

PL 01

ELECTRODIALYSIS, A MATURE TECHNOLOGY WITH A MULTITUDE OF NEW APPLICATIONS

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Electromembrane processes, such as electrolysis, electrodialysis, diffusion dialysis, etc. are used today on a large industrial scale in the production of potable and industrial process water as well as in the treatment of industrial effluents.

Currently desalination of brackish water and the chlorine-alkaline electrolysis are still the dominant applications of electromembrane processes. But interest in other processes such as diffusion dialysis or the electrodialytic water dissociation with bipolar membranes, continuous deionization or capacitive deionization is rapidly growing. A number of new applications in the chemical and pharmaceutical industry and energy conversion systems have more recently been identified. However, today's electromembrane processes and components used in these processes have still severe technical and commercial limitations and there is a substantial need for basic as well as applied research to improve the processes. In this presentation the state-of-the-art processes, their mayor areas of application as well as their present limitations pointed out. More recently developed products and processes will be discussed in more detail and their technical as well as economic advantages are described, and present and potential future applications indicated.

Fundamentals and major application of state-of-the-art electromembrane processes, such as electrolysis, electrodialysis, diffusion dialysis, etc. are briefly described and their industrial relevance and their technical and commercial limitations are pointed out. More recently developed processes such as the electrodialytic water dissociation with bipolar membranes and the electrochemical regeneration of ion-exchange resins are discussed in more detail and their application is illustrated in selected examples. Problems and technical limitations of these processes as well as commercial opportunities are indicated. Research needs for a sustainable growth of electromembrane processes are pointed out.

Key words: Electromembrane processes, ion-exchange membranes, bipolar membranes, electrolysis, electrodialysis, electrodialytic water dissociation

PL 02

MEMBRANE OPERATIONS IN REDESIGNING PROCESS ENGINEERING

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The rapid, recent progresses in the development of membrane operations covering practically all the most important unit operations necessary in process engineering are offering the opportunity to redesign successfully industrial productions, water desalination systems and waste water treatments, consistent with the basic requirements of a process intensification strategy. Significantly lower energy consumption, lower ecoenvironmental impact factors, higher final products quality and formulations characterize successful cases already realised. The development of new membranes and membrane operations as membrane crystallisers, membrane emulsifier etc. are offering more innovative opportunities for further progress for a sustainable industrial growth.

PL 03

ENZYMATIC MEMBRANE REACTORS

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Most of the time enzymatic reactions are carried out in classical batch reactors. At the end of the reaction the enzymes are inactivated before recovering the final products. The use of such reactors is relatively simple at any scale, with only the need to control the temperature and the pH. Nevertheless, this type of bioreactor presents a certain number of disadvantages, in particular when they must treat large quantities of raw material as it is often the case in industrial practice: low productivity, high operating costs, loss of catalytic activity due to inactivation, great variability of the quality of the products... (Rios *et al.* 2004)

To overcome those limitations, some attempts to operate in a continuous way and reusing enzymes came out. At the beginning of the twentieth century, the idea of immobilizing enzymes appeared as an interesting alternative. The objective was to ensure the localisation of biological catalyst in a definite space area, the preservation of its global activity and reuse. Immobilization of enzymes in fixed or fluidized bed was proposed to conduct the reaction in a continuous mode. A main disadvantage of fixed or fluidized bed systems is the occurrence of mass transfer limitations due to diffusion at the surface or inside particles which decreases conversion. Moreover, if enzyme stability generally increases as a consequence of immobilization, specific activity more often drops due to structural modifications or hiding of active sites. Finally, cost of immobilization must be accounted for.

By introducing membrane technologies, some of these disadvantages could be circumvented and the concept of enzyme immobilisation could be considerably enlarged. The enzyme membrane reactor (EMR) is a specific mode for running continuous processes in which enzymes are separated from end products with the help of a selective membrane. Whatever the EMR configuration, the main objective is to ensure the complete rejection of the enzyme in order to maintain the full activity inside the reacting volume. Depending on the case, enzyme molecules may be freely circulating on the retentate side or immobilised onto the membrane surface or inside its porous structure. In the first case, the function of the membrane is to reject free enzymes in order to keep them inside the system and the reaction occurs on the retentate side. In the second process, the membrane became the catalyst media and reaction occurs during membrane crossing.

This presentation will endeavour to give a broad overview of the different systems now under consideration, and their various applications for food production, biotechnologies, effluent treatments, new energy devices, sensors....

PL 04

THE PERSPECTIVES IN THE DEVELOPMENT OF ELECTROMEMBRANE SEPARATION PROCESSES

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Historically, electro dialysis has appeared about 10 years earlier than reverse osmosis. However, now reverse osmosis displaced electro dialysis in water desalination occupying about 90% of the membrane technology market in this domain. It is well known that electromembrane processes are intensively used in a number of emerging technologies such as fuel cells, electrokinetic microfluidic devices for medicine, microelectronics, and other. In this paper we consider the axes of development of electromembrane processes in separation technologies applied for natural and waste water treatment, as well as for the treatment of biological, pharmaceutical and food industry solutions. Really, there are at least three directions where electromembrane processes are 'hors concours' (which cannot or hardly can be realized with other techniques):

- 1) production of high purity water;
- 2) production of brines with highest possible concentration close to saturation;
- 3) pH correction of solutions with their simultaneous desalination or concentrations.

Each type of processes demands ion-exchange membranes with special properties. Thus, the treatment of diluted solutions and, in particular, production of high purity water (electrodeionization) can be improved when using the membranes enhancing the rate of mass transfer and reducing generation of H^+ and OH^- ions at membrane surface. Production of brines requires the membranes with reduced water transfer. pH correction can be realized with bipolar or asymmetric membranes allowing the control of H^+ and OH^- ions generation.

To be competitive, electromembrane techniques should apply cost efficient membranes. The ways of obtaining novel membranes dedicated for deep deionization, ultimate concentration and pH correction are analyzed. The main idea is to use as precursors not expensive commercial ion-exchange membranes and then improve them through surface of bulk modification.

Note that these electromembrane techniques are especially effective when combined with other membrane processes. They complete perfectly reverse osmosis by transforming its permeate stream into high purity water and the retentate stream into a highly concentrated brine. Examples of hybrid technologies applied for production of makeup water in heat-and-power engineering, for regeneration of processing liquids and water recycling in production of synthetic fibers and ammonia fertilizers are discussed.

PL 05

ION EXCHANGE MATERIALS FOR ENERGY PRODUCTION

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Ion exchange materials can be used in a variety of sustainable energy production systems such fuel cells, batteries and salinity gradient power generation (pressure retarded osmosis and reverse electrodialysis). This contribution shortly reviews the properties of polymers used in membrane based energy production systems based on salinity gradients. In particular, the contribution zooms in on the transport properties of ion exchange materials used for the production of energy through the process of reversed electrodialysis. A set of experimental techniques is required to precisely decouple transport in the hydrodynamic boundary layer from the properties of the membrane material itself. Understanding both hydrodynamic and membrane transport properties is necessary to guide membrane development and module design.

KL 01

EFFECT OF MEMBRANE SURFACE PROPERTIES ON THE MEMBRANE BEHAVIOR IN ELECTRODIALYSIS

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The way to prepare cost effective ion-exchange membranes with specified properties by surface modification of not expensive heterogeneous membranes seems quite attractive. For this aim, the relation between the state of the membrane surface and its electrochemical behavior is of great interest. In this paper, we will consider several types of membrane surface modification and the corresponding responses in variation of the surface properties and the overall membrane behavior. The effects of surface homogenization/heterogeneization, geometrical shape, hydrophilic/hydrophobic balance, change in the nature of functional fixed groups are considered.

An increase in overlimiting mass transfer is observed in case of MK-40 membrane coated with a homogeneous conducting film (MK-40+F), Fig. 1. This behavior is explained by appearance of electroconvective vortices: the presence of the coating film leads to an increase in the size of the conducting “gates” at the membrane surface that results in growing size of vortices, Fig. 2.

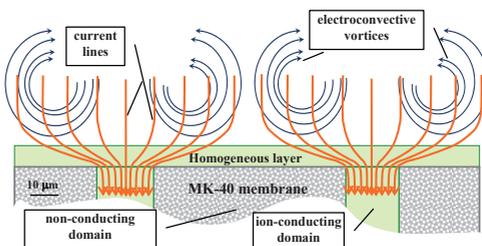
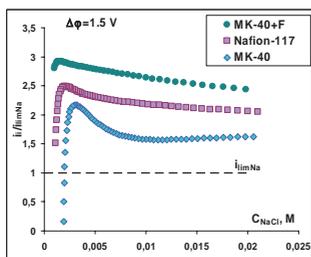


Fig. 1. Overlimiting current of Na⁺ ions across different membranes as a function of the feed solution concentration

Fig. 2. Scheme of electroconvective vortices in case of tailored MK-40+F membrane

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KL 02

POLYMERIC MATERIALS FOR MEMBRANE: NEW ASPECTS OF EMPIRICAL APPROACH FOR PREDICTION OF GAS PERMEABILITY PARAMETERS

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The amount of gas permeability data for polymers drastically increased during last decades. Thus, there is opportunity to check the more general hypothesis based on representative selection of the parameters choice including different polymeric materials such as homopolymers (polyimides, polyamides, polysulfones, polycarbonates, silicon-containing polymers, polyolefins, polyphosphasenes, etc.), copolymers, composite membrane materials and surface-modified membranes. In spite of accumulated data for more than 2000 polymers only a few of them are using at present as membrane gas separation materials. One of the reasons is problem of preliminary estimation of gas permeability parameters of polymeric material in relation to permanent gases, lower hydrocarbons and toxic gaseous components. This task can be carried out by systematic study of empirical regularities and comparison with some existing models of gas diffusion by using DATABASE containing of the most published gas permeability data. Paper presents the first step of this study including the DATABASE (more than 1400 polymers) organization algorithm, results of empirical statistical treatment of these data and consideration of the most understandable correlations between gas permeability parameters (permeability, diffusivity and solubility coefficients) of polymeric materials and key physical chemical properties of diffusing molecules. As a result the “empty spaces” of DATABASE for permanent gases were filled. Based on diffusing molecule configurations and their Lennard-Johnes potentials consideration the approach to the preliminary estimation of polymeric materials permeability in relation to permanent gases based on limited experimental data is considered. Particularity of estimation for lower hydrocarbons and toxic gaseous components permeability are discussed.

Acknowledgements

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SL A01

MORPHOLOGY TRANSITIONS AND ELECTROTRANSPORT PHENOMENA IN THE NANOCOMPOSITES BASED ON THE PERFLUORINATED SULFOCATIONIC MEMBRANES MF-4SC INCORPORATING POLYANILINE

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The synthesis of composite ion-exchange materials and investigation of their functional properties are relatively new research area in membrane electrochemistry and high-molecular chemistry. This area has attracted the interest of researches, which is due to the development of fuel cells and various sensor devices. The investigation of composites based on ion-exchange membranes and polyaniline (PAni) in a “free standing” state is of special interest because such composite materials can be used to promote the efficiency of electromembrane separation processes.

Most often such materials are obtained by chemical template synthesis, where various redox systems are electron acceptors during the oxidative polymerization of aniline. Various combinations of the aniline polymerization conditions, which allow to incorporate polyaniline both on the surface and in the membrane bulk, have been elaborated in this investigation. AFM, SEM images and curves of water distribution on the effective pore radii in the composite membranes testify to a morphology transition from the nano- to the microsize of polyaniline inclusions with increasing the aniline polymerization time. This work summarizes results on the synthesis, morphology and transport properties of the new grade nanocomposite materials based on polyaniline and ion-exchange membranes MF-4SC (Russia).

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References

1. N.P. Berezina, A.A.-R. Kubaisy (Sytcheva), S.V. Timofeev, L.V. Karpenko // *J. Solid State Electrochem.* 2007. Vol. 11. P. 378-389.
2. N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin // *Advances in Colloid and Interface Sci.* 2008. Vol.139. P.3-28.

SL A02

THE EFFECT OF INORGANIC ION EXCHANGE RESIN ON PROPERTIES OF HETEROGENEOUS ION EXCHANGE MEMBRANE

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This case study deals with relationships between characteristic properties of anorganic ion exchange resins and heterogeneous ion exchange membranes.

At the first stage the chemical and temperature stability, humidity and particle size distribution of different type of ion exchange resins was analyzed. At the second stage the membranes with different filler/polymer matrix ratio and different particle size of distribution of milled resins was prepared. Finally the different ion exchange resins were used for preparing of heterogeneous ion exchange membranes at fixed filler/polymer matrix ratio.

We analyzed many characteristic properties of input materials, intermediate and final products including process parameters during preparing of membranes.

We have found some important relationships between type of resins and membranes including influences to process of membrane preparation.

Our results show that most of ion exchange resins should be used for ion exchange membranes but with different characteristic properties. We also established that increasing of filler/polymer matrix ratio or using very fine particle size distribution improve electrochemical properties of membranes at the expense of worst mechanical properties and membrane preparation.

On the basis of these results we are able to modify composition of ion exchange membrane to reach required properties.

SL A03

ELECTRIC TRANSPORT OF SULFURIC AND PHOSPHORIC ACIDS THROUGH ANION-EXCHANGE MEMBRANES IN AQUEOUS SOLUTIONS

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The results on the separation of phosphoric acid from the sulfuric acid by the electrolysis method using anion-exchange membranes are presented. Two types of membranes have been tested – Neosepta ACM (Tokuyama Co., Japan) and Selemion AAV (Asahi Glass Engineering Co., Japan). The experimental results have been described by the model based on the extended Nernst-Planck equation and the Donnan equilibrium. The model includes two kinds of fitting parameters characterizing the membrane – the concentration of fixed charges, \bar{c}_m , and the parameter $k_{DV\theta,i} \equiv V_p \theta^{-2} \bar{D}_i D_i^{-1}$ being a combination of the volume fraction of pores, V_p , tortuosity, θ , and the ion diffusivity inside, \bar{D}_i , and outside the membrane, D_i . Regarding the ionic equilibria only the first stage of dissociation of H_3PO_4 has been assumed, however also the reactions leading to H_3PO_4^- and $\text{H}_6\text{P}_2\text{O}_8$ have been taken into account. The thickness of the polarization layer, necessary in the model fitting has been calculated from the experimentally determined limiting current density.

It has been found that the separation of H_2SO_4 and H_3PO_4 is possible only in a limited range. The limitation is caused not only by the increased dissociation of H_3PO_4 when the concentration of H_2SO_4 becomes low but also because of the loss of selectivity of the investigated membranes. The decreased current efficiency has also been reflected in the obtained optimal values of \bar{c}_m – for a pure H_2SO_4 solution it was 0.6 M, for the mixture $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ – 0.2-0.3 M, whereas for a pure H_3PO_4 solution \bar{c}_m was close to zero. Evidently, phosphate anions associate with functional groups of ACM and AAV membranes thus reducing their effective positive charge. Comparing the model fitting based on the species H_2PO_4^- and H_3PO_4 with that including also $\text{H}_5\text{P}_2\text{O}_8^-$ and $\text{H}_6\text{P}_2\text{O}_8$ no significant differences have been found except the fact that in the second case the time of computations was much longer.

SL A04

ION-EXCHANGE MEMBRANES FOR FUEL CELLS BASED ON VINYLPHOSPHONIC ACID COPOLYMERS

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Proton-exchange membranes for fuel cells must possess high proton conductance, and excellent thermal and chemical stability. Membranes based on sulfonated aromatic polymers have limited oxidation stability, and often poor mechanical properties, whereas sulfonated perfluorinated membranes are costly. An alternative is the development of proton-conductive, non-fluorinated aliphatic polymer membranes as they have excellent mechanical properties and a high thermal stability.

