

Performance of PEG on immobilization of zero valent metallic particles on PVDF membrane for nitrate removal

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(Received July 10, 2016, Revised February 27, 2017, Accepted March 21, 2017)

Abstract. The principal objective of this study is to investigate the effect of Polyethylene Glycol (PEG) crosslinking in Polyvinylidene Fluoride (PVDF) in immobilization of Fe and bimetallic Fe/Cu and Cu/Fe zero valent particles on the membrane and its efficiency on removal of nitrate in wastewater. PVDF/PEG polymer solution of three weight compositions was prepared to manipulate the viscosity of the polymer. PEG crosslinking was indirectly controlled by the viscosity of the polymer solution. In this study, PEG was used as a modifier of PVDF membrane as well as a cross-linker for the immobilization of the zero valent particles. The result demonstrates improvement in immobilization of metallic particles with the increase in crosslinking of PEG. Nitrate removal efficiency increases too.

Keywords: zero-valent iron nanoparticle; bimetallic nanoparticle; membrane grafting; nitrate removal

1. Introduction

The high performance nano-scale zero valent iron (nZVI), and its bimetallic, iron/nickel (Fe/Ni), iron/palladium (Fe/Pd), and iron/copper (Fe/Cu) are getting tremendous attention from the industries. They are largely adopted in treating organics such as trichloroethylene compounds, and nitrate compound in waste water (Parshetti and Doong 2009, Zin *et al.* 2013). nZVI is reported to have large active surface area, high heavy metal adsorption capacity, reduction and precipitation of toxic and carcinogenic metals. For instance, it is used to convert toxic or unstable form of chromium, Cr (III) to a more non-toxic form via in situ remediation (Liu 2010). Besides that, nZVI can stabilize halogenated hydrocarbons, carbon tetrachloride and polychlorinated biphenyls (PBCs). It is used to perform effective transformation of many common environmental contaminants like chlorinated organic solvents, organochloride pesticides, organic dyes and various inorganic compounds and metal ions (Fu *et al.* 2013). Zin *et al.* (2013) report that degradation of dichlorodiphenyl trichloroethane (DDT) improves significantly by using Fe/Cu bimetallic compare to nZVI. Fe/Cu bimetallic metallic particles embedded within ordered mesoporous carbon is also studied for degradation of organic contaminants (Wang *et al.* 2015).

These zero valent nanomaterials are unfavourable in many applications due to several drawbacks. Firstly, its large surface area increase its reactivity which causes it to oxidize easily. The oxide layer on the zero valent nanoparticles decreases its capacity to treat a targeted

compound. In addition, it has high tendency to agglomerate because of interparticle interactions such as Van der Waals forces and magnetic interaction. The agglomeration of nanoparticles results in volumetric expansion of elemental metals upon oxidation and compaction or cementation by metal (hydr) oxides. The presence of these effects will subsequently reduce the accessible surface area and emasculate the reactivity of nZVI (Yaacob *et al.* 2012). Furthermore, the recovery of nZVI in aqueous solutions after the water treatment process was also a major concern in the application of nZVI (Yuvakkumar *et al.* 2011, Jiang *et al.* 2012).

Several strategies have been developed to overcome the weaknesses of nZVI and other zero valent metallic nanoparticles. For instance, stabilizers and capping agents are used to stabilize the iron nanoparticles and to reduce the possibility against oxidation reactions (Allabaksh *et al.* 2010). The addition of various stabilizers including thiols, carboxylic acids, surfactants and polymers were investigated to be used in prevention of agglomeration of nano scale iron oxide and zero valent nanoparticles. Unfortunately, stabilizer such as thiols and carboxylic acids tend to be reduced by nZVI and therefore were found to be unsuitable for stabilizing nZVI (Jiang *et al.* 2012). Another strategy to enhance the performance of nZVI was to make use of the characteristics of microfiltration membrane such as their open structures and large pore sizes as a support for nZVI (Parshetti and Doong 2009, 2012). This strategy can be done by immobilization of iron nanoparticles in polymers or co-polymers with applications of coating, grafting and blending techniques to modify the surface of the membrane.

