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Removal of acetic acid from wastewater by esterification in the membrane reactor

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Abstract. Acetic acid can be removed from wastewater by esterification in a membrane reactor. Pervaporation membrane reactor (PVMR) is an alternative process to conventional separation processes. It is an environmentally friendly process. The main advantages of the PVMR are simultaneous water removal and production of an ester economically. In this study, the synthetic wastewater has been used. Esterification reaction of acetic acid with isopropanol has been studied in the presence of tungstosilicic acid hydrate as a catalyst in a batch reactor and in a PVMR. The effects of important operating parameters such as reaction temperature, initial molar ratio of isopropanol to acetic acid and catalyst concentration has been examined. Removal of acetic acid (conversion of acetic acid) was obtained as 85% using a PVMR by removal of water from the reaction mixture.

Keywords: acetic acid; esterification; pervaporation membrane reactor; removal; wastewater

1. Introduction

Purification of industrial wastewater is a serious environmental problem in recent years. However, these wastewater may contain a huge number of organic chemicals. Removal of these products are significant as economically (Yagyu *et al*. 2013 and Cloete and Marais 1995).

Wastewater containing diluted acetic acid (AcAc) is one of the poisonous industrial waste in chemical processes. Aqueous streams of AcAc are produced in large quantities by some of the organic chemical industry such as the manufactures of cellulose esters, polyvinyl alcohol, terephthalic acid or dimethyl terephthalate (Ragaini *et al*. 2006). The removal of AcAc from these wastewater may be feasible; it has significant economic limitations as well. The conventional separation methods such as distillation, liquid-liquid extraction are not economical and adequate processes. Distillation process cannot be used alone due to azeotropic property of acetic acid and water mixtures. For achieving each stream as pure, distillation columns must have high number of plates and high reflux ratios. In this condition, the costs of installation and operation of the required equipments would be high. Another method extraction is limited by the phase separation (Bianchi *et al*. 2003 and Saha *et al*. 2000). Also some application of membrane bioreactor has been seen in literature (Palmarin and Young 2016 and Nam *et al*. 2015).

Alternative methods were investigated to find a solution for these problems. In this study, the pervaporation membrane reactor (PVMR) has been considered as an energy saving solution for

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removal of acetic acid.

Pervaporation (PV) is a membrane assisted separation process for liquid-liquid mixtures. One of the important applications of PV separation is industrial dehydration of aqueous–organic mixtures (Wang *et al*. 2014 and Marszałek *et al*. 2014). The chemical potential difference is the driving force for molecular transport in PV. Feed liquid transports by diffusion through membrane and product permeated vaporizes on the other side. Combination of PV unit with reactor called as PVMR (Vijayakumarnaidu *et al*. 2005 and Naidu and Aminabhavi 2005).

The reaction products are separated in the PVMR by using selective membranes in reversible reactions. Reaction equilibrium in the PVMR shifts towards to products thus reaction yield is increased (Zhang *et al*. 2014). Using a large excess one of the reactants in batch reactor or additional separation step such as distillation for removal of products are required for obtain higher efficiency in conventional esterification reaction. The using of excess reactants can cause an increased operating costs. The distillation is useful only when the components of the reaction mixture have different boiling point liquids. Usage of the membrane reactor is preferable for the equilibrium-limited reaction systems, because the operating cost of the membrane reactors is reduced due to using of small reactor volume and short reaction time (Khajavi *et al*. 2010 and Wasewar *et al*. 2009).

In PVMR, membranes allow the selective permeation only one of the components from a reaction mixtures. Removal of the desired component from the reaction mixture enhances the conversion. In the esterification reaction, by-product water is usually removed from the reaction mixture. If the water is removed from the reaction mixture, the thermodynamic limitations of the reaction would be overcome and the catalyst wouldn't be poisoned (Parulekar 2007 and Diban *et al*. 2013).

