FABRICATION OF POLYETHERSULFONE MEMBRANE BY POLYETHYLENEGLYCOL COATED COBALT-DOPED IRON OXIDE FOR COPPER (II) REMOVAL

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ABSTRACT

Today, research and development of membrane technology are focused towards the improvement of properties and performances through membrane modification by using nanoparticles. In this research, hydrophobic cobalt-iron oxide nanoparticles were coated with polyethylene glycol (PEG) molecular weight MW-600 to prevent the agglomeration of nanoparticles and to improve its dispersion before adding into the dope solution containing 20 wt% polyethersulfone (PES) in dimethylformamide (DMF). The nanomodified membranes were characterized in terms of flux permeation (Q), wetting ability and solute separation. The prepared modified ultrafiltration membranes were then subjected to the separation of copper (II) ions and the separation efficiency of the nanoparticles modified membrane were found to improve significantly. This may be due to synergistic interaction between two additives that improved the structure as well as the performance of PES ultrafiltration membrane in terms of copper (II) rejection. The incorporation of 6% nanoparticles in the membranes had improved the copper (II) rejection from 10% to >90% with initial concentration of copper (II) at 20 ppm in cross flow filtration cell at pH 7. The membrane modified with nanoparticles also exhibited good regeneration ability and could be reused for more than five times without significantly drop in performances. In conclusion, incorporating of cobalt iron oxide nanoparticles coated with PEG can improve the copper (II) rejection of modified ultrafiltration membrane.

ABSTRAK

Pada masa kini, penyelidikan dan pembangunan teknologi membran menumpu kepada penambahbaikan sifat dan prestasi melalui pengubahsuaian dengan menggunakan nanopartikel. Dalam kajian ini, kobalt-besi oxida yang hidrofobik telah disalut dengan polietilena glikol (PEG) berat molekul MW-600 untuk mengurangkan pengumpalan nanopartikel dan meningkatkan kelarutannya sebelum ditambahkan ke dalam campuran yang mengandungi 20 wt% polietersulfon (PES) dalam dimetilforamida (DMF). Membran yang dinano-ubahsuaikan telah dicirikan dari segi fluks (Q), kebasahan dan pemisahan bahan larut. Membran ultraturasan yang disediakan seterusnya digunakan untuk memisah kuprum (II) dan kecekapan pemisahan didapati telah meningkat. Ini mungkin disebabkan terdapat interaksi sinergistik antara kedua-dua bahan tambah yang telah meningkatkan struktur dan prestasi membran dari segi penyingkiran kuprum (II). Penambahan 6% nanopartikel dalam membran telah meningkatkan penyingkiran 20 ppm kuprum (II) dari 10% kepada >90% dalam pH 7 menggunakan sel penurasan aliran silang. Membran yang diubahsuai menggunakan nanopartikel mempunyai kemampuan untuk dikitarguna sebanyak lima kali tanpa mempunyai penyusutan prestasi yang ketara. Kesimpulannya, penambahan nanopartikel kobalt-besi oxida yang disalutkan dengan PEG dalam membran ultraturasan telah meningkatkan penyingkiran kuprum (II) .

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LIST OF ABBREVIATIONS

Copper (II)	-	Cu(II)
DMF	-	Dimethyl formamide
EELS	-	Electron Energy Loss Spectrometer
FT-IR	-	Fourier transform infa-red
Magnetic nanoparticle	-	MNP
Microfiltration	-	MF
MWCO	-	Molecular weight cut off
Nanofiltration	-	NF
Natural organic matter	-	NOM
NMP	-	N-methyl-2- pyrrolidone
PEG	-	Polyethylene glycol
PES	-	Polyethersulfone
PS	-	Polysulphone
PVDF	-	Polyvinylidine floride
PVP	-	Polyvinylpyrrolidone
PWP	-	Pure water permeation
SEM	-	Scanning electron microscope
SR	-	Solute rejection
TEM	-	Transmission Electron Microscope
UF	-	Ultrafiltration
XRD	-	X ray diffraction Spectrometer

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CHAPTER 1

INTRODUCTION

1.1 Overview

A membrane has been defined by the European Society of Membrane Science and Technology as “an intervening phase separating two phases and/or acting as an active or passive barrier to the transport of matter between phases”. Membranes and membranes processes have become industrial products of substantial technical and commercial importance which are used to treat industrial effluents, to recover hydrogen from off gases, or to concentrate, and purify molecular solutions in the chemical and pharmaceutical industry. Due to its low energy consumption and easy control of operation, membrane technology has been very effectively used for the removal of natural organic matter (NOM) from surface and ground water (Celik *et al.*, 2011).

