doi:10.2533/chimia.2020.423 Chimia 74 (2020) 423–425

FH HES Universities of Applied Sciences

Fachhochschulen – Hautes Ecoles Spécialisées

Membrane Filtration: Expanding the Areas of Application by Chemical Modification – Examples from the FHNW

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Abstract: Membrane filtration applications are omnipresent in production processes of the food and beverage industry, in pharmaceutical production and the petrochemical industry but also in water purification for drinking water production and wastewater treatment. The main separation principle in membrane filtration is based on size exclusion which is dependent on the pore size of the membrane. Current developments based on chemical modification of these membranes have the goal to confer an additional chemical selectivity to membranes in order to broaden their areas of application. Here we present two examples of chemical membrane modifications pursued at the University of Applied Sciences and Arts Northwestern Switzerland (FHNW) which are based on a) polyelectrolyte multilayer (PEM or LbL) coatings and b) coating with stimulus responsive polymer brushes. Applications of such modified filtration membranes are *e.g.* selectively gated filtration and phosphorous P-recovery from acidic disintegrated sewage sludge.

Keywords: LbL coating · Membrane filtration · Phosphorous recovery · Polymer brush · Stimulus responsive

LbL-modified Filtration Membranes for Phosphorous Recovery

Recovery of resources from waste streams is becoming hugely important when striving for circular economies. Several industry branches are aiming increasingly at zero-liquid-discharge. Nanofiltration (NF) is a well-known separation technique and applied in many industries such as the food and pharma industry. Recently, NF has become attractive for resource recovery applications from acidic waste streams. For instance, studies have shown that NF is a suitable technology for P-recovery from acidic disintegrated sewage sludge.[1] We demonstrated that the application of layer-by-layer (LbL) modified membranes could enhance the process performance in terms of P-yield and energy consumption.[2,3] Currently the scientists at the FHNW are going a step further by identifying LbL-membranes that are not only stable in acidic environments, but also resistant to multiple and consecutive backwashing cycles. Furthermore, they investigate the upscaling of a selected LbL configuration into larger modules, demonstrating that LbL-membranes are a viable treatment technology in the field of resource recovery.

Fig. 1. Deposition of a polycation (red) and polyanion (blue) on a porous ultrafiltration membrane (left) and a schematic description of the transport mechanisms of a LbL membrane during phosphorous recovery from acidic disintegrated sewage sludge (right, P = phosphorous, M = metal ion).

LbL membranes are fabricated by depositing consecutive layers of oppositely charged polyelectrolytes (PE) on a charged support material, typically a porous ultrafiltration (UF) membrane (Fig. 1). The support UF plus the LbL multilayer assembly will create a nanofiltration (NF) membrane (see also Fig. 2). Typically the used support is a hollow fiber type UF membrane. Due to reported high fluxes, this novel technique