In this paper, the removal of acetic acid is carried out by esterification with isopropanol in batch reactor and in PVMR under the same reaction conditions. Isopropyl acetate is used as a solvent for cellulose, plastics, oil, printing inks or perfumes. For this experiment, chitosan membrane has been prepared in the laboratory. The effects of temperature, catalyst concentration and the ratio of molar feed reactants were examined and the performance of the reaction and pervaporation were interpreted.

2. Experimental

2.1 Materials

Chitosan (high molecular weight polymer) powder was received from Sigma Aldrich. Acetic acid, isopropanol (IPOH), acetone, sodium hydroxide and crosslink agent sulfuric acid were purchased Merck Chemicals. The catalyst tungstosilicic acid hydrate was also supplied by Sigma Aldrich.

2.2 Membrane preparation

Chitosan flakes were first dissolved in dilute acetic acid aqueous solution. The obtained chitosan solution was cast on a plate for drying. The dried chitosan membrane was treated with NaOH in a 50% v/v aqueous ethanol solution to make insoluble in water. The membrane was dried and cross linked with H_2SO_4 in 50% aqueous acetone solution. The cross-linked chitosan membrane was washed with distillate water to eliminate residuals and then dried at ambient conditions (Won *et al*. 2003).

2.3 Characterization

The membrane was characterized by analytical results of Fourier Transform Infrared Spectroscopy (FTIR) and the Scanning Electron Microscopy (SEM). FTIR was used to analyze and identify the variations of the bonds before and after the cross linking. Surface and cross section images of membrane were checked by SEM analysis.

2.4 Analysis

Acetic acid, isopropanol, water and isopropyl acetate in the reaction mixture and the permeate were analyzed using gas chromatography (GC) device (Agilent GC-7820A), supplemented by a thermal conductivity detector (TCD) and HP-FFAP capillary column to prove the accurate results. The injector and detector temperatures were maintained at 220°C. The temperature of the oven was maintained at 60°C. Acetic acid concentration was also determined by titrating the sample with 0.1 (N) sodium hydroxide solution by using phenolphthalein as indicator. Conversion was calculated by Eq. (1).

$$x = \frac{N_{A0} - N_A}{N_{A0}} \tag{1}$$

N_{A0} is the initial mole of acetic acid, N_A is the mole of acetic acid at any time.

2.5 Batch reactor and PVMR experiments

The schematic batch reactor and pervaporation membrane reactor apparatus are shown in Figs. 1 and 2.

The effect of membrane on the conversion was examined. The total reaction volume of the

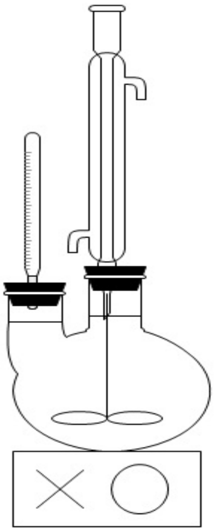

Fig. 1 Batch reactor set-up

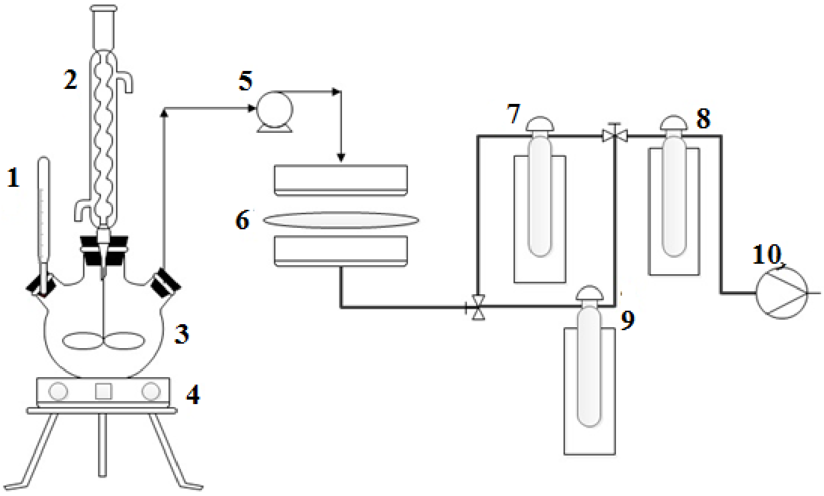

Fig. 2 PVMR configuration. (1) thermocouple; (2) reflux condenser; (3) magnetic stirrers with heating; (4) reactor; (5) feed pump; (6) membrane; (7), (8) and (9) Dewar flasks; (10) vacuum pump