A series of vinylphosphonic acid copolymers with various contents of vinylphosphonic acid units were synthesized by radical polymerization using photopolymerisation. All the polymers were characterized by elemental analysis, ionic conductivity, water sorption, phosphoric acid sorption, TGA and oxidation stability. The resulting films displayed good mechanical properties and ability to adsorb phosphoric acid. The films based on vinylphosphonic acid copolymers exhibited high proton conductivity, therefore seem to be promising in proton exchange membranes for fuel cells.

SL A06

BEHAVIOR OF NAFION MEMBRANE AT ELEVATED TEMPERATURE AND PRESSURE

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In recent years production of electricity from renewable sources as are windmills and solar cells significantly increases. Despite ecological point of view its dependency on actual weather conditions is its crucial disadvantage. To ensure regular energy supply efficient energy storage is required. Hydrogen economy represents one of the generally accepted concepts of the energy production and storage in the future. As hydrogen production method from renewable sources water electrolysis is logical choice.

Water electrolysis can be realized by alkaline or acidic way. However alkaline water electrolysis is already well established industrial process, for intermittent operation acidic polymer electrolyte membrane (PEM) reactor is more suitable due its high current densities, compact and module design, good separator effect of product gases, etc. The application of PEM electrolysis suffers from several problems. High platinum metals catalysts loading is one of most important. Most promising method for catalyst loading reduction is to operate at elevated temperature above 1 (V) \square . The electrode kinetics will be enhanced and therefore the overpotentials at both electrodes reduced together with decreased of catalyst loading demand.

To elevate operation temperature requires new materials more chemically stable than currently used. Also the proton conductive membrane must be able to operate at desired conditions. The most often used membrane in conventional PEM fuel cells and PEM electrolyzers is perfluorinated membrane Nafion. The problems of Nafion operation at temperature above 100°C are widely known. In case of water electrolysis it is possible to operate at high pressure to ensure saturation of water also at higher temperature. The data about Nafion behavior at these conditions are missing. The Nafion conductivity was measured in temperature range 100 - 160°C and pressure up to 0.65 MPa. It was proven that Nafion exhibits sufficient conductivity also above 100°C in case of 100% relative humidity. Its capability to operate was tested during preliminary experiments in laboratory PEM electrolyser.

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SL A07

DIALYSIS OF AQUEOUS SOLUTION OF NITRIC ACID AND FERRIC NITRATE

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The separation of an $\text{HNO}_3 + \text{Fe}(\text{NO}_3)_3$ mixture using an anion-exchange membrane Neosepta-AFN has been investigated in a two-compartment dialysis cell with stirrers. The experiments and the subsequent data treatment have revealed that the partial flux of ferric nitrate is below 3 %, so that the membrane can be considered a very good separator for an $\text{HNO}_3 + \text{Fe}(\text{NO}_3)_3$ mixture. The analysis of ionic equilibria in aqueous solution of nitric acid and ferric nitrate has showed that no complexes of Fe^{3+} with NO_3^- ions bearing negative charges are formed by complexation reactions. Iron is preferably present in the form of Fe^{3+} ions. This results in large repulsive forces between Fe^{3+} ions and charged sites in the membrane phase, so that the transport of iron through the membrane is efficiently decelerated. The dialysis process can be quantified by four phenomenological coefficients, which are dependent upon the initial acid and salt concentrations in the compartment initially filled with $\text{HNO}_3 + \text{Fe}(\text{NO}_3)_3$ solution.

SL B01

INTENSIFICATION OF ELECTRODIALYSIS : MIXED CONTROL MODE WITH PULSE ELECTRIC FIELD

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These last years, the interest to lead electrodialysis in pulsed electric mode was shown [1-3]. The pulsed mode can make it possible to decrease the membrane fouling by organic species. Scaling can also be reduced. Lastly, a notable gain on the transferred electric charge was observed during desalination by pulsed electrodialysis. However, the precise mechanisms which are at the origin of these effects are not all clearly identified. For this purpose, a study modelling the transport within the diffusion boundary layers in pulsed mode was undertaken. The model used is particular from its boundary conditions because it must reflect the specific control mode of the current and potential in pulsed mode. Indeed, the devices used for chopping the current in pulsed electrodialysis relies on a transistor functioning in commutation. It results from this a mixed regulation mode for the electrodialytic cell. When the transistor is busy, it behaves like a closed switch and the potential difference at the boundaries of the electrodialysor is the one imposed by the potential source: the regulation mode is potentiostatic. When the transistor is blocked, it behaves like an open switch and the current is then imposed on a null value: the regulation mode is galvanostatic. These conditions taken into account, the simulation can be done for a simple 1D geometry or a 2D electrodialysor channel. The intensification of electrodialysis in pulsed mode can then be explained by regeneration of the diffusion boundary layer content by diffusion during switch off time, regeneration of the channel content by convection for low frequency mode.

[1] Ruiz, B., Sistat, P., Hugueta, P., Pourcelly, G., Aray-Farias, M. and Bazinet, L. Effect of pulsed electric field on anion-exchange membrane fouling during electrodialysis of a casein solution. *Desalination*, 200(1-3):208-209, 2006.

[2] Ruiz, B., Sistat, P., Hugueta, P., Pourcelly, G., Araya-Farias, M. and Bazinet, L. Application of relaxation periods during electrodialysis of a casein solution: Impact on anion-exchange membrane fouling. *Journal of Membrane Science*, 287(1):41 - 50, 5/1/2007.

[3] Casademont, C., Sistat, P., Ruiz, B., Pourcelly, G. and Bazinet, L. Electrodialysis of model salt solution containing whey proteins: Enhancement by pulsed electric field and modified cell configuration. *Journal of Membrane Science*, 2008.

SL B02

ELECTRODIALYSIS OF CHLORIDE SOLUTIONS CONTAINING MERCURY (II) IONS

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Despite worldwide reduction of usage of highly toxic mercury its application in chlorine industry, measuring and lighting device productions is still in use. To decrease ecological danger of such productions it is necessary to find effective methods which lower mercury losses from a production cycle and exclude mercury containing wastes. In the present work the process of electrodialysis of sodium chloride solution of 0,085M containing mercury (II) ions (from $2,5 \cdot 10^{-4}$ till 0,1M) with heterogeneous membranes MC-40, MA-40 and MA-41 is studied.

Calculations with the use of equilibrium and material balances have shown that in solutions under investigation neutral particles of HgCl_2 and complex anions of HgCl_3^- and HgCl_4^{2-} prevail and Hg^{2+} cations are practically absent. It explains intensive absorption of mercury by anion-exchange membranes MA-40 and MA-41 in quantity up to 6 and 4 mg-equiv/g respectively and practically inertness of the cation-exchange membrane MC-40 towards mercury containing ions.

It is stated that electrical conductivity of the membrane MA-40 on the average twice as lower as MA-41 membrane while their ion-exchange capacities are quite the contrary. Increase in absorption and decrease of counter-ions mobility in membrane MA-40 is connected with formation of $\text{Hg}(\text{OH})_2$ particles obtained as a result of hydrolysis of weakbase anion-exchange membrane and formation of coordination compound of $[(-\text{N})_2\text{Hg}]\text{Cl}_2$ type with the participation of deprotonised secondary and tertiary amino groups. This fact is proved by changes in IR-spectra and X-ray diagrams of the membranes in the areas corresponding to fluctuations of C-N links of amino groups.

The electrodialysis of sodium chloride solutions containing mercury ions with "hollow" channels formed by membrane pairs of MC-40 and MA-40 under current densities below limiting ones has shown presence of material balance, absence of hydroxides formaton and decrease of mercury concentration in desalination cells by 70-76 %. Filling the desalination channels with granules of ion-exchange resin of AV-17-8 type and cutting off the feed solution to the concentration channels has allowed increasing the degree of desalination up to 95-97 % calculating on mercury.

SL B03

SEPARATION OF SMALL ORGANIC IONS FROM SALTS BY ION EXCHANGE MEMBRANES IN ELECTRODIALYSIS

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Electrodialysis can be applied in the food and fermentation industry for separating inorganic salts and organic ions from other fractions. However, the separation efficiency for small organic ions has not been systematically studied. In this paper, the separation efficiency and transport properties of small organic ions from mixed salts by ion-exchange membranes are investigated. It was observed that separation of inorganic ions from organic solutes was feasible, but the efficiency was dependent on the size and charge of organic ions. The influence of key parameters, i.e., pH and current density on the solute flux (organic ions and inorganic ions) and on selectivity (between organic ions and inorganic ions; and between different organic ions) in electrodialysis was studied. It was shown that the selectivity can be influenced by changing pH and current density. Furthermore, competition between the small organic ions and inorganic ions is discussed. Finally, the effect of molecular size, charge (barrier effects) and hydrophobicity (diffusion) on solute transport in the electrodialysis stack will be systematically discussed based on the experimental results.

SL B04

BIOHYDROGEN PRODUCTION IN INTEGRATED SYSTEM

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Hydrogen – as a promising alternative energy carrier (“clean fuel”) – can be produced in several ways, including environment-friendly methods such as biological systems. The gas mixture – containing hydrogen – obtained in the fermentation process, however, is not suitable for direct utilisation, therefore it should be separated, which can be carried out by membrane gas separation.

Biohydrogen formation during the fermentation carried out by an *Escherichia coli* strain was studied in an integrated system, where a membrane module was built in.

Purified product was brought into fuel cell with proton exchange membranes based on aliphatic copolymers of vinyl phosphonic acid. The productivity and efficiency of integrated process was optimized.

The research work was supported by the Czech-Hungarian Science and Technology Cooperation Programme, grant No. CZ-8/08.

SL B05

SEPARATION OF THE PLATFORM CHEMICAL ITACONIC ACID OUT OF FERMENTATION BROTH

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Itaconic acid or methylenesuccinic acid ($C_5H_6O_4$) is a platform chemical with one methylene group and two carboxylic acid groups. Many fine chemicals and polymers derive from it like from the chemically similar acrylic acid derivatives. Specialised yeasts and moulds produce itaconate salts under limited conditions environmentally sound. We apply electrodialysis with bipolar membranes to separated itaconic acid together with other organic acid and metal ions from the fermentation broth into an acid and a caustic stream respectively. This separation is one process step of the green biomass process of the project "tailor made fuel from biomass" in which regenerative combustion fuels of the future shall be synthesised.

Our project aim is to develop an applicable and environmentally friendly process containing fermentation of green biomass, pre-treatment of fermentation broth and separation of purified itaconic acid. In the first project phase the fermentation and the separation of the itaconic acid by electrodialysis with bipolar membranes are studied separately.

For this project we bought an automated labplant which allows a production process similar to the industrial scale and an EDBM module with membranes from FuMA-Tech. For the energetic optimisation of the process with regards to the long term stability we study

- the influence of the pH-Value in the feed,
- the influence of temperature on the separation, and
- the acceptable concentration of bivalent ions.

Regarding the information available today, production of itaconic acid out of green biomass by fermentation and separation by electrodialysis with bipolar membranes is feasible and seems to be economically promising.

Acknowledgement: This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

SL B06

RECOVERY AND CONCENTRATION OF AMINO ACIDS BY ELECTRODIALYSIS WITH BIPOLAR MEMBRANES

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Amphoteric nature of amino acids one can consider a basis for their recovery and concentration from various solutions. Lecture focuses on the possibilities and quantitative characteristics of amino acids recovery and concentration in an electromembrane system with bipolar membranes. Two types of bipolar membranes are used for the concentration effectiveness comparison. Concentration factor has been calculated in a wide range of current density for amino acids with various side chains. The influence of monopolar membranes hydration on concentration effectiveness is discussed. The peculiarities of neutral amino acids electrodialysis recovery from the mixtures with sugars are discussed. The procedure is suggested as one of the last stages during microbiological synthesis of amino acids.

SL B07

DEMINERALIZATION OF NATURAL SWEET WHEY BY ELECTRODIALYSIS AT PILOT-PLANT SCALE

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Demineralization of sweet whey was performed in a pilot electro dialysis unit EWDU-P1 provided with EDR stack with 50 membrane pairs of membranes RALEX CMH-PES and AMH-PES. Experiments were carried out at 15 °C, which was chosen to reduce microbial growth and to minimize microbial degradation of organic components with nutritional value (especially lactose). Batch process of whey demineralization was ended when the conductivity of diluate decreased of 90 % (87 % decrease of ash content). During the process constant outer voltage was kept. The influence of different outer voltage and spacer width (0,8 mm and 1 mm) on the velocity of salt transport and energy consumption was studied. At higher outer voltage 90 % demineralization was reached earlier, but energy consumption increased too. The spacer width did not have significant effect on the length of the process and energy consumption. The transport of individual salts and losses organic components was studied too. The most effective was removal of chloride (up to 99 % removed) and potassium (95 %), the lowest cut was for magnesium (75 %) and sodium (80 %). Losses of lactose were negligible; decrease of crude protein content was maximally 5 %. Decrease of titrable acidity was observed too.

SL B08

DOW™ EDI MODULES PERFORM WELL AT BIOENERGY COMBINES IN SCANDINAVIA

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A Dow Chemical Company case study is presented here to introduce Dow spiral wound electrodeionization (EDI) technology and its optimum operation in one of the most modern bioenergy powerplants in Sweden.

EDI technology is a separation process that combines electro dialysis and conventional ion exchange. EDI is used to polish RO permeate of any residual ionic impurities. EDI is acquiring popularity in Europe due to the environmental and economical benefit of eliminating acid and caustic regenerants used for mixed bed deionizers and because it is a continuous process not a variable batch operation.

Dow EDI technology already has several reference plants in the USA and China in the water treatment market including several cogeneration installations that were designed using Dow EDI technology.

The bioenergy combine powerplant in Sweden generates around 48 GWh of electricity and 40 GWh of heat every year. The water available to feed the turbine is high conductivity tapwater with a high silica concentration which could deposit in the turbine and interrupt its correct work. Reverse osmosis doesn't entirely eliminate silica compounds. Higher water purification is done using EDI technology. The most common water treatment sequence in the Nordic countries is to use a softener followed by RO and EDI systems.

In the present study Water Processing turns to Dow for a complete water treatment. Water Processing is a loyal Dow OEM that relies on Dow Water Solutions products to guarantee its success in the water treatment market

Tapwater is pretreated using a complete Dow Water Solutions plant that consists of a softener with DOWEX(TM) Ion Exchange Resin, DOW(TM) FilmTec Reverse Osmosis elements and DOW(TM) EDI 210 modules. The capacity of the RO system is 6 m³/h and that of the EDI is 5, 5 m³/h. The RO feed water has a silica concentration of 1 ppm and 71, 44 ppm of TDS. EDI product water comes out completely satisfying client's needs, with a silica concentration reduced to < 20 ppb and product water resistivity increased to more than 15 Megohm-cm.

Dow Water Solutions can offer a broad range of top of the line state of the art component technologies designed for water purification. Dow EDI is the most economical and reliable technology available in the market for water boiler powerplants.

SL B09

APPLICATION OF ELECTROMEMBRANE PROCESSES IN DAIRY INDUSTRY

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Electrodialysis is one of the most important Electromembrane processes which is used in the Dairy Industry. The most common and ecologically necessary application of the Electrodialysis process is whey treatment.

The company MEGA is engaged in the given problematic from the beginning of 2003 and has already achieved some results in this direction:

- Possibility of processing not only sweet whey but acid with its further application in the baby food production;
- Improvement of technological lines on production of the different dairy products due to use of Electrodialysis equipment;
- Non-waste production of casein, curd, cheese and milk sugar;
- Possibility of producing of new generation products: lactulose, bifidogenic concentrate etc.

Lately greater work on studying influence of casein whey treatment by Electrodialysis has been made. As a result the demineralized casein whey (up to 90%) can be applied also in the baby food products.

