SUPPLEMENTARY MATERIAL TO ARTICLE

The Critical Zeta Potential of Polymer Membranes: How Electrolytes Impact Membrane Fouling

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Supplementary Material to Section 3.1.1 Zeta Potential of Polymer Membranes and PS Beads

Following the reaction mechanism of a radical emulsion polymerization polystyrene beads are formed as described in section 2.2. The surface charge is determined by the charged moieties of the initiator molecules (figure S1a). The bead diameter was adjusted to a value of around 0.2 µm. The polydispersity index (PDI) was maintained in the monodisperse range below 0.05 (figure S1b). SEM images confirmed the bead size (figure S1c).

Figure S2 shows the zeta potential vs. pH curves for cationic an anionic PS beads at sodium chloride concentrations of 0.001 M and 0.01 M.

The modification of polymer membranes was carried out as described in section 2.4. Due to the electron beam irradiation radical species are formed leading to grafting reactions. This way, chemical bonds between the membrane and the used modification reagent are formed. Modifications with PSS follow a grafting-to reaction mechanism. No further steps are needed to gain the PSS modification (PES-PSS and PVDF-PSS). In the case of modification with AEMA a grafting-from reaction takes place. Membranes modifies with AEMA will subsequently brought into reaction with GA forming a Shiff base. Afterwards, a second reaction with either TEPA (intermediate to PES-TEPA and PVDF-TEPA) or lysine (PES-Lysine and PVDF-Lysine) takes place forming another Shiff base structure. In the case of modifications with TEPA moieties the reactions with GA and TEPA are repeated to create a second generation of dendrimeric structures (PES-TEPA and PVDF-TEPA).

The modified membranes were characterized regarding their morphology (SEM), pore size distribution, porosity, water permeation flux, water contact angle, chemical composition (XPS), and zeta potential.

SEM images (figure S3) of modified PES and PVDF membranes do not show pore blocking due to the modification when compared to the reference membranes. This is in agreement with the data for average pore size, porosity and water permeation flux (table S1). No significant changes were found.

The chemical composition (table S1) of the membranes changed according to the applied modification. Increased values for oxygen and sulfur were found for modifications with PSS. Membranes modified with TEPA show high amounts of nitrogen and increased oxygen values while lysine groups lead to small increases of both nitrogen and oxygen.

The water contact angles (table S1) of all modified membranes decreased after modification. Due to the charged moieties the membrane surfaces become more hydrophilic.

Figure S4 presents the zeta potential of PES- and PVDF-PSS and PES- and PVDF-TEPA membranes at sodium chloride concentrations of 0.001 M and 0.1 M.

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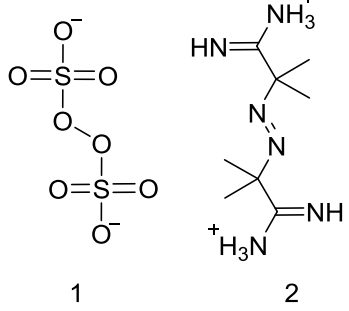
a



b

bead charge	diameter	PDI
cationic	183	0.015
anionic	220	0.018

c

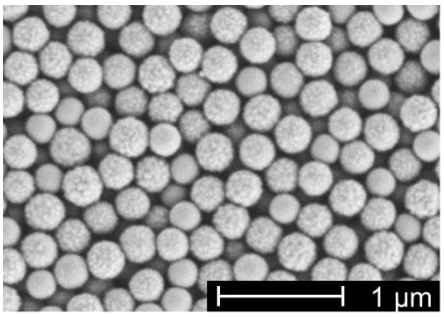


Figure S1 (**a**) Initiator molecules (**1**) KPS and (**2**) AIBA; (**b**) SEM picture of cationic PS beads, (**c**) SEM of cationic PS beads.