experiments was 400 ml. The experiments were carried out with different initial molar ratios (IPOH to AcAc) at different temperatures of 50-60-70°C. The different concentrations of the catalysts (tungstosilicic acid hydrate) were added in the reactors. The membrane was located in a Teflon membrane cell. The effective surface area of membrane was 25.26 cm^2. The vacuum pressure at the permeate side was maintained by a vacuum pump. The compositions of permeate and reaction mixture were analyzed by using an Agilent GC-7820A GC.

Membrane performance was evaluated by flux and separation selectivity. Flux was calculated by Eq. (2)

$$J = \frac{m}{A.t} \tag{2}$$

$m\{g \text{ or } kg\}$ is the weight of the permeate, A is the effective membrane area$\{m^2\}$, t is the time$\{\text{sec or min}\}$. PV selectivity is defined by Eq. (3)

$$\alpha = \frac{y_i / y_j}{x_i / x_j} \tag{3}$$

Where x and y are the weight fractions of components in the feed and permeate sides. The component i was water and the component j was the other components in this study. The selectivity of the membrane was described by the separation of water compared to the other organic components.

3. Results and discussion

3.1 Characterization results of FTIR and SEM

The FTIR spectra of uncross linked and cross linked chitosan membrane by sulfuric acid were

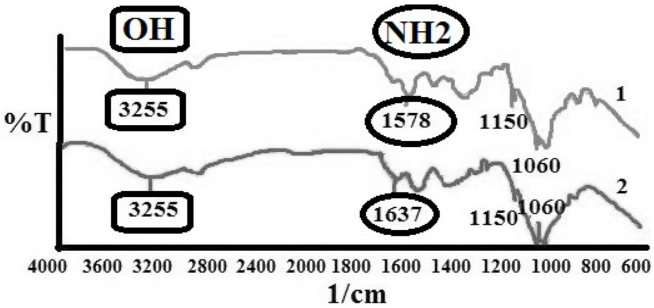

Fig. 3 FTIR spectra of (1) uncross linked; and (2) cross linked chitosan membrane

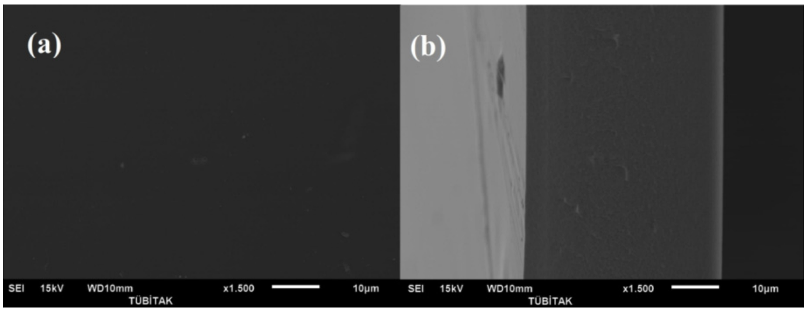

Fig. 4 SEM photos of chitosan membrane (a) surface; (b) cross-section

scanned in the range of wavelength 600-4000 cm^{-1} using Perkin Elmer Spectrum 100 FTIR spectrophotometer. FTIR spectra of uncross linked and chitosan cross linked by sulfuric acid can be seen in the Fig. 3 (Unlu and Hilmioglu 2014). The characteristic peak of NH_2 is obtained at 1578 cm^{-1} is shown in spectra 1 in Fig. 3. After crosslinking, the signal of NH_2 appearing at 1637 cm^{-1}. Groups of NH_2 in chitosan chain is protonated with groups of H^+ in H_2SO_4. Free hydroxyl group can be seen at 3255 cm^{-1} (Cui *et al*. 2008 and Mulder 1991).

