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Novel carbohydrate polymeric blend membranes in pervaporation dehydration of acetic acid ☆

K.S.V. Krishna Rao [a], B. Vijaya Kumar Naidu [b], M.C.S. Subha [a], M. Sairam [b], N.N. Mallikarjuna [1], T.M. Aminabahvi [b,*]

[a] *Department of Chemistry, Sri Krishnadevaraya University, Anantapur-515 003, India*
[b] *Membrane Separations Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad-580 003, India*

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Abstract

Due to the widespread usage of carbohydrate polymers in a variety of areas, the present study is undertaken to develop novel graft copolymers of hydroxyethylcellulose and acrylamide (HEC-*g*-AAm). Grafting reaction was confirmed by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The graft copolymers were blended in different ratios with a natural polymer, sodium alginate (NaAlg). Using these polymers, membranes were prepared by solution casting and were crosslinked with glutaraldehyde for testing in pervaporation (PV) dehydration of acetic acid. Swelling experiments have been performed on the blend membranes at 30 °C to test their stability in water–acetic acid mixtures. The present membranes, being hydrophilic, were able to successfully recover 89% of water from acetic acid solutions when tested for feed mixtures ranging from 10% to 50% (w/w) of water. Membrane flux and selectivity to water was increased at increasing amount of HEC-*g*-AAm grafted copolymer in the mixed blend of NaAlg. The membranes of this study showed selectivity of 27.9 with a flux of 0.058 kg/m^2 h to dehydrate 10% (w/w) water from aqueous acetic acid feed mixture through the blend membrane. Flux values increased with increasing concentration of water in the feed, while selectivity decreased considerably. To the best of our knowledge, this is indeed the first example of the use of this type of combination carbohydrate polymers for pervaporation dehydration of acetic acid, which is a well-known industrial solvent.

Keywords: Blend membranes; Pervaporation; Swelling; Sodium alginate

1. Introduction

Classes of compounds that are basic components of plants of all types, collectively known as carbohydrates, are composed of carbon, hydrogen and oxygen. Such carbohydrate polymers comprise of all varieties of starches, seaweeds, natural gums, polysaccharides and cellulose. Use of carbohydrate polymers in place of man-made polymers has been increasing in recent years due to stringent environmental regulations. Sodium alginate (NaAlg), a well-known natural polysaccharide, derived from the brown seaweeds, is composed of D-mannuronic acid and D-guluronic acid. This polysaccharide is used in food industry as a gelling agent (Lim & Moss, 1981; Cai, Shi, Sherman, & Sun, 1989; Hertzberg, Moen, Vogelsang, & Oestgaard, 1995). In the earlier literature, NaAlg has been used as a pervaporation (PV) membrane for dehydrating several-organic compounds from their aqueous feed solutions (Kurkuri, Kumbar, & Aminabhavi, 2002; Wang, 2000; Toti & Aminabhavi, 2004; Toti, Kariduraganaver, Soppimath, & Aminabhavi, 2002; Naidu, Krishna Rao, & Aminabhavi, 2005; Naidu, Sairam, Raju, & Aminabhavi, 2005). NaAlg has also been used as a membrane or matrix material in pesticide and drug delivery applications

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* Corresponding author. Fax: +91 836 2771275.
E-mail address: aminabhavi@yahoo.com (T.M. Aminabahvi).
[1] Present address: US Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH 45268, USA.

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(Kulkarni, Soppimath, Aminabhavi, Dave, & Mehta, 2000; Xing, Dawei, Liping, & Rongquing, 2003). Another widely used carbohydrate polymer viz., hydroxyethylcellulose (HEC), a non-ionic water-soluble and water swellable cellulose ether, that is compatible with a wide range of water-soluble polymers has also been widely tested as a PV membrane in liquid separations (Savage & Thers, 1971; Dalal & Narurkar, 1991; Naidu, Sairam et al., 2005). However, due to intrinsically poor mechanical properties of some carbohydrate polymers, attempts have been made to develop their blends/grafts with the other well-known man-made polymers. Graft copolymerization of vinyl monomers on carbohydrate polymers has been widely studied since radical sites can be generated on cellulose backbone using the chemical initiators. Earlier, Mino and Kaizerman (1958) grafted monomers like acrylamide, acrylonitrile and methyl methacrylate on poly(vinyl alcohol) using Ce^{+4} initiator. Several vinyl monomers were also grafted on cellulosic backbones by the direct oxidation method using Ce^{+4} (Lepoutre, Hui, & Robertson, 1973; Lepoutre & Hui, 1975; Zhran, Williams, & Stannet, 1980).

