

Mixed Matrix Membranes for Adsorption Application

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Mixed matrix membrane (MMM), a currently popular research field, is a type of membrane formed by incorporating fillers in polymer matrix. Its preparation procedures mainly involve with only blending and phase inversion. According to its structure, MMM can typically be divided into two categories. The first one is with a dense structure, mostly developed for the applications in gas separation, pervaporation, fuel cell, and so on. The fillers employed for improving the MMM performance in this category are usually inorganic nanomaterials (zeolite, carbon nanotube, metal organic framework, etc.) with specific features (shape, pore size, surface interaction, etc.). The other category is with a porous structure, specially designed for adsorption purpose. Micro-to-nano-size particles with functionality are regularly adopted as the fillers for this kind of MMM to provide the adsorptivity with target solutes. The polymer matrix is principally served as the support of particles. On the other hand, membrane pores provide the pathways for solutes to pass through and then easily reach the adsorption sites on the filler particles. Their size is generally in the macropore range to avoid unwanted clogging and fouling. This paper will focus on discussing the latter MMM case.

Traditional adsorbents are primarily of particle form. However, either the batch or semi-continuous operations of particulate adsorbents encounter a few crucial problems. In the batch process, difficulties may arise in maintaining uniform particle suspension at a large vessel and additional cost for final solid-liquid separation by filtration or centrifugation is required. These problems could be intrinsically exempted with the use of adsorbent in membrane form such as MMM. In the semi-continuous process of particles-packed bed, problems such as high pressure drop slow mass transfer, long process time, bed compression, and clogging may associate with low bed porosity and long bed height. Furthermore, non-uniform packing (e.g. channeling and dead volume) usually happens in the cases with a wide and short bed. MMM does not have the non-uniform packing or bed compression problem. Besides, it also provides shorter bed height, higher bed porosity, and larger pores for convective flow, leading to the operation at lower pressure drop and smaller residence time [1-8]. Consequently, the MMM process offers the benefits in time and energy savings with respect to the conventional packed bed process.

The fillers adopted in the literature of adsorptive MMMs [1-14] include commercial ion-exchange resins, clays, chitosan beads, functionalized silica particles, metal ion charged beads, and plant waste particles. Most of these filler particles contain ionic groups that could provide charge interaction with proteins and contaminant species. Ion exchange mode is more popularly applied because its interaction rate is normally faster than other adsorption modes. In addition, ion exchangers are usually cheaper than the specific affinity adsorbents. Since the adsorptivity of MMM comes from the entrapped filler particles, the particle characteristics (particle size, pore size distribution, surface area, ion exchange capacity, etc.) and batch adsorption properties (adsorption isotherm, adsorption kinetics, and various effects of adsorption conditions) are crucial and thus require intensive evaluations. Desorption study is also important because it could help elucidate the adsorption mechanisms between adsorbate and adsorbent [8,15]. Moreover, the economic feasibility of using adsorbents for practical applications relies on the adsorbent

regenerability during multiple adsorption/desorption cycles. To find an appropriate desorption condition for breaking the attractive forces between adsorbate and adsorbent, the variations in solution pH, salt concentration (ionic strength), and organic solvent percentage need to be extensively examined.

Mass transfer mechanisms are also the key factors governing the adsorption performance and have to be investigated. The transport of adsorbate molecules in a batch container with the particles-filled MMM include the following steps in serial: (1) external mass transfer from bulk liquid to the frontal membrane surface, which could be accelerated via shaking of the container; (2) diffusion through the membrane pores in the direction of membrane thickness (axial diffusion), which has been found to dominate the whole adsorbate transport [5,8]; (3) radial diffusion in membrane pores to reach the outer surface of particles; (4) diffusion inside the particle pores (intraparticle diffusion), which is usually the rate-limiting step for the adsorption onto pristine particles [8,15]; (5) intrinsic adsorption onto the active sites of particle surface. It is evident that the adsorbate diffusion through the membrane support of MMM is supplementary compared to the passage in batch particle system and hence prolongs the time duration to attain the equilibrium state of batch adsorption.

