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# Graphene oxide incorporated novel polyvinyl alcohol composite membrane for pervaporative recovery of acetic acid from vinegar wastewater

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ABSTRACT

A novel polymeric composite membrane consisting of graphene oxide (GO) and poly (vinyl alcohol) (PVA) has been developed and applied in the recovery of acetic acid from vinegar wastewater in a pervaporation unit. The resultant composite membranes designated as $(PVA\text{-}GO)_1$ and $(PVA\text{-}GO)_2$ were characterized by using X-ray diffractions, scanning electron microscopy, Fourier-transform infrared spectroscopy, atomic force microscopy and thermogravimetric analysis. Membranes were found to attain semi-crystalline to amorphous nature by incorporation of GO to PVA. GO incorporation in the PVA membrane was observed to have a profound influence, as it helped achieve better thermal stability and higher tensile stress compared to pristine PVA membrane. The composite membranes were prone to swelling in presence of water. GO imparted better hydrophilicity of the composite membranes as displayed by a reasonably high degree of volumetric flux of water and separation factor. The study demonstrates that GO can be effectively incorporated within the polymer matrix to tune the mechanical and permeation characteristics of nanocomposites.



## 1. Introduction

Physico-chemical modification is an attractive means of tailoring the properties of a polymeric membrane according to the end use. The use of graphene oxide (GO), the oxygenated derivative of graphene, as a filler, to fabricate nanocomposite membranes has drawn considerable attention in recent years [1,2]. GO can be incorporated into a ceramic or polymeric matrix to improve its chemical tunability and mechanical strength in a myriad of applications including treatment of aqueous streams. Due to the presence of different covalently bonded oxygen functional groups (such as hydroxyl and epoxy) on the basal planes together with carboxyl and carbonyl moieties lining the nanosheet edge of carbon atoms GO exhibits excellent hydrophilicity [3]. It has a quasi-two-dimensional honeycomb lattice type structure and can be easily dispersed in water and some organic solvents, to form a stable colloidal suspension. GO can be potentially used as a free standing membrane, as a surface modifier and as casted GO incorporated composite membranes [4]. These GO incorporated membranes are reported to exhibit enhanced performance in terms of flux and solute permeation.

Combining the excellent film forming ability of polyvinyl alcohol (PVA) and the mechanical stability of graphene oxide (GO), a polymer-inorganic hybrid composite could be a unique option in the pressure driven membrane processes for aqueous system. Through incorporating GO into different polymer matrices, the hybrid membranes are observed to exhibit higher water fluxes and better fouling resistance for nanofiltration or ultrafiltration [5,6]. The GO film is stabilized by hydrogen bonding and the van der Waals forces between the sheets [7,8]. Stronger interaction between the GO sheets lead to laminates with a more ordered and denser structure facilitating the effective separation performance of composites. Wang et al. reported the preparation of "pore-filling" membrane by dynamic pressure-driven assembly of a poly (vinyl alcohol)–graphene oxide (PVA–GO) nanohybrid layer onto an asymmetric polyacrylonitrile ultrafiltration membrane for the pervaporation of toluene and *n*-heptane mixture [9]. Graphene-loaded sodium alginate (NaAlg) nanocomposite membranes were used to enhance the pervaporation (PV) dehydration of isopropanol at varying feed concentrations and temperatures [1]. In another study graphene oxide (GO) was deposited on modified polyacrylonitrile (mPAN) for the dehydration of 1-butanol mixtures by pervaporation. The composite membrane thus prepared exhibited

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**Nomenclature**

| | |
|---|---|
| HAc | Acetic acid |
| TGA | Thermogravimetric analysis |
| FTIR | Fourier transformed infrared |
| AFM | Atomic force microscopy |
| FE-SEM | Field emission scanning electron microscopy |
| PVA | Polyvinyl alcohol |
| $W_{wet}$ | Weight of swallow membrane (g) |
| $W_{dry}$ | Weight of dry membrane (g) |
| $P_i^G$ | Permeability of component i (Barrer) |
| $J_i$ | Mass flux (kg/m$^2$h) |
| $C_i$ | Concentration of component I (kg/m$^3$) |
| $l$ | Membrane thickness (mm) |
| $x$ | Mole fraction of feed |
| y | Mole fraction of permeate |
| $P_p$ | Permeate pressure |
| $P^{sat}$ | Saturated vapor pressure |
| $j_i$ | Volumetric flux (m$^3$(STP)/m$^2$ h) of component 'i' |
| $v_i^G$ | Molar volume of gas i (22.4 l(STP)/mol) |
| $m_i$ | Molecular weight of component i |
| $D_i$ | Diffusion coefficient or diffusivity of component i (m$^2$/s) |
| $\delta$ | Diffusion length (m) |
| T | Temperature (°C) |

*Greek letters*

| | |
|---|---|
| $\beta$ | Separation factor |
| $\gamma$ | Activity coefficient |

exceptional pervaporation potential at 30 °C. The concentration of water at the permeate side and flux was reported to be 9.6 wt% and 2.54 kg/m$^2$ h$^{-1}$ respectively [10]. Poly (ethyleneimine) and polyacrylic acid modified GO nanohybrid membranes were used in the pervaporative dehydration of ethanol/water mixture at 50 °C [11]. Free standing GO membranes were synthesized by a simple drop-casting method. The resulted nanofiltration membranes showed significant potential in separation of sodium salts from a mixture of copper salts and organic contaminants [12]. Performance of a free-standing graphene oxide (GO) thin films were reported in the pervaporation of ethanol-water mixture. For a feed containing 85 wt% ethanol the membrane selectivity was found out to be 227 at a temperature of 24 °C [13].