Among all the organic polymer materials, Polyvinylidene fluoride (PVDF) was reported as a good support to nZVI due to its significant properties such as excellent chemical resistance and thermal stability which was the reason for application of this membrane on

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ultrafiltration and microfiltration. (Parshetti and Doong 2009) Unfortunately, the hydrophobicity of this membrane has limited its application on immobilization of metallic particles. The hydrophilicity of PVDF plays an important role in immobilization of metallic particles. Therefore, modifications of this membrane are needed (Parshetti and Doong 2012). Previous study has shown that polyelectrolytes can be used to functionalize microfiltration membrane. Such polyelectrolytes are polyelectrolytes with the presence of functional chelating groups such as $-OH$, $-NH_2$ and $-CONH_2$. However, poly (ethylene glycol) (PEG) was found to be the most suitable polyelectrolytes due to its advantages with the presence of reactive OH groups on both ends which is beneficial for surface modification for metal ion adsorption, high water solubility (hydrophilic), non-toxicity, inexpensive, environmentally friendly and ease of thermal grafting (Yuvakkumar *et al.* 2011).

In this study, the effect of PEG crosslinking on the immobilization of metallic particles onto PVDF/PEG membrane was investigated. In this experiment, we manipulate the content of polymer to produce membrane with different thicknesses and PEG crosslinking. The PEG crosslinking was investigated by using Fourier Transform Infrared spectroscopy (FT-IR). The efficiency of immobilization and distribution of metallic particles onto the membranes were obtained through Field Emission Scanning Electron Microscopy (FE-SEM) and Energy-Dispersive X-ray Spectroscopy (EDX), and percent nitrate removal was inspected by using UV-spectroscopy to confirm our hypotheses.

2. Materials and methods

2.1 Materials

Polyvinylidene fluoride (PVDF) powder, Polyethylene glycol (PEG) 4000 purchased from R&M chemicals, N, N-Dimethylformamide (AR grade), Iron (II) sulphate (ACS Reag. grade) from R&M chemicals, Copper (II) chloride dehydrate (ACS Reag. Grade) from Merck KGaA and Sodium borohydride (>98%, GR grade). The washing and storing solution for the grafted membrane are alcohol mixture containing Methanol (>99%, AR grade), Ethanol (>95%, AR grade) from J. Kollin chemicals and Propan-2-ol (AR grade) from Fisher chemical.

2.2 Methods of Metallic particles-membrane preparation

2.2.1 Preparation of PVDF/PEG membrane

PVDF/PEG membranes were prepared via wet phase inversion method. To create membrane with different thicknesses and structures, M1, M2, and M3 were prepared based on the weight composition shown in Table 1. PVDF and PEG-4000 resins were dissolved in DMF (solvent) with continuous stirring at 400 rpm and heating at 50°C. Clear homogenous polymer solutions were obtained after agitation. The polymer solutions were stored in oven at 50°C for 24 hours. An appropriate amount of polymer solutions were poured uniformly on a glass plate at room

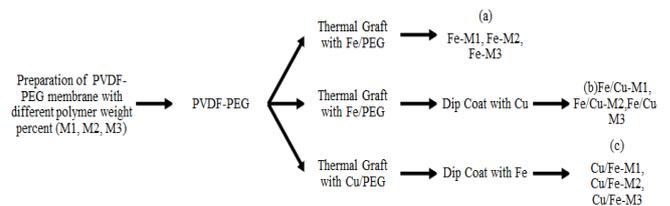


Fig. 1 Schematic illustration of Sample Preparation, (a) Thermally Grafted Fe Membrane, (b) Thermally Grafted and Dip Coated Fe/Cu Membrane, (c) Thermally Grafted and Dip Coated Cu/Fe Membrane

Table 1 Composition of PEG/PVDF membrane

Type of membrane	Weight Composition (%)		
	PVDF	PEG 4000	DMF
M1	6	12	82
M2	8	16	76
M3	9	18	73

temperature for membrane casting followed by immersing membranes into 15 L of reversed osmosis(RO) water bath for phase inversion. The membranes were conserved with RO water.