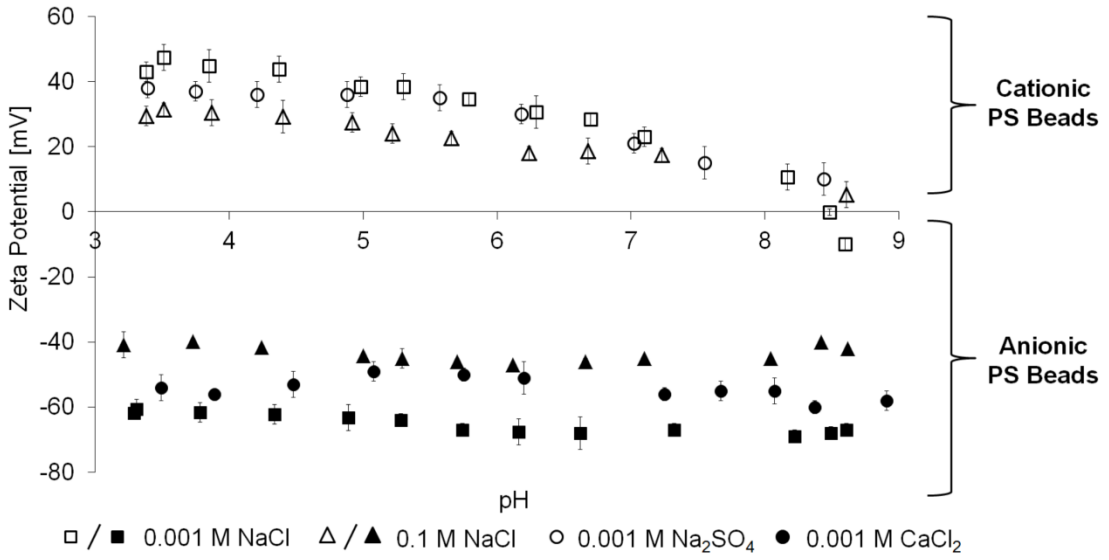


Figure S2 Zeta potential of charged PS beads *vs*. pH at different salt concentrations.

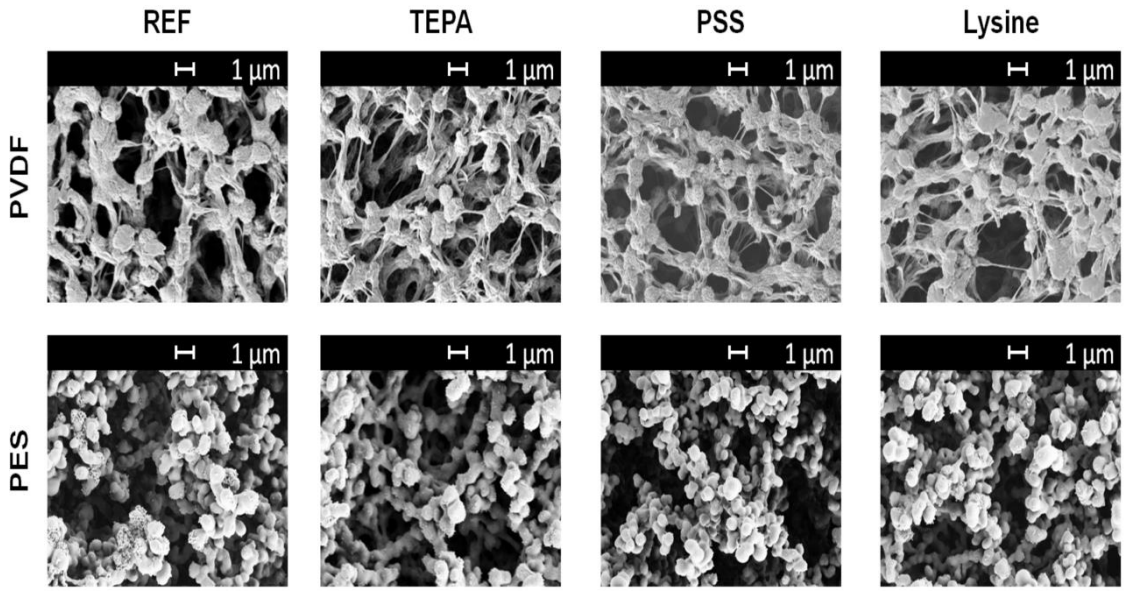


Figure S3 SEM images of modified membranes top side.