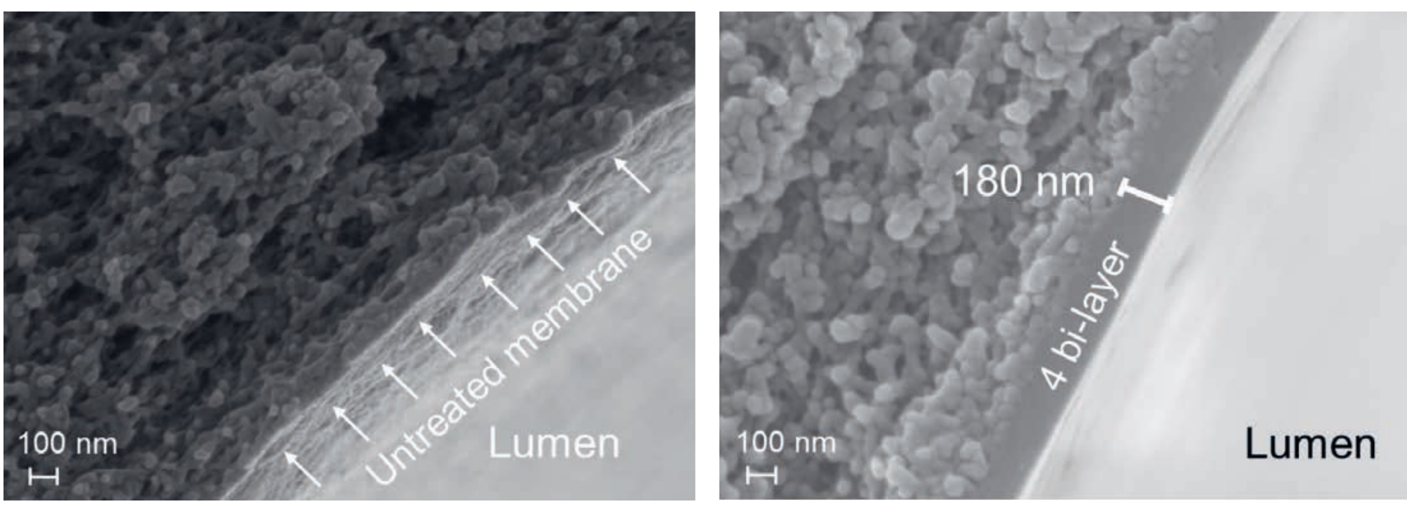

Fig. 2. Scanning electron microscopy (SEM) images of uncoated hollow fiber ultrafiltration membrane lumen (left) and coated hollow fiber ultrafiltration membrane lumen (right).

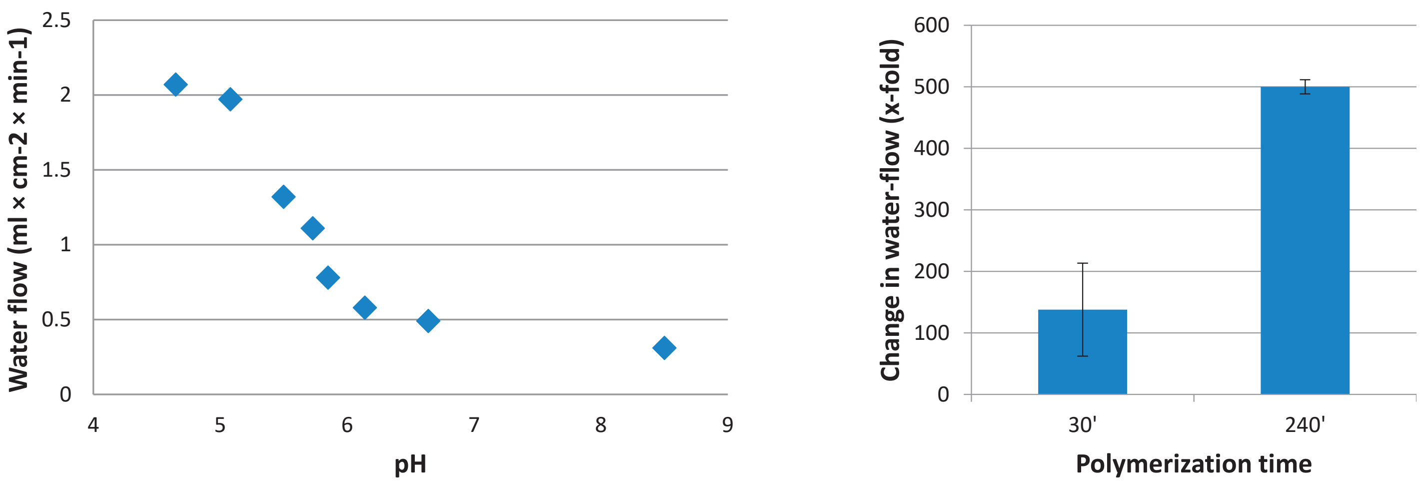

Fig. 3. pH-dependent water flow through poly-MES modified cellulose filtration membranes. 10 mM buffer solution was adjusted to the indicated pH values and the liquid flow determined. The graph on the left shows the pH-dependent flow rate of the modified membranes, the graph on the right indicates the changes in water flow between pH 3.2 and pH 8.5 for membranes modified with polymer brushes synthesized for either 30 min or 240 min.

has the potential to be a suitable solution for overcoming the drawbacks of current commercially available NF membranes such as low flux and static retention properties. Indeed, LbL-coated UF membranes have significant higher fluxes (up to 10–16 times) than UF membranes and can be tailored for specific filtration tasks.[2–4] Besides their use for phosphorous recovery, other groups have shown the application of LbL-coated membranes for micropollutant removal as well as the efficient separation of lactose and protein, demonstrating the usefulness of such membranes for the food processing industry.[5,6]

In this regard, the recent technological development of LbL-coated membranes introduces this type of membrane as a viable solution because they are resistant to harsh, *e.g.* acidic environments, and their performances can be tailored on demand by modifying the LbL coating procedure. The latter property makes LbL membranes a flexible tool, capable of addressing very specific needs and, thus, filling a gap in the market.