2.2.2 Immobilization of Fe metallic particles on PVDF/PEG membrane

The preparation of coating solution was done by dissolving 1.60 g of PEG and 11.12 g of ferric chloride hexahydrate ($FeSO_4 \cdot 7H_2O$) in 50 ml of RO water. The membranes were cut into a dimension of 4 cm×1 cm and immersed in coating solution at 120°C for 3 hours. The iron metallic particles on the membranes were formed by soaking the grafted membranes into 0.5 M of 300 ml sodium borohydride ($NaBH_4$) solution for reduction reaction. The membranes were then washed with ethanol and store methanol/ethanol/isopropanol (90:5:5, v/v/v) solution to prevent oxidation.

2.2.3 Immobilization of bimetallic Fe/Cu metallic particles on PVDF/PEG membrane

0.8524 g Copper Chloride ($CuCl_2$) was added into 50 mL of RO water. Fe/Cu (10:1) membrane was prepared by dip coating the Fe membrane prepared earlier into the solution for 30 minutes. The membrane was then dip into $NaBH_4$ for reduction of bimetallic metallic particles. The membranes were then washed with ethanol and store methanol/ethanol/isopropanol (90:5:5, v/v/v) solution to prevent oxidation.

2.2.4 Immobilization of bimetallic Cu/Fe metallic particles on PVDF/PEG membrane

The preparation of Cu coating solution was done by dissolving 1.60 g of PEG and 0.85 g of $CuCl_2$ in 50 ml of RO water. Similar to the preparation of Fe membrane, PVDF/PEG membrane was soaked in the coating solution at 120°C for 3 hours for thermal grafting.

Fe solution was prepared by dissolving 11.12 g of $Fe_2SO_4 \cdot 7 H_2O$ into 50 mL of RO water. Cu membrane

formed was later dip coated with Fe solution.

2.2.5 Membrane characterization

The distribution of iron and bimetallic metallic particles on membranes were inspected on Field Emission Scanning Electron Microscopy (FE-SEM, NOVA NANOSEM 230). For the cross section image inspection, samples were carefully fractured in liquid nitrogen before test. The samples were observed under the FE-SEM with different magnifications. Furthermore, the cross-sectional membrane morphology as well as its composition were observed and studied by using Field Emission Scanning Electron Microscope (FESEM)-Energy-Dispersive X-ray (EDX) Spectrometer (Model: JSM7800F) from Jeol.

2.2.6 Removal of nitrate test using immobilized membranes

50 strips of the membrane were added into 100 mL of 100 ppm nitrate solution. For Fe-membrane samples, the nitrate tests were conducted under pH 2 by adding in hydrochloric acid as it is reported to perform under acidic condition. (Choe *et al.* 2004). For the bimetallic membrane, tests were performed without pH adjustment. The conical flask was then placed in orbital shaker for 60 minutes at room temperature at 200 rpm. 1 ml of NaNO₃ solution sample was taken out from each conical flask after treating process and diluted with 19 ml of RO water before testing it by using Shimadzu UVmini 1240 UV visible scanning spectrophotometer (wavelength=220 nm). The nitrate concentration of the sample is measured according to the APHA Method 4500-NO₃-B.

The reduction in nitrate concentration at time *t* (*C_t*) was calculated as

$$\text{Percentage of nitrate removed (\%)} = \frac{(C_0 - C_t)}{C_0} \quad (1)$$

where *C₀* is defined as the initial concentration.

3. Results and discussion

3.1 PEG Crosslinking by various polymer concentration

The effect of PEG crosslinking in PVDF/PEG by manipulating the polymer concentration was studied via Fourier transform infrared spectroscopy (FT-IR). From Fig. 2, the signature absorption peaks for PVDF membrane can be observed where the peak at 1110-1280 cm⁻¹ was due to the presence of C-F₂ and 1346-1461 cm⁻¹ for the C-H. (Chen 2016). Broad OH bands were observed in all modified PVDF membranes (M1, M2 and M3) due to the presence of PEG-4000 in the membrane. This proves that the hydrophilicity of the membrane was improved.