Table S1 Characteristics of modified polymer membranes.

membrane property	PES-REF	PES-TEPA	PES-PSS	PES-Lysine
water permeation flux [mL/(min cm² bar)]	32 ± 6	35 ± 2	32 ± 4	37 ± 1
porosity [%]	73 ± 3	71 ± 7	68 ± 2	75 ± 1
average pore size [µm]	0.83 ± 0.04	0.74 ± 0.05	0.64 ± 0.01	0.76 ± 0.03
elemental composition [%]				
C	74.9	71.3	73.3	72.1
O	19.8	20.6	20.4	21.6
S	5.3	4.7	6.3	4.8
N	-	3.4	-	1.5
	PVDF-REF	PVDF-TEPA	PVDF-PSS	PVDF-Lysine
water permeation flux [mL/(min cm² bar)]	33.7 ± 1.6	30.8 ± 0.9	36.3 ± 1.5	30.0 ± 1.8
porosity [%]	72 ± 2	72 ± 2	69 ± 1	72 ± 2
average pore size [µm]	0.9 ± 0.04	1.0 ± 0.09	0.9 ± 0.05	0.9 ± 0.03
elemental composition [%]				
C	51.8	53.8	45.2	50.3
O	0.2	8.5	2.1	6.4
N	-	3.9	-	1.0
F	48.0	33.8	52.5	42.3
S	-	-	0.2	-

