Metal organic frameworks (MOFs) based mixed matrix membranes for separation applications. Dehydration of ethanol/water mixture.

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Abstract

The most effective separation process for dehydration of ethanol/water mixture as well as the other organic mixture is pervaporation process. Pervaporation process does not rely on the liquids present reaching equilibrium with each other and so can break these azeotropes without the need for additional chemicals [1]. It has significant advantages in azeotropic system where traditional distillation is only able to recover pure solvents with the use of entrainers, which are hard to separate from the mixture. Hence the pervaporation process is the most promising technology in the molecular-scale liquid/liquid separations existing in biorefinery, petrochemical, pharmaceutical industries, wine industry etc. for being highly selective, economical, safe and ecofriendly [2].

For the dehydration of ethanol/water mixture a series of mixed matrix membranes (MMM) were prepared comprising polymer (Matrimid 5218) matrix and different types of metal organic frameworks as a molecular sieve with various loading. Metal organic frameworks (MOFs) are relatively a new family of nanoporous materials, the organic ligands as an inherent part of MOFs allow them to interact well with the polymer material and its functionalities. This way, the formation of gaps between the filler and the polymer phase, which would cause losses in selectivity, can be avoided [3]. Their incorporation into membranes is a promising application because mixed matrix membranes could combine the molecular sieving effect of MOFs and process ability of the base polymers. Nowadays MOFs play an important role in membrane technology because of their porosity and easy tunability of their pore size and shape from microporous to mesoporous scale by changing the connectivity of the inorganic part and the nature of organic linkers [4]. Therefore, they could be readily scaled up for industrial applications using the established fabrication techniques for polymer membranes [5]. Mixed matrix membranes containing MOFs have a great success in gas separation but up till now they were not well studied for separation applications of liquids. This study looks at the application of MOFs in a comparatively new application area which is the separation of liquid/liquid mixtures. So far our experiments have provided good separation results.

In this study the effect of typical membrane processing conditions on the structure, interfacial morphology, nature of MOFs and liquid separation performance of MOF/polymer nanocomposite membranes is investigated. In particular, mixed matrix membranes containing molecular sieves such as MIL-101, silica and ZIF-8 is examined, and it was confirmed that ultrasonication which is a commonly employed particle dispersion method [6] induces significant changes in the shape, size distribution, and structure of MOFs particles suspended in an organic solvent during membrane processing. The interaction between molecular sieves and polymer was studied by scanning electron microscope and differential scanning calorimetry. The measured contact angle between a drop of water and the membrane indicated the hydrophilicity of the membranes.

The prepared membranes were tested in the separation process of ethanol/water (90 wt% of ethanol and 10 wt% of water respectively) mixture by pervaporation. The trade-off between two main parameters that are generally used to characterize a pervaporation process, namely mass flux across the membrane and membrane separation factor [7], was achieved at the feed temperature 55 °C. To obtain this optimum processing temperature[1] initially pervaporation experiment was done with the membrane based on neat Matrimid 5218 at two different temperatures. In the following figure 1 it is represented that steady state of the system was achieved. Depending on the temperature permeate flux was varying from 0.28 to 0.43 kg/(m^2·h) and the membrane separation factor was varying from 501 to 818.

Since molecular sieves can have very small pore size (shown in table 1) the selectivity of the mixed matrix membranes can be increased just by adding a small amount of these molecular sieves. Also another important factor is the hydrophilic or hydrophobic characteristic of these sieves, in the case

[1] Optimum temperature is the temperature at which it is more convenient to achieve the steady state of the pervaporation system. The steady-state mass transport regime depends on several parameters, i.e., upstream pressure, downstream pressure, temperature and film thickness [8].

of ethanol/water separation hydrophilic sieves are needed to favor the permeation of water molecules through the membrane. The effect of this sieving and hydrophilicity provided by the molecular sieves was confirmed by using mixed matrix membrane containing silica where the membrane selectivity was increased from 501 to 525 and MMM containing MIL-101 where the membrane selectivity was increased from 501 to 710.

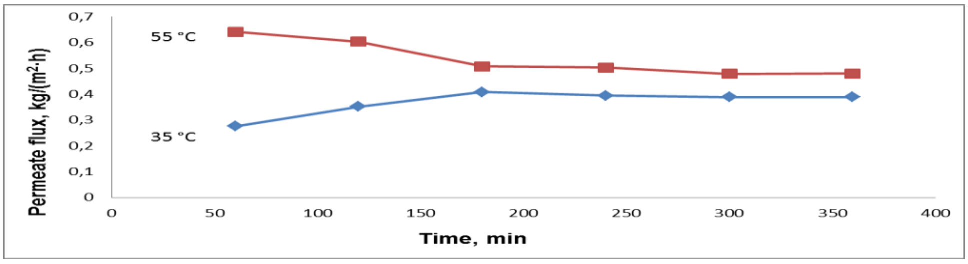
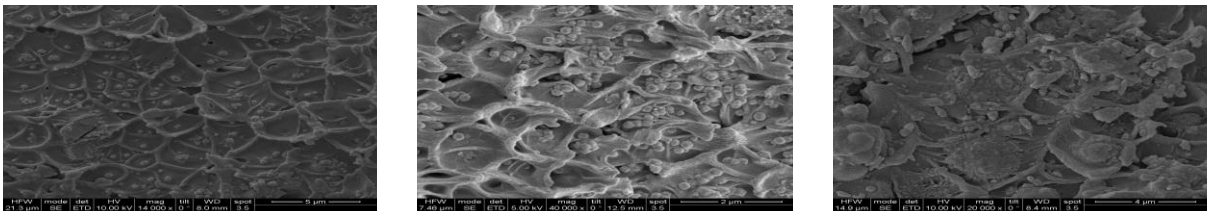


Figure 1. Permeate flux versus operating time. Membrane based on neat Matrimid 5218.

MOFs type	Pore topology	Pore diameter	S BET, m^2/g	Particle size
ZIF-8	cage/window	11.6 / 3.4 A	1214	127 nm
MIL-101	cage/window	3.4 / 1.6 nm	2074	175 nm
Silica	hexagonal symmetry	2.7-3 nm	939	3.1 µm

Table 1. Textural properties of the different filler materials according to BET isotherm results.

On the other hand the higher loading of fillers into the polymer matrix will lead to higher permeability of water molecules through the membrane. These molecular sieves will fill the dense matrix of polymer phase allowing the water molecules to diffuse through the membrane, resulting in a higher total permeate flux. In the figure 2 the cross section SEM images of MMM containing different fillers demonstrate the polymer-sieve interaction. We observe that only in the sample C containing 12% of silica the interaction was not good and currently this is the limitation that needs to be improved in our mixed matrix membranes, we are currently introducing various amount of different fillers into the polymer phase. We are trying to find the optimum amount of particular filler which will results in a good membrane separation performance.



a) b) c)

Figure 2. Cross section SEM images of mixed matrix membranes containing a) 12% of MIL-101, b) 8% of ZIF-8, c) 12% of silica

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