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Recovery of hydrochloric acid and glycerol from aqueous solutions in chloralkali and chemical process industries by membrane distillation technique

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ABSTRACT

Membrane distillation (MD) is a rapidly advancing process for separation of azeotropic and close boiling liquid mixtures besides dewatering of high boiling solvents. Recovery of hydrochloric acid (HCl) from a chloralkali industrial effluent and dehydration of glycerol/water mixture was performed using MD technique. HCl was recovered using chemically resistant polytetrafluoroethylene (PTFE) membrane of 0.22 μm pore size and 78% porosity. The effluent feed contained 32.8 wt.% of aqueous HCl with color forming Fe compounds and heavy hydrocarbon (C_9–C_{14}) impurities that gave an oily appearance. Permeate obtained was colorless aqueous HCl (33 wt.%) at a high flux with negligible impurity levels. An increase in permeate pressure from 5 to 15 mmHg resulted in a gradual reduction in flux from a high value of 8.57 kg/m^2/h to a moderate 1.02 kg/m^2/h at ambient temperature of 28 °C. Effect of feed composition in terms of acid and inorganic salt contents besides feed temperature (25–60 °C) on flux and separation efficiency was demonstrated at a constant downstream vacuum of 8–10 mmHg. Dehydration of glycerol was performed using novel indigenously synthesized ultraporous hydrophobic polystyrene (PS) membrane of 0.72 μm pore size. Permeate was found to contain pure water due to the low vapor pressure and larger molecular size of glycerol which cannot penetrate PS as it does not get wetted by water. This indicated a selectivity of infinity (∞) which is associated with a reasonable water flux in the range 0.56–0.02 kg/m^2/h at a vacuum of 5 mmHg for feed glycerol concentration varying from 10 to 90 wt.%. PS membrane was characterized by SEM, FTIR, XRD and TGA to assess surface and cross-sectional morphologies, structural elucidation, crystallinity and thermal stability of the membrane, respectively. A detailed economic estimation of HCl recovery for a feed effluent capacity of 2 m^3/h is presented. The study showed that commercial grade HCl and glycerol could be recovered from aqueous streams at a reasonable price by employing MD technique.

1. Introduction

The separation of useful chemical entities such as solvents and acids from aqueous waste streams released from industries is important from both economic and environmental points of view [1–8]. Glycerol is a nontoxic, edible, bio-sustainable and biodegradable compound used as a versatile industrial organic solvent and more recently as a reactant for producing several important chemicals. It has a high boiling point of 290 °C and decomposition temperature. The hygroscopic nature of glycerol results in water absorption and formation of an aqueous solution of 80% glycerol which requires to be dehydrated before reuse [9]. With rapid growth in both population and industrialization, there is an urgent need to utilize biofuels such as biodiesel as alternative sources of energy since they are renewable, biodegradable and clean. Due to the large surplus of glycerol formed as a by-product during the production of biodiesel, many studies are focused on finding new applications of glycerol as a low cost feedstock for converting it into value-added chemicals. Glycerol is used in food and beverages, drugs, cosmetics, surface coating resins, textiles industries and in production of acrolein [10–14]. Several conventional methods, for instance, adsorption onto activated carbon [15,16], multiple-effect evaporation [17] and distillation [1,6,18–27] have been in use for recovery of solvents such as glycerol since past few decades. The technologies evaluated so far involve high capital and operating costs due to regeneration procedures and phase change.

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Inorganic acids such as HCl have manifold uses in a variety of industries including metal and woodwork, textile dyeing, petroleum, explosive and photography besides being employed as catalysts in several important chemical reactions. Several approaches have been proposed for the recovery of acids from effluents which includes ion retardation, diffusion dialysis, and electrodialysis [28–32]. Nevertheless, these regeneration processes produce lots of dilute acid solution. Thus, a novel efficient technology needs to be proposed to concentrate the acid solution. HCl is a strong inorganic acid having several applications in chemical and electroplating industries [5,33,34]. Aqueous HCl is used for industrial acidizing, refining ores of tin and tantalum, converting corn starch to syrup, etc. Since the past few decades, various techniques have been in use for separation of acids and solvents from aqueous solutions. In comparison to these processes, MD is an emerging technology due to inherent features of process safety and environmental friendliness for radioactive waste treatment, removal of volatile organic compounds, concentration of agro-based and organic solutions and other specific applications [34,35]. The key advantages of MD over conventional separation processes are relatively lower energy consumption compared to distillation, considerable separation of dissolved and non-volatile species, reduced vapor space as compared to conventional multistage flash distillation, lower operating pressure than pressure-driven membrane processes, lower operating temperature and corrosion related problems as compared to evaporation [36]. The large vapor space required by a conventional distillation column is replaced in MD by the pore volume of a microporous membrane, which is generally around 100 μm thick. While conventional distillation relies on extensive vapor–liquid contact, MD employs a hydrophobic microporous membrane to support a vapor–liquid interface. Membrane fouling is a smaller problem in MD than in other membrane processes because the pores are relatively large compared to the 'pores' or diffusional pathways in nanofiltration or ultrafiltration, and do not get easily clogged since vacuum is applied at downstream side in MD rather than pressure at the upstream surface [37].