SL C01

COMBINING MEMBRANE SEPARATION TECHNOLOGY AND FERMENTATION PROCESSES FOR IMPROVED PERFORMANCE

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Fermentation processes are often inhibited by the build-up of cell expressed products or by-products. Growth inhibitors like small organic acids or bases act by limiting the duration of the fermentative exponential growth phase resulting in less biomass reduced maximum product concentration, and limited overall production rates.

Novel electro membrane separation techniques like the patented REED™ technology (Reversing Electro-Enhanced Dialysis) are able to remove process inhibitors effectively, offering a healthier bioreactor condition, which results in prolonged exponential cell growth, more biomass and more products.

The ability of the REED separation system to extract and control growth inhibiting organic acids like lactic acid during fermentations has yielded significant increased productivities and product yields in various fed-batch fermentation setups (5-35 folds).

In a REED fermentation setup with anion-exchange membranes, anion inhibitors (e.g. lactate, acetate, etc.) generated in the complex fermentation broth are replaced by hydroxide ions from the dialysate. The result is an optimized controlled fed-batch fermentation process sustaining constant growth at a stable concentration of organic acids below the inhibition level.

Potential applications are in Bio refinery production of high-value bio-based chemicals, in the production of food ingredients, and in Biopharmaceutical productions using recombinant protein expressions systems.

SL C02

ENERGY EFFICIENT DEWATERING OF ETHANOL BY INDUSTRIAL SCALE NaA-ZEOLITE MEMBRANES

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As an alternative to the conventionally used processes of azeotropic distillation or pressure swing adsorption hydrophilic NaA-zeolite membranes can be used in a very energy efficient way to dewater ethanol by vapour permeation.

NaA-zeolite membranes (Fig. 1) in four channel geometry are produced by the German company inocermic GmbH (inocermic) in an industrial scale. These membranes show high flux and high selectivity in ethanol dewatering by pervaporation or vapour permeation. Since November 2007 the inocermic NaA-zeolite membranes



Fig. 1: NaA-zeolite membranes by inocermic in four channel geometry

demonstrate their good performance under production conditions with real feed mixtures in a demonstration plant (Fig. 2). These convincing separation properties led to the construction of an industrial plant with strongly enlarged membrane area (120 m²). In the meantime several industrial plants with 30,000 l/day, 60,000 l/day, 80,000 l/day, 100,000 l/day and 200,000 l/day bio ethanol production with inocermic NaA-zeolite membranes have been built or are under construction by GFT.

By an optimised combination of distillation, rectification and dehydration the steam consumption for the whole ethanol concentration could be reduced down to less than 1 kg of steam per 1 litre of dry ethanol. In combination with a mechanical vapour compression system it is also possible to operate the whole ethanol concentration process without steam with an electricity consumption of only 0.15 KW per 1 litre of dry ethanol.



Fig. 2: Installed vapor permeation membrane modules in the demonstration plant

SL C03

MINE WATERS IN THE CZECH REPUBLIC – CURRENT SITUATION AND TREND DEVELOPMENT

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Mine waters belong to unique waters, defined by §40, Directive No. 254/2001 (Water Directive) and by §40, Directive No. 44/1988 (Mine Directive). As unique waters are considered underground waters, surface waters and precipitation waters, which penetrate into the underground and strip mines areas by infiltration or gravitation from top wall, subsoil, side walls or by simple inflow of precipitation waters.

Pumped mine waters from strip or underground mines are affected by increased volumes of iron cations, manganese cations, sulphates anions, acid carbonates and by acid pH. Excess limit volumes of dissolved matters are typical.

According to Statutory Order No. 229/2007, which presents limit values of surface waters pollution, the concentration of characterised pollution of mine waters from specific mines (bituminous coal mines or lignite mines) does not allow direct discharge of these waters into the surface waters, not even their utilization without previous modification or treatment.

Mine waters treatment technology on particular localities of coal mining could be characterised as mechanical-chemical processes, including processes of solid matter sedimentation and further neutralization, oxidation and processes of chemical precipitation of metal ions.

This procedure ensures quality of treated waters for its discharge into the surface waters almost in all limited parameters of pollution. Exception is formed by excess limit concentration of dissolved matters (over 1000mg/l) and excess limit concentration of sulphates (over 300mg/l).

Principal possibilities of mine waters desulphurisation lie between section of biological, chemical and physico-chemical procedures. Selected desulphurisation bacteria are able, in respect to the specific conditions; reduce sulphates to nondissolved sulphides, which could be mechanically separated. This procedure is

SL C04

PIEZOELECTRICITY OF FERROELECTRET FILM

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Recently, the study of ferroelectrets with the perpendicular piezoelectric constant d_{33} larger than that of lead zirconate titanate (PZT) ceramics has progressed rapidly [1,2]. We investigated the piezoelectric motion of ferroelectrets fabricated from porous polyethylene (p-PE) film with the thickness of $30\mu\text{m}$ and porosity of 58%, by the piezoresponse force microscopy (PFM). Figure 1 shows the atomic force microscope (AFM) image of the ferroelectret p-PE (Fp-PE) film with d_{33} of 100 pC/N . Pores with the diameter of about $0.3\mu\text{m}$ is almost homogeneously distributed in the Fp-PE film. Figure 2 shows the PFM image of Fp-PE film under the application of ac voltage with the frequency of 10 kHz and the amplitude of 1V. Upon comparison of Figs. 1 and 2, it was found that the surroundings of the pore change position in one direction following the application of ac voltage, but positions other than those near the pore concerned are not allowed to move freely. These results indicate that the electrical charge in a cavity formed from a number of

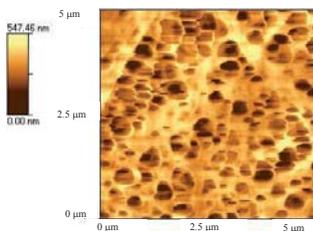


Fig. 1. AFM images of p-PE film. The color corresponds to the microscopic roughness on the surface of Fp-PE film.

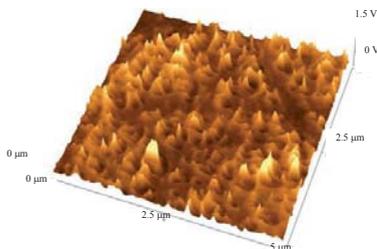


Fig. 2. Three-dimensional image of PFM of Fp-PE film. The height (voltage) corresponds to the displacement due to the piezoelectricity of Fp-PE film.

pores in Fp-PE film plays an important role in the piezoelectricity.

References

- [1] E. Fukada, IEEE Trans. of Diel. & Electr. Ins. 13 (2006) 1110.
- [2] S. Bauer, R. Mulhaupt, G. Sessler, Physics Today 57 (2004) 37.

SL C05

FERMENTATIVE METHANE GAS PRODUCTION FROM MUNICIPAL SEWAGE USING ANAEROBIC MEMBRANE BIOREACTOR

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A laboratory scale anaerobic membrane bioreactor (AnMBR) system for the fermentative methane gas production was operated for 60 days with municipal sewage as a sole carbon source. The AnMBR system utilized the external cross-flow membrane module and was equipped with on-line data acquisition which enables continuous monitoring of the performance of both bioreactor and membrane through the analyses of pH, temperature, gas production, permeate flow rate, and trans-membrane pressure (TMP). Such a configuration also provides an efficient tool to study rapid variations of monitoring parameters in the system, which would be impossible to explore in general.

The AnMBR resulted in a gradual increase of methane gas production from 63 to 71% which was normalized to the total chemical oxygen demand (COD) processed (i.e., VFAs- and methane-COD) from sludge waste along with the operation time. The residual COD in the effluent was attributed to acetic acid mainly and propionic acid.

Based on the resistance in-series model ($J = \Delta P / [\mu(R_m + R_{if} + \theta \cdot \Delta P)]$), the permeate flux is a function of TMP and there are two distinct pressure-dependent and pressure-independent regimes. The viscosity of permeate measured using a falling ball-type viscometer was 0.82 cp at 35°C and the biomass concentration in the reactor was 5.8 ± 0.3 gVS/L. Each resistance value (R_m and R_{if}) was determined from a flux profile on a clean and a fouled membrane after the surface rinsing. For the PVDF MF (0.07 μm) membrane, resistance values of R_m and R_{if} were $1.2 \cdot 10^{12}$ and $3.5 \cdot 10^{12} \text{ m}^{-1}$, respectively at the end of 60-d operation period. The obtained regression parameter value (θ) from a non-linear regression of the membrane performance data was $6.82 \cdot 10^{11}$ ($r^2=0.96$) $\text{psi}^{-1} \cdot \text{m}^{-1}$. The close fit between the model-estimated and experimentally measured permeate flux as a function of TMP confirms that the applicability of the resistance in-series model for the AnMBR system for the fermentative methane gas production from municipal sewage.

SL C06

INTEGRATED SOLUTION FOR BORON REMOVAL FROM SEAWATER USING RO PROCESS AND SORPTION-MEMBRANE FILTRATION HYBRID METHOD

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In this study, the possibility of implementing a new hybrid system which combines RO process with sorption-membrane filtration method was investigated (Fig. 1). RO tests were performed using a small-scale SWRO system which was established in Izmir-Urla region. Dowex (XUS 43594.00) ion exchange resin with a particle size of 0-20 μm was employed for removal of boron from RO permeates. A submerged-style hollow-fiber module containing two polypropylene membranes (diameter: 1.3 mm, thickness: 200 μm , pore diameter: 0.4 μm) was used throughout the sorption-membrane filtration hybrid system. Sorption of boron was performed on a fine powdered boron selective ion exchange resin and boron loaded resin was separated by microfiltration later on. The main advantage of sorption-membrane filtration hybrid process is the opportunity of using very fine particles of the resin, which increases specific surface and results in faster kinetics. The usage of very fine sorbents is not possible in fixed bed systems because it causes significant pressure drop and that results in a high pumping costs of the fluid through sorbent. Process variables such as resin concentration in the suspension, flow rates of fresh and saturated resins, and permeate have been evaluated in order to determine the efficiency of the hybrid process.

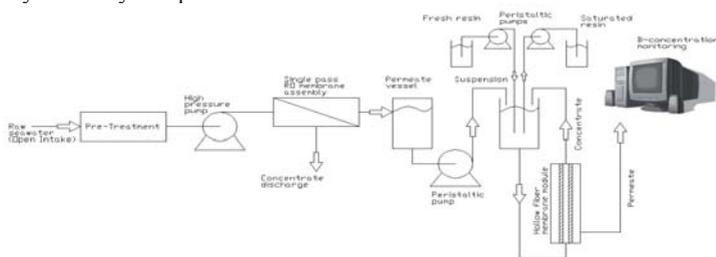


Fig. 1. Integrated RO process with the sorption-membrane filtration hybrid system

SL D01

CONTINUOUS BORON REMOVAL FROM WATER BY SPECIALLY SYNTHESIZED POLYMERS VIA POLYMER ENHANCED ULTRAFILTRATION

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Separation of borate anion from water down to very low concentration levels is required due to environmental considerations. Waste water with several ppms of boron can be hazardous to the surrounding vegetation. In Polymer Enhanced Ultrafiltration (PEUF) technique, the borate anions are bound to water soluble polymer molecules in homogeneous aqueous feed solution and this feed solution is to be passed through an ultrafiltration membrane to filter polymer-borate complexes.

In this study, special polymers were synthesized and used in the borate anion separation by PEUF. The synthesized polymers are polyglycidyl methacrylate functionalized with hydroxyl ethyl amino glycerol at three different molecular weights (PNSH, PNSM, and PNSL), a copolymer (COP) poly (4-vinyl-1, 3-dioxalan-2-on-co-vinyl acetate) and polyvinyl amine functionalized with glycidole (GPVA). Each polymer is dissolved in boric acid solution of 10ppm with several loading (boron/polymer mass ratio) values and this feed solution is filtered continuously by UF membrane. During the ultrafiltration experiments, samples from feed and permeate streams were taken and then boron concentrations in these samples were analyzed by ICP-OES. Retention values are calculated from boron concentration readings. Moreover, dynamic and static light scattering analyses were performed except for GPVA to investigate the conformational changes of the polymers in response to pH change and to the addition of boron into the feed solution. TOC measurements of the feed and permeate samples were also carried out in order to assure that the polymer molecules do not pass to the permeate stream.

Boron retention increased with increase in pH for all the polymers. The decrease in loading increased the retention for PNSM and PNSL but there was a problem of dissolution of PNSH for low loading values. The boron retention was constant when COP was used with loading values lower than 0.005. Maximum retention value was determined as 64% for PNS polymers and as 55% for COP. GPVA polymer showed a pH-sensitive boron uptake which increase steeply with pH increase from 7 to 9. Results have shown that the synthesized polymers are highly promising in borate removal from water.

Key Words: Ultrafiltration, borate anion separation, functional polymer.

SL D03

ENHANCED Cu/Zn SEPARATION AND POLYMER REGENERATION BY MEANS OF POLYMER SUPPORTED ULTRAFILTRATION (PSU) AND ELECTRODEPOSITION

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Nowadays, there exists a wide variety of industries that produce wastewater effluents with variable quantities of heavy metal ions. The finding of a suitable treatment technology for this kind of effluents is necessary from both, economical and environmental points of view. Within the last decades, several techniques have been developed to face up the treatment of diluted streams with heavy metal ions. Among them, Polymer Supported Ultrafiltration [1] offers clear advantages as compared to conventional techniques such as precipitation or ionic exchange. Several studies have showed the technical viability of this method, which most important advantages are low energetic and inversion costs, the use of compact units and a simple operational procedure.

In order to make economical and technically feasible a continuous process for metal ions recovery with this technique, it is necessary to face up the regeneration of the bonding agent and the recovery of the metal/s. In our research group, this regeneration is currently been done by electrodeposition of the retentate stream [2].

In the present work, we have taken advantage of a previous PSU study that dealt with the selective separation of the couple Cu/Zn. Here, we propose to join both, PSU and electrochemical steps to obtain a whole process in which the overall selectivity is higher than that obtained with each single step. In the electrochemical step, the retentate and/or the permeate stream pass through an electrochemical cell where the heavy metal ions can be selectively deposited. Taking into account the great difference between the standard reduction potentials of both metals (0.34 for Cu and -0.76 for Zn, vs. H^+/H_2) and the presence of the polymer (partially ethoxylated polyethylenimine), it is possible to enhance selectivity of the single PSU process.

The influence of the most important variables (presence of the polymer, Cu/Zn ratio and pH) on the selectivity of the whole process has been investigated.

References

[1] Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, G.; Dytnerky, Y., J. Membrane Sci. 1993, 79, 253.

[2] J. Llanos, Á. Pérez, P. Cañizares, Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration, J. Membr. Sci., 323 (2008) 28-36.

SL D04

SEPARATION OF CHROMATE ANION FROM AQUEOUS SOLUTIONS BY A WATER SOLUBLE FUNCTIONAL POLYMER VIA POLYMER ENHANCED ULTRAFILTRATION

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Many industrial waste water streams contain various metal ions. Many of these metals such as chromium, boron, mercury, cadmium are dangerous to human health and to the environment. Separation of these ions from aqueous solutions especially of low concentration is difficult. Polymer Enhanced Ultrafiltration is a method for separating species from low concentration solutions.

In Polymer Enhanced Ultrafiltration, a special polymer is dissolved in a solution including various metal ions which are attracted by the polymer dissolved. Then, this feed solution is filtered by UF membrane which does not allow the passage of polymer complexes through the pores.