Due to its excellent chemical and mechanical properties, polyethersulfone (PES), a popular membrane material have been studied for many centuries for the synthesis of microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) membranes (Villaverde, *et al.*, 2012; Barth *et al.*, 2000). However, its hydrophobic nature has limited its applications especially in membrane separation processes (Ng *et al.,* 2013). Thus, several techniques were developed in order to solve these disadvantages which include hydrophilic modifications on the membrane surface to increase its permeability and reduce membrane fouling.

Today, the research and development of membrane technology are focused towards the improvement of anti-fouling properties (Cheng *et al.,* 2011), antibacterial properties (Liu *et al.,* 2009) and mechanical properties (Cheng *et al.,* 2011). Currently, many researchers have modified the membrane with nanoparticles such as TiO_2 (Rajesh *et al.,* 2013), CuO and ZnO (Liu *et al.,* 2012), polyniline (Shivkalyan *et al.*, 2012; Teli *et al.*, 2012), and silver (Cao *et al.*, 2010; Huang *et al.*, 2012) to improve the properties and performance of the membranes.

Among various types of nanoparticles, magnetic nanoparticles (MNP) have attracted a wide range of interest in many areas for example in material processing, desalination and water treatment. These nano size particles can be easily integrated with other adsorbents to produce magnetic composite adsorbent for water purification (Philipova *et al.*, 2011; Repko *et al.*, 2013). Idris *et al.* (2011) have used the iron oxide nanoparticle embedded in the form of beads to remove Pb(II) through adsorption process under various condition and they successfully removed 95.2% Pb(II) from the solution, which indicated that iron oxide act excellently as an adsorbent to remove the toxic heavy metal. Besides having excellent affinity towards heavy metals, iron oxide also proved to be a good adsorbent for the dyes (Tuutijärvi *et al.*, 2009; Zhou *et al.*, 2010; Mahapatra *et al.*, 2013) due to:

i.) large surface area which promotes adsorption,
ii.) metal-loaded magnetic adsorbent can be immediately and easily separated from treated water by the use of an external magnetic field,
iii.) no secondary toxic waste are produced

In water treatment process, removal of heavy metals can be conducted using techniques such as precipitation, ion-exchange and electrochemical (Caetano *et al.*, 1995; Fu *et al.*, 2011). In industry, chemical precipitation is widely used because it is relatively simple and inexpensive to operate (Ku and Jung, 2001). Chemical precipitation has been reported to be ineffective when metal ion concentrations are low and can also produce large amounts of sludge that needs subsequent treatment (Fu *et al.*, 2011). Due to high removal efficiency and fast kinetics, ion exchange resins are advantageous (Kang *et al.*, 2004). However, domestic applications of ions exchange are economically impractical especially at low metal concentrations and the regeneration of resins can cause secondary pollution (Fu *et al.*, 2011).

Electrochemical wastewater treatments such as electrocoagulation, electroflotation, and electrodeposition, have been established to be rapid and well-controlled techniques. However, they have not been widely applied due to high investment and operational costs (Fu *et al.*, 2009). Therefore, new environmental friendly and affordable processes are yet to be designed to remove the heavy metal and recover the valuable heavy metal from waste.

Besides the above mentioned techniques, membrane filtration technologies such as ultrafiltration, nanofiltration and reverse osmosis show great promise for toxic heavy metal removal due to its ease of operation and high efficiency (Fu *et al.*, 2009). Compared to nanofiltration and reverse osmosis membrane that operated at high transmembrane pressure, ultrafiltration membrane has low working pressure and therefore is less expensive and more applicable for household drinking water purification. Although ultrafiltration offers a higher permeation or filtration rate, it usually has low metal ions rejection due to its larger pore sizes, therefore these ions can pass easily through the membrane matrix. In order to increase the metallic ions rejection, micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) were studied. (Ferella *et al.*, 2007; Barakat *et al.*, 2010). These techniques used the chelating agents or complexing agents to bind the metallic ions to form larger structure that could be retained by the ultrafiltration membrane. However, the heavily consumption of expensive complexing agents such as sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate rendered its practical usage in household drinking water application due to the complexity in the design of this treatment system.