Acetic acid is an important base chemical for a number of applications ranking among the top-20 intermediates. Nearly two-thirds of its total production is used to produce vinyl acetate and cellulose acetate. It is also used as a solvent in plastic industries and in the production of resins. A trace amount of acetic acid is used in pharmaceutical and biochemical industries in the production of some antibiotics. Currently used processes for acetic acid production include carboxylation of methanol, liquid phase oxidation of hydrocarbons and oxidation of acetaldehydes (King, 1983). One way to reduce the cost of acetic acid is in fermentation of biomass, forestry residues, municipal wastes and other byproducts (Bungay & Hadson, 1987). Acetic acid concentrations obtained in these processes are usually small i.e., <10–15% (w/w) and it must be recovered from the fermentation broths. Even though water and acetic acid do not form azeotropes, their separation by simple distillation is not very easy due to their close relative volatility. As a viable alternative, pervaporation dehydration membranes have been used (Aminabhavi & Toti, 2003). PV process consists of preferential sorption of one of the components of the feed mixtures across a membrane and desorption or evaporation as a permeate vapor due to vacuum applied on the downstream side of the membrane. PV differs from all other membrane processes because of the phase change of the permeate. Transport through the membrane therefore occurs due to vapor–pressure gradient across the membrane. Innumerable types of polymeric membranes have been used in PV separation research (Aminabhavi et al., 1994; Aminabhavi & Toti, 2003).

In our continuing efforts to tackle acetic acid separation problem using membranes (Aminabhavi & Toti, 2003) and to search for new environmentally benign polymeric materials, we thought of combining the properties of NaAlg and acrylamide grafted HEC carbohydrate polymer to develop the type of novel membranes for the PV dehydration of acetic acid. Earlier studies from this laboratory (Toti et al., 2002; Aminabhavi & Nayak, 2002) have dealt with the use of hydrophilic membranes prepared from guar gum-*grafted*-acrylamide blends with NaAlg and poly(vinyl alcohol)-*grafted*-acrylamide (PVA-*g*-AAm) for PV dehydration of acetic acid. In continuation of this research, we now report the preparation of blend membranes of NaAlg and hydroxyethylcellulose-*grafted*-acrylamide (HEC-*g*-AAm) comprising varying compositions of HEC-*g*-AAm for the PV dehydration of acetic acid. PV performance of the blend membranes, when compared with the pristine NaAlg membrane as well as with other literature data on similar types of membranes, revealed an improved performance of the present membranes. Particularly, the developed membranes are found to be much better than those of the earlier blend membranes of NaAlg with guar gum-*grafted*-acrylamide in terms of selectivity and flux. To the best of our knowledge, this type of blend combination is used first time for the PV dehydration of acetic acid from its feed aqueous solution.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg), glutaraldehyde (GA), acrylamide, analytical reagent grade acetic acid, acetone and hydrochloric acid (HCl) were all purchased from s.d. fine Chemicals, Mumbai, India. Hydroxyethylcellulose (HEC) powder was purchased from Polysciences Inc., USA. Deionized water having a conductivity of 20 μS/cm was produced in the laboratory itself from the Permeonics pilot plant (Vadodara, India) using nanofiltration membrane module.

2.2. Synthesis of poly(acrylamide-grafted-HEC)

Acrylamide-*grafted*-HEC copolymer was synthesized by solution polymerization using ceric ammonium nitrate (CAN) as an initiator (Lepoutre et al., 1973). In brief, HEC solution was prepared by dissolving 5 g of solid polymer in 100 mL of HNO_3 (5×10^{-3}M) for overnight under constant stirring in an inert atmosphere of nitrogen gas. To this solution, 0.070 moles of acrylamide was added and stirred thoroughly for about 1 h at 60 °C. The initiator solution containing 5.47×10^{-4} moles of CAN were added to the mixture under continuous stirring at 60 °C for about 5 h. The reaction mixture was then cooled and a pinch of hydroquinone was added to quench the reaction. The mass obtained was precipitated in acetone and washed with an aqueous methanolic solution to remove the polyacrylamide homopolymer formed. The solid copolymer thus obtained was dried in an electrically controlled oven at 40 °C before further use.