In this study, a functional polyelectrolyte was synthesized for the removal of chromate from its aqueous solutions and the effects of parameters such as pH, loading (metal/polymer mass ratio) and concentration of competing ions on the chromate separation by PEUF (Polymer Enhanced Ultrafiltration) were investigated. Poly (N, N-diallyl morpholinium bromide) (PDAM), a quaternary ammonium polymer, was synthesized for the removal of chromate anions from water by PEUF. The polymer and potassium chromate were dissolved in the same aqueous solution with various loading values. Feed solution was then circulated through continuous ultrafiltration set-up maintaining constant feed concentration. Samples from feed and permeate streams were taken and analyzed for their chromium content by Atomic Absorption Spectrophotometer. Chromate retention values were calculated from feed and permeate concentration data.

Decrease in the loading values caused an increase in the chromate retention. However, for the loading values lower than 0.01, a slight decrease was observed in the retention values. The chromate retention was experimentally found to have increased at low pH values. In addition, the effect of competing anions, sulfate and chloride, on the chromate retention was investigated. It was found that sulfate decreased the retention of chromate more than chloride did and this is most probably because sulfate has higher negative charge than chloride has. Maximum retention was 70% at pH 7 and loading 0.01. In this study, satisfactory chromate retention values were obtained even at high competing anion concentrations.

Key Words: Ultrafiltration, chromate separation, functional polymer, polyelectrolyte.

SL D05

BALLAST WATER TREATMENT BY MEMBRANE FILTRATION FOR INDUSTRIAL APPLICATIONS

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Global shipping transports over 90% of the world's commodities in intercontinental traffic. In ships, ballast water is widely used to stabilize maritime vessels during voyage, it is also reported that three thousand species of animals and plants are transported around the world in ballast water every day. Ballast water is discharged at ports where cargo is loaded and the introduction of nonindigenous aquatic species along with the discharge of ballast water into these new environments may cause serious ecological and economical problems. Without natural predators in the new environments, these species might rapidly multiply and significantly alter the biodiversity of an ecosystem.

The significance of the ballast water issue was already acknowledged in an International Maritime Organization (IMO) resolution. Despite the global efforts of industry and IMO's guide, efficient, financially feasible, environmentally friendly and safe methods of preventing the translocation of harmful organisms via ballast water are still developing. Based on the National Research Council, it is recommended that filtration is the most promising ballast water treatment technology. However, granular media filtration, screen/disk filtration, and porous filter might not be economically and technologically feasible for shipboard ballast water treatment because of its heavy weight, low filtration rate, and large space requirements.

The objective of this study is to investigate the applicability of membrane filtration technology for ballast water treatment. The removal of particles, turbidity and organisms by membrane filtration was evaluated under various design, operational and water quality conditions. In addition, the effect of membrane types on removal efficiency was conducted in order to evaluate the filtration rate as an applicability of this technology. All filtration experiments showed a very good agreement with IMO guidelines, indicating the applicability of technology for membrane filtrations.

Key words: Ballast Water, Filtration, Marine, Membrane, Ship

SL D06

PERVAPORATION OF VOLATILE ORGANOHALOGEN COMPOUNDS THROUGH POLYDIMETHYLSILOXANE MEMBRANE

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Chlorinated hydrocarbon solvents (especially tetrachloroethene - TCE and dichloromethane - DCM) are often used for the dry-cleaning of clothes. These solvents (also at very low concentrations) are suspected of carcinogenic, mutagenic and teratogenic properties and thus represent a direct health risk to workers. Volatile organohalogen compounds can enter the human body by inhalation, dermal contact or inadvertent ingestion *via* hand-mouth contact. After intake, the chemicals may enter the bloodstream, they may either be accumulated or be excreted, usually with urine (in a non-metabolized form) [1]. Results of analysis of biological fluid samples such as blood, saliva and urine can be essential source of information about the level of human exposure to chloroorganic compounds.

Urine as a biological material is characterised by complex matrix what makes analytical work much more difficult and direct urine samples analysis impossible. Samples of this medium require special preparation which is based mostly on isolation (changing matrix) and/or analytes preconcentration prior to final determination.

The aim of this study was to find a new integrated procedure for the determination of tetrachloroethene and dichloromethane in water and human urine samples. Pervaporation, applying hydrophobic nonporous membranes, is one of separation techniques which could be used for the isolation of trace volatile substances from liquid samples [2].

Selective preconcentration TCE and DCM from aqueous solutions was performed using polydimethylsiloxane membranes. The pervaporation permeates were then analyzed by a direct aqueous injection (DAI) into a thick-film, non-polar gas chromatographic (GC) column with electron capture detector (ECD).

The basic parameters of this integrated pervaporation-DAI-GC-ECD procedure (e.g. temperature, time, fluxes) were determined. The new procedure has been validated, and the full uncertainty budget has been also calculated. This procedure presents a large opportunity for the analytical purposes.

[1] Hellweg, S., Demou, E., Scheringer, M., McKone, T.E., Hungerbühler, K., Confronting workplace exposure to chemicals with LCA: examples of trichloroethylene and perchloroethylenen metal degreasing and dry cleaning. *Environ. Sci. Technol.* 39, 7741-7748 (2005).

[2] Jakubowska N, Kujawski W, Polkowska Ż, Konieczka P, Namieśnik J, Procedure of determination of volatile trihalomethanes in human urine with pervaporation and gas chromatography, *Intern. J. Environ. Anal. Chem.* 87, 449-457 (2007).

SL D07

RECOVERY OF n-BUTYLALCOHOL USING PERVAPORATION MEMBRANE

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The aroma compounds of foods can be damaged in big rate or lost during the course of processing in connection with the applied pressure and temperature. The pervaporational membrane separation is available to eliminate the organic compounds solved in water. The application of high temperature can be avoid during this process, so the separation of heat-sensitive and volatile compounds can be separated as well.

We can meet the problem of the volatile organic compound loss caused by evaporation during the process and concentration of foods. The concentration of fruit juices and drinks is carried out by evaporation widespread. The deposition, heat degradation, the evaporation loss of volatile compounds and the burning to the evaporator can cause problem during the concentration by evaporation. We have to take in account the remarkable loss of the aroma compounds near the vaporization of water. The evaporated aroma compounds are recovered in the industry by rectification made on high temperature and washing the gas. The high rate of the aroma compounds can be found in steam come off the evaporation can be recovered by vapour permeation (in case the vapour is lead directly to the membrane) or pervaporation in case condense is lead to the membrane surface. Earlier experiences show that a part of the aroma compounds get to permeate during multi level membrane concentration, so the recovery of these can be reasonable as well.

In the fuel-industry n-butyl-alcohol is sustained to be a new organic material in case of the bio-fuel production. The ABE synthesis results in a 2w% concentration of n-butyl-alcohol content in aqueous mixture, so the separation and purification is necessary. Pervaporation could be an effective and economical way to produce bio fuel.

During my experiments the separation of model solutions were studied. My primary goal was to determine the factors used to the characterisation of separation efficiency such as permeate flux, activation energy and separation factor.

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SL D08

APPLICATION OF MEMBRANE PROCESSES FOR CONCENTRATION OF RASPBERRY (*RUBUS IDAEUS L.*) JUICE

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Last few years customers choose healthier lifestyle, and they are seeking for products which are rich in vitamins and minerals. The raspberry is rich in C-, P- and B9-vitamin, and anthocyanin, organic acid and phenolic contents are remarkable in it. These valuable components of raspberry have a good effect on human organism.

Mild concentration of raspberry by membrane-filtration was the aim of our experiments. For prefiltration, to remove suspended solids, ceramic tube microfiltration-membrane (MF) was applied. The prefiltered raspberry juice was concentrated by nanofiltration (NF) and reverse osmosis (RO). The effect of operational parameters, like transmembrane pressure and recycle flow rate, on the permeate flux and concentrations of retentate were studied. In case of RO the further concentration of the retentate juice of NF and RO were carried out by osmotic distillation (OD). On the basis of the experimental results using the resistance in series model, the membrane-, fouling- and the polarization layer resistance were determined in case of micro- and nanofiltration. In the experiments of prefiltration and concentration total soluble solid (TSS) content, the total acid, phenolics, capacity of antioxidants and anthocyanin content of samples were determined. The RO and OD permeate were compared with fresh raspberry juice by sampling. Sensory analysis was performed to compare the colour, odour, flavour, acid taste and general impression of different raspberry samples. The total number of cells and number of yeasts were determined with microbiological examination.

On the basis of the experimental results it should be concluded, that the applied microfiltration membrane (MF) was suitable for prefiltration. The Nanofiltration (NF) was competent for preconcentrating the fruit juice until 18% TSS. The reverse osmosis (RO) was suitable for concentration until 25-28% TSS and with osmotic distillation (OD) we reached 67% TSS. The competence of membrane filtrations was supported by chemical analysis.

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SL D09

SELECTIVE SEPARATION OF AMINO ACIDS BY REACTIVE EXTRACTION WITH TOMAC IN HOLLOW FIBER CONTACTORS

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Amino acids are often used as raw materials in the chemical, food and pharmaceutical industries. This study examines two amino acid models in increasing use nowadays: phenylglycine, used in the synthesis of β -lactam antibiotics, and aspartic acid, mainly used in the production of aspartame. Ion exchange or chromatographic techniques are used to carry out amino acids separation from fermentation broths or wastewaters, involving several concentration and separation stages, the cost of which may reach up to 50% of the production costs.

New separation processes are being investigated in order to lower processing costs and to improve their separation yield. Membrane processes have the advantages of large-scale separation, energy-saving and easy operation. Extractive ultrafiltration using membrane contactors in connection with the reactive liquid-liquid extraction are being used as a novel hybrid membrane process. This avoids many of the shortcomings associated with solvent extraction in conventional processes. The aqueous-organic interface is immobilized at the membrane pores by applying a higher pressure on the side having the non-wetting phase.

The aim of this work was to study and optimize the membrane-based solvent extraction of phenylglycine and aspartic acid from aqueous solutions at pH=11 containing individual or binary mixtures of the aforementioned amino acids by trioctylmethylammonium chloride (TOMAC) in decanol, and the simultaneous membrane-based solvent stripping by chloride aqueous solutions (1N HCl + 2N NaCl) using two Celgard X-50 hollow-fiber membrane contactors. This integrated extraction-stripping membrane process allows regenerating of the organic phase and concentrating the amino acid. An easy predictive mathematical model that considers the competitive extraction of each amino acid with the TOMAC has been developed to estimate the overall mass transfer coefficient and simulate the concentration profiles of the three phases. The effect of the hydrodynamic conditions on the mass-transfer rates was analyzed.

The treatment of the final feed and stripping phases was also investigated in order to achieve the separation of both amino acids.

SL D10

BIO-MICROCAPSULES PREPARATION BY MEMBRANE PROCESS FOR A CONTROLLED RELEASE OF NATURAL ANTIMICROBIALS

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Capsules of different materials can be employed for many industrial applications such as cosmetic, pharmaceutical, chemical and food packaging.

In particular, micro-encapsulation is a promising technology for protecting the natural active substances from the stresses and damages that can occur during the food package manufacturing, for improving the capsules distribution in film, for preventing or minimising the loss of efficacy and for modulating the water resistance of the biodegradable materials. Thanks to these effects and according to their structure, the microcapsules could better control the release of the active substances and promote the interaction of the film with the active substances carrier.

In this work, bio-microcapsules of chitosan have been developed by a membrane process using a mono-porous polymeric film. This technique permitted the formation of monodispersed bio-polymer droplets which were then cross linked with a natural additive adapted for this polymer structure that enhanced the water resistance of chitosan. The capsule size and morphology was adjusted changing the ingredient parameters such as the cross-linking concentration and tailored with the pore diameter of the mono-porous film employed. Furthermore, two different types of natural antimicrobial, were included in the capsules making the loading both during their production and after the droplet formation. The most effective entrapping method was then selected considering the amount of natural antimicrobial incorporated. The chemical-physical analysis of the new chitosan microcapsules was carried out by means of SEM and EDX. The antimicrobial activity of the microcapsules was assayed by turbidimetric methods against *S. aureus* and *Pseudomonas spp*, selected as dangerous and common microorganisms respectively, which may be present in fresh food.

Results are reported about the relationship between the amount of natural active substances released by microcapsules and the different degree of crosslinking, as well as the effects of the technological variables investigated on the kinetics of antimicrobial release.

SL D11

ABSORBING PERVAPORATION - A NEW TYPE OF MEMBRANE CONTACTORS FOR GAS SEPARATION

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Research and development of the membrane gas separation had shown the high efficiency of this method. But for some pairs of separated gases there is no membrane with according selectivity. In this case the hybrids separation method which is combining membrane gas separation with another traditional separation method is promising for investigation.

In the present work gas separation and high purification by combined method of absorbing and pervaporation design in one mass-transfer apparatus was analyzed. This method is named absorbing pervaporation and looks like a type of membrane contactor in which the advantages of both absorbing (wide range of absorbents) and pervaporation (continuous operating) are combined. And also there are the advantages of hybrid method which are multiplicative selectivity and low energy and material consumption.

The math model was considered for separation processes realized in apparatus consisting of few membrane modules filled by absorbent. The gas mixture consistently follows through these membrane modules being gradually separated from more soluble and more penetratable component. Gas mixture follows through absorbent by bubbling.

In calculation of separation process the two-film model of mass-transfer was used. The mass-transfer equation for single membrane module was found. In the case when the pressure of the low pressure cavity of membrane module is close to zero it was shown that separation degree of apparatus consisting of N membrane modules is equaled to $(P_{in}/P_{out})^N$, where P_{in} and P_{out} – pressure of input and output of membrane module, respectively. This value is enough for separation of the most of gas mixtures.

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SL D12

SEPARATION OF LACTIC ACID WITH HOLLOW FIBER SUPPORTED LIQUID MEMBRANES BASED ON IONIC LIQUIDS

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A typical example of a bioproduction process using whole-cell and organic solvents is the extractive fermentation of ethanol, acetone-butanol or organic acid. Particularly, lactic acid production by fermentation has gained interest because optically pure lactic acid is the raw material of a biodegradable polymer. The economics of the process, however, depend on the development of an effective recovery method for lactic acid from the broth because the separation and purification steps account for up to 50% of the production costs. Solvent extraction has been proposed as a promising recovery technique and as an alternative to the conventional precipitation process. The suitability of ionic liquids as green solvents for chemical processes has been extensively recognized due to their having effectively no vapor pressure, which lends them to be replacements for volatile, conventional organic solvents.

However, using a large amount of ionic liquids as solvents in liquid-liquid extraction systems is expensive due to the extremely high cost of ionic liquids compared with conventional organic solvents. Recently, a supported liquid membrane system has been studied using ionic liquids as membrane solutions. Although a supported liquid membrane process, which combines extraction and stripping processes, reduces the amount of solvent more than liquid-liquid extraction systems, membrane stability was critical. In our study concerning penicillin G permeation through supported liquid membrane using ionic liquids, we found that the membrane solution was retained without leaking. In this paper, hollow fiber supported liquid membrane using ionic liquids were examined for recovering lactic acid. A porous polypropylene hollow fiber was used. The membranes were prepared by immersing the hollow fibers in the ionic liquid for 24 hours in a desiccator. The experiments were carried out in a batch mode. The recovery ratio of lactic acid in the hollow fiber membrane system reached 87.1% after 10 h. Uphill transport of lactic acid was achieved by using the ionic liquids having hydrophobic cation and hydrophilic anion, such as Aliquat 336, Cyphos 101 as a membrane solution and hydrochloric acid as a stripping agent.

SL D13

THE PRESSURE MEMBRANE TECHNIQUES AS BAT IN DAIRY INDUSTRY

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Progress of industrial development since years has been causing problems with increasing amount of environmental pollution as well as the levels of sources and energy consumption. Finally the environmental problems were considered as the prior value in the European Union law regulations.

In the 1996 year common rules for permitting and controlling industrial installations were adopted by the European Council as the Integrated pollution Prevention and Control (IPPC) Directive which is one of the most important law regulations in EU. The idea of integrated approach which focused on to a high level of environmental protection taken as a whole was introduced as one of the IPPC Directive principles.