Stimulus Responsive Filtration of Polymer Brush-functionalized Filtration Membranes

The modification of filtration membranes with polymer brushes has been shown to introduce new properties to these membranes.[7,8] Polymer brushes are well known for their stabilizing effect on colloids as well as their potential to reduce surface fouling and friction between surfaces. In recent years their potential for the improvement of filtration processes has been demonstrated and here we present data on the introduction of stimulus responsive properties to filtration membranes by modification with pH- and divalent ion-sensitive polymer brushes. Cellulose-based filtration membranes were modified with a covalently bound atom transfer radical polymerization (ATRP) initiator followed by polymerization of the carboxy-functionalized monomer 2-(methacryloyloxy)ethyl succinate (MES), a process which has been shown to result in the surface functionalization with polymer molecules with up to 200 nm length.[9] Following functionalization of the cellulose membrane we determined the pH-dependent water flow through the modified membrane at a pressure of 0.1 bar. While the water flow at low pH was uninhibited, with increasing pH there was a strong reduction on water flow with the largest flow change in the region between pH 5 and 6, being slightly higher than the pKa value of 2-(methacryloyloxy) ethyl succinate (Fig. 3, left). As can be expected, the pH-effect on the reduction of the water flow was increasing with poly-MES polymerization time and thus polymer length, cumulating in a 500× factor observed on samples functionalized for 240 min (Fig. 3, right), corresponding to a change in water flow from around 2 ml/(cm^2 × min) at pH 3.2 to a nearly closed state with flow rates below 1 µl/(cm^2 × min) at pH 8.5.

At neutral pH, when water flow is nearly absent, it can be reconstituted by the addition of divalent ions like Ca^{2+} (Fig. 4). The effect was already observable at a concentration of 1 mM $CaCl_2$ which increased the water flow by a factor of 4 as compared to calcium-ion free water.

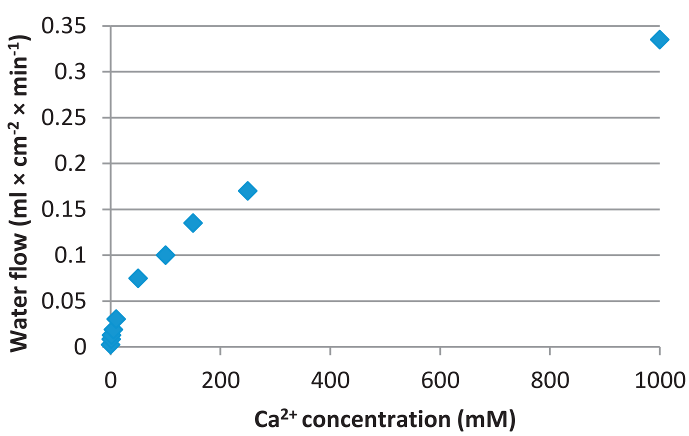

Fig. 4. Calcium ion concentration dependent water flow through poly-MES modified cellulose filtration membranes. Buffer solution with neutral pH and increasing concentration of calcium ions was filtered through the modified membranes at 0.1bar pressure and the water flow was recorded. Note the nearly complete prevention of water flow for calcium free solutions.

Summarizing, here we describe a method to introduce stimulus-induced switchable water flow through filtration membranes by modification with polymer brushes. To date the main exploited stimuli of polymer brush modified materials are divalent cations and pH, however current research in the field is evaluating different methods to introduce other stimulus responding chemical functionalities to polymer brushes.[10,11] In the future, scientists even envisage substrate specific filtration by mimicking principles of selective biological pores like ion channels and pumps as well as the highly protein type selective intracellular barrier of the nuclear pore complex.[12,13]

Received: March 12, 2020

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