2.3. Differential scanning calorimetric (DSC) studies

DSC thermograms of HEC and HEC-*g*-AAm copolymers were recorded using Rheometric Scientific differential scanning calorimeter (Model-DSC SP, Surrey, UK). The analysis was performed by heating the samples at the rate of 10 °C/min under an inert atmosphere. The procedure followed was the same as described in the literature (Hatakeyama & Quinn, 1999).

2.4. Membrane preparation

Blend membranes of NaAlg with HEC-*g*-AAm were prepared by solution casting. The procedure used to fabricate the membrane remained the same as used before (Aminabhavi & Nayak, 2002). A required quantity of NaAlg was dissolved in 100 mL distilled water by stirring over a magnetic stirrer (Jenway, model 1103, UK) for about 24 h. To this, 10%, 20% and 30% (w/w) different amounts of HEC-*g*-AAm were added. The solution was mixed uniformly and filtered to remove the suspended particles. It was poured onto a clean glass plate leveled perfectly on a tabletop kept in a dust free atmosphere and dried at room temperature. Dried membranes were peeled off carefully from the glass plate. Membranes were crosslinked by immersing in 70% (v/v) aqueous-acetone mixture containing 2.5 mL HCl and 2.5 mL GA for up to 12 h. After removing the membrane from the crosslinking bath, it was washed with water repeatedly and dried in an oven at 40 °C. The measured membrane thickness was around 40 μm. The membranes prepared with 10%, 20% and 30% (w/w) of HEC-*g*-AAm were designated as NaAlg-HEC-*g*-AAm-10, NaAlg-HEC-*g*-AAm-20 and NaAlg-HEC-*g*-AAm-30, respectively, while the pristine sodium alginate membrane was designated as NaAlg.

2.5. Swelling experiments

Equilibrium swelling experiments on all the membranes were performed in water–acetic acid mixtures ranging from 10% to 90% (w/w) of water at 30 ± 0.5 °C in an electronically controlled incubator (WTB Binder, Model BD-53, Tuttilgen, Germany) as per the procedures published earlier (Aminabhavi, Munnolli, & Ortego, 1995; Harogoppad & Aminabhavi, 1991; Aminabhavi, Phayde, Ortego, & Vergnaud, 1996). Circularly cut (diameter = 2.5 cm) disk-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30 °C for about 48 h before performing the swelling experiments. Mass of the soaked samples were measured using a digital Mettler microbalance (Model AE 240, Greifensee, Switzerland) sensitive to ±0.01 mg.

2.6. Pervaporation experiments

Pervaporation experiments were performed in an apparatus designed indigenously (Aminabhavi & Nayak, 2002). The PV apparatus consists of a stirred stainless steel cell through which retentate is circulated to the feed tank. The effective surface area of the membrane in the cell is 32.43 cm^2 and the diameter is 6.4 cm. Volume capacity of the cell is 250 cm^3. Temperature of the feed mixture is kept constant using a thermostatically controlled water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a DC current motor in the feed compartment. Downstream side of the PV apparatus was continuously evacuated using a vacuum pump (Toshniwal, Mumbai, India) at a vacuum pressure of as low as 10 torr.

The test membrane was equilibrated for about 2 h with the feed mixture before starting the PV experiment. For each feed mixture, PV runs lasted up to 5–6 h. After establishment of a steady state, permeate vapors were collected in traps immersed in liquid nitrogen. PV experiments were performed with 10–50% (w/w) water-containing feed mixtures. Each time, adding the required amount of fresh solvent mixture continuously enriched the depleted solvent mixture in the feed compartment. Mass of permeate collected in the trap was taken and its composition was determined by measuring its refractive index and comparing it with a standard established graph of refractive index vs. mixture composition. Permeate composition was determined at 30 °C by measuring refractive index of the liquid mixture on a refractometer (Atago, model 3T, Tokyo, Japan). From the PV data, selectivity, α was calculated as

$$\alpha = \left(\frac{y_A}{1-y_A}\right)\left(\frac{1-x_A}{x_A}\right), \tag{1}$$

where x_A is mole fraction of water in the feed and y_A is mole fraction of water in the permeate. Flux, $J(\text{kg/m}^2\text{h})$ was calculated from the weight of permeate, $w(\text{kg})$, effective membrane area, $A(\text{m}^2)$ and time, $t(\text{h})$ using the relation

$$J = w/At. \tag{2}$$

3. Results and discussion

3.1. DSC studies

DSC scans of the pristine HEC and HEC-*g*-AAm are displayed in Fig. 1. Plain HEC has a glass transition temperature, T_g at 65 °C. However, the T_g of HEC was shifted to higher temperature (135 °C) in the graft copolymer, which confirmed the grafting of acrylamide onto HEC.