Although polymer–GO membranes have drawn much interest in diverse separation processes, its potential for pervaporative separation of highly diluted water -acetic acid system has not been explored so far. High concentration of vinegar (containing up to 15% acetic acid) is commonly used as cooking ingredients, food flavourant, pickling and perishable food preservation. Additionally it is also used as effective cleaning agents for crockery. Wastewater generated from the vinegar processing units contains up to 15% of recoverable acetic acid with a COD of 66.3 gL$^{-1}$ [14]. This dilute acetic acid (along with few other ingredients like salts, edible color etc) in vinegar is not amenable to separation from water by conventional distillation or rectification owing to their proximate boiling points. Separation and concentration of aqueous acetic acid – one of the important organic intermediates in the chemical industry, has become a priority area of industrial research for quite some time. However, very few studies have focused on the concentration of vinegar or recovery of acetic acid from spent vinegar. Vinegar containing 12% w/v acetic acid was concentrated by electrodialysis (ED) to produce triple-strength vinegar (30–33% acetate) [15]. Electrohydrolysis of vinegar fermentation wastewater was carried out for simultaneous COD reduction and hydrogen production [16]. Justin et al. reported the treatment of wastewater from a wine and apple vinegar production unit and detergent unit in a hybrid constructed wetland [17].

At present, majority of the large-scale pervaporation units are employed for the dehydration of ethyl alcohol, isopropyl alcohol and other organic solvents. Therefore, development of pervaporation process for acetic acid recovery from dilute waste stream, which may partly supplement, if not fully substitute distillation processes, is quite encouraging. Taking these considerations into account, we chose to work on polyvinyl alcohol-graphene oxide composite membrane for the recovery of acetic acid from vinegar wastewater. To the best of our information this is the first report of the feasibility of GO incorporated PVA membrane for the pervaporation of vinegar wastewater. The selection of PVA is reasoned for its affordable cost, commercial availability, hydrophilicity and good film forming properties. Preparation of composite membrane needs proper selection of a solvent as it governs the monomer solubility and diffusivity in the reaction zone, which in turn affect the performance and morphology of the membrane. PVA can form gel in various solvents and therefore two different solvents, water and dimethyl sulphoxide (DMSO), were used for PVA gel formation. Three sets of membranes namely pristine polyvinyl alcohol $(PVA)_0$, polyvinyl alcohol-graphene oxide-composite prepared from PVA dissolved in water $(PVA\text{-}GO)_1$ and polyvinyl alcohol-graphene oxide-composite prepared from PVA dissolved in dimethyl sulphoxide (DMSO) $(PVA\text{-}GO)_2$ were used in this study. The as-prepared membranes were characterized by wide angle X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transformed infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM), and Atomic force microscopy (AFM) analyses. Permeation performance of the membranes was evaluated in terms of flux, permeability, separation factor and diffusion coefficient under various experimental conditions. The results obtained in the present study should facilitate the synthesis of PVA-GO composites and thin films using different solvents. It provides additional insight into fundamental aspects and could be useful as guidelines for scale up of pervaporation system for the recovery of dilute acetic acid from spent vinegar.

## 2. Materials and methods

### 2.1. Materials

Polyvinyl alcohol (MW ~72000; 98–99% conversion from acetate) granules were obtained from Loba Chemi Pvt. Ltd., India and was used as received. Glutaraldehyde and DMSO were procured from Qualigens and used as such. Simulated vinegar wastewater was prepared by diluting raw vinegar purchased from a local provision store at Anand, Gujarat. It was used as received without further purification. Preparation of stock solutions was carried out with deionized water, having a conductivity of 20 μS/cm, produced from a reverse osmosis system. All other chemicals were of reagent grade and were used without additional processing.

### 2.2. Preparation of graphene oxide

Pristine graphene oxide was prepared by modified Hummers method [18] as reported in the literature. In a typical reaction, 5 g of graphite powder and 2.5 g of $NaNO_3$ were mixed with 108 mL of 98 wt% $H_2SO_4$ and 12 mL of $H_3PO_4$ in an ice bath for 10 min. Then 15 g of $KMnO_4$ was slowly added in batches to keep the temperature under 5 °C. After stirring for 60 min, the mixture was transferred into an oil bath at 35 ± 2 °C and stirred for 30 min at 40 °C for another 60 min. The temperature of the mixture was adjusted to a constant 98 °C for 60 min while water was added continuously.

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