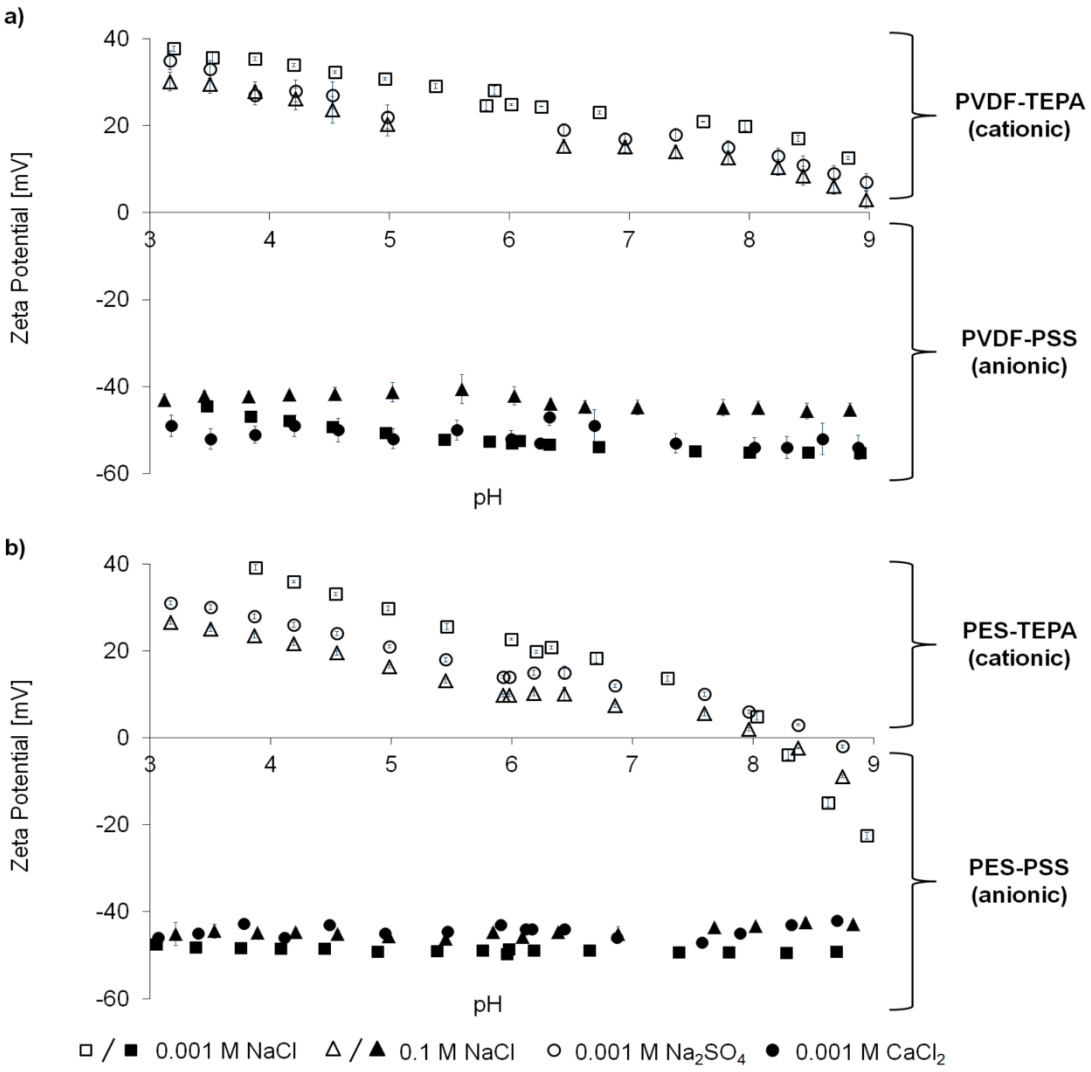


Figure S4 Zeta potential *vs*. pH at different salt concentrations of (**a**) PVDF-TEPA and -PSS membranes; (**b**) PES-TEPA and -PSS membranes.