3.2. Membrane swelling

It has been well recognized that sorption properties exhibited by the membrane materials are helpful in selecting the appropriate membrane because PV performance of the membrane depends upon its sorption characteristics in the presence of the feed mixture. Since sorption does not correspond to permeability because diffusion through the

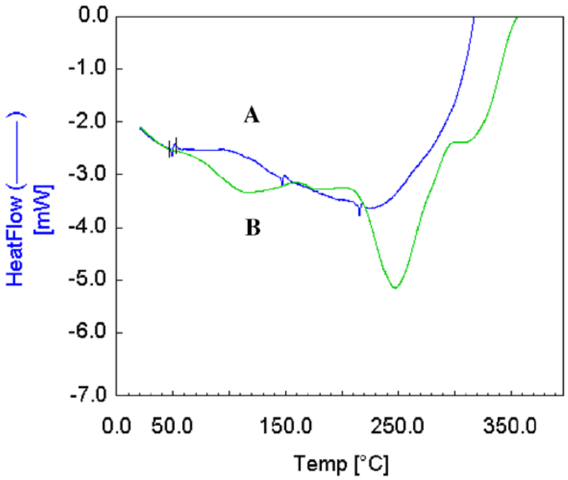

Fig. 1. DSC thermograms of (A) HEC and (B) HEC-*g*-AAm copolymer.

membrane also contributes significantly to the overall permeation process. In any case, membrane swelling controls its PV performance (Toti et al., 2002). Hence, it is important to determine the degree of swelling (*DS*), which was calculated as

$$DS = \frac{W_\infty - W_0}{W_0}, \tag{3}$$

where W_0 is initial dry weight of the membrane and W_∞ is swollen weight of the membrane at equilibrium.

Results of degree of swelling of the membranes in water–acetic acid mixtures ranging from 10% to 90% (w/w) of water at 30 °C are presented in Table 1. *DS* of the membranes increased with increasing amount of water in the feed and also, with increasing HEC-*g*-AAm content of the blend membrane. This could be due to increased solublization of carbohydrate polymers at higher concentrations of water in the feed mixture. As the amount of graft-copolymer increased, the blend membrane will become more and more hydrophilic due to higher amount of HEC-*g*-AAm of the matrix making it more hydrophilic than NaAlg itself. This effect further increased the free volume of the membrane matrix as a result of increased swelling (Harogoppad, Aminabhavi, & Balundgi, 1992; Duda & Zielinski, 1996). Degree of membrane swelling in water–acetic acid feed mixture varied as per the sequence from higher grafting to lower grafting ratios i.e., NaAlg-HEC-*g*-AAm-30 > NaAlg-HEC-*g*-AAm-20 > NaAlg-HEC-*g*-AAm-10 > NaAlg. Notice that least swelling of NaAlg membrane is directly related to its somewhat poor PV performance as compared to the blend membranes.

3.3. Pervaporation results

There have been many attempts and investigations in the previous literature to develop homogeneous or heterogeneous polymeric membranes (grafted or blend matrix) giving high performance in terms of flux and selectivity. These attempts include the modification of a pristine polymeric membrane by introducing another hydrophilic polymer, blending a polymer with a high flux and one with a high selectivity for the same component of the feed mixture, incorporation of functional groups interacting with the permeants into a membrane through graft co-polymerization and/or crosslinking. The principal objective of this research is to develop a novel mixed-blend membrane by using a suitable graft copolymer such as HEC-*g*-AAm with another hydrophilic NaAlg polymer to obtain a better PV performance to dehydrate acetic acid from its aqueous feed solutions.

