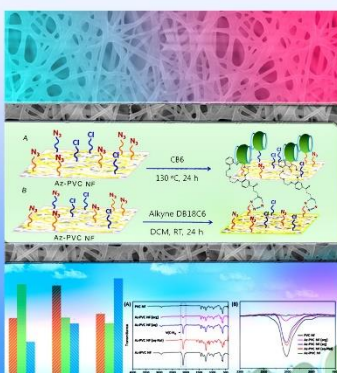




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Facile preparation of azido functionalized polyvinyl chloride (PVC) nanofiber (NF) membrane for various applications

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ABSTRACT

Polyvinyl chloride (PVC) nanofiber (NF) membrane functionalized with azido groups (Az-PVC NF) was prepared using various techniques with the aim of enhancing azide substitution of chlorine in the PVC backbone. Azidation strategies that were investigated include: (1) catalyst-assisted azidation in organic solvent, (2) phase transfer catalyzed azidation in aqueous media, (3) phase transfer catalyzed azidation in aqueous media using pre-iodinated membrane, and (4) phase transfer catalyzed azidation in aqueous media of electrospun pre-iodinated PVC granules prepared via Finkelstein reaction. Results showed that azidation was greatly enhanced when PVC NF membrane or PVC powder underwent pre-iodination prior to azidation. As far as it is known, this is the first time that preparation techniques for azidized PVC NF membrane in aqueous media that involve halogen exchange have been studied. Hence, the optimized conditions for the preparation of azidized PVC NF membranes and the resulting membrane properties are hereby reported. Furthermore, the utility of Az-PVC NF in the development of water treatment technologies was demonstrated with successful grafting of cucurbiturils via nitrene insertion.

Keywords: azide, covalent attachment, halogen exchange

INTRODUCTION

Polyvinyl chloride (PVC) is among the most widely produced and among the cheapest plastic materials (Pham et al. 2021). It has been used in a great variety of industrial, construction, and household products, and its applications continue to grow as new material processing technologies emerge. For example, with the development of electrospinning techniques for the production of nanofibers (NF) and nanofiber mats, PVC is now being used as membrane in air and water filtration systems, as protective layer in textiles, as anti-corrosion material, and many others (Ouerghui et al. 2016; Pham et al. 2021). These nanofiber-based applications of PVC take advantage of new or

improved properties such as increased porosity and increased surface area resulting from the fabrication process.

Meanwhile, the use of PVC NF membrane in the development of air or water treatment technologies may be expanded by allowing attachment of molecules with desired functionalities. A convenient way to carry out this functionalization is to introduce azido groups on the PVC chain by substitution of chlorine. Thereafter, other molecules can be covalently tethered to PVC NF via nitrene or click chemistry. As such, azidized PVC NF (Az-PVC NF) membrane can be customized to possess features useful for functions other than filtration. In other words, azidation opens



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PVC NF membrane to a multitude of modifications and applications.

Successful azidation of PVC NF membrane, however, is difficult to accomplish through conventional methods such as the use of organic solvents because these cause the fiber to deteriorate or they entail an exceedingly long time for substantial replacement of chlorine to take place. Process economics and occupational safety considerations require that azidation must be as pervasive and as swift as possible. Thus, strategies for the effective and efficient preparation of Az-PVC NF membrane need to be developed.

In this study, an assortment of techniques for the preparation of Az-PVC NF membrane were employed with the aim of achieving as much replacement of chlorine by azido groups as possible. It was found that remarkable improvements in azidation can be achieved using aqueous systems in the presence of a phase transfer catalyst, and that further improvements occur when prior replacement of chlorine by iodine is performed. This is the first report on the efficient and effective preparation of azidized PVC NF membrane in aqueous systems employing halogenation pretreatment. To demonstrate the utility of Az-PVC NF membrane in the development of water treatment technologies, it was grafted via nitrene insertion with cucurbit[6]uril or CB6—a pumpkin-shaped molecule capable of host-guest interactions with organic molecules and selective sequestration of large metal ions such as Cs^+ on two of its carbonyl rims.