In essence, the IPPC Directive is about minimising pollution from various industrial sources. According to the Annex I of the IPPC Directive operators of industrial installations are required to obtain an authorisation (environmental permit) from the authorities in the EU countries. The conditions of the authorisation are mainly based on Best Available Techniques (BAT), the second principle of the IPPC Directive.

BAT definition is held indications for the technologies in practical usage as well as the way in which installations are operated to ensure an integrated approach to various environmental problems. On the other hand BAT takes into account the balance between the costs and environmental benefits [1].

As for many other food processing industries, the main environmental impacts related to the dairy industry are: the high consumption of water, the discharge of effluent with a high organic load like whey in the wastewater, and the consumption of energy for heating and cooling.

Increasing demand for the processed food technology related to the high level of environmental protection is offered by membrane processes.

The benefits being a result of the membranes techniques go far beyond the direct balance of expenditures and profits – the practical employment of membranes is one of the methods leading to rationalization of industrial technologies what is the aim of the new European law regulations such as the IPPC Directive.

References

1. The IPPC Directive (Directive 1996/61/EC) has been recently codified (Directive 2008/1/EC)

SL D14

COMPARISON BETWEEN STIRRED AND VIBRATED UF MODULES

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Whey, a co-product of the cheese-making and casein industry, is a nutritious protein source. The process of whey concentration was important historically, as the application of ultrafiltration (UF) in the dairy industry started with the separation and concentration of whey proteins from whey. In order to improve the performance of UF, it is beneficial to limit the extent of fouling of the membranes.

In this study, the performances of a vibratory shear-enhanced filtration process and a batch-stirred dead-end ultrafiltration process for the concentration of cheese whey were investigated with UF, C-30F regenerated cellulose and polysulfone 30 kDa nominal molecular weight limit membranes. The separations of protein and dry matter were examined by means of an IR technique and the Kjeldahl method. The turbidity and the chemical oxygen demand were also measured during concentration experiments. The volume of the pretreated (pasteurized) feed whey was decreased to 50% and 17.6% in the stirred and vibrated membrane processes, respectively.

The concentrates or retentates of the membrane separations were examined as energy sources for the possibilities of further utilization. In order to increase the biodegradability and biogas production of the concentrated whey conventional heating and microwave irradiation were compared. The results demonstrated that microwave pretreatment is the most appropriate process for enhancement of the biodegradability by hydrolysis of large molecules of whey concentrates.

Keywords: Whey, Ultrafiltration, Regenerated cellulose membrane, Polysulfone membrane, C30F, VSEP, Membrane resistance, Biogas, Biodegradability

SL D15

SORPTION OF C₁-C₆ ALCOHOLS IN PERFLUORINATED POLYMERS

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Excellent thermal and chemical properties of amorphous glassy perfluoropolymers (PFPs) make them interesting for ‘wet’ gas treatment or organic-organic separations but their potential is still not fully explored yet¹. Samples of flat membranes from copolymers of Teflon AF 2400 {2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole with tetrafluoroethylene, Du Pont} were used for C₁-C₆ vapour sorption experiments with vapour activity from 0.1 to 0.9. Measurements were performed gravimetrically at 298.15 K by the sorption apparatus equipped with the calibrated quartz (McBain’s) spiral balance² and from experimental data the sorption isotherms and the values of diffusion coefficients were determined^{1,2}.

Reference

1. J. C. Jansen, K. Friess, E. Drioli, Transport of alcohol vapours in amorphous glassy perfluoropolymer membranes with high fractional free volume: evaluation of clustering through time lag measurements (in preparation)
2. K. Friess, J. C. Jansen, O. Vopička, A. Randová, V. Hynek, M. Šípek, L. Bartovská, P. Izák, M. Dingemans, Jo Dewulf, H. Van Langenhove, E. Drioli: Comparative study of sorption and permeation techniques for the determination of heptane and toluene transport in polyethylene membranes. (Submitted into *J. Membrane Sci.* in November 2008)

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SL D16

BIOMETHANE PRODUCTION BY GAS SEPARATION MEMBRANES

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Biogas produced from agro wastes is a gas mixture containing mostly methane (45-85%), carbon dioxide (23-50%), hydrogen (up to 2%) and hydrogen sulphide usually is saturated with water. Biogas can be used for several purposes: direct energetic usage, power generation, compression and usage as fuel, or usage as a natural gas substitute (biomethane) after purification and compression.

For the usage as a natural gas substitute it is important to develop an efficient and reasonable technology to provide necessary BTU value and H₂S, CO₂, N₂, O₂, H₂O concentrations under limitation. Membrane technologies provide several advantages for this gas separation problem: environmental safe process, high effectiveness, low energy demand, mobile module system...etc.

The aim of this work was to develop a membrane separation technology and to test the technology in combination with a biogas fermentation for the digestion of different agro-wastes.

We have tested different commercially available polymer membranes (UBE, Japan) and some supported liquid membranes (SLM) using room temperature ionic liquids (RTIL). The polymer membranes are efficient and reliable in CO₂ and H₂S separation, but they need high pressure thus high energy, to provide affordable methane loss during the separation. SLM membranes usually work at lower pressure and have excellent selectivity. The membranes are evaluated with single gases and model gas mixtures while the online analysis was provided by photo acoustic detection (PAD). Biogas fermentation was performed in batch fermentors, inoculated with mesophilic methanogenic culture using different agro wastes.

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SL D17

MEMBRANE PROCESSES IN WATER TREATMENT AT THE URANIUM CHEMICAL MILL

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Uranium ore mined in the Rožná deposit is treated at a chemical mill situated in the close vicinity of the Rožná mine. The final product of the milling is a uranium concentrate, ammonium diuranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$, a so-called “yellow cake” which is treated into a fuel for nuclear power plants in conversion facilities abroad.

The milling is carried out under the condition of the closed cycle of technology water. Due to the positive annual precipitation balance, the over balance of technology water in tailing ponds has to be purified before discharging into a river. The water in the tailing ponds has high salinity – about 33 g/l. It is a complicated system of a lot of inorganic and organic compounds where the predominant contaminant is sodium sulphate. Evaporation and membrane processes (electrodialysis and reverse osmosis) are used to purify the water.

Electrodialysis has been tested at the mill since 1980s. There was installed a laboratory equipment and then a pilot plant. The small-scale plant of 10 electrolysers with capacity $70\,000\text{m}^3$ of dilute annually has been working at the mill since 1996. The full-scale plant of 30 electrolysers (type ED II-II made by MEGA a.s.) was put into operation in 2007. The plant is used for desalination of the tailing ponds’ water from TDS 33 g/l to 15 g/l. The capacity of the equipment is $70\text{ m}^3/\text{hour}$. All got parameters show that this technology is very suitable for purification of the technological water.

Tests with application of reverse osmosis for water treatment were started in 2000. Treating of the raw technological water from a tailing pond, the water after pretreatment and the diluate with various concentrations of salts were tested. The full scale application with annual capacity of $230\,000\text{ m}^3$ permeate for desalination of diluate with TDS about 15 g/l started in 2007.

During the operation a great force is devoted to optimization of pretreatment to save membranes and to prolong their lifetime period.

SL D18

INTEGRATED MEMBRANE/PSA SYSTEMS FOR HYDROGEN RECOVERY FROM GAS MIXTURES

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The problems of hydrogen recovery from multicomponent gas mixtures assume the development of safe technologies with low power consumption. Membrane and adsorption methods are examples of such processes, since they do not require energy for phase transition. The paper presents the results of efficiency estimation of the membrane-adsorption systems combining the gas separation by membrane module based on commercially available polymeric membranes with pressure swing adsorption (PSA) based on new porous carbon adsorbents for hydrogen recovery (for example, from bio-hydrogen produced by bacteria, from bio-synthesis gas obtained from solid organic wastes and wood or from acetylene production processes). The use of integrated gas separation system consisting of membrane modules and well known PSA unit has been examined in this study. We also present the results of comparison of modules based on commercially available membranes (GENERON hollow fiber membranes and flat sheet membranes based on PVTMS) for hydrogen recovery from multicomponent gas mixtures containing CO, CO₂, N₂, and H₂S. The estimation of H₂S, CO, H₂O permeability of membranes was carried out by the correlation method. The comparative analysis of membrane modules mentioned above for pre-concentration of H₂ from multicomponent gas mixtures including CO, CO₂, N₂, and H₂S has been made. Taking into account the principle of gas separation under operating conditions of PSA we considered the basic classes of adsorbents for effective hydrogen recovery. It is known that the particular problem of this process is the presence of acid gases. This problem can be solved by the combination of membrane and adsorption processes.

It is shown that hydrogen recovery degree may achieve 90-97% for bio-synthesis gas and petrochemical gas in case of 70% hydrogen pre-concentration at the membrane stage. As a result, the hydrogen of 99.9 % purity may be obtained at the PSA stage. The obtained data correspond to well known membranes and adsorbents and can be considerably improved by using of new effective membrane materials and adsorbents.

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SL D19

OPTIMAL OPERATIONAL DESIGN IN BATCH DIAFILTRATION

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The traditional diafiltration (TD) process may involve three steps: (i) pre-concentration step; (ii) constant volume diafiltration step, to reduce microsolite concentration; and (iii) post-concentration step, which is used to concentrate the macrosolute. In contrary with that, variable volume diafiltration (VVD) is an operation mode in which fresh water is continuously added to the feed tank at a rate that is less than the permeate flow. This causes a simultaneous concentration of macrosolute and reduction of microsolite. These concepts of membrane diafiltration are widely used for many fields of industrial separations, including also virus purification and recovery. Although diafiltration is generally considered as a proven technology, there is still a real need for model-assisted process design. In this study, a mathematical frame for modeling various diafiltration modes is provided. The approach followed in this work hands separately the design equations of the system configuration and the models of mass transfer through the membrane. The numerical solution of the proposed set of ordinary differential equations allows the prediction of the dynamic behaviour of diafiltration systems. The presented simulation technique is a useful tool for evaluating the optimal system design, operation, and control. The purpose of the optimization is to find the set of operational parameters which result in the most economical process and satisfy the given technological demands of the final product. The different diafiltration operations are compared in respect to total operation time, total product loss, and wash water utilization.

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SL D20

EFFECTIVE FOULING CONTROL ON A NF MEMBRANE MODULE: A THREE YEAR LONG CASE STUDY

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The continuous operation for three years of a spiral wound NF membrane for olive vegetation waste water treatment will be discussed. The membrane module was firstly used at the beginning of year 2006, and after that continuously operated for critical flux studies on a 100 litre batch system for the purification of olive vegetation waste water.

The olive vegetation waste water is a waste stream produced by the olive oil mill factories, characterized by a very high organic matter (COD values equal to 50-150 g/l).

Without fouling control, membranes would reach zero-flux condition very fast, within days. This was not the case of the analyzed NF membrane module, which was successfully operated for three years within the continuous Laboratory work of many different Students at the Department of Chemical Engineering. This result can be reached only by proper fouling control, which relays on both critical flux measurements and optimized operation methods previously developed by the Authors.

Since fouling control especially on real waste water stream does not mean necessarily that the membrane performances didn't change at all, the present work aims to review the collected data on the pure water permeability, the COD and polyphenols rejection and the critical flux values of this NF module. The changes of these key parameters throughout the years will be discussed, and moreover how fouling control may (or not) maintain satisfying separation performances.

Nowadays, the NF module is still used in Laboratory works since it has still flux values above the sustainable flux and rejection values compatible to waste water purification purposes, and thus represent the best possible validation for the adopted fouling control methods.

SL D21

ENZYMES MODIFIED MEMBRANES BY USING POLYELECTROLYTE LAYER

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Immobilization of enzymes on a solid support is absolutely among the most important problems in modern biotechnology. The immobilization of enzymes increases their stability in many cases. However, the enhancement of stability is advantageous for the industrial application of enzymes. Only a few of practical applications of the immobilized enzymes have been reported, and this because of the choice of appropriate support material and simple immobilization method. The purpose here is to integrate both functions (biocatalysis and separation) in the membrane structure by direct enzyme immobilization on synthetic ultrafiltration membranes. In these processes the membrane is only a separator, and to improve these processes it would be interesting to use the membrane to achieve other functions as it is in the natural membrane that makes, beyond the selective permeability, conversion of energy and chemical synthesis. The layer-by-layer technique, which was introduced by Decher, opens new possibilities for enzyme immobilization. Since enzymes are multiply charged molecules, electrostatic adsorption seems to be one of the simplest ways to perform the immobilization.

We show here the efficiency of the physical adsorption method to immobilize enzyme on the surface of polyacrylonitrile (PAN) and PAN modified with polyelectrolytes membranes. We studied here 2 types of immobilization: the first was inside the pores (case of trypsin) and the second one was onto the surface (case of urease). Moreover transport experiments through these catalytic materials have been carried out in ultrafiltration cell. Permeability of substrate and buffer have been calculated and correlated to the enzymatic activity of the modified membrane. A mathematical model was derived to determine rate of mass transfer of substrate through trypsin immobilized membranes.

We have shown the efficiency of the physical adsorption method to immobilize enzyme on the PAN and PAN modified membranes with a very good storage stability. However, the immobilization of enzymes on polymeric membrane has become an good approach for enhancing their utility in biotechnology. Besides, the method proposed for surface modification seems to be versatile and its main advantage consists of its simplicity and stability. The effect of coupling between enzymatic reaction and transport has been also demonstrated.

SL D22

MEMBRANE-ASSISTED SEPARATION OF MICROBIAL LIQUID AND GASEOUS FUELS FROM RENEWABLE SOURCES

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Microbial production of gaseous or liquid products for the fueling is known for a long time. Biomethane and bioethanol is used for the car engines as well as biodiesel. But for the new challenges with renewable energy resources there must be a new technology evolved for the new fuels obtaining and recovery. Lot of fuels and its derivatives could be produced from renewable sources with microbial processes aerobically and anaerobically. Basically, the microbial products are produced as the mixtures and with application of membrane technologies it could be separated into individual pure components. Developed continuous pure methane obtaining process from algae biomass will be demonstrated with effective sunlight energy conversion into gaseous fuel, as well as hydrogen generation process from lignocellulose, both with membrane-assisted recovery of pure methane and hydrogen. The problems with submerged membrane technology for the recovery and concentration of liquid fuels (ethanol, butanol) from microbial processes will be discussed and solutions for the implementations of non-porous membranes will be explained. New horizons for the using of membranes in the future “microbial chemistry” processes and use of pure cultures and stable microbial consortia for the production of bulk chemicals for large-scale synthesis will be discussed.

SL E01

THE EFFECT OF THE CONCENTRATION POLARIZATION AND THE MEMBRANE LAYER MASS TRANSPORT ON THE MEMBRANE SEPARATION

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The negative effect of the stagnant concentration boundary layer on the mass transport through a membrane has been investigated for a long time. It was proved that this layer can be a major limiting factor in various membrane separation processes as e.g. gas separation, pervaporation, etc. The well known polarization equation $[(C_m - C_p)/(C_b - C_p)] = \exp(Pe)$, e.g. Baker et al., 1997] does not give, however, any information how the mass transport parameters of the membrane matrix, e.g. the solubility coefficient, membrane Peclet number, can affect the concentration profile of the boundary layer, and consequently, the separation efficiency. The question to be answered is how the C_p value (concentration in permeate) is affected by the mass transport properties of the membrane layer in presence of the concentration polarization layer containing convective flow, as well. This is not investigated in detail yet. This paper gives the suitable mathematical expressions, in order to predict the well known parameters as polarization modulus, enrichment factors, etc., taking into account the transport parameters for both the concentration boundary and the membrane layers, and discusses the concentration distribution and the polarization modulus. The developed model involve as limiting case the polarization equation mentioned above, as well. It will be shown that the transport properties of the membrane layer have significant effect on the concentration profiles of the boundary layer and thus, on the polarization modulus, enrichment factors, etc., as well. As a case study pervaporation of dilute organic components will be discussed.