PV results (flux and selectivity) of the blend membranes of this study as well as the pristine NaAlg membrane are presented in Table 2. Flux and selectivity results are graphically displayed in Fig. 2. The pristine NaAlg membrane has a flux of 0.005 kg/m^2 h at permeate concentration of 68.32% (w/w) of water for 10% (w/w) water in the feed. These values are quite lower than those observed for the present blend membranes. Nearly, ten-times increase in flux i.e., up to 0.058 kg/m^2 h was observed for NaAlg-HEC-*g*-AAm-30 membrane, due to its increased swelling at higher content of the grafted copolymer. Consequently, selectivity has also increased in the same ratio i.e., higher the grafting ratio higher would be the selectivity. With increasing concentration of water of the feed mixture, flux values have increased due to hydrophilic-hydrophilic interactions, but selectivity values decreased considerably. This

Table 1
Equilibrium swelling (w/w) data of different membranes in water + acetic acid mixtures at 30 °C

Water composition % (w/w)	NaAlg	NaAlg-HEC-*g*-AAm-10	NaAlg-HEC-*g*-AAm-20	NaAlg-HEC-*g*-AAm-30
Membranes				
10	1.131	1.318	1.499	1.796
20	1.320	1.526	1.743	1.954
30	1.426	1.674	1.895	2.090
40	1.517	1.840	2.037	2.512
50	1.653	1.914	2.235	2.659
60	1.760	1.991	2.453	2.846
70	1.820	2.115	2.568	3.169
80	1.958	2.301	2.756	3.247
90	2.155	2.412	2.987	3.478

Table 2
Pervaporation results of water–acetic acid mixtures at 30 °C

Feed water composition % (w/w)	Water flux (kg/m^2 h)	Selectivity	Permeate water composition % (w/w)
NaAlg			
10	0.005	19.4	68.32
20	0.020	16.0	80.01
30	0.042	10.2	81.32
40	0.054	7.0	82.32
50	0.072	5.0	83.23
NaAlg-HEC-*g*-AAm-10			
10	0.021	25.4	73.83
20	0.079	16.1	80.08
30	0.150	11.2	82.80
40	0.200	08.1	84.32
50	0.285	5.8	85.32
NaAlg-HEC-*g*-AAm-20			
10	0.031	25.9	74.23
20	0.148	17.3	81.23
30	0.217	11.6	83.21
40	0.264	10.6	87.65
50	0.363	7.4	88.12
NaAlg-HEC-*g*-AAm-30			
10	0.058	27.9	75.63
20	0.193	18.7	82.35
30	0.230	12.5	84.32
40	0. 290	11.6	88.52
50	0. 386	8.2	89.12

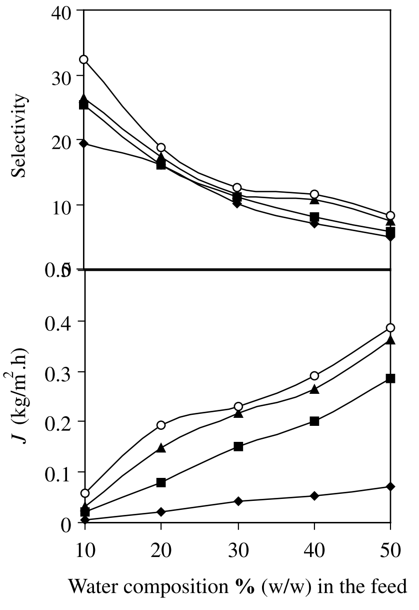

Fig. 2. Water flux and selectivity vs. % (w/w) of water in the feed for NaAlg and its blend membranes with HEC-*g*-AAm at 30 °C. Symbols: NaAlg (◆); NaAlg-HEC-*g*-AAm-10 (■); NaAlg-HEC-*g*-AAm-20 (▲); NaAlg-HEC-*g*-AAm-30 (○).

type of increase in flux is due to an increase in swelling of the membranes at higher concentrations of water in the feed. However, a noteworthy observation is that by blending NaAlg with increasing grafting ratio of HEC-*g*-AAm portion of the backbone polymer, both permeation flux and selectivity have increased. This type of simultaneous increase in flux and selectivity with increasing grafting ratio of the grafted copolymer supports the increased selective permeation of water molecules through the swollen membranes at higher grafting ratios. Such type of simultaneous increase in flux and selectivity of PV membranes is quite difficult to achieve. Among the three blend membranes prepared, NaAlg-HEC-*g*-AAm-30 has shown the highest flux ranging from 0.058 to 0.386 kg/m^2 h with a removal of as much as 89.12% (w/w) of water from the feed solution to the permeate side. However, permeation flux and % (w/w) of water in permeate increased with increasing concentration of water in the feed. This is the result of increased blend membrane swelling at higher concentrations of water in the feed.

