Derivatized Polymeric Nanoparticle Layers on Porous Surfaces

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1. Introduction

Composite membranes with porous layers of polymer nanoparticles on or between supporting membranes have been produced in the last decade. Investigations on the gas- and water-permeabilities [1] as well as on the porosity [2] of such composites have also been performed and published and the properties have been described with the Carman-Kozeny-Equation for packed beds [2,3]. As shown such separation layers can provide micro- or ultrafiltration properties depending on the size of the applied nanoparticles. Diffusion coefficients for different solutes through partially coalesced porous particle films have also been reported [4,5].

Polymeric nanoparticles can be produced with a variety of different chemical groups on the surface as reported numerously in literature for more than three decades. The aim of this work was to build layers of derivatized polymer particles on porous supports.

2. Experimental

Synthesis of nanoparticles

Styrene nanoparticles with a diameter of 458nm (PS1) were synthesized by emulsifier-free emulsion polymerization. The sulfonated particles (PS2) were synthesized by emulsion polymerization using the sulfonated comonomer NaSS. For (PS3) a core-shell approach was used and NaSS was implanted only in the shell. In all cases $K_2S_2O_8$ was used as initiator leaving a small amount of sulphate groups at the surface. All particles were cleaned with dialysis in NADIR-dialysis tubings which were washed with distilled water before use to remove glycerol. The particles were analyzed using different methods as shown in Table 1.

Particle	Characterization method	Av. Diam. [nm]	$\sigma[\mu C/cm^2]$
PS1	DLS, SEM	458	1,05
PS2	DLS, SEM	86	4,55
PS3	SEM	106	10,5

Table 1: Properties of the synthesized particles

A Brookhaven 90plus size analyzer using DLS was mainly used to analyze the particle size. The particle sizes seen in SEM (JEOL JSM-6400) were in good agreement with the particle sizes measured with DLS.

The amount of functional groups (SO_4-, SO_3-) was determined by conductometric titration.

Deposition of the particles on porous supports

Different amounts m_p of PS1 particles were deposited on cellulose nitrate micro-filtration membranes (SM 113, Sartorius, Pore size 450nm) by filtration in an Amicon 8050 test cell (A = 12.9 cm^2). Pure water fluxes were determined before and after the application of nanoparticles. The resistances of the particle layers were evaluated from filtration experiments at a constant pressure of 200 mbar (Table 2).

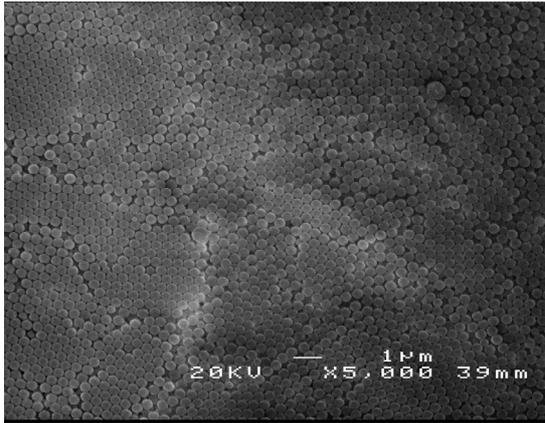| m_p [mg]	V_{H2O} [m^3/h^{-1}m^{-2}bar^{-1}]	α [m^{-2}]
0	27,2	
13,3	2,4	5,63E+16
39,9	0,77	9,46E+16

Table 2: Properties of 450nm layers on CN-membrane

Fig. 1: SEM image of layers of PS1 particles

In another filtration experiment suspensions of PS2 nanoparticles in water were prepared with five different concentrations. The suspensions were filtered in an Amicon 8010 dead-end membrane test cell (A = 3.59 cm^2) containing a PVDF membrane (MWCO 3000). The specific cake resistances for the applied masses are shown in Fig. 2.
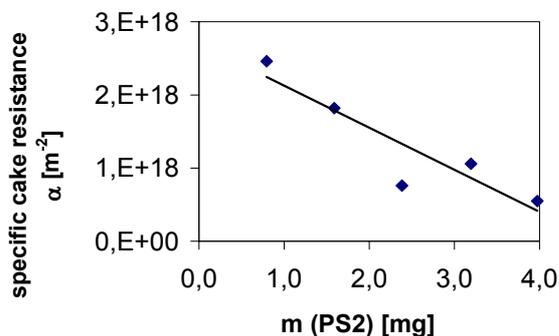

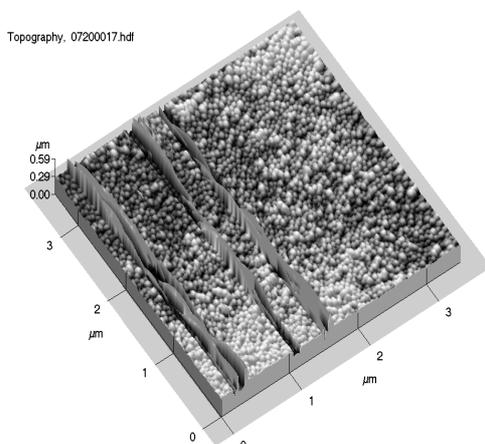Fig. 2: Specific resistances of PS2 particle layers vs. particle mass applied

Fig. 3: AFM image of the surface of layers of PS2 particles

After application of the nanoparticles the membranes were carefully removed from the test cells and dried in an oven at 80°C. In all cases the layers tended to break and brittle in the dry state. Particles were removed by touching with finger or spatula.

3. Results
Different nanoparticles with negatively charged surface groups were synthesized and the size and surface charges were determined. Layers of underivatized and sulfonated particles were applied onto commercially available micro- and ultrafiltration membranes and cake resistances of the separation layers were determined to gain first data on the properties of these kinds of layers.

4. Outlook
Further works are planned to make reproducible and more stable layers. The main research work is then focused on the investigation of such layers regarding the influence of functional groups on the mass transfer of charged and uncharged components to describe the separation properties as a function of respective nanoparticle and layer properties.

5. References
[1] S. Jons, P. Ries, C.J. MacDonald, J. Memb. Sci. 155 (1999), p79-99
[2] S. Ramakrishnan, C.J. MacDonald, et. al, J. Memb. Sci. 231 (2004), p57-70
[3] M. Lehmann, H. Brunner, G. Tovar, Desalination 149 (2002), p315-321
[4] P. Steward, J. Hearn, M. Wilkinson, Polym. Int. 38 (1995), p1-32
[5] O.K. Lyngberg, C.P. Ng, et. al, Biotechn. Prog. 17 (2001), p1169-1179