METHODS

Materials

Polyvinyl chloride (PVC, average $M_w \sim 62000$, average $M_n \sim 35\,000$) and cucurbit[6]uril hydrate were purchased from Sigma-Aldrich. Sodium azide (NaN_3 , 99%, extra pure) and tetrabutylammonium bromide (TBAB, 99+%) were purchased from ACROS Organics, South Korea. Sodium iodide (NaI , 99+%) was manufactured by Showa Chemical Co. Ltd. (Japan). Solvents used include dimethylformamide (DMF, anhydrous, Fisher Scientific U.K. Ltd.), acetone (99.8%, DaeJung Chemicals and Metals, Korea), ethanol (99.9%, Samchun Chemicals, South Korea) and tetrahydrofuran (THF, 99.9%, Samchun Chemicals, South Korea). Deionized water ($18.2\text{ m}\Omega\cdot\text{cm}^{-1}$ at 25°C) was processed through a Millipore Milli-Q system. Reagents and solvents were used as received.

Preparation of PVC NF Membrane from pristine PVC Granules

An electrospinning solution was prepared by dissolving PVC granules (15 wt. %) in a 1:2 volume ratio of THF to DMF. Polyvinyl chloride nanofiber

membrane was produced by electrospinning this solution at 22 kV at an ejection rate of 4 ml h^{-1} through a 21G needle and a rotating drum collector speed of 230 rpm at a distance of 100 mm.

Preparation of Iodinated PVC Granules

Iodinated PVC granules were prepared via Finkelstein reaction using sodium iodide as source of halogen nucleophile. Polyvinyl chloride granules (30 g) and NaI (71 g) were mixed in 215 ml acetone for 23 h. The iodinated granules were collected by filtration and dried overnight in an air-circulating oven at 65°C . Iodinated granules were vigorously washed multiple times with deionized water and then dried in a vacuum oven at 80°C for 12 h.

Preparation of PVC NF Membrane from Iodinated PVC Granules

Electrospinning solution was prepared by dissolving iodinated PVC granules (15 wt. %) in a 1:1.5 volume ratio of THF to DMF. Iodinated PVC NF membrane was produced by electrospinning this solution at 22 kV at an ejection rate of 2 ml h^{-1} through a 21G needle and a rotating drum collector speed of 230 rpm at a distance of 110 mm.

Preparation of Az-PVC NF Membranes

Four preparation techniques were employed to produce Az-PVC NF membrane. The first three involved use of PVC NF membrane prepared from pristine PVC granules (Figure 1) while the fourth involved PVC NF membrane prepared from iodinated PVC granules (Figure 2).

The first membrane underwent azidation by soaking for 24 h in saturated NaN_3 in DMF with 2% NH_4Cl as catalyst to produce Az-PVC NF (org) (Figure 1A). The second was soaked for 4 h in $6.15\text{ mol L}^{-1}\text{ NaN}_3$ and $0.037\text{ mol L}^{-1}\text{ TBAB}$ in H_2O to produce Az-PVC NF (aq) (Figure 1B). The third was subjected to halogen exchange by soaking for 5 h in $6.15\text{ mol L}^{-1}\text{ NaI}$ and $0.15\text{ mol L}^{-1}\text{ TBAB}$ in H_2O , followed by soaking for 4 h in $6.15\text{ mol L}^{-1}\text{ NaN}_3$ and $0.037\text{ mol L}^{-1}\text{ TBAB}$ in H_2O to produce Az-PVC NF (aq- NaI) (Figure 1C). The fourth membrane which was prepared from iodinated PVC granules was soaked for 4 h in $6.15\text{ mol L}^{-1}\text{ NaN}_3$ and $0.037\text{ mol L}^{-1}\text{ TBAB}$ in H_2O to produce Az-iPVC NF (Figure 2). After azidation, the membranes were washed with copious amounts of deionized water followed by 70% ethanol, and then dried in a vacuum oven at 80°C for 12 h.

Preparation of CB6-loaded PVC NF Membrane

Azidized PVC NF membrane was soaked in an aqueous CB6 solution in HCl at 100°C . After reaction, the membrane was washed vigorously with deionized water followed by 70% ethanol, and then dried in a vacuum oven at 80°C for 12 h.

Instrumentation

Functional groups in membrane materials were identified using a Fourier transform infrared (FTIR) -attenuated total reflectance (ATR) (Varian Scimitar 2000, USA) spectrometer. Morphology and approximate surface elemental compositions were determined using a scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM-EDX, Hitachi S-3500 N, Japan) while fiber diameters ($\varnothing$) were measured from SEM images using

ImageJ (Schneider et al. 2012). Mechanical properties were determined using a Universal Testing Machine (UTM LFPlus, Lloyd Instruments, UK) equipped with a 1 kN load cell. Azide loadings were quantified by elemental analysis using an Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). Water droplets for contact angle (θ) measurements were visualized with a video microscope (SCALAR VL-11S, Japan).