Supplementary Material to Section 3.1.2 Electrostatic Repulsive Interactions

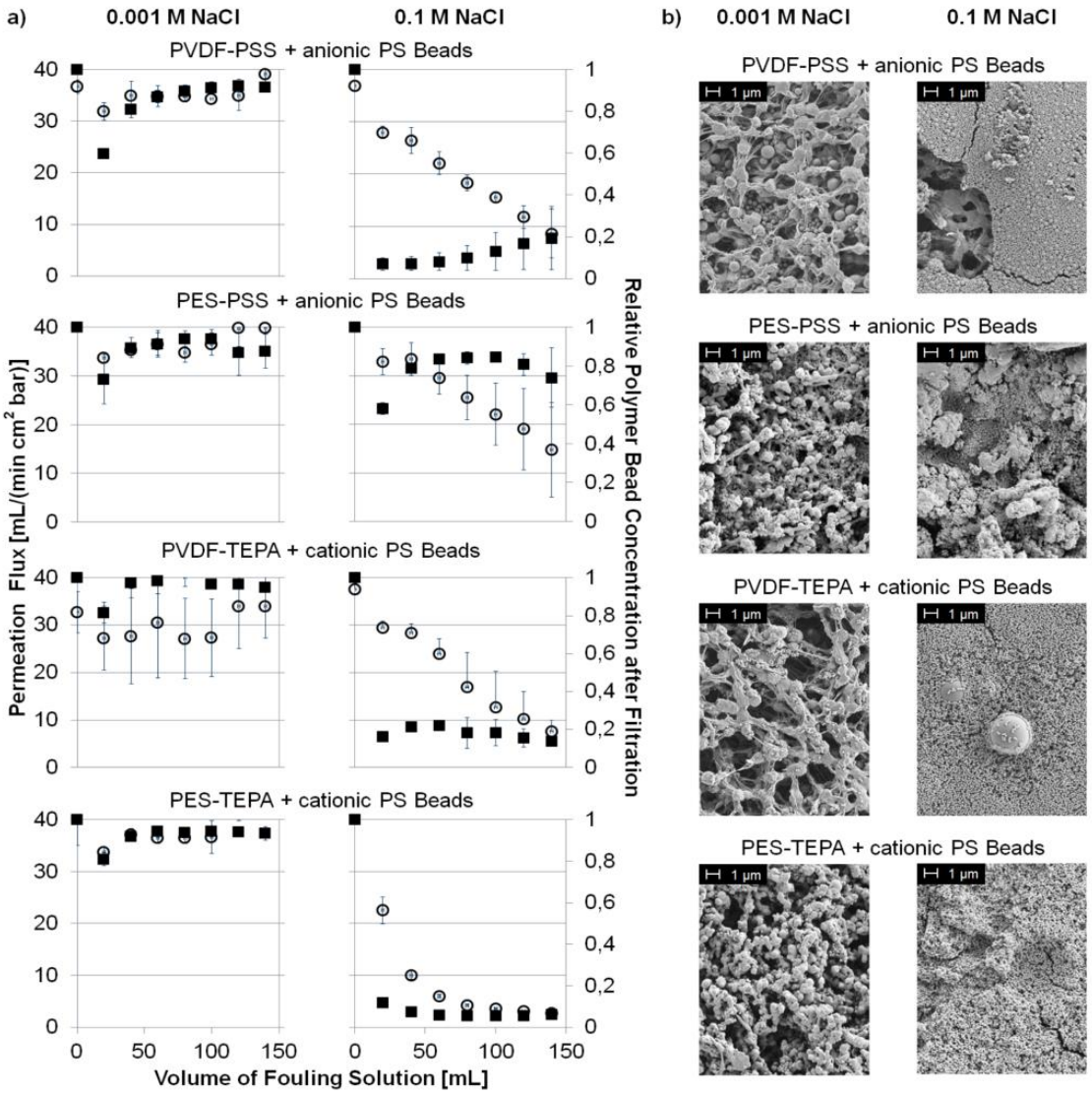


Figure S5 Repulsive Interactions at 0.001 M and 0.1 M NaCl (**a**) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) *vs*. volume of PS bead suspension; (**b**) corresponding SEM picture of the membrane after fouling.

