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WHEY ELECTRODIALYSIS USING ORGANIC-INORGANIC MEMBRANES

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Organic-inorganic membranes based on heterogeneous ion exchange polymer supports, which were modified with hydrated zirconium dioxide (anion exchange membrane) and zirconium hydrophosphate (cation exchange separator), were used for whey desalination as well as for concentrate and permeate of whey nanofiltration. Comparing with pristine polymer membranes, the composite materials are characterized by stability against fouling inside pores. The membranes were applied to desalination of whey and products of its baromembrane treatment. Exponential decay of electrical conductivity over time has been found for the solutions being purified. The membrane resistance grew simultaneously.

Large amounts of liquid wastes produced by dairy industry are dropped into rivers and lakes resulting in deterioration of water quality due to occurrence of turbidity and unpleasant odor, development of pathogens and so on. Recycling of milky whey allows one to solve not only ecological but also economical problems, since the end products (protein supplements or infant formula) can be sold. However, deep desalination of whey is needed to obtain these products [1]. Since milky whey contains high amount of inorganic salts (the order is 1 g dm^{-3}), electrodialysis (ED) is attractive for this purpose [2].

As a rule, polymer membranes are used for the ED processes, however they accumulate organic and inorganic matters not only on their outer surface, but also inside pores [3]. Thus, a durable procedure, which involves large amount of aggressive reagents and deionized water, is needed for regeneration of the membrane system. However, polymer material containing intraporous active layer of inorganic ion-exchanger is stable against fouling during baromembrane separation [4]. A similar approach could be applied to ion exchange membranes [5]. Before ED treatment, whey proteins are concentrated by means of nanofiltration, this process gives both concentrate and permeate [6]. After desalination, the concentrate is used for manufacture of valuable products. Salts are removed from the concentrate, which is used further for manufacture of valuable products. Desalinated permeate can be returned to fresh whey in order to enrich it with lactose. The aim of the investigation is application of organic-inorganic membranes to desalination of whey and products of its baromembrane treatment.

Research Methodology

The ion exchange separators were obtained by modification of heterogeneous CM-40 cation exchange and AM-40 anion exchange polymer supports (Schekinoazot, RF) with zirconium hydrophosphate (ZHP) and hydrated zirconium dioxide (HZD) respectively [5]**.** These membranes were manufactured from CU 2-8 cation-exchange resin and EDE-10P anion-exchanger. The resins were modified by similar manner for visualization of small incorporated particles using a JEOL JEM 1230 transmission electron microscope (Jeol) and a scanning electron microscope JEOL JSM 6700 F (Jeol).

Experimental set-up involves seven-compartment cell, power supplier, measuring instrumentations and three independent liquid lines [10]. The first line provides circulation of whey (300 cm^3) throw three desalination compartments with a flow velocity of 0.3 $cm^3\ s^{-1}$, the second line was through two concentration chambers filled with a 0.1 M HCl solution (1 dm^3). The electrode compartments were filled with a 0.05 M Na_2SO_4 solution. A thickness of each compartment was 6 mm, the desalination compartments contained turbulators for intensification of mass transport.. Only composite membranes (further CM) or only pristine membranes (PM) were used for separation of the compartments from each other.

Milky whey and products of its nanofiltration (NF) treatment (concentrate and permeate) were purified from inorganic ions. The ED processes were performed at 15 V.

Results and Discussion

Both single nanoparticles (4-20 nm in the case of ZHP and 3-6 nm fo HZD) are visible in TEM image of ion exchange resins. Aggregates of the nanoparticles (≈300 nm) have been also found (Fig. 1). Single nanoparticles are placed in clusters and channels of the polymers and improve ion transport [5]. The aggregates are placed in pores outside clusters and channels, where hydrophobic parts of the polymer chains are located. The aggregates prevent adsorption of organics (fouling).

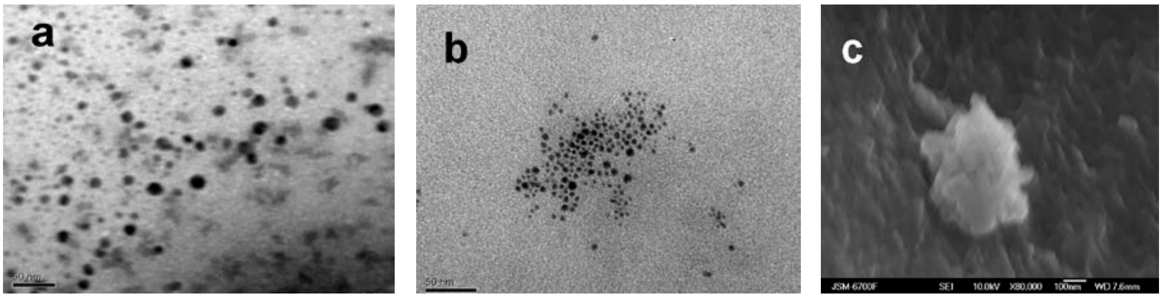

Fig. 1. *TEM and SEM images of ZHP (a, c) and HZD (b) particles in cation-(a, c) anion-(b) exchangers contain.*