As regards selectivity, the pristine NaAlg membrane has a selectivity of 19.4 at 10% (w/w) water of the feed mixture, which decreased drastically to a lower value of 5 at higher concentrations of water i.e., up to 50% (w/w). On the other hand, blend membranes of NaAlg with HEC-*g*-AAm have all exhibited an improved selectivity as compared to pristine NaAlg membrane. For instance, NaAlg-HEC-*g*-AAM-10 membrane has a selectivity of 25.4 with a flux of 0.021 kg/m^2 h for 10% (w/w) of water in the feed, whereas NaAlg-HEC-*g*-AAm-30 membrane has a selectivity of 27.9 with a still higher flux value of 0.058 kg/m^2 h. In case of blend membranes also, selectivity has decreased with increasing concentration of water. Higher swelling of blend membranes at higher water concentrations of water in the feed is the cause of this effect since, both permeate molecules will pass through the membranes with a decreased selectivity.

In most PV dehydration experiments, efforts have been made without much success to simultaneously increase flux and selectivity. However, in the present study, as shown in Fig. 3, both flux and selectivity have increased with increasing % (w/w) of HEC-*g*-AAm in the blend membrane. Permeation flux values have increased from 0.005 to 0.058 kg/m^2 h, while selectivity has increased from 19.4 to 27.9 with increasing copolymer composition of HEC-*g*-AAM from 0% to 30% (w/w) in the blend membrane. It is possible that at higher content of HEC-*g*-AAm in the blend, the rigid chains of NaAlg might have become somewhat flexible due to plasticization effect induced by the hydrophilic chains of the blends as a result of higher swelling than the pristine NaAlg. This in turn, has increased the free volume of the overall matrix membrane in order to accommodate more of water molecules for easy transport through the membrane. These results agree with the swelling results given in Table 1.

Acetic acid is one of the basic chemical commodities having a great industrial importance and its recycling after separation from aqueous streams is industrially challenging. As a result, innumerable efforts have been made in the literature to study its separation by the PV technique. A comparison of the present PV results is attempted with the available literature data. Poly(vinyl alcohol), PVA,

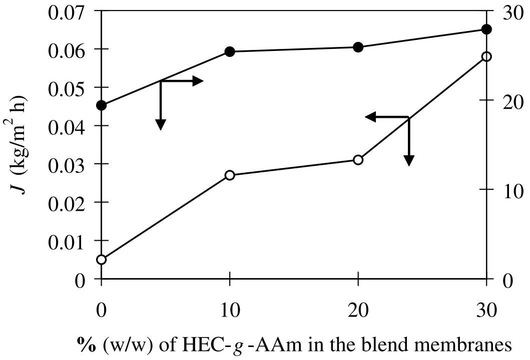

Fig. 3. Water flux (○) and selectivity (●) vs. wt% of HEC-g-AAm in the blend membrane for 10% (w/w) of water in the feed.

has been one of the most widely used membranes in PV dehydration of acetic acid. In one of the earliest studies by Nguyen, Essamri, Clement, and Neel (1987), three different membranes with PVA of different hydroxyl contents were prepared by solvent evaporation method. These membranes were tested for 10% (w/w) of water–acetic acid mixtures. The 100% hydrolyzed PVA membrane gave a selectivity of 7 with a flux of 0.05 kg/m^2 h giving 70% (w/w) of water in permeate. However, the blend membrane of PVA with poly(N-vinyl-2-pyrrolidone) gave an improved flux of 0.19 kg/m^2 h with a decrease in selectivity of 2.4. Recently, Aminabhavi and Nayak (2002) used the grafted copolymeric membranes of PVA with poly(acrylamide) for PV dehydration of acetic acid. Separation selectivity of 23 and flux of 0.006 kg/m^2 h were observed for 10% (w/w) water–acetic acid feed mixture. Toti et al. (2002) used blend membranes of NaAlg with guar gum-*grafted*-acrylamide in different ratios for the PV dehydration of acetic acid and found an improvement in flux (0.08 kg/m^{2}h) with a loss in selectivity ($\alpha = 7.4$) for the feed solution containing 10% (w/w) of water in acetic acid. The composite membrane of poly(sodium acrylate) prepared by Ruckenstein and Chen (1992) gave a flux of 0.41 kg/m^2 h with a selectivity of 12 for water–acetic acid mixtures. Wang (2000) prepared the modified NaAlg composite membranes crosslinked with 1,6-hexanediamine and obtained a selectivity of 28 with a flux of 0.182 kg/m^2 h to separate water from 15% (w/w) water containing acetic acid feed solution, but the PVA-crosslinked NaAlg composite membrane gave a selectivity of 26 with the a flux of 0.044 kg/m^2 h. It is thus realized that aromatic polyimide membranes yielded very high separation selectivity of $>10^4$ with a good permeation flux (Maeda, Tsuyumoto, Karakane, & Tsugaya, 1991). It is thus realized that the presently developed membranes are quite stable in the feed media and exhibited good PV performance characteristics compared to other membranes developed in the previous literature.