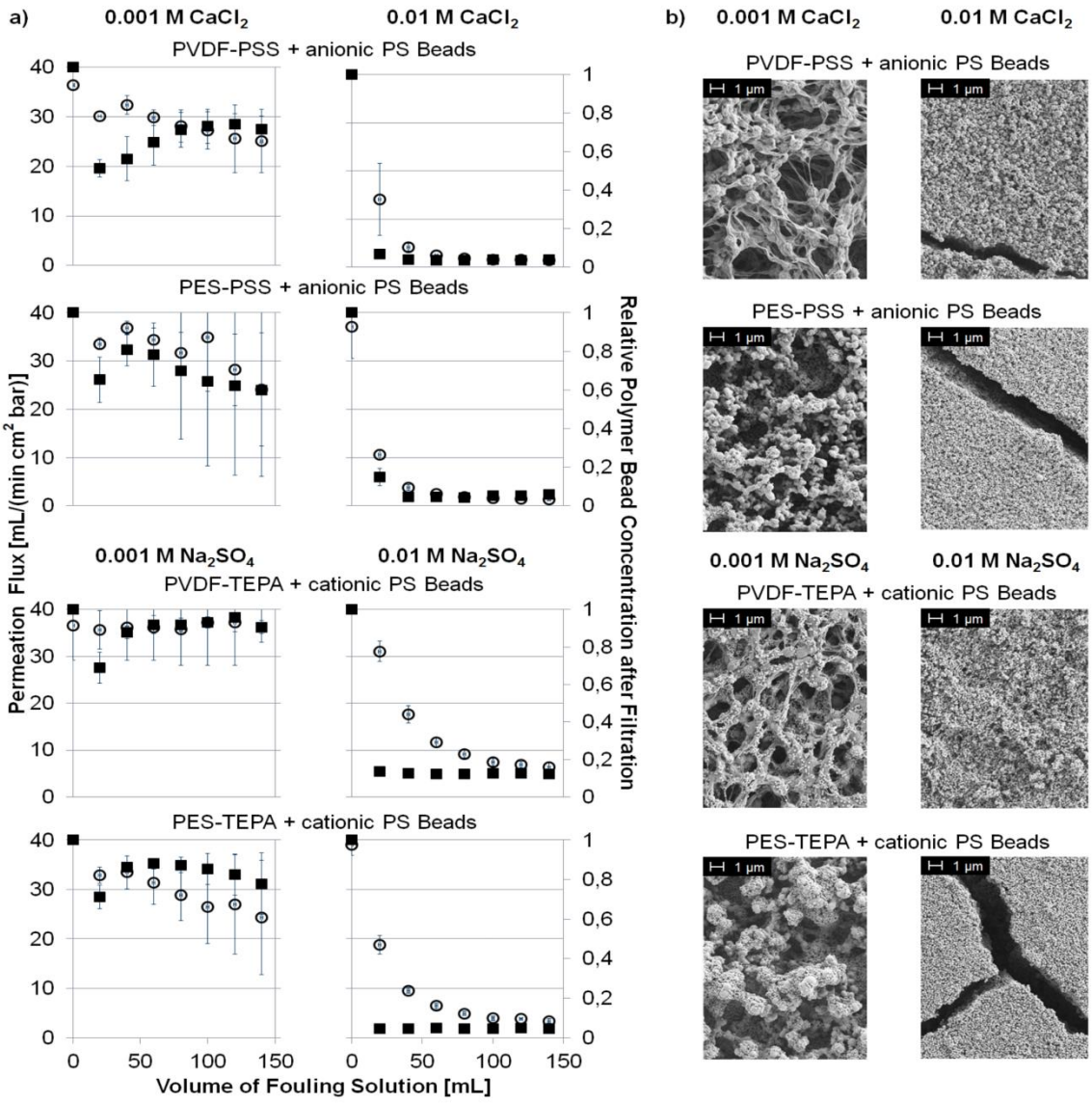


Figure S6 Repulsive Interactions at 0.001 M and 0.1 M $CaCl_2$ or Na_2SO_4 (**a**) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) *vs*. volume of PS bead suspension; (**b**) corresponding SEM picture of the membrane after fouling.

Supplementary Material to Section 3.1.3 Electrostatic Attractive Interactions

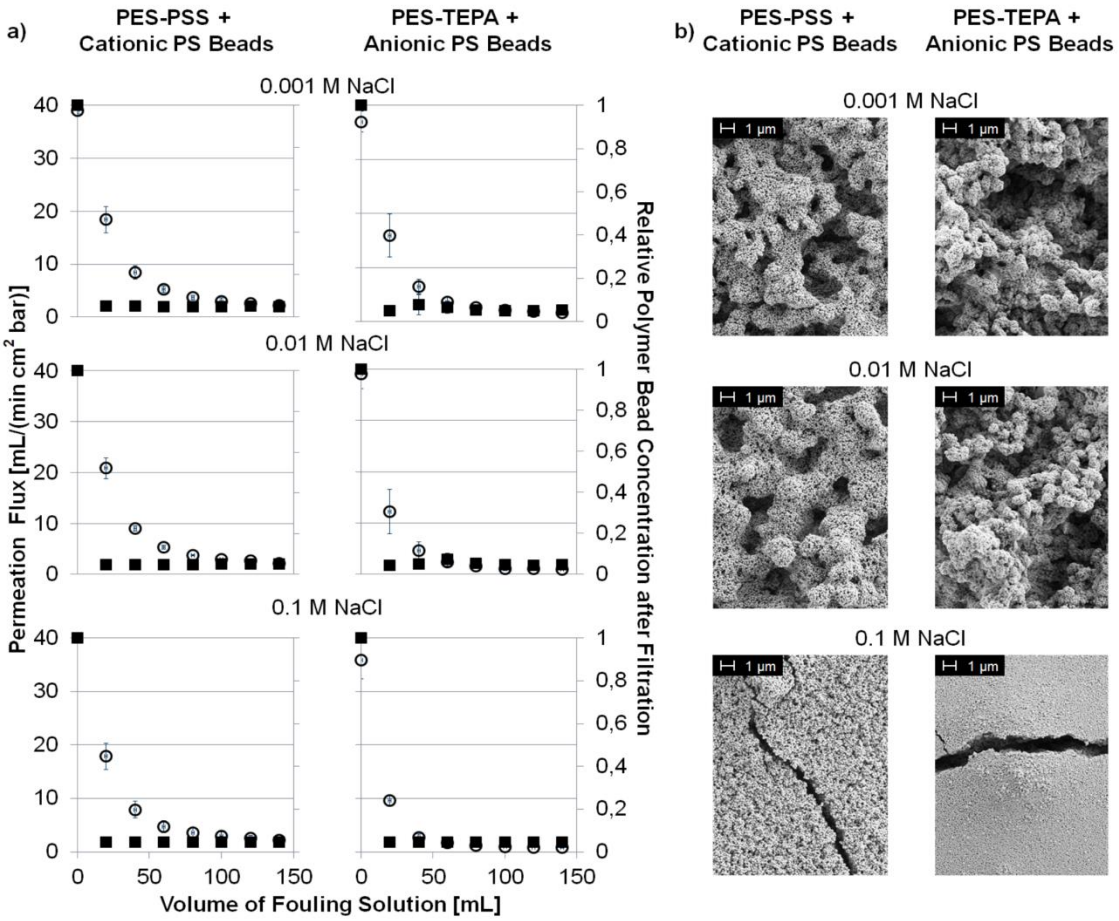


Figure S7 Attractive Interactions at 0.001 M, 0.01 M, and 0.1 M NaCl (**a**) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) *vs*. volume of PS bead suspension; (**b**) corresponding SEM picture of the membrane after fouling.