During electrodialysis using PM and CM, the whey conductivity (κ) decreased over time (τ) due to removal of mineral components (Fig. 2). The conductivity changed according to the relation:

$$\kappa = 10^{a - b\tau}, \tag{1}$$

where a (initial conductivity) and b (related to desalination rate) are the empirical coefficients. The b parameter corresponds to slope of the κ – τ curve, which is plotted in semi-logarithmic coordinates, i.e. $b = d(\log \kappa)/d\tau$. Modified membranes demonstrate higher rate of desalination than PM (Table 1). The cell voltage (U_c) is determined as:

$$U_c = E_{cath} + E_{an} + I\left(\sum_i R_{s,i} + \sum_j R_{m,j}\right). \tag{2}$$

Here E_{cath} and E_{an} are the electrode potentials, I is the current, R is the resistance, the s and m indexes correspond to solutions and membranes, i and j are the numbers of compartments and membranes. Since U_c is the constant, the current is determined by a resistance of the membranes and solutions, $R = p\frac{l}{S} = \frac{1}{\kappa}\frac{l}{S}$ (here ρ is the specific resistance, l is the thickness, S is the area), it is possible to write:

$$I = \frac{S\left[U_c - (E_c + E_a)\right]}{l_{comp}\left[3\rho_{s,des} + 2(\rho_{s,conc} + \rho_{s,el})\right] + l_m \sum_j \rho_{m,j}}. \tag{3}$$

Here the des, $conc$ and el indexes correspond to the desalination, concentration and electrode compartments ($comp$) respectively. The terms of $2(\rho_{s,conc} + \rho_{s,el})$ and $\frac{3l_{comp}}{S\left[U_c - (E_c + E_a)\right]}$ can be neglected, thus:

$$\frac{\rho_{s,des}}{I} = S\left[U_c - (E_c + E_a)\right]\sum_j \rho_{m,j} \ . \qquad (4)$$

In other words, the $\rho_{s,des} / I$ – τ plot reflects a change of the membrane resistance (due to depletion of whey and fouling) over time. As seen, PM are characterized by higher $\rho_{s,des} / I$ value despite lower desalination degree of whey. Thus, the composite membranes demonstrate higher stability against fouling than PM. ED process involving CM requires also lower energy consumptions (see Table 1).

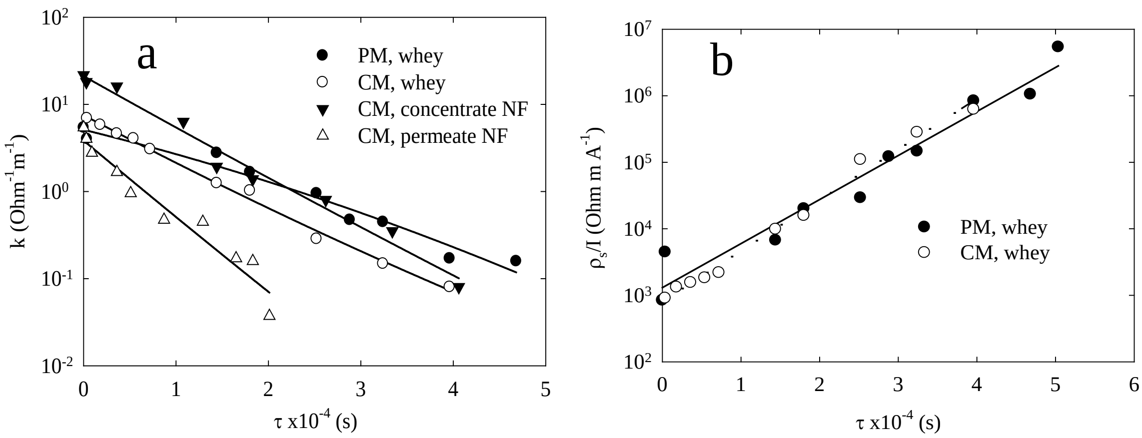

Fig. 2. Conductivity of liquid through desalination compartments (a) and ρ_s / I ratios (b) as functions of time.

Table 1. Electrodialysis of biological liquids

Liquid	Membranes	$d(\log \kappa) / d\tau$, (Ohm^{-1}m^{-1})s^{-1}	Energy consumptions for 1 kg salts / kWh
whey	PM	-3.8×10^{-10}	3.8
	CM	-5.1×10^{-10}	1.7
NF concentrate	CM	-5.7×10^{-10}	1.5
NF permeate	CM	-8.7×10^{-10}	2.4

The modified membranes were also applied to desalination of NF concentrate and permeate. Higher rate of desalination was found for the permeate evidently due to an absence of proteins, which form precipitation on outer surface of the membranes. However, the precipitate can be easy removed by polarity reversal or by hydrodynamical pulsations.

Conclusions

Modified separators demonstrate higher stability against fouling evidently due to nanoparticle aggregates, which prevent penetration of organics inside the membranes. Higher desalination rate and lower energy consumptions were found for these materials than for pristine membranes evidently due to this stability and improved ion transport, which is provided by single nanoparticles. Normally ≈1 kWh is necessary per 1 kg salts, needed decrease of the consumptions could be provided by optimization of the cell geometry.

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