A new absorption band at 990-1055 cm⁻¹(C-O) is also detected in all modified PVDF membranes. Notice that this peak is not detected in the pure PVDF or PEG-4000. The peak indicates ether linkages (C-O) which connects PEG and PVDF. Further observation shows a significant increase in intensity of the mentioned absorption band as the polymer weight percent increases from M1 to M3. The

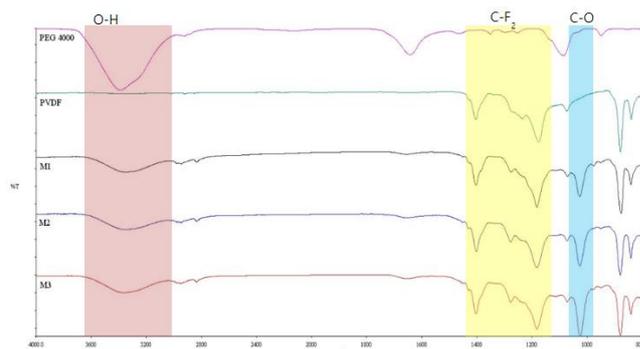


Fig. 2 FT-IR spectrum of PEG 4000, PVDF, and PVDF/PEG with different weight% (M1, M2, M3)

Table 2 Total Area for C-O the absorption band at 990-1055cm⁻¹

Type of Membrane	Total Area(% T cm ⁻¹)
M1	5919.22
M2	5922.33
M3	5979.78

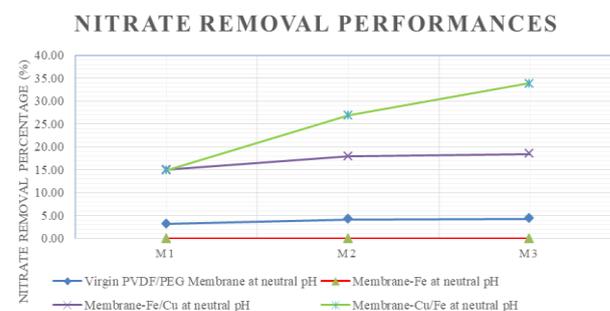


Fig. 3 Nitrate removal test result

relative total area of C-O peaks were tabulated in Table 2.

Apart from that, a broad OH peak was observed in PEG-4000 and the modified PVDF membrane. During the phase inversion process, the hydrophilic hydroxyl groups (O-H) in excess PEG is likely to have moved towards the surface of the membrane, where water molecules were abundant. Some of the PEG might have escaped from the polymer matrix during this process. However, some excess PEG might be trapped and remained on the surface of the polymer which is why OH peak is observed in the modified PVDF.

3.1.1 Nitrate removal performance of PVDF/PEG membrane

All nitrate removal test results are presented in Fig. 3. Nitrate test was conducted for the PVDF/PEG membrane before immobilization of metallic particles to study the effect of PEG cross-linkages or membrane structure in nitrate removal. Nitrate reduction seems to have occurred at a very minimal percentage in the range of 3 to 4% according to the results where the performance improves from M1 to M3. However, there are no functional groups present in the cross-linkage of PVDF and PEG that are effective or responsible for nitrate removal through adsorption or chemical reduction. The probable cause of the

result could be that water molecules within the membrane diffuse out into nitrate solution via osmosis process, which reduced nitrate absorption value through dilution instead of adsorption or chemical reduction. As the PEG cross-linkages increases, the more hydrophilic the membrane becomes which increases the amount of water molecules carried by the membrane itself. Hence, dilution increases from M1 to M3.

3.2 Immobilization of Fe on PVDF/PEG membrane

The immobilization of metallic particles on the polymeric membrane can be proven by color observation and magnetism. Table 3 shows the color of pure membrane (M1, M2, and M3) to be white with no magnetic responses. On the other hand, all metallic membranes are black in color and respond to magnet.

Apart from that, a collective FE-SEM images of the monometallic and bimetallic membrane is presented in Fig. 4. Fe-Membranes images are shown in Fig. 4(a). The membrane's morphology are greatly influenced by polymer solution viscosity. This correlate with the PEG crosslinking degree which was discussed in the previous section. From Fig. 4(a), it is found that excess PEG molecules remain on the nascent membrane and dispersed on the surface of the membrane uniformly. The surface of M1 (Fig. 4(a,i)) has larger pore diameter compared to M2 (Fig. 4(a,ii)) and M3 (Fig. 4(a,iii)). As discussed earlier, some PEG escaped into the coagulation bath during grafting process, leaving larger pores on the surface and inner part of the membrane. Meanwhile, M2 and M3 has little to no pores as PEG were fully grafted on top of the membranes. This resulted in denser surface rather than a porous surface.