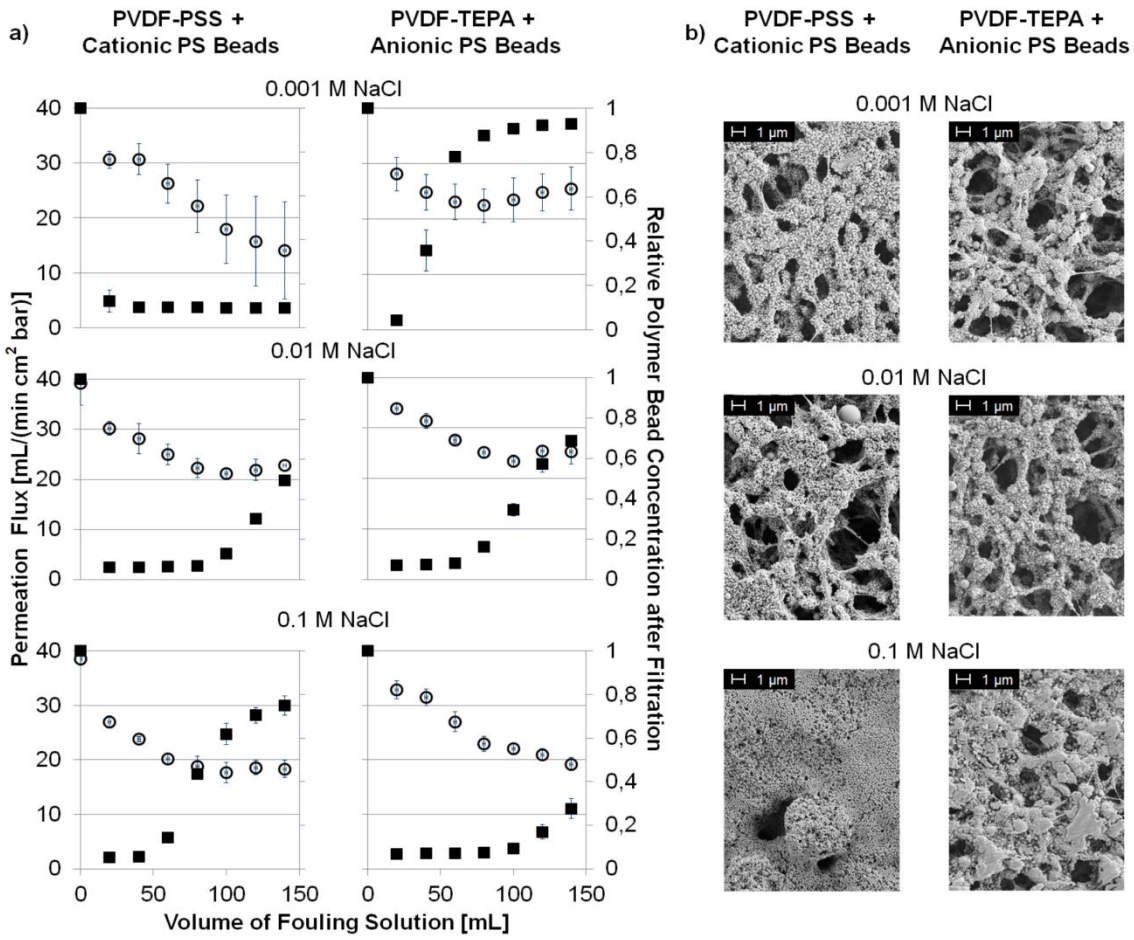


Figure S8 Attractive Interactions at 0.001 M, 0.01 M, and 0.1 M NaCl (**a**) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) *vs*. volume of PS bead suspension; (**b**) corresponding SEM picture of the membrane after fouling.