R.W. Baker, J.G. Wijmans, A.L. Athayde, R. Daniels, J.H., Ly, M.Le, The effect of concentration polarization on the separation of volatile organic compounds from water by pervaporation, *J. Membrane Sci.*, 137 (1997) 159-172.

SL E02

INFLUENCE OF IONIC LIQUID CONTENT ON PROPERTIES OF DENSE POLYMER MEMBRANES

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The polydimethylsiloxane membranes containing 0, 10, 20 or 30 wt. % of ionic liquid (benzyl-3-butylimidazolium tetrafluoroborate) were used for separation of butan-1-ol from water. Differential scanning calorimetry measurements showed that PDMS and [BBIM][BF₄] are not compatible and therefore PDMS-[BBIM][BF₄] membranes (though optically homogeneous) contain amorphous and crystalline phases of PDMS and also a dispersed phase of [BBIM][BF₄].

Pervaporation selectivity increased and the butan-1-ol flux through the membrane raised with the increased content of [BBIM][BF₄] in the PDMS-[BBIM][BF₄] membranes.

Since equilibrium separation factor in liquid is nearly independent on ionic liquid amount in PDMS, diffusion is the major factor contributing to pervaporation selectivity from butan-1-ol + water mixture. The PDMS-[BBIM][BF₄] membrane showed high stability as well as selectivity (the separation factor raised up to 37, if 30 weight % of ionic liquid was accommodated in PDMS) during all experiments.

Acknowledgement

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SL E03

APPLICATION OF PHOSPHONIUM BASED IONIC LIQUIDS AS SUPPORTED LIQUID MEMBRANES FOR GAS SEPARATION

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Gas separation is not only indispensable for certain industrial processes but it is also important from the environmental point of view. Therefore its continuous improvement is essential and can be realized by combining the advantages of environmentally sound membranes and ionic liquids.

In this work first supported liquid membranes were prepared with seven types of phosphonium based ionic liquids (Table 1.). Then the permeability and stability of the membranes were investigated using H₂, N₂, CO₂ and CH₄. Further experiments were carried out under various temperatures (20°C, 30°C, 40°C, 50°C, 60°C) and trans membrane pressures (1 bar, 2 bar, 3 bar, 4 bar, 5 bar) to study the permeation's temperature and pressure dependence.

Table 1. Phosphonium based ionic liquids used for the experiments

Cyphos 102	Trihexyltetradecylphosphonium bromide
Cyphos 103	Trihexyltetradecylphosphonium decanoate
Cyphos 104	Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate
Cyphos 106	Triisobutylmethylphosphonium tosylate
Cyphos 163	Tetraethylphosphonium bromide
Cyphos 166	Tetraoctylphosphonium bromide
Cyphos 169	Ethyltributylphosphonium diethylphosphate

It was found that while Cyphos 106, 166 and 169 destroyed the membrane material, the membranes prepared with the other ionic liquids showed quite high permeabilities and high CO₂/H₂, CO₂/N₂ and CO₂/CH₄ ideal selectivities, so they can be successfully used in gas separation.

Experiments concerning the permeation's temperature and pressure dependence showed that the permeability decreased with the increase in pressure and increased with the increase in temperature.

SL E04

DEVELOPMENT OF PDMS MEMBRANES FOR APPLICATION IN BOTH NANOFILTRATION AND PERVAPORATION

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PDMS (polydimethylsiloxane) is a hydrophobic, dense and selective material, from which it is possible to obtain membranes suitable for both solvent resistant nanofiltration (SRNF) and pervaporation PV).

SRNF-fluxes through PDMS membranes cast from 10 wt% solutions showed that the highest fluxes were obtained for toluene/IPA (isopropanol) mixtures with high toluene concentration. A mixture with 60 vol. % or 20 vol % toluene gave a flux of 19 and 4 kg m⁻² h⁻¹ respectively. These high fluxes can be related to the swelling of PDMS in IPA and toluene (0.48 and 1.1 cm³/g, respectively). From the series of solvents with less swelling, the highest flux was obtained for sec-butanol (2 kg m⁻² h⁻¹), which also can be related to the relatively high swelling. Fluxes of ethanol and propanol were comparable (~ 1 kg m⁻² h⁻¹). The lowest fluxes were obtained for methanol and hexanol (~ 0.3 kg m⁻² h⁻¹). For methanol, the lowest swelling degree was observed, which explains the obtained result. On the other hand, the low hexanol flux could be linked to its high viscosity.

Retention measurements were done using bengal rose (a negatively charged dye) / isopropanol mixtures, and bromothymol blue (neutral dye) / isopropanol or n-propanol. The highest bengal rose retention (99 %) was found for the PDMS membrane prepared from a 10 wt% coating solutions. The PDMS-membranes prepared from more dilute solutions (7.5 wt% and 5 wt% respectively) gave lower retentions (86 % and 76 %, respectively). In case of bromothymol blue, a slightly higher retention was obtained in IPA (93 %) than in n-propanol (89 %).

Compaction was studied by doing experiments by first increasing the pressure from 4 bar to 30 bar, followed by decreasing the pressure and finally again a pressure increase. A partially reversible PDMS membrane compaction was observed. Due to the applied pressure, the relatively swollen dense PDMS top-layer, is being slowly squeezed till equilibrium. This creates a higher resistance for the migrating compounds. Therefore, PDMS can be considered as a "soaked sponge".

In pervaporation, 15% unfilled PDMS-membrane coated on PI-support showed a lower flux but higher selectivity (4.3 and 3.8, respectively) than the one coated on PAN-support. Permeate flux decreased with the increase of the polymer concentration in the top layer. Commercial Pervap 1060 had a higher flux but lower selectivity, being cast from a more hydrophilic PDMS material.

SL E05

THE INFLUENCE OF ORIENTATION ON THE PROPERTIES OF POLYETHYLENETEREPHTALATE FILMS IRRADIATED WITH HEAVY IONS

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The influence of irradiated PET-films orientation onto its mechanical characteristics (strength and elongation), kinetics of process of chemical etching and shape of pore formation was studied. Double-axis-oriented PET film (thickness of 10 mkm) and not oriented (thickness of 50 mkm) film were used in this investigation. Irradiation has been done normally to the film surface with Ar and Kr heavy ions with $10^6 - 10^9$ fluence range and 3 - 5 Mew/a.m.u. energy in cyclotron U-400 (JINR LNR, Dubna, Russia). Thermo-elongation has been done with orientation machine under different temperatures (80 - 130°C). Process of the samples etching was carried out in KOH solution of different concentrations (0.25 - 2 M) under 70°C. Microphotography of oriented PET-film, irradiated with Kr (fluence $3 \cdot 10^8$) (400%), etched with alkali solution as shown on fig. 1 b. It was shown, that considerable TM pore shape changing occurs in film orientation course in compare to the control sample (fig. 1 a). Ellipticity was about 350% in this case.

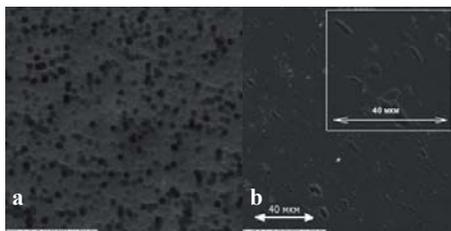


Fig. 1. Electronic microphotography of PET film, irradiated with Kr (fluence $3 \cdot 10^8$) (400 %, 800C, not heat-treated). Etching agent KOH, 2 M; etching time: 3 h. a - not oriented film; b - oriented (400 %, 80°C, not heat-treated).

Thus, we have shown the ability of TM preparation with crack shape pores, characterize with increased productivity.

SL E06

INVESTIGATIONS OF RUBBERY COPOLYIMIDES FOR THE PREPARATION OF ASYMMETRIC PERVAPORATION MEMBRANES

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As the regulations applied in the chemical industries are getting more stringent, the need to develop economical environmental-friendly processes is increasing. In that field, it is now well recognized that membrane technologies may have a major role to play either in gas separations or liquid-liquid separations. However one of the challenging issues is to design and prepare polymers and membranes with suitable separation properties, in particular for liquid separations where the polymer has to survive to the exposure of liquid solvents at various temperatures.

If aromatic polyimides are known to exhibit a fairly good stability to a great number of solvents, their uses are mainly focussed in gas separation as dense membranes or in micro- and ultra-filtration processes as porous membranes.

Indeed, as glassy polymers, they possess remarkable mechanical and chemical properties for organic materials, but in general their permeability coefficients are limited because of their rigid carbon skeleton and hence of their low available free volume. To broaden the scope of these very stable polymers with the aim of achieving liquid-liquid separations, we have studied the properties of a block-ether aromatic polyimide series comprising a flexible block; we describe attempts to produce asymmetric PEI membranes by using various experimental conditions of dry/wet phase inversion.

We report the physical properties of the obtained PEI membranes and the related morphologies by scanning electronic microscopy. The pervaporation properties of these membranes were then studied with model liquid mixtures, i.e. water - ethanol. For some of these copolyether-imide membranes, it was shown that high permeation fluxes together with fairly good selectivity could be reached. These results demonstrated that rubbery copolyimides are promising materials and membranes for liquid-liquid separations.

SL E07

NEW INSIGHT IN TUNING THE MORPHOLOGY OF POLY(VINYLDENE) FLUORIDE MEMBRANES

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The present work focuses on the effect of polymer dissolution temperature on the morphology and crystalline behaviour of poly(vinylidene fluoride) (PVDF) membranes, prepared by the vapor-induced phase separation method (VIPS). In this contribution, 20wt% PVDF solutions were prepared in N-methylpyrrolidone (NMP) at temperatures ranging from 33 to 110 °C \pm 1°C. Based on the membrane morphology and crystalline type, we define minimum and critical dissolution temperature (MDT and CDT) for PVDF dissolution process. Dissolution of PVDF between MDT and CDT resulted in membranes with bi-continuous structure and consisting of mixed α and β crystallites. When polymer was dissolved above CDT, membrane had particulate structure with mainly β crystallite. Therefore, the dissolution temperature can be regarded as a key point for controlling the morphology, crystallization and mechanical properties of PVDF membrane prepared by VIPS.

It has been found that MDT is dependent on the polymer concentration and solvency. For instance, compared to NMP as solvent, higher MDT is required to completely dissolve PVDF with DMF to produce bi-continuous membranes.

We assume that chain mobility governs the difference observed in the final membrane morphology. No noticeable variation was found in terms of viscosity and elasticity for the studied dissolution temperatures. To get a deeper insight, single steel ball sedimentation measurement was investigated. In this case, differences were observed by adding small amount of water to the polymer solution and by increasing the time scale of measurement. For polymer solutions dissolved below CDT and premixed with 0.5 to 2 wt% of water, the viscosity increased more quickly than for solutions dissolved above CDT. We propose that water intake in polymer solution during the VIPS stage might induce with time differences of chain mobility depending on dissolution temperature meaning that the structure of polymer aggregates are of different nature. At dissolution temperature below CDT, the chain mobility is supposed to be limited, entailing that polymer chains may not nucleate and grow easily when crossing the solid-liquid phase separation region. This phenomenon may account for the bi-continuous morphology of obtained membranes in this case. For dissolution temperature above CDT, polymer chains still have higher mobility and may undergo nucleation and growth mechanism giving rise to membrane with particulate structure.

Keyword: Poly(vinylidene) fluoride (PVDF); Vapor-induced phase separation; Dissolution temperature; Chain mobility ; morphology ; crystallization.

SL E08

THE HYDRODYNAMIC EFFECT OF MICROPARTICLES FOR THE MEMBRANE RESISTANCE

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The membrane technique of microfiltration (MF) was used to investigate the reduction of membrane resistance. The experiments were carried out in a tubular ceramic membrane (MF/K1) microfiltration equipment. Concentration polarisation, cake formation lead to a performance loss of microfiltration membranes in terms of reduced permeate flux. Causes of these phenomena are depend largely on components and properties of the feed suspension. In this paper, an investigation has been carried out to look for a way to improve filtration performance.

To prevent fouling of microfiltration membranes during processing of chalk-dust solutions, a high degree of turbulence should be introduced in the feed solution. For this purpose, the application of microparticle (bakelite) was investigated. The influence of microparticles on the flux was investigated with a 0.45 μm tubular ceramic membrane. The mass transfer is increased considerably by addition of bakelite particles. The main mechanism of fouling reduction is by an increased diffusion of rejected solutes from the membrane interface back to the bulk solution.

Effects of shear rate and particle size on the cake resistance are investigated. The larger particles induce much higher shear-induced diffusion and therefore dramatically improve mass transfer. The shear force is dependent on the square of the particle radius. The size of bakelite used was 90-125 μm , 125-160 μm , 160-200 μm and a 200-400 μm respectively.

It was concluded that the applied bakelite in all cases increased the permeate fluxes. Increasing size of bakelite was associated with an increasing flux. The largest size of bakelite (200-400 μm) caused by the highest fluxes and the smallest cake (R_C) and total (R_T) resistance. This work gives new experimental results in the alternative approach to reduce of fouling.

SL E09

FABRICATION OF THE POLYETHERSULFONE MEMBRANES WITH BROAD OPEN PORES AND SPONGE-LIKE STRUCTURE AS FUTURE SCAFFOLD FOR CELLS AND TISSUES CULTURES

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The method of obtaining broad-pore membranes for application as scaffolds for chondrocyte cultivation is described. These membranes were obtained from polyethersulfone. They are characterized by the presence of both macropores of relatively large diameter, as well as micropores. These membranes are predicted first of all for use in the cultivation of cartilage cells (chondrocytes). The membranes are obtained by the phase inversion method followed by dissolving cellulose present in the membrane. Cellulose is a macropore precursor. Cellulose is dissolved by means of a copper hydroxide ammonia complex. As a result of the work carried out, three types of broad-pore semi-permeable membranes were obtained of 0.8-1.0 mm thickness. The first obtained and studied membrane was that with two skin layers. This membrane showed good mechanical properties. Unfortunately, as cultivation scaffold it did not fulfill the requirement of rapid and efficient penetration inside the membrane. The second type of membrane completely lacking of skin layers appeared to be mechanically too weak and practical working with it by surgeons was extremely difficult. However, this membrane perfectly performed as a cultivation scaffold. The above reservations caused that we concentrated on the development of a membrane which would not have the faults of both previous types. The membrane comprising one solid layer and the second skin layer with perforation appeared to be such a membrane. The upper perforated skin layer did not constitute a barrier for chondrocytes. They penetrated inside the membrane where they freely developed. The membranes obtained are not cyto-toxic. The culture of chondrocytes derived from White New Zealand breed rabbits developed very well on these membranes. The results of these experiments did not show a negative effect of the membranes on the cell culture. Just the opposite, the cartilage cells development on the membranes proceeded very well. The results obtained show that the membrane developed is a very good scaffold for cell cultivation.

SL E10

PREPARATION OF THE GAS DIFFUSION ELECTRODES FOR HIGH TEMPERATURE PEM TYPE FUEL CELLS

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Proton Exchange Membrane Fuel Cells (PEMFCs) represent a perspective alternative as an energy source mainly for the mobile applications (vehicles, notebooks). Nowadays it suffers from several serious drawbacks. They are related mainly to the slow electrode reactions kinetics. It thus requires high load of the platinum metals based electrocatalysts. At the same time it is sensitive to the several catalyst poisons. Majority of these problems may be solved by the increase of the PEMFCs operating temperature up to 200 °C. An increase in the operating temperature results important changes in the fuel cell water management. This concerns polymer electrolyte membrane as well as the gas diffusion electrode (GDE). Whereas to the first issue significant attention was paid during the last years, the problem of the GDE is solved into a significant degree less systematically. This research is devoted to the development of the novel high temperature PEMFC membrane based on the polymer supported ionic liquid (IL). The aim of this contribution is to develop the electrode compatible with the novel type of the membrane. It has to allow for a reproducible determination of the performance of the fuel cell equipped with this membrane.

