Steric Pore Model
EDX	- Energy-dispersive X-ray
EPS	- Extracellular Polymeric Substances
EVOH	- Ethylene-Co-Vinyl Alcohol
FESEM	- Field Emission Scanning Electron Microscopy
FRR	- Flux Recovery Ratio
GO	- Graphene oxide
FTIR	- Fourier Transform Infrared
GRAS	- Generally Recognised as Safe
HM	- Hybrid Model
HM	- Heavy Metal
HPI	- Heavy Metal Pollution Index

HRA	- Health Risk Assessment
IEP	- Isoelectric Point
IP	- Interfacial Polymerisation
IR	- Infrared
IV	- Arsenic
KATS	- Ministry of Water, Land and Natural Resources’
MBR	- Membrane Bioreactor
MF	- Macrofiltration
MP	- Megapascal
MW	- Molecular Weight
MWCO	- Molecular Weight Cut-off
NAHRIM	- National Water Research Institute of Malaysia
NF	- Nanofiltration
NIH	- National Institutes of Health
NMP	- N-Methylpyrrolidone
NOM	- Natural Organic Matter
NP	- Nanoparticle
ODS	- Office of Dietary Supplements
PA	- Polyamide
PAE	- Phthalic Acid Esters
PAH	- Polycyclic Aromatic Hydrocarbons
PDA	- Polydopamine
PDIP	- Pre-diffusion Interfacial Polymerization
PEI	- Polyethyleneimine
PES	- Polyethersulfone
PSBMA	- Poly (sulfobetaine methacrylate)
PSf	- Polysulfone
PVA	- Poly (vinyl alcohol)

PVC	- Polyvinyl chloride
PVDF	- Poly(vinylidene fluoride)
PVP	- Polyvinyl pyrrolidone
PZC	- Point of Zero Charge
QD	- Quantum Dots
RO	- Reverse Osmosis
SEDE	- Steric, Electric, and Dielectric Exclusion
SEM	- Scanning electron microscope
SHP	- Steric Hindrance Pore Model
SK	- Spiegler–Kedem
TDS	- Total Dissolved Solid
TFC	- Thin Film Composite
TMC	- trimesoyl chloride
TMS	- Teorell-Meyer-Sievers
UF	- Ultrafiltration
UHT	- Ultra-High-Temperature
UV	- Ultra-Violet
WCA	- Water Contact Angle
WHO	- World Health Organization
XDA	- Xylylenediamine

LIST OF SYMBOLS

C_p - Feed concentration (mg/L)

C_f - Permeate concentration (mg/L) ε - Porosity r_m - Pore size

J - Water/permeate flux (L/m^2.h)

R - Rejection (%)

Q - Amount of water collected (L) l - Membrane thickness d_w - Density of water ΔP - Applied pressure (bar)

A - Membrane surface area (m^2) T - Absolute temperature (K)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Water is an essential element in life because body needs water to function at its topmost competence. Frequently drinking water can improve skin condition and help control weight, emotions, and alertness (An & McCaffrey, 2016; Krecar et al., 2014; Pross et al., 2014). According to data provided by The Department of Statistics Malaysia (DOSM) in 2023, the estimated population of Malaysia in the first quarter of that year was 33.2 million. This represents a 1.6% increase compared to the first quarter of 2022, when the population was recorded at 32.6 million Based on the sustainability report published by Air Selangor, a total of 4991 million litres of clean and safe water is generated on a daily basis (Air Selangor, 2022). Hence, it has been established that access to clean water is of utmost significance and is a critical necessity in everyday existence. In Malaysia water supply shortage are either scheduled (usually for maintenance) or unscheduled. However, a journalist for Malay Mail, Ida Lim, wrote that according to Ministry of Water, Land and Natural Resources' (KATS), out of many states in Malaysia, Selangor is the state that suffered the greatest for unscheduled water supply disruption (Lim, 2019). One of the alternative ways to counter this problem was to extract fresh groundwater. Mridha and co-researchers affirmed that in Selangor, about 10.8 billion litres of fresh groundwater is being extracted and used as water supply especially for factories (Mridha et al., 2019).

However, over the past century, there has been a significant increase in the rate of industrialization. The increased demand for exploiting the Earth's natural resources at an unsustainable rate has worsened the global issue of groundwater pollution. Groundwater pollution is primarily caused by various contaminants, including phosphorus, nitrogen found in sewage and heavy metals (Denchak, 2023). Heavy metals could come from both natural and anthropogenic sources. Heavy metal contaminants that come from anthropogenic sources are agriculture (pesticides and fertilizer), sewage sludge, domestic and mining (Cesar Minga et al., 2023; Perumal et al., 2021; Sidabutar et al., 2017; Thai-Hoang et al., 2022). Meanwhile, Ali et al. (2019) stated that heavy metals that come from natural sources are usually originate from natural processes such as weathering of metal-bearing rocks and volcanic eruptions. Groundwater often contains various heavy metals, such as zinc (Zn), manganese (Mn), chromium (Cr), copper (Cu), cadmium (Cd), iron (Fe), cobalt (Co), and lead (Pb) (Belkhiri et al., 2018; Lou et al., 2017; Vetrimurugan et al., 2017). However, Fe and Mn, are the heavy metals that are frequently detected in groundwater that is provided to houses area. These two heavy metals are common in deeper wells since the water has been in contact with rocks for a long time. According to Swistock & Sharpe (2022), Fe and Mn frequently coexist in groundwater, although Fe typically manifests in significantly higher concentrations compared to Mn.