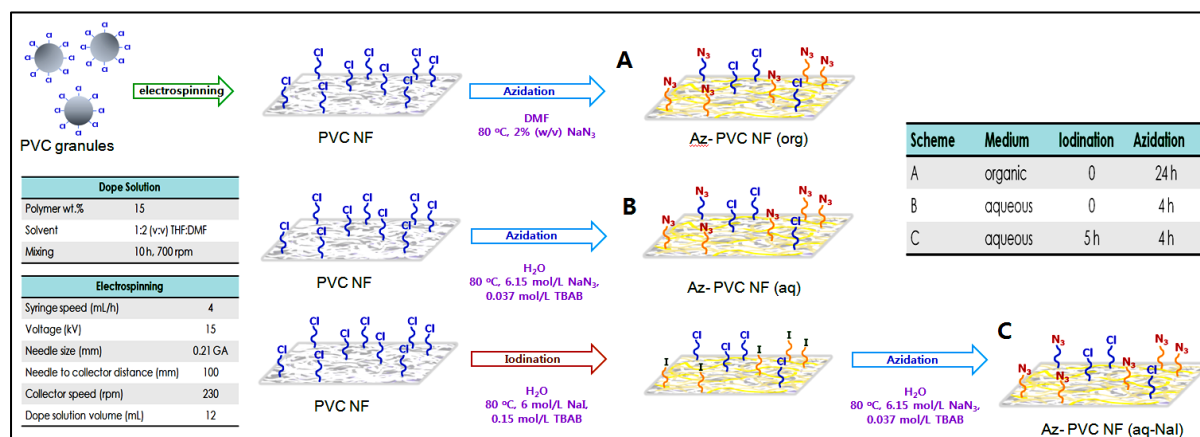


Figure 1. Preparation of membranes (A) Az-PVC NF (org), (B) Az-PVC NF (aq), and (C) Az-PVC NF (aq-NaI) using electrospun pristine PVC granules.

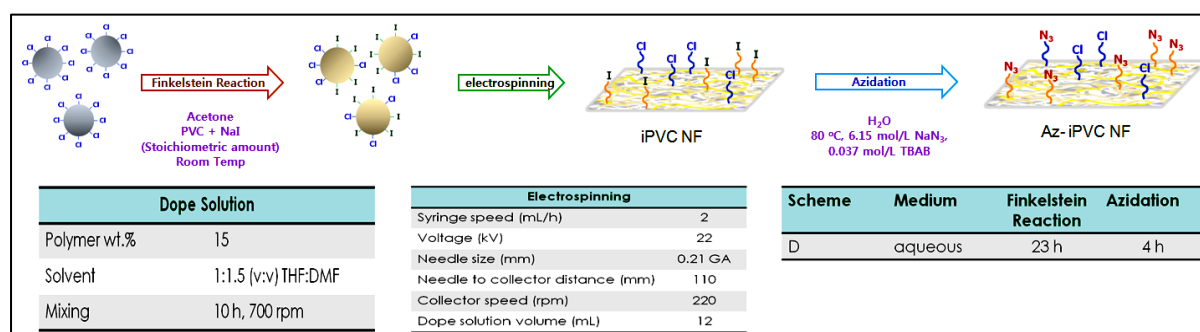


Figure 2. Preparation of Az-iPVC NF using electrospun iodinated PVC granules.

RESULTS

Characterization of azidized PVC NF Membranes

The FTIR spectra of pristine and azidized PVC NF membranes are provided in Figure 3A. The emergence of the azide peak at 2100 cm^{-1} suggests the presence of azido (-N_3) groups in the membrane which can be attributed to successful substitution of chlorine (Ouerghui et al. 2016). Results revealed a remarkable increase in the intensity of the azide peak in azidized PVC NF membranes prepared using aqueous azidation media. The superposition of the azide peaks (Figure 3B) provides a more vivid comparison of the peak intensities, with Az-iPVC NF exhibiting the strongest.

The azide peak intensity follows the trend Az-iPVC NF > Az-PVC NF (aq-NaI) > Az-PVC NF (aq) > Az-PVC NF (org).