Besides membrane technologies, adsorption is also recognized as one of the effective and cost saving methods in heavy metal ions water treatment (Fu *et al.*, 2009; Tizaoui *et al.*, 2012). The adsorption process can produce high-quality treated water even at low heavy metal concentration. Activated carbon adsorbent is one of the common, low cost adsorbent that is widely used in domestic drinking water purification system for the removal of heavy metals ions as well as the organic matter (Lo *et al.*, 2012; Hu *et al.*, 2014; Largitte *et al.*, 2014; Njoku *et al.*, 2014). Besides activated carbon, many studies were also performed on the iron oxide nanoparticle or modified iron oxide nanoparticle as an effective adsorbent in waste water treatment especially in heavy metal ions adsorption or dye adsorption (Basu *et al.*, 2011; Ahmad *et al.*, 2012; Khatiri *et al.*, 2013; Burks *et al.*, 2014; Debnath *et al.*, 2014; Habibi *et al.*, 2014; Mittal *et al.*, 2014). However, iron oxide nanoparticle is hydrophobic in nature; therefore many methods such as coating or functionalization were used to modify the iron oxide to be more hydrophilic (Woo *et al.*, 2005; Park *et al.*, 2011).

1.1.1 Problem Statement

In our domestic drinking water, copper contamination constantly takes place during the water delivery process because of the leaching and micro-corrosion of copper piping or fitting in the water plumbing system (Girardi *et al.*, 2014; Camarillo *et al.*, 2010). The copper contamination of the domestic drinking water always goes unnoticeable by the consumers since the presence of copper does not alter significantly the taste, color or smell of the drinking water. Although copper is an essential micronutrient for the human, excess accumulation of copper in human body may cause intestinal disease such as nausea, vomiting, diarrhea, and even deaths (Fu and Wang, 2011). Therefore, a mixed matrix ultrafiltration membrane loaded with nanoparticles with better Cu(II) rejection properties should be developed.

Although nanoparticles such as, carbon nanotube (CNT), ZnO, Al_2O_3, SiO_2 and TiO_2 are seen promising to improve the performance and function of membranes, their low dispersion ability and high aggregation effect have rendered its uniform distribution throughout the membrane matrix. Such ununiformed distribution and agglomeration further lead to microdefects and thus lost their enhancement purposes (Liu *et al.,* 2011; Hong *et al.,* 2012; Liang *et al.,* 2014). Therefore, the amount of nanoparticles used are widely kept in small amounts (<4% wt) in the membrane solution preparation.

To further improve the dispersion of the nanoparticles as well as to prevent agglomeration, polyether glycol (PEG) is widely used as the coating agent for iron oxide nanoparticle and its derivative (Qu *et al.,* 2013). In addition, PEG also is commonly studied in membrane preparation due to its pore forming ability and its hydrophilicity characteristic in membrane flux improvement as well as antifouling properties (Long *et al.,* 2012; Hu *et al.,* 2013; Rahman *et al.,* 2013; Prince *et al.,* 2014). It was reported that PEG of low molecular weight would act as a macrovoid suppressor and give the membrane its hydrophilic character (Chou *et al.,* 2007). By increasing the molecular weight of PEG, the pure water permeation (PWP) would increase greatly therefore it is often used to improve the PWP of hydrophobic membrane such as PES, PS and PVDF membrane (Idris *et al.,* 2006; Chakrabarty *et al.,* 2008; Ma *et al.,* 2011).

The objective of this study is to fabricate dual function ultrafiltration membrane which has high permeation rate as well as high heavy metal ions rejection by incorporating the heavy metal adsorbents (cobalt doped iron oxide) coated with PEG with enhanced and uniform dispersion throughout the membrane matrix conceptually depicted in Figure 1.1. During ultrafiltration, the cobalt doped iron oxide will act as an heavy metal ions adsorbent to adsorb the Cu(II) that pass through the membrane matrix, therefore further reduce the Cu(II) concentration in the filtrate.