E-TEK commercial gas diffusion layer (GDL) was used as an electrode support. Commercial carbon supported Pt catalyst was used for the electrode construction. Important problem represents incorporation of a suitable polymer used as a binder. It is at the same time responsible for the occurrence of the three phase contact. In the first instance polybenzimidazole (PBI) was used. The results obtained using this electrode were used as a reference point for the subsequent experiments using as a binder polymer supported ionic liquids identical with the membrane material. The reproducible way of electrode preparation and fuel cell assembling was identified. New membrane materials perspective for application in high temperature PEMFC were tested using these electrodes.

Acknowledgement

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SL E11

HYBRID PROCESSES WITH MEMBRANES IN WATER TREATMENT AND BIOTECHNOLOGY

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A short overview of hybrid processes utilising membrane separation combined with other separation process or (bio)chemical reaction will be presented. Two case studies will be discussed in more detail. Adsorption-microfiltration processes for boron removal from the reverse osmosis permeate in the sea water desalination and a fermentation-pertraction process for production of butyric acid.

Application potential of a new hybrid process combining adsorption of a target solute on microparticulate sorbent and microfiltration (AMF process) in water treatment applications is high. Fast adsorption kinetics in microparticulate adsorbent and the possibility to achieve rather high concentrations of adsorbent in suspensions by microfiltration, as well as the concept of the whole system are the key aspects of the process design. Impressively low flux of adsorbent is needed in the adsorbent regeneration loop. Diafiltration of regenerated adsorbent suspension is an effective way of decreasing of the adsorbent flow rate and consumption of chemicals in the desorption loop of the adsorbent. The inventory of adsorbent needed in this unit is much lower compared to IEX columns. Lower consumption of chemicals in the desorption loop and a lower overall power demand have been estimated what makes this process competitive to classical IEX processes.

Strategy of design of a hybrid fermentation-separation process for production of butyric acid (BA) is discussed based on available data on fermentation, pertraction through supported liquid membrane (SLM) with ionic liquid and L/L equilibria for this system. Pertraction through SLM containing phosphonium ionic liquid is advantageous comparing to classical carriers (extractants) and their application in hollow fibre contactor is considered. Continual removal of product in fermentation is an effective way of obtaining high substrate utilisation at reasonable product formation rates by preventing the product inhibition and better utilisation of biomass. Based on results of simulation of the hybrid process is shown that decreased pH in the feed into pertraction to about 4 can substantially decrease the surface area of membrane required in pertraction. It is advantageous to have the BA concentration in the broth as high as possible, but this should be optimized in connection with the bioreactor productivity.

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SL E12

THE PAST AND PRESENT TREATMENT OF WATER USED FOR THE BREWING OF PILSNER URQUELL BEER

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Brand Pilsner Urquell from Plzeňský Prazdroj brewery is a world-famous beer. The important impact on taste of beer has the brew water. Brewery Plzeňský Prazdroj use own source of ground water. Water treatment is focused on iron and manganese removing and for finally brew water quality is used reverse osmosis, because brew water standards request low hardness and non-detected concentration of iron and manganese. The waste water from reverse osmosis – concentrate with high salt concentration is utilized for malthouse.

Keywords

Brew water, Pilsner Urquell beer, water treatment, reverse osmosis

SL E13

COMPOSITE MEMBRANES: STRUCTURE, ION TRANSPORT, APPLICATIONS

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Membrane materials find wide application in modern technologies. They are traditionally used for gas and fluid sensor production, and for a wide range of electrochemical cells. Leading positions among them belong to the purification and separation systems. Proton conducting membranes for fuel cells have been developed especially fast in last years.

A number of problems can be mentioned, which restrict membrane applications. Membrane use in hydrogen power engineering is limited by necessity of temperature and humidity control and by their chemical degradation. It has led to necessity of development of membrane materials with improved properties. One of the most popular ways is a synthesis of hybrid inorganic/organic membranes. High ionic conductivity and improvement of mechanical properties can be mentioned among their advantages. Changes of composite membrane properties are caused by both synergism of properties of their components and phenomena proceeding on phase boundary.

In this report we discuss the composition, structure of hybrid ion exchange membrane obtained in our laboratory in recent years and their transport properties, which are the most important for practical application. These membranes are based on Nafion or MF-4SC (Russian analog of Nafion) membranes incorporating nanoparticles of silica, zirconia, hydrogen zirconium phosphate and polyaniline. Properties of membranes with uniform or gradient distribution of additives are described. The main attention is paid to the study of ionic conductivity and transport properties of hybrid ion exchange membranes, including comparison of various ions transport numbers, dependences of ionic conductivity on relative humidity and possible mechanisms of ion migration. The main reasons of composite materials properties change are also discussed.

SL E14

THE METHOD OF STANDARD CONTACT POROSIMETRY FOR STUDY OF MEMBRANES AND OTHER OBJECTS

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The porous structure properties of membranes, separators, electrodes, catalysts have a great influence on performances of different electrochemical systems: fuel cells, electrodialyzators, batteries, electrolyzers, sensors, etc. The wide known method of mercury porosimetry have several of great disadvantages, for example, the necessity to apply high pressures of mercury (up to thousands of atmospheres), which can lead to a deformation or even destruction of the samples and to a distortion of the porosimetric curves (porograms). Other drawbacks of this method are: distortion of the results owing to amalgamation of most metals, different values of the mercury wetting angle for different materials, complexity of the equipment, toxicity of mercury.

We developed a new method - the Method of Standard Contact Porosimetry (MSCP). MSCP has not these disadvantages and gives the possibility of measurements in a widest range of pore sizes for any materials including soft or frail materials or materials amalgamated by mercury [1]. The method is based on the laws of capillary equilibrium. If two (or more) porous bodies contacted one another and partially filled with a wetting liquid are in the state of capillary equilibrium then the values of the capillary pressure P of the liquid in these bodies are equal. The capillary pressure can be represented by the Laplace equation: $P = -2\sigma (\cos \theta) / r$, where σ - the surface tension of the liquid, θ - the wetting angle, r - the maximum radius of pores filled with the liquid. If for one of the porous bodies (the standard sample) the pore size distribution is known, then by determining an equilibrium dependence of liquid content for a test sample on liquid content for standard sample, the pore size distribution for the test sample can be calculated. The amount of liquid in the samples is determined by weighing. As working liquid can be used any wetting liquid, for example, hydrocarbons, water, etc. The porous standard and test samples preliminary are (under vacuum) filled with the liquid. The stack of porous samples is assembled in a special clamping device in which the samples are tightly pressed to each other. From this assembly a small portion of the liquid is evaporated through the open surface by or vacuum treatment or by a flow of dry inert gas. After establishment of a capillary equilibrium the stack is disassembled and each sample and weighed. After this the stack is reassembled and all listed operations are continued periodically until all the liquid has practically completely evaporated from the test samples. These operations can be made as by manual so automatic methods. The Automated Standard Porosimeter (ASP) was developed based on the MSCP [2]. ASP includes the following parts: a personal computer, an electronic balance, an automatic manipulator for the assembling and disassembling of the stack of samples and for the transfer of the samples to the balance; a device for drying of the stack by a controlled flow of dry gas, and an electronic device. Any porous and dispersed bodies can be investigated by MSCP and ASP, for example, different membranes (ion- exchange, ultrafiltration, inverse osmotic, etc.), electrodes, separators, filters, filters, soil, peat, oil and gas rocks, wood, catalysts,

adsorbents, ceramics, metallic ceramics, textiles, artificial and natural leathers, medicines, construction materials, polymers, etc.

MSCP allows to obtain a many of different information about porous and dispersed bodies:

- Distribution functions of pore volume of pore radii (in the range ~ from 1 nm to 3×10^5 nm).

- Specific surface area (in range ~ from 0.001 to $3000 \text{ m}^2/\text{cm}^3$) and its distribution of pore radii.

- Differential and integral information about a shape (corrugation) of pores.

- Liquid distributions of values of its binding energy with the testing material (in the range ~ from 0.003 to 10000 J/mole) and of the capillary pressure (~ from 0.003 to 10000 bar). The capillary pressure function is very important for different goals. For example, it is possible to calculate a distribution of water and conductivity in the proton exchange membrane fuel cell (PEM FC) [1,3,4].

- Differential characteristics of swelling. The characteristics is very important, for example, for ion-exchange membranes and conducting polymer electrodes, operating in electrolyte. In this case porous structure of these materials changes in comparison with a structure of the same materials in dry state. MSCP gives the possibility to obtain information on porous structure in real conditions, namely in electrolyte [1,3,4,5,6].

- Contact angle and its dependence on pore radii. The characteristic is very important, for example, for carbon electrodes [1,7].

- Structural and surface properties of multicomponent hydrophobic-hydrophilic bodies, for example PEM FC electrodes [1,7].

- Adsorption isotherm, etc.

The MSCP is widely used for investigation of porous materials (electrodes, membranes, separators, catalysts et al.) for different electrochemical systems (fuel cells, primary and secondary batteries, electrochemical supercapacitors, electrolyzers etc.) and for different non-electrochemical subjects. It was made many of investigations of different porous and dispersed materials for different companies and universities, for example, UTC Fuel Cells (USA), Ballard (Canada), Kompozit (Russia), SAFT Batteries (France); KFA (Germany), Honda (Japan), Samsung Electronics, DAEWOO (Korea), etc.

References

1. Yu.M. Volkovich, V.S. Bagotzky, V.E. Sosenkin, I.A. Blinov. In: Colloid and Surfaces A: Physicochemical and Engineering Aspects. 187-188 (2001) 349.
2. Y.M. Volkovich, I.A. Blinov, A.V. Sakars. Porosimeter. Patent 7, 059,175. (USA). 2006.
3. J.Divisek, M. Eikerling, V. M. Mazin, H. Schmitz, U. Stimming, Yu. M. Volkovich, J. Electrochem. Soc., 145 (1998) 2677.
4. M. Eikerling, Yu.I. Kharkats, A.A. Kornyshev, Yu.M. Volkovich. J. Electrochem. Soc., 145 (1998) 2684.
5. Yu. M. Volkovich, A. G. Sergeev, T. K. Zolotova, S.D. Afanasiev, O.N. Efimov, E.P. Krinichnaya. Electrochimica Acta, 44 (1999) 1543.
6. V.L.Sigal, V.L.Ponomarev, V.A.Semirenkov, Yu.M. Volkovich. J. Membrane Science, 81 (1993) 263.
7. J. Gostick, M. Fowler, M.A. Ioannidis, M.D. Pritzker, Y.M. Volkovich, A.V. Sakars. Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells, J.Power Sources, 156 (2006) p. 375-387.

SL E15

MODIFICATION OF THE MEMBRANE STRUCTURE BY MEANS OF A WEAK SOLVENT OF POLYMERS

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Control of porosity and pore size in semi-permeable membranes is from the beginning one of the basic problems in membrane development and production. Especially the size of pores and uniformity are of importance in medicine and biotechnology. Polysulfones (PSF) and polyethersulfones (PES) are one of the best membrane-forming materials for biomedical purposes. This results from their properties, and especially biocompatibility. Unfortunately, direct obtaining of (PS) or (PES) hollow fiber membranes permeable for proteins is difficult and complicated. Many methods of membrane modification leading to this are known, such as change of their surface leading to an increase in hydrophilicity or change of structure. These are often unstable and expensive methods. Modifications of a membrane-forming polymer often considerably worsen its properties, and especially its biocompatibility and biochemical resistance.

In our work we undertook an attempt to increase the cut-off point of ready PSF or PES membranes by increasing the pore size of these membranes. For this a method of increasing the size of pores should be developed, or cause some degradation of its structure should be performed. We assumed that it is possible to efficiently increase the membrane pore size without its degradation by acting on the membrane with a weak solvent of the polymer. We found several weak solvents of the membranes and confirmed their efficient action on ready membranes. Since their action on ready membranes was too strong, we diluted the solvent with a non-solvent. We studied a dozen or so membranes of PSF and PES made by us on our own hollow fiber spinning apparatus. The membranes differed between each other in the membrane-forming solution composition, hydraulic permeability (UFC) and cut-off point. For each membrane we selected the etching conditions. When permeating the solvent/non-solvent solutions through the membrane walls we found slight degradation of the membrane structure. Due to such etching, we obtained membranes of very high hydraulic permeability. Membranes before etching stopped from 90 to 100% of beef albumin, whereas the etched membranes were characterized by scanty retention for beef albumin. The results obtained show that this method can serve for controlled increase of the pore size in our membranes.

SL E18

NAFION-POLYBENZIMIDAZOLE-ZIRCONIUM PHOSPHATE COMPOSITE MEMBRANES FOR FUEL CELL AND STEAM ELECTROLYSER APPLICATIONS

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Ionically cross-linked Nafion and polybenzimidazole blend membranes were prepared by solution casting. The blend membranes were then swollen and loaded with zirconium (Zr^{4+}) cations by ion exchange within the confines of the hydrophilic region of the membranes. Further treatment of the composite membranes in phosphoric acid converted the zirconium ions to α -zirconium phosphate within the polymer microstructure. At the same time the polybenzimidazole was doped with phosphoric acid. At temperatures above $100^{\circ}C$ the composite membranes exhibit high proton conductivity and much improved mechanical strength and flexibility. Figure 1 shows the tensile strength at break, being as high as 26-30 MPa for the composite membranes at $130^{\circ}C$, which is above the glass transition temperature of Nafion. At $118^{\circ}C$ and 40% relative humidity, conductivity as high as 0.09 s cm^{-1} was obtained (see Figure 2).

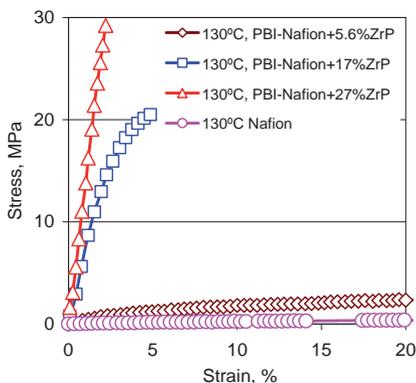


Fig. 1. Tensile strength of Nafion and Nafion-PBI-ZrP composite membranes at $130^{\circ}C$ and under dry atmosphere. The polymer blend consisted of 88% Nafion - 12% PBI based into which ZrP was loaded.

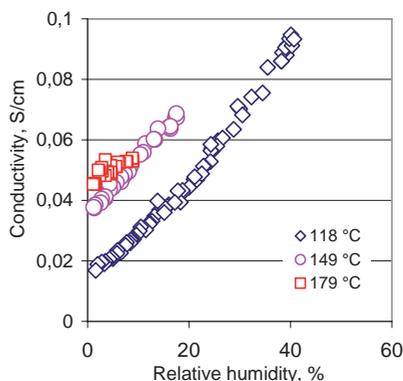


Fig. 2. Proton conductivity of the composite membrane consisting of 82% Nafion and 18% PBI into which 25 wt% ZrP was loaded and phosphoric acid is further doped (ca. 8 H_3PO_4 per PBI unit).

SL E19

LOCAL PROBE ANALYSIS OF MEMBRANES

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The membrane technologies are actively used in different fields of modern industry. Directions and depth of the membrane application in biomedical, milk and other industries are broadened while transferring to a nanoscale. The pore diameter for nanomembranes varies from hundreds to tens of nanometers. The methods of an express-control of the nanomembrane parameters on the basis of a scanning probe microscopy (SPM) and, particularly an atomic force microscopy (AFM), turn out to be effective.