The actual azide load of each membrane was quantified via elemental analysis and results are summarized in Table 1. Results showed that the nitrogen content and consequently the azide load follow the trend Az-iPVC NF > Az-PVC NF (aq-NaI) > Az-PVC NF (aq) > Az-PVC NF (org) which is the same trend observed in the FTIR azide peak intensities. Az-iPVC NF membrane which registered the highest nitrogen content has an azide load of approximately 2.36 mmol g^{-1} .

Scanning electron microscopy images of pristine and azidized membranes show that electrospun PVC features thin, long fibers with nanosized diameters (Figure 4). Polyvinyl chloride nanofiber (PVC NF, $\varnothing \sim 413 \pm 195$ nm) and Az-PVC NF (aq-NaI, $\varnothing \sim 426 \pm 201$ nm) membranes are essentially morphologically similar which means that iodination and subsequent azidation of PVC NF membrane cause no change in the physical structure of the membrane (Figures 4A and 4B). On the other hand,

having been prepared using a different set of electrospinning conditions, Az-iPVC NF ($\varnothing \sim 187 \pm 53$ nm) features thinner, densely meshed nanofibers (Figure 4C). Results from surface elemental analyses via EDX further confirmed the presence of azide groups in Az-PVC NF and Az-iPVC NF, which contain approximately 6.8% and 9.8% nitrogen, respectively (Figures 4B and 4C).

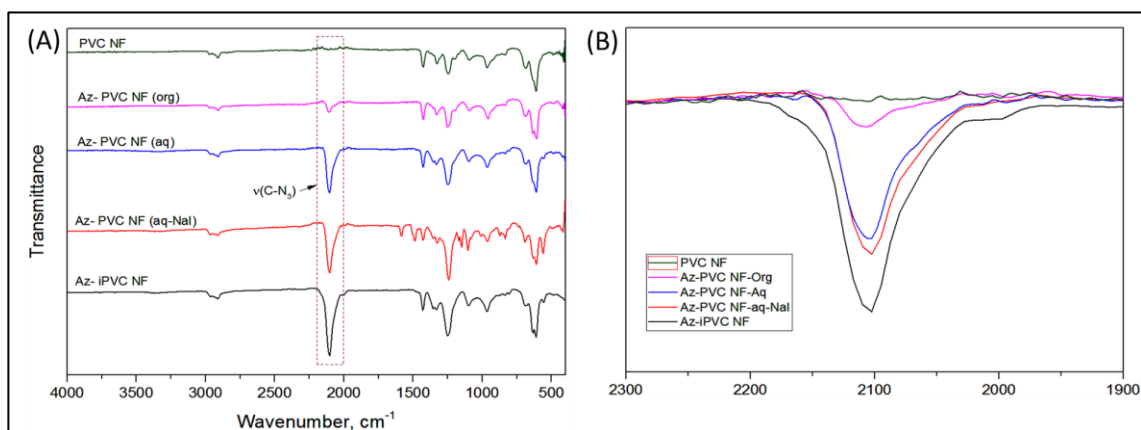


Figure 3. Fourier transform infrared spectra of (A) pristine PVC NF membrane and azidized PVC NF membranes prepared using different techniques, and (B) a superposition of their azide peaks.