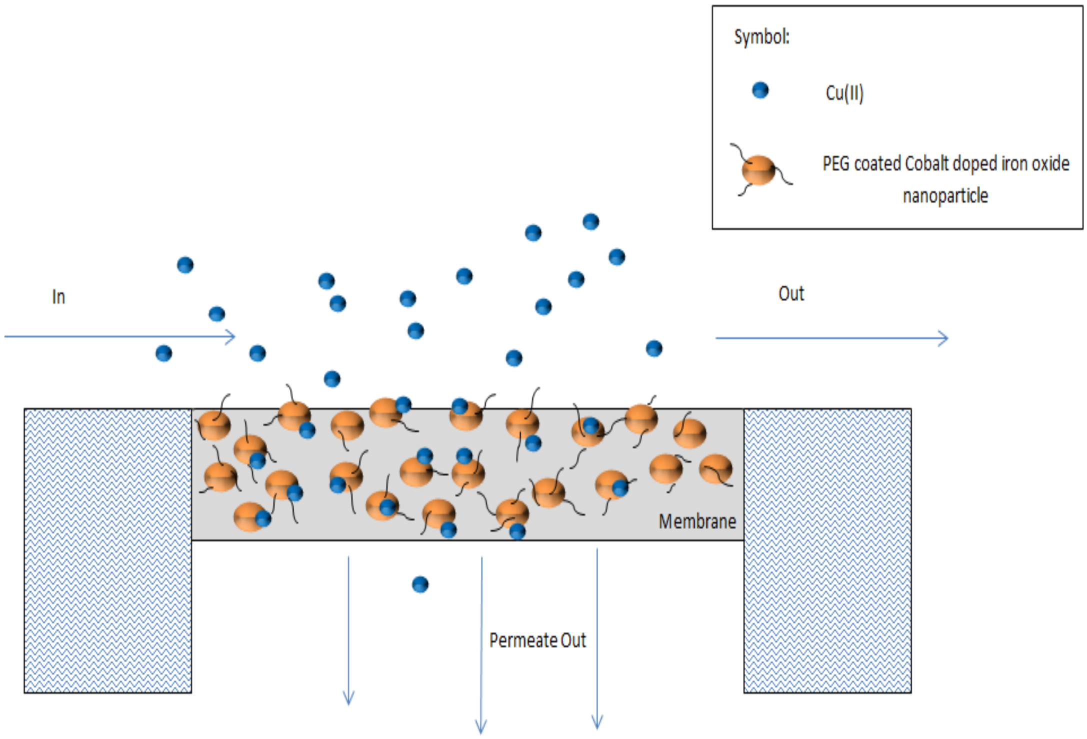

Figure 1.1 Schematic diagram of PES membrane modified with PEG-coated Co-Fe_2O_3 in cross flow filtration

1.3 Objectives and Scopes

The main objectives of this research are to:

i. Fabricate PES membranes containing cobalt-doped iron oxide nanoparticles coated with PEG.

ii. Study the influence of the cobalt doped iron oxide nanoparticle coated with PEG as the additive on PES membrane were investigated for Cu(II) removal.
iii. Determine the recyclability and antifouling properties of the modified membrane.

In order to achieve the mentioned objectives, the scopes of work need to encompass the following:

i. Preparation of cobalt doped iron oxide nanoparticles coated with PEG with uniform dispersion in the solvent
   -Characterization of nanoparticle using X-ray diffraction (XRD), fourier transform infra-red spectroscopy (FT-IR), electron energy loss spectroscopy (EELS) and transmission electron microscope (TEM).
ii. Preparation of dope solution formulations by varying the weight composition of nanocomposite in 20% wt PES by conventional heating method.
iii. The performance of the casted flat sheet membranes was analyzed in terms of MWCO and permeation rate using various PEG solutions ranging from 1000-35000 Dalton. The theoretical pore size was determined based on the MWCO profile.
iv. Surface hydrophilicity is evaluated using contact angle measurement and the chemical and structural properties of the membranes are then investigated using SEM and FT-IR.
v. The performance of modified PES membrane in term of Cu(II) removal was done at various pH condition ranging from pH 3-7 in the cross flow cell.
vi. The recyclability of the modified membrane was also performed in cross flow filtration cell for 20ppm Cu(II) for 5 treatment cycles.
vii. The antifouling properties of the membrane were also determined where BSA was used as model foulant through the flux recovery ratio calculation.

1.4 Significance of the Study

The aim of this project is to develop dual function ultrafiltration membrane which can be applied in various fields especially in the household water purification system. The introduction of cobalt doped iron oxide nanoparticles coated with PEG into the membrane matrix is believed to provide the antifouling properties to the PES membrane. Coated Iron oxide nanoparticle is often usely in waste water treatment as one of the advanced technologies in heavy metal removal such as Cu(II) (Wong *et al.*, 2014). However, coated iron oxide nanoparticle is hard to be separated out from the solution in the shortest time even by magnetic means due to the hydrophilicity of its coated surfactant. Hence, by integrating the coated iron oxide nanoparticle into the membrane matrix, membrane with better Cu(II) removal properties can be designed. Besides acting as the filtration membrane, this membrane can act as the adsorption membrane which can be used to adsorb and therefore capture the heavy metal such as Cu(II) from the solution therefore term as dual function membrane. These features make the nanoparticle modified membranes an attractive and ecofriendly separation tool to be applied in domestic water purification system.

1.5 Outline of the Thesis

The thesis is divided into four chapters. The first chapter encompasses the overview of the project which includes objectives, scope and significant of the study. Chapter 2 would surveys latest research on membrane development especially in membrane modification using nanoparticles. In Chapter 3, the methodology and experimentation design of this study were discussed in detail. Chapter 4 discusses the important findings of this research. Finally, Chapter 5 would recapitulates major findings of the thesis, and propose issues inviting future research

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