Generally speaking, flow process is more efficient for practical adsorption applications. Similar to a chromatographic process, the semi-continuous operation of adsorptive MMMs should contain four stages: loading (adsorption), washing, elution (desorption), and regeneration. Minor desorption conditions are commonly employed for washing the impurities either specifically or unspecifically adsorbed on the adsorbents, in order to raise the purity of target adsorbate product. Regeneration stage may not be necessary unless the functionality of adsorbent has to be re-activated. The most common mode for the semi-continuous operation of adsorptive MMMs is dead-end (flow-through) [1,3-10,13,14]. This kind of MMM process is analogous to low-pressure liquid chromatographic process. Accordingly, examination of breakthrough curve is the main approach for evaluating its process efficiency. Breakthrough volume is usually determined as the volume of feed solution loaded when the effluent adsorbate concentration attains 0.01-0.1 of the feed concentration. This volume could then be used to calculate the dynamic adsorption capacity. Through the ratio of dynamic capacity to static capacity at the same feed condition, it would be easy to recognize the process efficiency. Once the breakthrough volume and the conditions for individual stages are decided, the loading/washing/elution/regeneration cycle may be repeated consecutively to check the reusability and lifetime of MMM.

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The mass-transfer mechanisms for adsorption in the flow-through MMM process are similar to the batch process. The main difference is that the first step in the flow-through process is the convective transport of adsorbate molecules through the membrane thickness (axial convection) and slow axial diffusion may be neglected. Since the membrane is thin, the residence time of adsorbate by axial convection is small. The short residence time offers an advantage of time efficiency. In many cases, however, axial convection may not provide sufficient time for adsorption and allow some adsorbate molecules to pass through the membrane without binding [5,7,8]. This phenomenon will result in an earlier breakthrough and thus get a smaller dynamic adsorption capacity. A useful method for increasing the retention time is to recycle the effluent back to the feed container, i.e. in a recirculation mode [5,7,8]. This way, the whole system will be operated in a batch mode and the static capacity could be achieved as the recirculation time is long enough. On the other hand, a slow uptake may be observed in the late stage of breakthrough curve [8], which should be governed by the time-consuming intraparticle diffusion in MMM.

The main feature for cross-flow mode is supposed to combine filtration and adsorption in one step [11]. Nevertheless, it does not really work as well as expected. The adsorbates could be adsorbed on the frontal surface and the internal pore surfaces of membrane so that they would be eluted to not only permeate side but also retentate outlet. This phenomenon would cause the loss or dilution of adsorbates in the permeate product [8,16-18]. To attain a better separation efficiency, the cross-flow process must be delicately designed at the cost of complicating the whole process. For example, a cross-flow MMM cell was employed in the literature [11,12] with recirculation mode in loading stage by recycling both the retentate and permeate streams back to the feed reservoir in order to achieve good performance for separating the important proteins from whey mixture.

The popular forms for adsorptive MMMs are flat shape and hollow fiber. The related module types include disc holder, cylindrical tube, spiral-wound module, and hollow fiber cartridge. The scale up of these MMMs can be simply implemented by either stacking more pieces of flat membranes together, using a spiral configuration with larger membrane surface, or developing a big bundle of hollow fibers [8,19]. By stacking flat membranes together, the overall thickness is enlarged to extend the residence time for achieving a larger breakthrough volume. When a cylindrical configuration (hollow fiber, tubular, or spiral) is used, the feed solution should be loaded in axial direction such that the solutes can touch the frontal surface tangentially and pass through the membrane in radial direction. With this setup, the residence time of solutes could be significantly increased.

In summary, the adsorptive MMMs exhibit several process benefits: time efficiency, energy saving, minimum membrane fouling and flux decline, simple and flexible large-scale operation. However, further improvement can still be explored on MMM materials and operations such as: selecting degradable polymer as matrix for eco-friendly purpose; utilizing smaller fillers to reduce the intra-filler diffusion limitation; employing a polymer with the functional groups similar to the fillers for raising the entire adsorption capacity of MMM; choosing a suitable cylindrical configuration to lengthen the convective residence time.

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