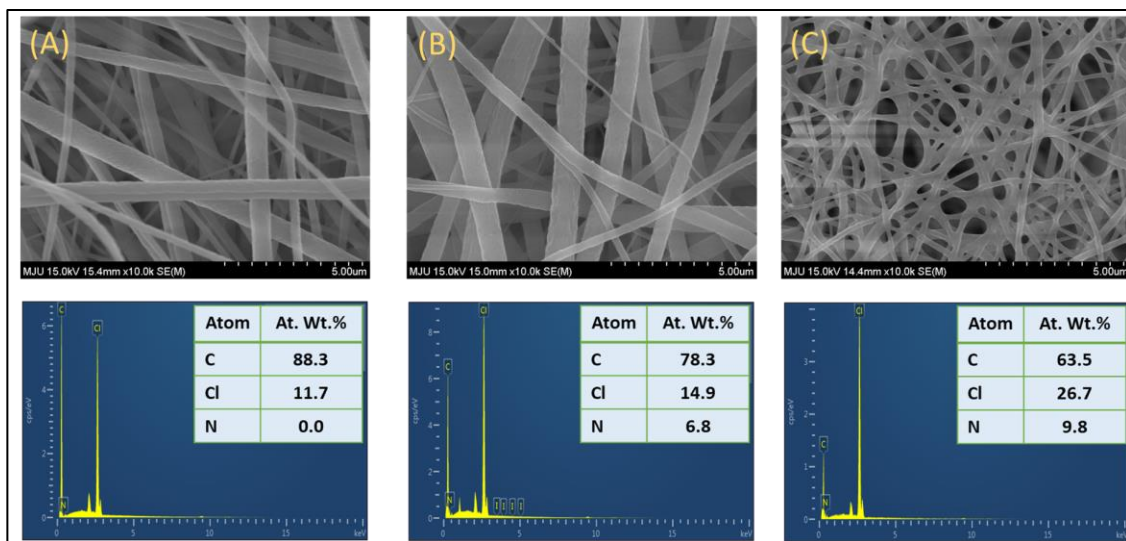


Figure 4. Scanning electron microscopy image and EDX spectra of (A) PVC NF, (B) Az-PVC NF (aq-NaI) and (C) Az-iPVC NF.

Table 1. Elemental composition and azide loading of PVC NF membranes.

Membrane	% C	% H	% N	Azide Load (mmol g ⁻¹)
PVC NF	38.64	4.992	0.35	0.08
Az-PVC NF (org)	38.64	4.974	2.80	0.67
Az-PVC NF (aq)	38.66	4.968	6.92	1.65
Az-PVC NF (aq-NaI)	39.23	4.905	8.51	2.03
Az-iPVC NF	39.00	4.868	9.91	2.36

The mechanical properties of the membranes were found to be at variance with one another. Young's moduli are around 20-35 MPa, stiffnesses are at 3900-6000 N m⁻¹ and stresses at maximum load are at 1.34-2.68 N mm⁻² (Figure 5). Despite the variability, the mechanical properties of all membranes prepared in this study are comparable with published data for which Young's moduli in the range 3.75-308 MPa and stresses at maximum load of 0.67-9.1 N mm⁻² have been reported (Pham et al. 2021).

Covalent Immobilization of CB6 in Az-PVC NF

Thermally induced generation of nitrenes led to successful immobilization of CB6, as confirmed by the subsequent weakening of the azide peak (2100 cm⁻¹) and the emergence of the carbonyl stretch (1740 cm⁻¹) in the FTIR spectra of CB6-loaded PVC NF membrane (Figure 6A). The SEM image of CB6-loaded PVC NF ($\varnothing \sim 418 \pm 173$ nm) membrane is

shown in Figure 6B while the corresponding surface elemental scan which confirms the existence of oxygen, and hence surface-immobilized CB6, is shown in Figure 6C. Significant changes in surface properties were observed from static water droplet contact angle measurements whereby the previously hydrophobic surfaces of pristine ($\Theta = 137.5^\circ$) and azidized ($\Theta = 139.7^\circ$) PVC NF membrane became more hydrophilic after CB6 immobilization (Figure 6D), causing the water droplet to be flatter ($\Theta = 90.4^\circ$). This improved hydrophilicity is likely due to increased attractive electronic interactions (e.g. hydrogen bonding) between water molecules at the droplet interface and the carbonyl groups of immobilized CB6 on the PVC surface which effectively disrupts the droplet surface tension. As with most surfaces, the static water droplet contact angle approaches 90° or less as a consequence of hydrophilicity (Law 2014).

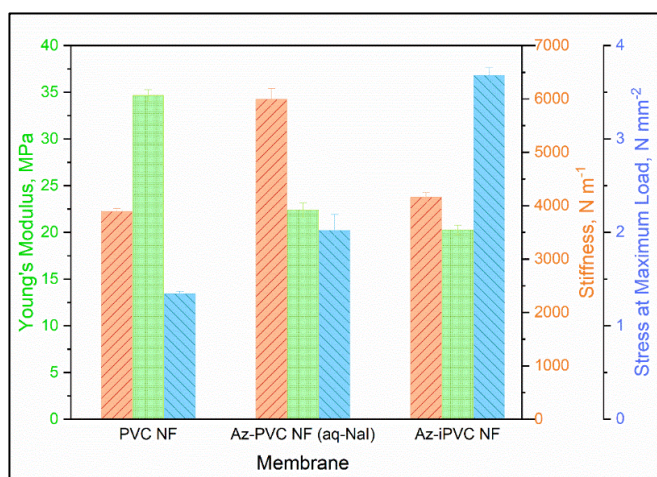


Figure 5. Mechanical properties of PVC NF, Az-PVC NF (aq-Nal) and Az-iPVC NF.