4. Conclusions

In industrial unit operations, wastewater is almost always contaminated with acetic acid, the separation of which is difficult by conventional distillation, due to their close relative volatilities. Moreover, the conventional extractive distillation will be expensive, since it consumes high energy. On the other hand, pervaporation dehydration using hydrophilic blend membranes of the type developed here are the better attractive alternatives. Blend membranes of this study exhibited better pervaporation performance than pristine sodium alginate membrane in separating water–acetic acid mixture. However, affinity of the developed membranes towards water is more than acetic acid and membranes are quite stable in the feed environment under cyclic PV experiments.

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References

Aminabhavi, T. M., Khinnavar, R. S., Harogoppad, S. B., Aithal, U. S., Nguyen, Q. T., & Hansen, K. C. (1994). Pervaporation separation of organic-aqueous and organic–organic binary mixtures. *Journal of Macromolar Science Reviews Macromolar Chemistry and Physics, C34*, 139–204.

Aminabhavi, T. M., Munnolli, R. S., & Ortego, J. D. (1995). Sorption and diffusion of *n*-alkanes into bromobutyl rubber membranes. *Polymer International, 36*, 353–363.

Aminabhavi, T. M., & Nayak, H. G. (2002). Synthesis of graft copolymeric membranes of poly(vinyl alcohol) and polyacrylamide for the pervaporation separation of water/acetic acid mixtures. *Journal of Applied Polymer Science, 83*, 244–258.

Aminabhavi, T. M., Phayde, H. T. S., Ortego, J. D., & Vergnaud, J. M. (1996). A study of sorption/desorption profiles and diffusion anomalies of organic haloalkanes into polymeric blend of ethylene–propylene random copolymer and isotactic polypropylene. *Polymer, 37*, 1677–1684.

Aminabhavi, T. M., & Toti, U. S. (2003). Pervaporation separation of water–acetic acid mixtures using polymeric membranes. *Designed Monomers and Polymers, 6*, 211–236.

Bungay, H. R., & Hadson, L. R. (1987). Calcium magnesium acetate from biomass. In M. Moo-Yong, J. Lamptey, B. Glicle, & H. Bungay (Eds.), *Biomass conversion technology, principles and practice* (pp. 189–192). New York: Pergamon Press.

Cai, Z., Shi, Z., Sherman, M., & Sun, A. M. (1989). Development and evaluation of a system of microencapsulation of primary rat hepatocytes. *Hepathology, 10*, 855–860.

Dalal, P. S., & Narurkar, M. M. (1991). In vitro and in vivo evaluation of sustained release suspensions of ibuprofen. *International Journal of Pharmaceutics, 73*, 157–162.

Duda, J. L., & Zielinski, J. M. (1996). In P. Neogi (Ed.), *Free-volume theory in diffusion polymers*. New York: Marcel Dekker.

Harogoppad, S. B., & Aminabhavi, T. M. (1991). Diffusion and sorption of organic liquids through polymer membranes, 5. Neoprene, styrene-butadiene-rubber, ethylene-propylene-diene-terpolymer and natural rubber versus hydrocarbons (C_8–C_{16}). *Macromolecules, 24*, 2598–2605.

Harogoppad, S. B., Aminabhavi, T. M., & Balundgi, R. H. (1992). Molecular transport of binary liquid mixtures into EPDM and NBR membranes at 25 °C. *Indian Journal of Chemistry, 31A*, 328–333.

Hatakeyama, T., & Quinn, F. X. (1999). *Thermal analysis: fundamental and applications to polymer science*. New York: Wiley.

Hertzberg, S., Moen, E., Vogelsang, C., & Oestgaard, K. (1995). Mixed photo-crosslinked polyvinyl alcohol and calcium-alginate gels for cell entrapment. *Applied Microbiology and Biotechnology, 43*, 10–17.