Fig. 4 shows the SEM micrographs of the chitosan membranes as surface and cross section. In surface and cross section image, the chitosan membrane shows homogenous structure.

3.2 Batch reactor and PVMR experiments

Esterification reaction between acetic acid and isopropanol in the presence tungstosilicic acid hydrate catalyst was carried out in a batch reactor and in a PVMR. Reaction products were ester, water and excess reactants. The presence of water in a reaction mixture has negative impact on the equilibrium yield of the esterification. Therefore, PVMR was used to remove water in order to increase yield of the reaction.

3.2.1 Effect of temperature on conversion

The esterification of acetic acid with isopropanol was studied both in a batch reactor and in a PVMR. The reaction temperatures were chosen as 50°C, 60°C and 70°C. Fig. 5 compares the conversions of AcAc at different temperatures when the ratio of isopropanol/acetic acid (M) was equal (1:1) with the presence of 10 g/l tungstosilicic acid hydrate.

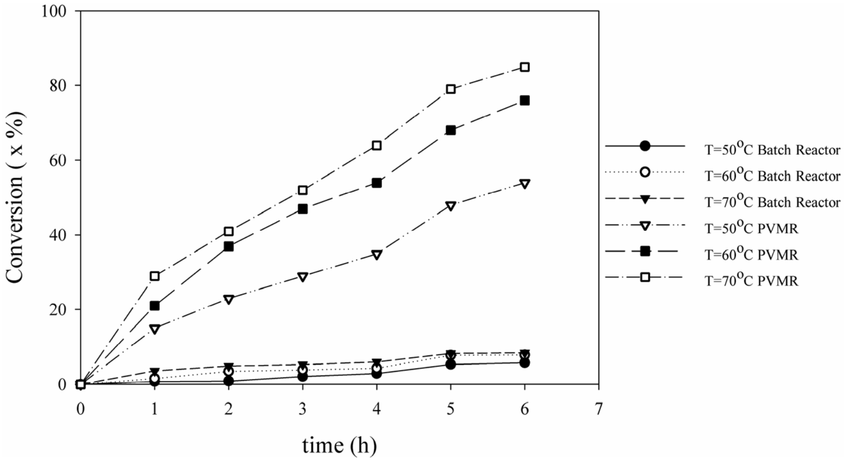

Fig. 5 Influence of the temperature on the conversion (C_{cat} = 10 g/l, M = 1:1)

Temperature is known an important factor as the rate of a chemical reaction depends on temperature. The reactants are needed to energy which is called “activation energy” in order to obtain products. When the temperature rises, molecules of reactants have higher kinetic energy. Therefore, increment in the reaction rate was observed (Menzinger and Wolfgang 1969).

Temperature not only affects the reaction rate, also accelerates the permeation rate from the membrane (Delgado *et al.* 2009). These increases in permeability are mainly due to an increase in chain mobility and free volume of polymeric membrane, caused by an increasing temperature. When the temperature varied from 50°C to 70°C, increasing the motion of the polymer chain induced increasing of free volume. Hence the transport of the water were accelerated, which caused to producing of ester in other words removal of AcAc. When process temperature increased, the driving force for mass transfer through the membrane increased, because the vapor pressure of the components increased (Xia *et al.* 2011). The diffusion of water molecules accelerated with high temperature and reaction equilibrium in the PVMR changed towards to products and formation of ester increased. Therefore, PVMR has higher efficient than batch reactor for increment conversion of AcAc (Wasewar *et al.* 2009). The highest AcAc conversion was obtained at 70°C. While conversion was calculated as 8% at the end of 6 h in the batch reactor, conversion was obtained as 85% at PVMR. Fig. 5 shows that the time required to reach a higher conversion value in PVMR is lower than in batch reactor.

3.2.2 Effect of initial molar ratio of isopropanol to acetic acid on conversion

Effect of initial molar ratio of isopropanol to acetic acid on conversion of acetic acid in batch reactor and in PVMR are shown in Fig. 6. The initial molar ratio of reactants was varied from 1 to 2 for a fixed value of temperature (T = 70°C), and of catalyst concentration (C_{cat}= 10 g/l).