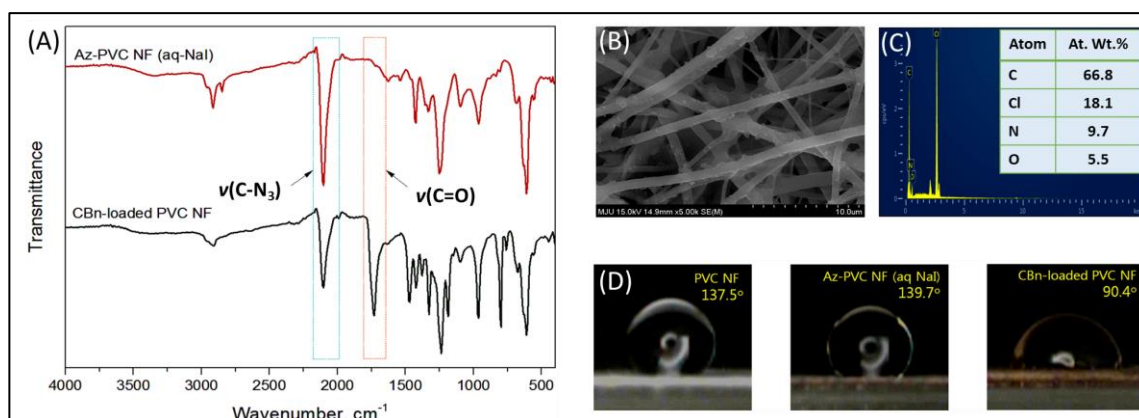


Figure 6. (A) Fourier transform infrared spectra of pristine and CB6-functionalized Az-PVC NF; (B) SEM image and (C) EDX spectrum of CB6-functionalized Az-PVC NF; and (D) water contact angles of PVC NF, Az-PVC NF and CB6-functionalized Az-PVC NF.

DISCUSSION

Azidation in Aqueous Systems and the Importance of Pre-iodination

Azidation of PVC is usually carried out in a polar aprotic solvent (e.g. DMF) since this favors S_N2 reactions by keeping the nucleophile prone to reactive collisions. This approach, however, cannot be applied to electrospun PVC NF membrane because the membrane deteriorates in DMF. Moreover, poor solubility of NaN_3 in DMF limits the amount of azide nucleophiles available. An azidation solvent system that keeps the PVC NF membrane intact and dissolves the azide salt easily had to be resorted to, and this was accomplished by performing the reaction in aqueous media in the presence of TBAB as phase transfer catalyst (Lakshmi and Jayakrishnan 2002). In this method, the soluble organic cation $\text{N}^+(\text{Bu})_4^+$ transports N_3^- from the aqueous phase to the organic solid phase of the PVC NF membrane where the nucleophilic substitution occurs. These explain the remarkable improvement in azide load of Az-PVC NF (aq) relative to Az-PVC NF (org).

Because a high loading of azide groups is desired, chlorine groups in the PVC NF membrane were pre-displaced with iodine, again by phase transfer catalysis using TBAB. Although a weaker base, iodine is a stronger nucleophile than chlorine if the reaction occurs in a polar protic solvent like water, which allows the replacement of chlorine to proceed spontaneously. Meanwhile, iodine is better than the azide ion at displacing chloride groups in the PVC backbone via nucleophilic substitution, which means that under the same conditions, more chlorine groups are replaced in PVC if it were reacted with iodine anions than when reacted with azide anions. In short, iodine ions are more effective than azide ions at sweeping off chlorine atoms from the PVC chain. Once attached to PVC, iodine atoms are not as firmly bonded as the chlorine groups that they displaced due to the larger atomic size of iodine. This causes iodine to have a greater tendency than chlorine to leave the alkyl backbone of PVC. As such, iodine atoms are more vulnerable to displacement by smaller nucleophiles like azide ions. This makes azidation of PVC more pervasive if preceded by iodination because iodination serves to facilitate the displacement of chlorine atoms and is easily substituted by azide ions thereafter. This explains the higher azide load of Az-PVC NF (Aq-NaI) than Az-PVC NF (Aq).