Vacuum MD (VMD) uses porous hydrophobic membranes that act only as support for the vapor–liquid interface and do not contribute to the separation performance. On the contrary, pervaporation requires dense and selective membranes and the separation is based on the relative solubility and diffusivity of each component in the membrane material. Therefore, VMD typically achieves fluxes that are several orders of magnitude higher than pervaporation mass transfer rates even though selectivity in pervaporation is considerably higher than in MD for close boiling mixtures. This phenomenon is attributed to the fact that in VMD the selectivity is mainly determined by temperature gradient and vapor–liquid equilibrium (VLE) conditions at the membrane-solution interface, although the diffusion step across the porous membrane may impart some assistance to the transport of lighter molecules [38]. MD is a thermally driven separation process, wherein a microporous hydrophobic membrane usually separates aqueous solutions maintained at different temperatures. The temperature difference across the membrane results in vapor pressure gradient, causing transfer of water vapor molecules though the pores of the membrane from the high to low vapor pressure side.

Several authors have studied recovery of hydrochloric acid from aqueous streams using MD. Gryta et al. (2006) investigated the performance of MD process by treating effluents containing residual HCl along with soluble salts [39]. A significant enhancement in flux was observed by increasing acid concentration in the feed mixture. Another study was carried out by Tomaszewska et al. (2001) for concentration of acidic spent solutions containing HCl and salts using capillary PP membrane module [40]. The experiments were performed using model or real metal pickling solutions of different compositions. The application of concentration or separation of HCl from spent acid solutions may have a limited practical significance therefore the studies on the influence of salts on HCl molar flux were demonstrated [41]. The presence of salts in feed solution improved the flux of HCl to a greater extent compared to the case wherein salt was absent. The same authors also studied mass transfer of HCl and water vapor through flat sheet membranes made of hydrophobic PTFE, PVDF and PP capillary membranes [42]. A transport model was developed by considering a set of possible equations. The study showed that experimental results obtained were in good agreement with theoretical predictions.

Polyvinylidenefluoride (PVDF), polytetrafluoroethylene (PTFE) and polypropylene (PP) are the most common membrane materials for MD applications due to their hydrophobic nature and high thermal stability. PTFE membranes show a better performance compared to PVDF due to better chemical inertness but are far more expensive. Thus, there is enough scope to study polystyrene membrane for dehydration of glycerol since not much work pertaining to this particular membrane has been reported in literature so far. In the present study, ultraporous hydrophobic polystyrene was indigenously synthesized and used for dehydration of glycerol from aqueous solutions. Commercial PTFE membranes were preferred for recovery of HCl from a chloralkali industrial effluent, which contained concentrated and fuming HCl, water and traces of impurities in the form of higher hydrocarbons (C_9-C_{14}) and Fe compounds which gave an oily appearance to the aqueous HCl rendering the acid unfit for utilization.

2. Theory

In MD a hot aqueous feed solution is brought into contact with one side (feed side) of a hydrophobic, microporous membrane. The hydrophobic nature of the membrane prevents penetration of the aqueous solution into the pores, resulting in a vapor–liquid interface at each pore entrance. Fig. 1 illustrates how the vapor–liquid interfaces are supported at the pore openings. The value of the contact angle θ of a liquid droplet on an ideal smooth homogeneous surface is described by Young's equation [43]:

$$\gamma_{lv}\cos\theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

where θ contact angle between liquid and membrane, γ_{lv} liquid–vapor interfacial tension, γ_{sv} solid–vapor interfacial tension, γ_{sl} solid–liquid interfacial tension. A droplet of water on a hydrophobic surface of a polymer film made of polymer like PS, PP or PTFE will give a contact angle which is larger than 90°. If the surface

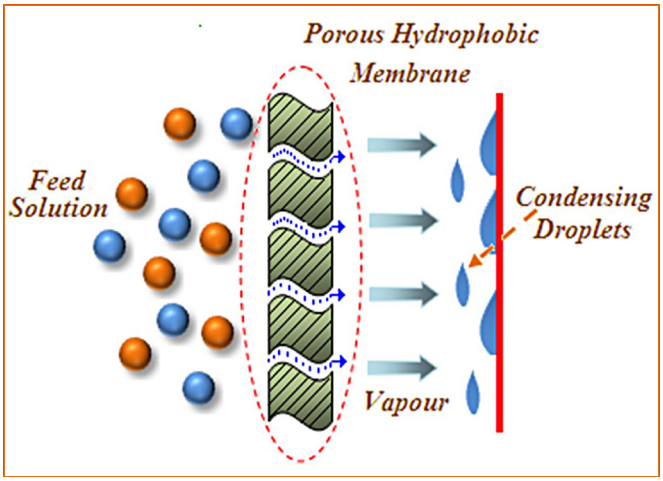

Fig. 1. Transport mechanism in MD process.

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