The esterification of AcAc with IPA is a reversible reaction. High conversion could only be achieved if the excess reactant is used or one of the products is removed from the reaction mixture. Thus equilibrium was shift towards the product side, rate of back reaction is minimized (Hasanoğlu *et al.* 2009).

Using excess reactant is a costly process, because great reactor volume is required. The continuous removal of one of the products from the reaction medium is an alternative solution

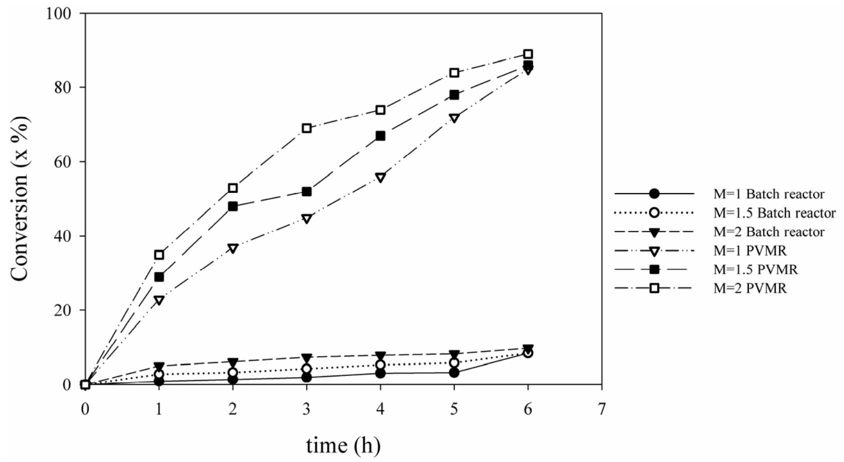

Fig. 6 Influence of the initial molar ratio on the conversion (T = 70°C, C_{cat} = 10 g/l)

(Zhu and Chen 1998). In this study, hydrophilic membrane was used in order to remove water from reaction mixture in a PVMR process. Comparison of the batch reactor shows that, the PVMR has higher conversion.

It is clear that, conversion values of AcAc increased with increasing molar ratios. In PVMR, higher conversion was obtained in a short time due to water removal by pervaporation. The highest degree of conversion of 9% was obtained for $M = 2$ at 6 h in a batch reactor. In the case of PVMR, the highest conversion was up to 89% when being esterified at $M = 2$ in 6 h.

3.2.3 Effect of catalyst concentration on conversion

The effect of catalyst concentration on conversion of acetic acid was investigated at fixed temperature (70°C) and the equal initial molar ratio of reactants (M = 1:1). Fig. 7 shows the conversion of acetic acid versus time at different catalyst concentrations (per unit volume of the reaction mixture containing the catalyst) 3 g/l, 6 g/L and 10 g/L.

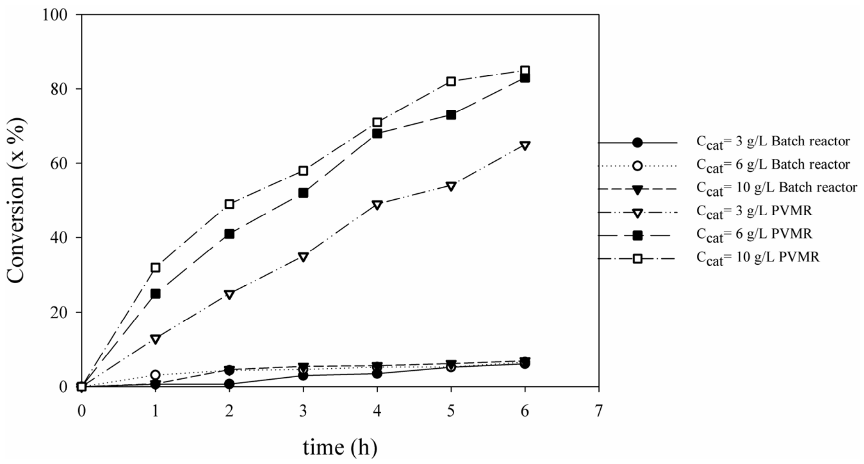

Fig. 7 Influence of the catalyst concentration on the conversion (M = 1:1, T = 70°C)