To further exploit the efficacious azidation of pre-iodinated PVC NF, a more vigorous iodination reaction through halogen exchange in acetone was performed. The procedure, however, cannot be applied to PVC NF membrane because the membrane dissolves completely in acetone. Fortunately, PVC granules are not so easily dissolved by acetone, and the halogen exchange reaction—also called Finkelstein reaction—may be performed successfully. Iodinated

PVC NF membrane prepared from such granules registered the highest azide loading among all the different azidation strategies employed.

Applications of Az-PVC NF Membrane

Azido groups on PVC NF membrane can participate in nitrene insertion or click reactions resulting in covalently bonded molecules (Figure 7). Covalent immobilization of molecules on solid supports, especially the custom-made expensive functional molecules such as cucurbiturils and crown ethers, allows the possibility of multiple reuse which helps offset costs (Escobar et al. 2021; Escobar et al. 2022).

The conversion of azido groups to nitrenes that insert non-selectively into C-H bonds is particularly useful in covalently immobilizing molecules devoid of functional attachments or are difficult to chemically modify such as the cucurbit[*n*]urils or CBN's where *n* represents the number of glycoluril units comprising the molecule. CBN's are a family of macrocyclic molecules that possesses highly symmetric structures with two identical negatively charged portal carbonyl groups and a hydrophobic cavity (Assaf and Nau 2015). Supramolecular assemblies built from CB6 with 4,4',4''-benzene-1,3,5-triyl tribenzoic acid as directing agent had been shown to exhibit high selectivity for Cs^+ —an abundant component of radioactive wastes—against common alkali ions in basic medium (Chen et al. 2014), while CB8 in free form had been reported to have a high adsorption capacity for Pb^{2+} (Sun et al. 2016). Meanwhile, CB6 by itself has been found to form CB6- Cs^+ complexes, registering stability constants that are several orders of magnitude higher than those formed with either 18-crown-6 ether or cryptand 222, an outcome attributed mainly to the strong negative charge of the carbonyl rim and a close cavity-ion size match (Buschmann et al. 1992). Because of their ability to interact selectively with solutes, the covalent immobilization of CBN's onto solid supports such as PVC NF is a huge step into their utilization for practical solute sequestration technologies. On the other hand, azido groups can participate in click reactions which permit fast and highly selective attachment of molecules that possess alkyne functionalities. Click reactions have been used extensively in the development of water decontamination technologies involving various specialized alkyne-bearing molecules on different azido-functionalized supports (Liang and Astruc 2011; Nisola et al. 2020; Ouerghui et al. 2016). With the azido-functionalized PVC NF membranes developed in this study, applications that take advantage of nitrene or click reactions might be extended over to membranes, thereby allowing the development of membrane materials with highly specialized functionalities.

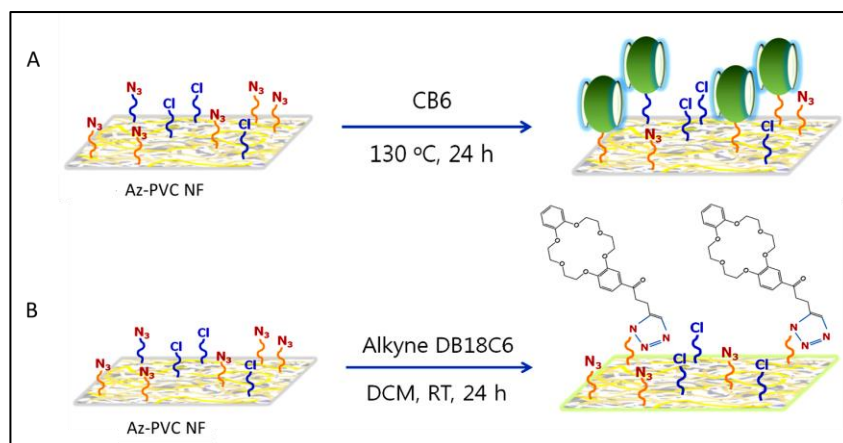


Figure 7. Examples of molecule attachment schemes in Az-PVC NF: (A) nitrene insertion in alkyl chains of cucurbiturils, or (B) click reaction with alkyne-functionalized crown ethers.

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ETHICAL CONSIDERATIONS

This research did not require human or animal subjects.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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ROLE OF AUTHORS: ECE- methodology, investigation, writing of original draft; GMN- conceptualization, project administration, investigation; WJC- resources, supervision, project administration.