The effect of polymer viscosity on PEG cross-linkages can be further supported by the cross section FESEM images of Fe-Membranes shown in Fig. 4(b). The PEG mesh became denser as the viscosity of polymer solution increased. The average thickness of PVDF/PEG membrane in this study were measured, where M1 is $160 \pm 7 \mu\text{m}$, M2 is $220 \pm 9 \mu\text{m}$ (M2) and M3 is $320 \pm 4 \mu\text{m}$. Dan-ying Zuo (2008) reported that an average viscosity of PVDF/PEG polymer solution of 8.8 to 9.6 Pa.s for PEG with molecular weight ranging from 200 to 20000. They also report that viscosity of the polymer solutions causes an increase in membrane thickness for PEG 200, PEG 1000 and PEG 6000. The reported thickness ranging from 39 to $56 \mu\text{m}$.

PEG crosslinking has significant impact on immobilization of Fe metallic particles. The effect is clearly demonstrated in Fig. 4(b). The thickest membrane (M3) shows the densest inner membrane structure with metallic particles residing within the membrane whereas the thinnest membrane (M1) shows the opposite. This is because of the higher contact area and higher PEG content in M3. The thicker the membrane, the larger contact area with the coating solution per unit time during dip coating and grating. Therefore, the possibility for Fe metallic particles to adhere on the pores of the membrane is higher. In addition, the $-\text{OH}$ functional group in PEG cross-linkage attracts the metal ion in the coating solution. Consequently, higher content of Fe metallic particles are observed in M3. Fe metallic particles on the membranes were shown to be uniformly dispersed in the pores of the membranes.

Table 3 Membrane's Color and Magnetic Responses

Types of Membrane	Color	Magnetic response
M1	White	No
M1-Fe	Black	Yes
M1-Fe/Cu	Black	Yes
M1-Cu/Fe	Black	Yes
M2	White	No
M2-Fe	Black	Yes
M2-Fe/Cu	Black	Yes
M2-Cu/Fe	Black	Yes
M3	White	No
M3-Fe	Black	Yes
M3-Fe/Cu	Black	Yes
M3-Cu/Fe	Black	Yes

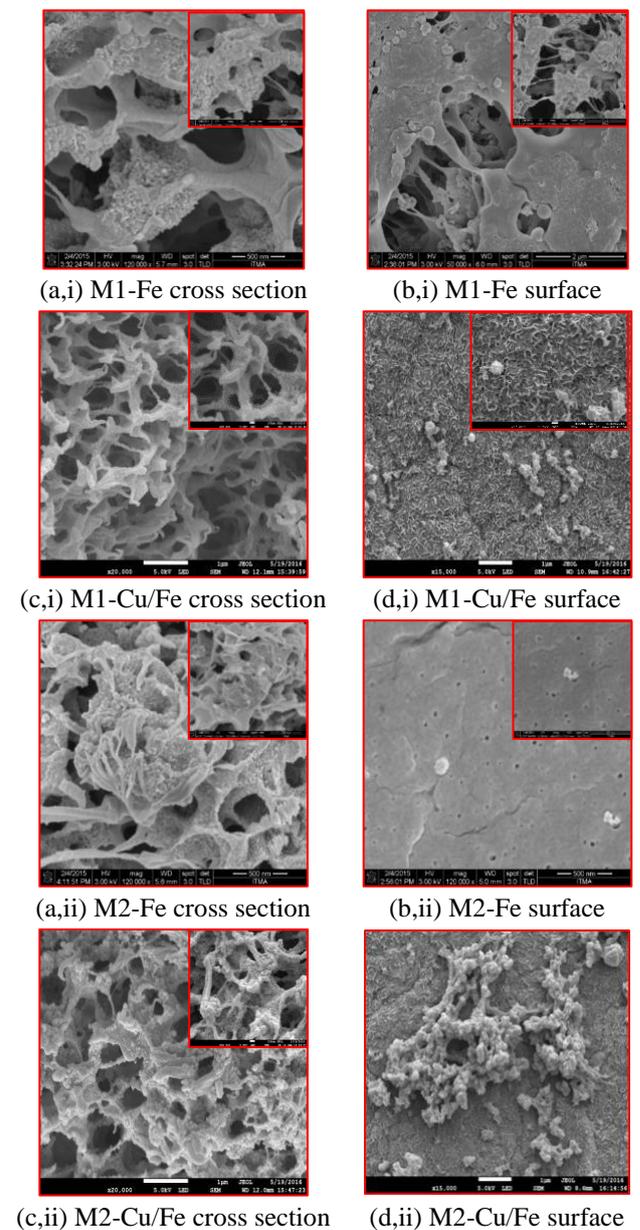


Fig. 4 FESEM images of surface and cross-section of monometallic and bimetallic membranes (M1, M2, M3)