There are two types of toxicity effect from heavy metals which are acute and chronic effect (Azeh Engwa et al., 2019). Based on a study done by Azizkhani and colleagues in 2018, diarrhea, kidney damage, lung insufficiency, bone lesions, nausea and renal disturbances can occur if one has consumed heavy metals for an extensive amount of time. Consequently, the World Health Organisation (WHO) has provided guidance stating that the safety of drinking water can only be assured if its iron content is below 0.3 mg L^{-1} and its manganese content is below 0.1 mg L^{-1} (World Health Organization, 2011). As per the guidelines established by the WHO, the Ministry of Health Malaysia (2023) has determined the maximum permissible concentrations of Fe and Mn to be 0.3 mg L^{-1} and 0.1 mg L^{-1}, respectively.

Igberase and co-researchers found that heavy metal removal from water is essential for disease-free health (Igberase et al., 2019). Hence, ion-exchange, water softening, activated carbon absorption, aeration, filtration, biosorption, and ionic liquid extraction have been used to remove Fe and Mn from groundwater (Abdul Kadir et al., 2012; Chaturvedi & Dave, 2012; Ellis et al., 2000; Hussin et al., 2014; Jusoh et al., 2005). According to Elsheikh et al. (2018), the authors found that effective removal of Fe and Mn can be achieved through oxidation using potassium permanganate, followed by the process of filtration. However, Genesis Water Technologies which is a company that specializes in drinking water & wastewater reuse solutions stated that oxidation processes are very high maintenance, very complex and removal of residual peroxide may need to be considered if the process utilizes hydrogen peroxide (Genesis Water Technologies, 2019).

In recent years, the use of membranes and membrane processes has found significant application within the realm of cleaning technology and the environmental sector (Badrinezhad et al., 2018; Kang et al., 2018). The need for novel membrane materials with excellent qualities has arisen due to membrane-based technologies' enhanced efficiency and effectiveness. Hence, the selection of materials and the techniques used in membrane fabrication have a crucial role in establishing the characteristics of the membrane. Many academics are interested in the topic of nanofiltration (NF) since it is quickly becoming a popular treatment method for water (Ainscough et al., 2021; Giacobbo et al., 2023; Mei et al., 2023; Yüzbasi et al., 2022). Furthermore, it is worth noting that NF membranes offer several advantages, including their ability to reject multivalent ions even at lower operating pressures effectively. This characteristic could lead to decreasing of permeate flux. Polysulfone (PSf) membranes have gained significant popularity due to their exceptional characteristics, including distinctive mechanical properties, low resistivity, high thermal and chemical stability (Mikhailenko et al., 2000; Min & Kim, 2010; Kaleekkal et al., 2017; Liu et al., 2014; Swier et al., 2006).

With a pore size approximately 0.5 – 5 nm (Zhang et al., 2022), NF membrane exhibits a noticeable sieving rejection mechanism called steric hindrance and at the same time it also exhibits non-sieving rejection mechanism. According to Andrij E. Yaroshcuk, non-sieving mechanism are donnan exclusion, dielectric exclusion and hydration mechanism (Yaroshcuk, 1998). Initially, it was renowned that NF is ruled by the Donnan exclusion caused by the electricity interactions of ionic solutes with established electrical charges attached to the membrane matrix. However, it has recently became clear that various NF membranes may have different dominant rejection mechanisms. Moreover, combinations of several rejection are also possible. Therefore, it is essential to investigate rejection mechanism of NF membranes to develop the best membrane for a particular application.

1.2 Problem Statement

Polymeric membrane is well known with its selectivity performance however the hydrophobic nature of polymeric membrane is inevitable and can lead to low permeation performance compared to inorganic membrane. According to Nguyen et al. (2019), PSf membranes are widely preferred in water treatment due to their notable thermal stability and commendable chemical resistance. However, it is important to note that the PSf membrane possessed hydrophobic characteristic which could lead low permeability and low water flux. In recent years, numerous strategies have been devised to enhance the properties of polymer membranes. The strategy of adding nanoparticles to a casting solution to create polymer-nanoparticles composite membranes is the most promising due to its straightforward preparation steps. The use of nanoparticles (NPs) such as silver (Ag) and Cu in water purification has garnered considerable interest (Mecha et al., 2023). The addition of NPs makes the membranes reactive instead of simply being a physical barrier, thereby performing multiple functions such as increasing water flux and improving contaminant rejection (Han et al., 2022; Mazani et al., 2020). A previous study has elucidated the incorporation of Ag NPs and Cu NPs into three-dimensional (3D) polymer nanocomposites with the aim of improving their mechanical strength, thermal stability, and electrical conductivity (Aktitiz et al., 2020).

In a study conducted by Chen et al. (2022), the successful integration of Ag into the polyamide layer was achieved using interfacial polymerization. This process involved the reaction between triethylenetetramine and 1,3,5-benzenetricarboxylic acid chloride. The experimental results indicate that there was a notable increase in