The catalyst concentration in this study was defined as the ratio of the catalyst amount to reaction mixture volume. It could be seen from Fig. 7, an increase of the catalyst concentration may be an alternative way to accelerate the removal of acetic acid as ester. As expected, the consumption of acetic acid increased with the increase of the catalyst concentration. Fig. 7 shows that an increase of the catalyst concentration leads to an increase of the reaction rate, because catalyst active site is increased and reaction activation energy which accelerate reaction rate is decreased (Ma *et al.* 2009).

Comparing to batch reactor, PVMR is an efficient process for improving the yield. This can be explained as follows. When the catalyst concentration was increased, water concentration in the reaction medium was increased. Permeation flux was higher at maximum water concentration in PVMR. Due to removing of water, the reaction equilibrium was shifted towards to products, conversion of AcAc was increased (Sanz and Gmehling 2006).

The conversion of AcAc in the batch reactor observed as the minimum values. After four hours, the almost identical conversion is obtained for all catalyst concentration values in the batch reactor. The highest conversion of AcAc of 6% was obtained at 10 g/L catalyst concentration in the batch reactor after 6 h. In PVMR, the maximum conversion of AcAc was obtained as 85% at the same catalyst concentration in 6h.

3.2.4 Flux and Selectivity in PVMR

Membrane performance in PVMR were determined by experiments for flux and selectivity calculations. Optimum conditions of flux and selectivity were $T = 70°\text{C}$, $M = 1$ and $C_{cat} = 10$ g/L.

Figs. 8 and 9 shows the variation of total flux and separation selectivity with time. As can be seen in Fig. 8, total flux was increased with the time. As increasing the water concentration of reaction mixture, swelling degree of hydrophilic chitosan membrane increased. As a result of this increment, the space of the between polymer molecules increased as volumetric.

Consequently, permeation of components was increased with great free volume. Permeation of components caused to decrease of separation selectivity (Veerapur *et al.* 2007). Because, the other components of mixture permeated through the membrane, the separation selectivity of water decreased with time as shown in Fig. 9.

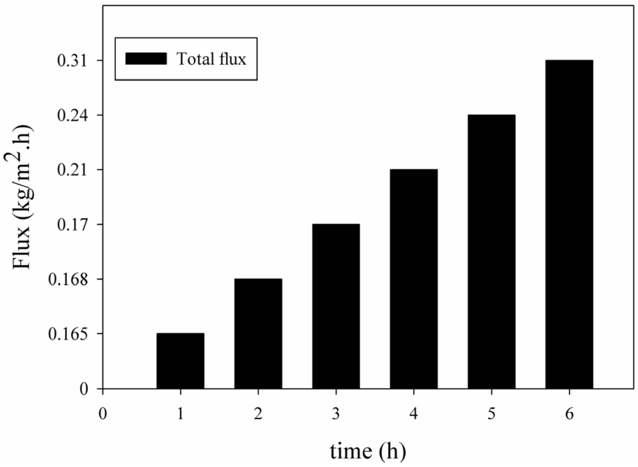

Fig. 8 Total flux to time at optimum operation conditions ($T = 70°\text{C}$, $M = 1{:}1$, $C_{cat} = 10$ g/l)