King, C. J. (1983). Acetic acid extraction. In T. C. Lo, M. H. I. Baird, & C. Hanson (Eds.), *Handbook of solvent extraction* (pp. 567). New York: Wiley.

Kulkarni, A. R., Soppimath, K. S., Aminabhavi, T. M., Dave, A. M., & Mehta, M. H. (2000). Glutaraldehyde crosslinked sodium alginate beads containing liquid pesticide for soil application. *Journal of Controlled Release, 63*, 97–105.

Kurkuri, M. D., Kumbar, S. G., & Aminabhavi, T. M. (2002). Synthesis and characterization of polyacrylamide grafted sodium alginate copolymeric membranes and their use in pervaporation separation of water + tetrahydrofuran mixtures. *Journal of Applied Polymer Science, 86*, 272–281.

Lepoutre, P., & Hui, S. H. (1975). Grafting acrylonitrile onto wood pulp: influence of process variables. *Journal of Applied Polymer Science, 19*, 1257–1268.

Lepoutre, P., Hui, S. H., & Robertson, A. (1973). The water absorbency of hydrolyzed polyacrylonitrile-grafted cellulose fibers. *Journal of Applied Polymer Science, 17*, 3143–3156.

Lim, F., & Moss, R. D. (1981). Microencapsulation of living cells and tissues. *Journal of Pharmaceutical Sciences, 70*, 351–354.

Maeda, Y., Tsuyumoto, M., Karakane, H., & Tsugaya, H. (1991). In R. A. Bakish (Ed.), Proceedings of the 5th international conference on pervaporation processes chemistry and industry, Bakish Material, Englewood, NJ, pp. 31–44.

Mino, G., & Kaizerman, S. (1958). A new method for the preparation of graft copolymers. polymerization initiated by ceric ion redox systems. *Journal of Polymer Science, 31*, 242–248.

Naidu, B. V. K., Krishna Rao, K. S. V., & Aminabhavi, T. M. (2005). Pervaporation separation of water + 1,4-dioxane and water + tetrahydrofuran mixtures using sodium alginate and its blend membranes with hydroxyethylcellulose-a comparative study. *Journal of Membrane Science, 260*, 131–141.

Naidu, B. V. K., Sairam, M., Raju, K. V. S. N., & Aminabhavi, T. M. (2005). Thermal, viscoelastic, solution and membrane properties of sodium alginate/hydroxyethylcellulose blends. *Carbohydrate Polymers, 61*, 52–60.

Nguyen, Q. T., Essamri, A., Clement, R., & Neel, J. (1987). Synthesis of membranes for the dehydration of water–acetic acid mixtures. *Macromolecular Chemistry, 188*, 1973–1984.

Ruckenstein, E., & Chen, H. H. (1992). Composite membranes prepared by concentrated emulsion polymerization and their use for pervaporation separation of water–acetic acid mixtures. *Journal of Membrane Science, 66*, 205–210.

Savage, A. B., & Thers, C. (1971). In N. M. Bikales & L. Segal (Eds.), *Cellulose and cellulose derivatives*. New York: Wiley, Part V.

Toti, U. S., & Aminabhavi, T. M. (2004). Different viscosity grade sodium alginate and modified sodium alginate membranes in pervaporation separation of water + acetic acid and water + isopropanol mixtures. *Journal of Membrane Science, 228*, 198–204.

Toti, U. S., Kariduraganaver, M. Y., Soppimath, K. S., & Aminabhavi, T. M. (2002). Sorption, diffusion, and pervaporation separation of water–acetic acid mixtures through the blend membranes of sodium alginate and guar gum-*grafted*-polyacryl amide. *Journal of Applied Polymer Science, 83*, 259–272.

Wang, X. P. (2000). Modified alginate composite membranes for the dehydration of acetic acid. *Journal of Membrane Science, 170*, 71–79.

Xing, L., Dawei, C., Liping, X., & Rongquing, Z. (2003). Oral colon-specific drug delivery for bee venom peptide: development of a coated calcium alginate gel beads-entrapped liposome. *Journal of Controlled Release, 93*, 293–300.

Zhran, A. H., Williams, J. L., & Stannet, V. T. (1980). Radiation grafting of acrylic and methacrylic acid to cellulose fibers to impart high water sorbency. *Journal of Applied Polymer Science, 25*, 535–542.