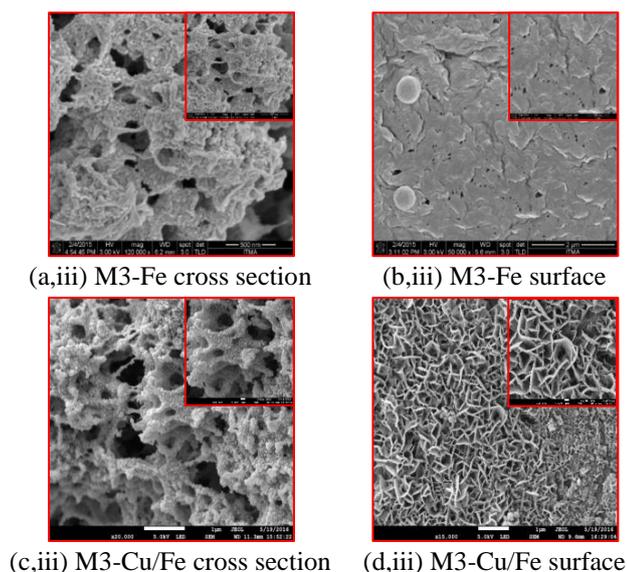


Fig. 4 Continued

Table 5 Atomic percentage and Ratio of Metallic Element in EDX analysis

Element	Atomic %	Element	Atomic %
Fe	23.26	Fe	15.53
Cu	1.87	Cu	1.22

However, there is slight agglomeration where some of the metallic particles were not in spherical shape. This can be explained as the interaction between PVDF/PEG membranes and metallic particles may undergo several reactions including ion exchange, chelation and electrostatic interaction to prevent particle agglomeration. However, since PVDF is mainly constitute from vinylidene fluoride only, the ability in minimization of particle agglomeration were reduced (Parshetti and Doong 2009) which resulted in slight agglomeration of iron metallic particles in membranes. As observed in all images of Fig. 4(a) and 4(b), the agglomeration of Fe particles does not show any significant changes between all three membranes of different thicknesses. Thus, PEG crosslinking does not affect the agglomeration of Fe metallic particles.

3.2.1 The effect of Immobilization of Fe on PVDF/PEG membrane in nitrate removal performance

For Fe-membrane, nitrate test was conducted under pH 2. pH of nitrate solution was adjusted to pH 2 by adding hydrochloric acid (HCl) drop-by-drop. It is reported by Choe *et al.* (2004) that pH plays an important role in nitrate reduction using nZVI. At neutral pH, zero valent iron nanoparticles only able to remove 9 percent of nitrate from a 100 mg/L nitrate solution even after 24 hours of reaction

time. At pH 2, Choe *et al.* (2004) successfully remove nitrate completely in 8 hours. However, in 1 hour reaction time, they were only able to remove approximately 10% of nitrate at pH 2. In our studies, the performance of nitrate removal is proven to improve from 28% (M1-Fe) percent to almost 80 percent (M3-Fe) in one hour. Free nZVI is reported to be highly reactive due to the large surface area and thus has higher tendency to agglomerate. Due to this reason, free nZVI could underperform the nitrate test when compare to the immobilized zero valent metallic particles. Results are summarized in Table 5.

3.3 Immobilization of bimetallic metallic particles on PVDF-PEG membrane

Similar to Fe-Membrane samples, the crosslinking of PEG in the Cu/Fe membrane are expected to increase from M1 to M3. This phenomenon also contributes to the grafting efficiency of the bimetallic metallic particles, Fe/Cu and Cu/Fe. The effect can be observed in Fig. 4(c) and 4(d). As reported earlier, M1 has the clearer surface as less metallic particles are grafted on it when compare to M2 and M3. By thermally grafting Cu/PEG during the initial stage of the membrane preparation, a “nucleus-like” seed is implanted for Fe to grow on top. This mimic the seed deposition method reported by many included Himadri (2016), in growing core-shell bimetallic metallic particles.