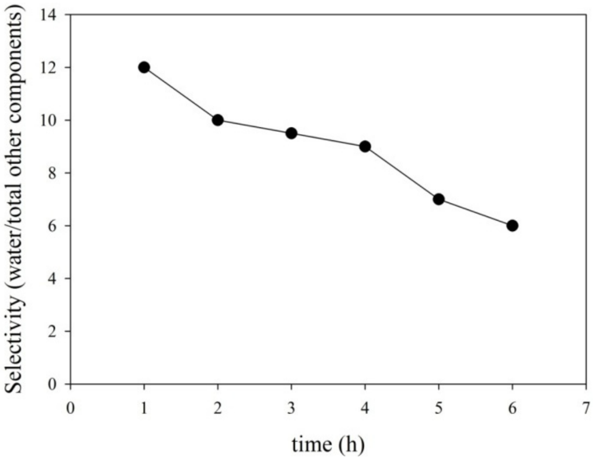

Fig. 9 Water selectivity to time at optimum operation conditions ($T = 70°C$, $M = 1:1$, $C_{cat} = 10$ g/l)

Table 1 Consumption of energy between processes (Huang *et al.* 2006)

Process	Energy requirement (kj/kg ethanol)
Distillation	10376
Azeotropic distillation	3305
Pervaporation	425

Table 2 Comparison of removal of AcAc values with the literature

Process	Reaction	Reaction conditions	Removal of AcAc (Conversion of AcAc) (%)	Reference
Evaporation condensation	AcAc-Butanol	$T = 99°C$, $t = 6$ h	70	Bianchi *et al.* 2003
Esterification	AcAc-2-ethyl-1-hexanol	$T = 99°C$, $t = 25$ h	70	Ragaini *et al.* 2006
Reactive distillation	AcAc-Butanol	M(AcAc/Butanol) = 1:2	52.7	Saha *et al.* 2000
Dehydrative esterification	AcAc-Ethanol	$T = 40°C$, $t = 20$ h	70	Yagyu *et al.* 2013
PVMR	AcAc-Isopropanol	$T = 70°C$, M(AcAc/Isopropanol) = 1:2, $t = 6$ h	89	This study

3.2.5 Comparison of data with the literature

PVMR has comparative advantages over conventional separation methods for removal of AcAc from wastewater. PVMR is energy saving and environmentally friendly process. Table 1 shows the energy consumption of process.

Table 2 compares the different separation methods used in the removal of AcAc from wastewater in literature. There is no study, which is used PVMR for recovery of AcAc from aqueous solutions.

In this study, removal of AcAc was higher than other separation methods. High conversion was obtained under mild reaction and process conditions such as short time, low reaction temperature and low energy consumption.

4. Conclusions

It is significant to have an energy efficient and sustainable process for the removal of acetic acids from the wastewater. PVMR is a encouraging green, innovative technology for separation/ removal of acetic acids from wastewater. Furthermore, isopropyl acetate which is used as a solvent for cellulose, plastics, oil, printing inks and perfumes is formed by the esterification of AcAc with isopropanol. The removal of acetic acid by esterification with isopropanol was performed in a PVMR. This esterification reaction was equilibrium limited reversible reaction. PVMR process is especially useful for equilibrium-limited reactions. The removal of acetic acid was improved by carrying out the reaction in a PVMR. The effect of temperature, the catalyst concentration and the molar feed ratio of reactants were studied and analyzed. The ideal operation conditions were determined as the initial reactant molar ratio of acid to isopropanol was 1, the temperature was 70°C, and the concentration of tungstosilicic acid hydrate catalyst that is compatible with the environment was 10 g/L. In these conditions, removal of acetic acid was increased from 8% value obtained using the batch reactor to 85% value obtained using the PVMR in which water was taken from the reaction mixture simultaneously. As can be seen, the PVMR exhibited higher performances than the batch reactor. Total flux was found 0.31 kg/m^2.h, water selectivity was found as 6 in the PVMR. PVMR is found as an innovative and successful process for removal and reuse of acetic acid.

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List of symbols

α	Selectivity
A	Effective membrane area (cm^2)
C_{cat}	Catalyst concentration (g/l)
J	Flux (g/cm^2.h)
m	Permeate weight (g)
N_A	The mole of acetic acid at any time (mol)
N_{A0}	The initial mole of acetic acid (mol)
t	time (h)
x	Conversion of acetic acid
x_i, x_j	weight fraction of *i* and *j* components in the feed
y_i, y_j	weight fraction of *i* and *j* components in the permeate