Supplementary Material to Section 3.2 pH Dependence

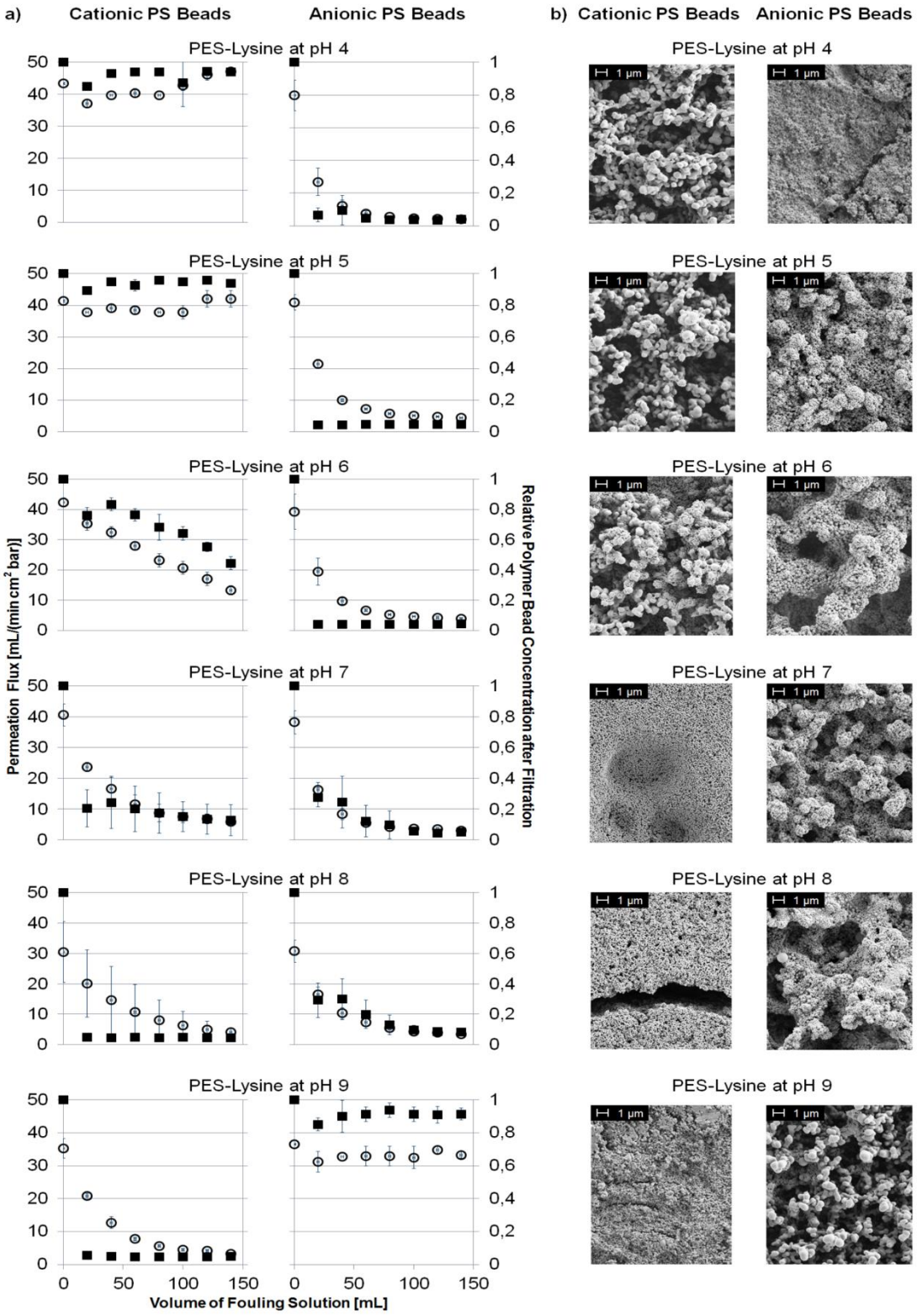


Figure S9 Fouling of PES-Lysine at different pH values (**a**) Permeation flux of fouling suspension (left axis, open circles) and normalized concentration of PS beads in filtrate (right axis, filled squares) *vs.* volume of PS bead suspension; (**b**) corresponding SEM picture of the membrane after fouling.