ABSTRACT

Organic pollutants in wastewater pose a great threat to the environment, as they are carcinogenic in nature. Nitrophenols and chlorophenols are such toxic pollutants responsible for significant health and environmental hazards due to their mutagenic and carcinogenic activities. N-methyl-2-pyrrolidone (NMP) and furfural are present in the wastewaters from chemical, petroleum refining and petrochemical industries. Selective removal and recovery of phenolic compounds, NMP and furfural is, therefore, a challenge to those industries.

Several membrane-based processes have attracted much attention of process industries for the separation of toxic pollutants from effluent streams. Pervaporation (PV) is one such membrane-based separation process in which a liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low-pressure vapor from the other side. As a result, both the more permeable species in the permeate, and the less permeable species in the feed are concentrated. This work is concerned with the selective removal of the above-mentioned organic pollutants from aqueous solutions by pervaporation using indigenously developed polymeric membranes.

The esters and alkyl aromatics have different important industrial applications such as in artificial perfume, flavoring extract, leather, photographic films, plastic and safety glasses, printing inks, surface-active agents, rubber chemicals, antioxidants, fungicides, petroleum additives. In most esterification and alkylation reactions equilibrium is reached without conversion to a sufficient level. There has been an engineering effort to combine reaction and separation into a single process unit to improve process performance. Since, PV permits selective permeation of a component over others from a mixture, pervaporation membrane reactor (PVMR) can help enhance the conversion of reversible esterification and alkylation reactions, generating water as a by-product, through removal of water from the reaction mixture immediately as soon as it is formed. A pat of the present work is, therefore, devoted to the intensification of esterification and alkylation reactions with the help of pervaporation.

Polyurethaneurea membranes of varying soft segment content were synthesized in the laboratory and suitably characterized. Porous membranes were prepared by using LiCl during synthesis and then leaching it out in hot water. Cross-linked polyvinyl alcohol (PVA) membrane was synthesized using tartaric acid as cross-linking agent and the synthesized membrane was used to study the effect of pervaporation on chemical reaction.

Separation of NMP from dilute aqueous solution was performed by pervaporation using polyurethaneurea membranes. The diffusion coefficient of NMP and water in the membrane were measured. The mass sorption coefficient of NMP in polyurethaneurea membranes was measured as 21.61-24.06. The NMP flux, concentration of NMP in permeate and separation factor was in the range of 1.0 - 4.0 g m^{-2} h^{-1}, 45.2-65.2 wt% and 2064-1791, respectively, having feed NMP concentration of 400-1000 ppm at 45°C with PUU100 membrane (synthesized with 100 mol% diamine chain extender) of thickness 0.20 mm. It was found that as the feed temperature increases NMP flux, concentration of NMP in permeate and separation factor increases. As the membrane thickness increases the NMP flux decreases, however, concentration of NMP in permeate as well as separation factor increases. The activation energy of permeation of NMP was calculated using Arrhenius plot.

Pervaporative recovery of furfural from aqueous solution using dense nonporous and porous polyurethaneurea membranes was performed. The total flux and furfural flux are 18.4 and 13.1 g m^{-2} h^{-1} for nonporous membrane and 24.2 and 18.7 g m^{-2}h^{-1} for porous membrane at 30°C with a feed furfural concentration of 6.0 wt%. The concentration of furfural in permeate and separation factor values were somewhat lower for porous membrane (75.2 wt% and 53) compared to nonporous membrane (78.4 wt% and 57). The membranes were, therefore, found to be highly furfural selective. Under certain experimental conditions a furfural separation factor as high as 638 and a permeate flux as high as 44.7 g m^{-2} h^{-1} were obtained. A comparative study of experimentally obtained furfural flux with that predicted by the solution-diffusion model using nonporous membrane was made.

o-Chlorophenol and p-chlorophenol were separated from aqueous solution by pervaporation using polyurethaneurea membranes. The membranes were found to be highly organic selective, with selectivity towards p-chlorophenol as high as 1177 with a permeate flux as high as 50.3 g m^{-2} h^{-1}. The total amount of liquid sorbed in the polyurethaneurea membrane increases with the concentration of chlorophenols and also with temperature. This indicates that chlorophenol has a higher solubility in hydrophobic polyurethaneurea membrane than that of water. The total flux was found to increase with temperature and concentration of chlorophenol in the feed. The preferential sorption of chlorophenol in polyurethaneurea membrane facilitated its permeation through the membrane. The modified Maxwell-Stefan model, which takes into account the non-ideal multi-component solubility effect, non-ideal diffusivity of all permeating components, concentration dependent density of the membrane and diffusion coupling, was used to predict various fluxes for o-chlorophenol-water mixture.

The separation of 2-nitrophenol (2NP), 4-nitrophenol (4NP) and 2,4-dinitrophenol (DNP) from synthetic wastewater by pervaporation was studied using the tailor-made polyurethaneurea membranes. The diffusion coefficients of nitrophenols in polyurethaneurea membrane were measured. Sorption of nitrophenols in PUU20 membrane was found to follow the order DNP > 4NP > 2NP. Sorption of nitrophenols was not influenced by the presence of other nitrophenols. NP flux and water flux increase with increase in NP concentration in the feed solution. The membranes were found to be NP selective, with separation factor of DNP as high as 8213 and a permeate flux of DNP as high as 10.5 g m^{-2} h^{-1}. The flux as well as separation factor for NP was seen to vary with concentration of diamine chain extender used for polyurethaneurea membrane synthesis. The organic flux was not influenced by the presence of other component in feed solution and hence there was no coupling effect of organic components in the system.

Pervaporation-assisted n-butyl acetate synthesis and tert-butyl phenol synthesis reactions were carried out using cross-linked polyvinyl alcohol (PVA) membranes. Due to selective removal of water from the reaction mixture immediately as soon as it was formed by pervaporation, conversion of n-butyl alcohol increased from 33.8% to 48.4% and the conversion of phenol from 26.73% to 39.47% by integration of the reaction with pervaporation under otherwise identical experimental conditions. The individual permeation fluxes follow the order water > acetic acid > n-butyl alcohol > n-butyl acetate for esterification reaction system, whereas for the alkylation reaction system, the individual permeation fluxes follow the order water > phenol > tert-butyl alcohol > 4-tert-butyl phenol. The influences of reaction temperature, reaction time, catalyst loading, and initial molar ratio of reactants on conversion were studied in order to find out the optimum operating condition for pervaporation facilitated esterification and alkylation reactions.

Keywords: Pervaporation; Sorption; N-methyl-2-pyrrolidone; Furfural; o-chlorophenol; p-chlorophenol; 2-nitrophenol; 4-nitrophenol; 2,4-dinitrophenol; Polyurethaneurea; Separation factor; Activation energy; Alkylation; Phenol; 4-tert-butyl phenol; Esterification; Acetic acid; n-butyl acetate; Mordenite; Membrane reactor.