The FE-SEM images shows that this bimetallic grafting method produced less homogeneous metallic membrane as the grafted area are not evenly distributed. Like seed deposition method mentioned earlier, Fe is found to grow on top of the Cu seeds on the surface of the membrane. As the content of Fe grafted on increases, the crystalline structure became more obvious. These crystalline surface mimic those reported in Metal-Organic-Framework (MOF). (Yeo *et al.* 2014) M3 shows a significant growth of crystalline area on its surface, indicating a higher grafting of metal compare to M2 and M1.

Similar to the monometallic membrane, Fig. 4(d) confirms the PEG crosslinking improvement from M1 to M3 as the membrane is denser internally. Immobilization of Cu/Fe metallic particles advances significantly from M1 to M3. This proves the grafting efficiency of monometallic and bimetallic metallic particles onto membrane is dependent on the crosslinking of PEG of the membrane.

FE-SEM imaging for Fe/Cu membrane was not conducted. It is expected to have similar grafting effect with that of Cu/Fe membrane.

Apart from that, Energy-Dispersive X-ray (EDX) Spectroscopy analysis was carried out to verify the immobilization of metallic particles on the membrane. M3-Cu/Fe was chosen for this test as it shows the best performance in the nitrate removal test. The EDX results shows that Cu/Fe metallic particles are successfully grafted onto the membrane. The atomic percentage and ratio of elements in EDX analysis as tabulated in Table 5 are not presenting its actual value as the amount of element carbon, fluorine and oxygen are varied at different part of membrane which would greatly affects the atomic percentage of metallic particles obtained.

3.3.1 Nitrate removal performance

Nitrate test was conducted under neutral pH. The results

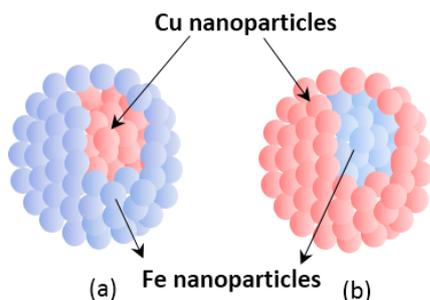


Fig. 5 (a)Cu/Fe core and shell structure and (b) Fe/Cu core and shell structure

in shows improvement from M1 to M3 in all three sets of samples in 60 minutes of treatment. Nitrate test for monometallic membrane (M1-Fe, M2-Fe and M3-Fe) was carried out under neutral pH as well to compare the nitrate removal efficiency with bimetallic membrane. The result is presented as zero percent of reduction because the calculated reduction rate was in negative value. The error in the result can be understood as no nitrate reduction.

The overall efficiency of metallic particles improves from M1 to M3. For bimetallic membrane, M3 gives the best result at 18 % for Fe/Cu and 34% for Cu/Fe. The result trend is identical to the monometallic's nitrate test at pH 2. By comparing the result of membrane with Fe/Cu and Cu/Fe, we find that by grafting Cu before Fe produced a better performance membrane. Hence, we proposed in Fig. 5, Cu/Fe and Fe/Cu sequence creates different bimetallic particles structure. As Fe is the important element that convert nitrate compound into nitrogen, it should be grafted as the shell but not the core. Fe/Cu membrane has the opposite structure and hence is not appropriate for nitrate removal purposes.

4. Conclusions

The higher the viscosity of polymer solution, the higher the crosslinking of PEG can be observed. PEG cross-linkage has a direct influence on the metallic particles grafting efficiency. The more the cross-linkages, the more metallic particles are immobilized on the membrane via thermal grafting as -OH group in PEG improves the affinity of metal ion with the membrane. This can be confirmed by the nitrate reduction performance where M3 is better than M2 and M1. Immobilization of the metallic particles improves the nitrate removal performance when compare to free metallic particles. Despite that, the grafting sequence of metal is also important and dependent on the applications of the membrane as this determines the core shell structure of the metallic particles grafted.

Acknowledgments

The research described in this paper was financially supported by the SEGi University Internal Grant, SEGIRF/2014-31/FOEBE-8/46.

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