Some examples of the AFM-utilization for the characterization of the different types of nanomembranes, such as porous alumina, polymer track radiation membranes, biological membranes based on the molecularly thin films are presented in the paper. Peculiarities of the contact and dynamic scanning modes, effectiveness of a joint use of the topography and contrast images (a lateral force map and a phase shift map) are described.

The fundamental scientific problem of the nanomembrane utilization consists in changes of the physico-mechanical properties of filtered matters in the nanoscale and, consequently, their transport mechanism in the nanometer channels. The SPM-technique allows realizing the force spectroscopy procedure that is the deformation of the surface layers of a sample with a force-displacement dependence registration. Local elastic and viscoelastic properties, as well as surface energy of materials on the nanometer areas can be estimated. In the paper, possibilities of the static and dynamic force spectroscopy modes for the evaluation of the viscosity and elasticity of the filtered liquid passing through a separate nanopore depending on its diameter are demonstrated. The obtained results allow to optimize the operational characteristics of the nanofiltering.

Single pore with the diameter from some nanometers up to some micrometers can be considered as a space, minimized in volume, that can act as nanoreactor for physicochemical processes and a receipt of materials in nanovolumes. The realization of an engineering process of the membrane-capillary transport of a matter to the AFM-tip permits to create the nanovolumes of different materials in the form of nano- clusters, wires and fibers on the tip. The subsequent utilization of the AFM force spectroscopy for the modified probe allows to measure physico-mechanical properties of materials in nanovolumes.

The perspectives of applications of the membrane local probe analysis for the industrial membrane technologies development are discussed.

SL F01

EFFECT OF SURFACE FORCES ON GAS MIXTURE SEPARATION IN NANOPOROUS BODIES

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In recent years, the flow of gas mixtures in nanodimensional channels has attracted steady interest. This is related to the development of new-generation membranes with nanometer channels and to the unusual behaviour of gases in these channels. It was shown [1] that in the case of free molecular flow of gases in nanodimensional capillaries under the action of temperature gradient, the effect of surface forces acting on molecules in the vicinity of capillary wall become appreciable.

In this work, we consider the effect of surface forces on the isothermal and nonisothermal gas mixture flow in nanodimensional capillaries. The surface forces are shown to considerably increase the thermomolecular pressure difference and make it possible to effectively separate the gas mixture components due to difference between the partial potentials of interaction with the walls. The effect of surface forces becomes especially notable when the flow is caused by a temperature gradient. Explicit expressions are derived for the thermomolecular pressure difference and mixture component separation efficiency in the steady-state regime, when the component flows through the cross section of capillary vanish. The possibility of determining the parameters of molecular-wall interaction by jointly measuring the thermomolecular pressure difference and separation efficiency is discussed.

It is shown that the surface forces somewhat change the expression for entropy production in a non-uniform gas flowing through a capillary under the action of temperature, concentration and pressure gradients. The modified expression for the entropy production is calculated. The new set of phenomenological equations of non-equilibrium thermodynamics are derived. The Onsager symmetry relations between cross kinetic coefficients are discussed.

1. V.I. Roldughin and V.M. Zhdanov. *Colloid Journal*, 2003, vol. 65, p. 652.

SL F02

UNDERSTANDING FUNCTIONING OF RO AND NF COMPOSITES: THEORETICAL ANALYSIS AND TOPLAYER CHARACTERIZATION

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Thin-film composite membranes for RO/NF owe their performance to decades-long and largely empirical effort that led to a unique combination of permeability and selectivity and robustness. Despite long manufacturing record, they still pose many questions regarding the structure, separation mechanism and possible ways to improve and diversify the existing membrane arsenal.

Theoretical analysis and direct microscopic observations reveal that the polyamide layer is fact a multilayer with characteristics (porosity, charge etc.) varying across it. This explains controversial surface characteristics obtained by different methods, such as streaming potential, XPS, ATR-FTIR spectroscopy, NMR and fitting of models to various transport data, all of which actually address different regions within the toplayer. In this situation methods, in which transport-related parameters are deduced from analysis of the whole toplayer (not including the porous support) or directly from transport experiments, should be preferred.

It has also become apparent that the analysis and modeling of transport must not view the transport through the membrane as a simple sieving process. For separation of small solutes in RO/NF both thermodynamics (partitioning of solutes between membrane and solution) and hydrodynamics (hindered transport of solute within the polymer matrix) should be considered separately. Unfortunately, separation of these factors is not possible using only filtration data. We show how such information may be experimentally obtained focusing on the impedance spectroscopy and ATR-FTIR spectroscopy.

SL F03

SHORT-RANGE FORECAST OF PERMEATE FLUX IN DETERGENT WASTE WATER ULTRAFILTRATION

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Waste water purification is very crucial nowadays and new techniques like low-pressure driven membrane processes are developed to obtain the sufficient productivity and quality of high efficiency of cleaning. However selection of membrane requires long-lasting tests. The new methods of modelling like artificial neural networks (ANN) are essential to avoid time consuming laboratory measurements.

The aim of the work was to forecast using ANN in short-range time series (one day) the permeate flux of detergent waste water. During two days of continuous measurements (every 5 minutes) the following parameters were measured: temperature of waste water, recirculation flux, feed pressure and pressure after process. Those parameters were considered as inputs to the network while permeate flux as output value. Waste water was ultrafiltrated with the use of 5kDa Romicon hollow fibre modules. 288 results from one day were used to learn ANN and also 288 from another day to verify created network. The selection of learning, testing and validating subsets was 117, 89 and 82 values, respectively. The best created network with the smallest learning error equal to 0.000653, one hidden layer with 8 neurones and activation functions in hidden and output layer (hyperbolic tangent and sine, respectively) was chosen to verify and to forecast in short-range the value of permeate flux. The time horizon was equal 0 and the number of late value amounted to 1. Due to different times of backwashing in analysed days, parameters of feed stream and permeate were random and divergent. Above mentioned problems caused the differences between convergence with experimental and forecasted values in learning and verifying processes. During backwashing permeate flux values were equal to zero. In this case created network generated sometimes the negative values of the flux which were treated as an error and replaced by real experimental values equal to zero. Analysing obtained results one can conclude that the results obtained in verifying process were sufficient from engineering point of view and that modelling using ANN gave proper results when the conditions of the membrane process and feed solutions were similar. Created network can be used to predict values of waste water permeate flux for other days, other installations working also with the same kind of membrane.

SL F04

ELECTROCHEMICAL CONTROL OF A pH GRADIENT FOR BIOMOLECULES SEPARATIONS BY ION EXCHANGE

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A classical method to separate amino-acids, peptides and proteins by column ion exchange is to use a pH^[1] and/or ionic strength gradients. The control of this pH gradient plays a key role on the resolution achieved, because it varies the velocity of molecules as their progress in column. This pH gradient is normally obtained in a chemical way with different buffers of variable dilutions. The objective of this work is to study the possibility to control electrochemically the pH gradients. So we avoid using the buffer solutions.

The experimental set-up is an electro dialysis cell involving ion exchange resin beds between membranes. The control of operating conditions, especially the potential difference at the boundaries of the cell, allows controlling water dissociation at the membranes or at the contact points between the cation and anion exchange beads^[2]. The produced protons and hydroxyl ions migrate to different compartments where the protein separation occurs in ion exchange resin beds. The choice of potential difference allows stabilizing different pH values in the compartments. The dynamic of the response to pH will be studied in the different compartments with potential variations imposed at the boundaries of the cell.

[1] T.M. Pabst, D. Antos, G. Carta, N. Ramasubramanian, A.K. Hunter, Protein separations with induced pH gradients using cation exchange chromatographic columns containing weak acid groups, *Journal of Chromatography A*, 1181 (2008) 83-94.

[2] J.H. Song, K.H. Yeon, S.H. Moon, Effect of current density on ionic transport and water dissociation phenomena in a continuous electrodeionization (CEDI), *Journal of Membrane Science* 291 (2007) 165-171.

SL F05

INVESTIGATIONS OF DIRECT METHODS FOR THE MEASUREMENT OF THE MASS TRANSFER COEFFICIENT OF HOLLOW FIBER MEMBRANE CONTACTOR

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In order to reduce greenhouse gases emissions, several technologies for the capture and removal of CO₂ from post-combustion flue gases are currently developed. Hollow fiber membrane contactors (HFMC) appear to be a promising technology which combines intensified gas-liquid absorption and the possibility to independently control gas and liquid flow rates.

The rigorous design of HFMC requires a precise computation of the mass transfer coefficients in the gas (k_g) and liquid (k_l) phases, as well as through the membrane (k_m). Numerous studies have been reported on the estimation of the fluid phase mass transfer coefficients. k_m has been however rarely investigated and it is most often estimated by correlations or through indirect methods:

1) for example, a classical approach is based on the following expression: $k_m = D \epsilon / \delta \tau$. The diffusion coefficient D is calculated by taking into account the bulk diffusion and the Knudsen diffusion. However the contribution of these 2 phenomena is not well determined and the coefficients τ (tortuosity) and ϵ (porosity) cannot be precisely established [1], [2], leading to a very large range of k_m values.

2) another approach is based on experiments with pure CO₂, so that k_g can be neglected in the overall mass transfer coefficient [3], [4]. Nevertheless, the exact contribution of k_l and k_m is difficult to estimate in that case.

In this study, direct experimental methods, which have been to our knowledge unexplored apart from a few studies for transmembrane distillation operations [5], will be described and the k_m values of different hydrophobic microporous membranes will be discussed and compared to the predictions. The interest of these methods in order to identify structural changes of membrane materials due to solvent influence (e.g. ageing effects after MEA exposure) will also be shown.

[1] P.S. Kumar and al., Approximate solution to predict the enhancement factor for the reactive absorption of a gas in a liquid flowing through a microporous membrane hollow fiber, *Journal of Membrane Science* 213 (2003) 231-245

[2] J.L. Li, B.H. Chen, Review of CO₂ absorption using chemicals solvents in hollow fiber membrane contactors, *Separation and Purification Technology* 41 (2005) 109-122

[3] Z.Qi, E.L. Cussler, Microporous hollow fibers for gas absorption II. Mass transfer across the membrane, *Journal of Membrane Science* 23 (1985) 333-345

[4] W. Albrecht and al., Selection of microporous hydrophobic membranes for use in gas/liquid contactors: an experimental approach, *Journal of Membrane Science* 263 (2005) 66-76

[5] C.M. Guijt and al., Determination of membrane properties for use in the modelling of a membrane distillation module, *Desalination* 132 (2000) 255-261

SL F06

OPTIMIZATION OF WATER ELECTROCHEMICAL ACTIVATION IN ELEMENT PEM-3

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Electrochemical activation (ECHA) is used for creation of highly effective and ecologically pure technologies in different areas of human activity. This activation includes a unipolar electrochemical effect on liquid under the minimum of heat release. Such influence is necessary for giving to it of the activated condition. This condition is characterized of nonequilibrium potential energy content. Water and other liquids can be activated by ECHA.

Potential of hydrogen (pH) and oxidation-reduction potential (ORP) are the main parameters which characterize of anolyte and alkaline fraction of water under ECHA. The highest deviation scope of these parameters from neutral numbers characterizes of fraction reactionary ability. Fractions with the greatest possible deviations pH (2,0 or 12,0) and ORP (about 1000 mV or a -800 mV) are used in many different innovative technologies. The value of pH and ORP for liquid system depends on many factors including design of the electroactivator and its elements. For each electroactivator the optimum combination of such factors may be found.

Basic element of the majority serial electroactivators is diaphragm flowing electrochemical modular block PEM-3. But using of serial electroactivator in scientific research is not efficiently. It is the most rational to create experimental devices on the basis of modular block PEM-3. However it is necessary to make some research for definition of optimum parameters of the liquids electrochemical activation for produce fraction with required values of pH and ORP.

For experiments the laboratory device containing module PEM-3 has been produced. Device allows changing intensity of the ECHA by means of a variation of the liquid flow through electrode chambers and voltage on electrodes, and also rates of ECHA processing. The analysis of the results of water electrochemical activation has allowed to define following optimum parameters: the water flow through electrode chambers – $4,1 \cdot 10^{-6}$ m³/s; the voltage on electrodes – 45÷50 V; triple of ECHA processing. Under this condition it is possible to receive anolyte with pH=2,4±0,05 and ORP =1000±20 mV, and alkaline fraction with pH=11,10±0,05 and ORP=-850±10 mV. The temperature of synthesised fractions is within the range 20÷28 °C.

SL F07

DEMINERALIZATION OF DIFFERENT MILK WHEY KINDS

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Process of electro dialysis is one of the most effective modern ways to prepare whey for its processing. Unfortunately electro dialysis of acid whey takes much time due to high concentration of lactic acid.

The purpose of our research was to investigate the process of electro dialysis of acidic whey and determine the way of its intensification.

Laboratory plant ED-mini and RE membranes produced by the company "MEGA" a.s., Czech republic have been used. Experimental conditions were similar to the industrial ones.

The main control parameters were:

- current strength to determine amount of ions permeated from whey to the concentrate;
- specific electrical conduction of whey and concentrate as indirect parameters of whey demineralization level.
- mass concentration of whey dry substances to estimate the losses non-connected with removal of inorganic ions.
- active and titratable acidity of dematerialized whey.

Various ways of whey acidity regulation have been considered and two of them have been investigated more in detailed.

1. Entering of reagents during electro dialysis process;
2. Entering of reagents at the final stage of electro dialysis process.

The obtained results showed that the second way of regulation of quark whey acidity was most preferable.

Deacidification of acidic whey made it possible to intensify its electro dialysis considerably and prepare product which can be used for further processing.

According to our research results we can propose different ways of application of demineralized acidic whey, e.g. manufacture of dairy products (infant formula, yogurts, ice-cream, milk desserts and beverages); confectionaries; bread; meat products and others.

SL F08

A MECHANISTIC STUDY OF ENTRAPMENT STRATEGY FOR HYDROPHILIC MODIFICATION OF POLYPROPYLENE MEMBRANE SURFACE

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One simple and effective method for polymer surface modification, the entrapment of hydrophilic macromolecules, has been studied occasionally in the recent decades and described as a two-step liquid immersion process so that the modifier can first disperse into the swollen base polymer and thereafter entrap within the deswollen base polymer [1]. Although polyethylene glycol (PEG) was more widely employed, our experiments showed that PEG is less effective than amphiphilic PEG block copolymers, when the polymer substrate is a nonpolar polyolefin. No work has yet been done to reveal the reasons. Therefore it is the aim of this study to verify the influences and different entrapping mechanisms of PEG homo- or copolymers and to evaluate the potential of the method for hydrophilic and anti-fouling modification of polypropylene (PP) microfiltration membranes.

PEG with different molar mass as water soluble homopolymer, and several amphiphilic copolymers with varied structure and PEG content such as dodecyl PEG (C₁₈E₈), PEG distearates, or triblock copolymers with polypropylene glycol (PPG), Pluronic[®] (PEG-b-PPG-b-PEG), were used as modifiers. The surface and membrane characterization of these 'modified' PP membranes indicated that only the amphiphilic copolymers, containing ca. 50% PEG, were efficient for hydrophilic and antifouling modification of PP surface. This might be attributed to the special conformation of surfactants in certain solvents. Hence, the amphiphilic molecules' structures in dichloroethane (used in swelling / embedment step) were characterized by NMR spectroscopy and fluorescence probe based determination of critical micelle concentration (CMC), which confirmed only the efficient polymers can form reverse micelles in nonpolar solvent. Therefore it is deduced that during the first step, the reverse micelles with hydrophobic shell tend to disperse into the swollen PP due to their good compatibility. And the orientation happen in the second step when this embedded PP was immersed into water, so that PEG chains had an inclination of stretching out of the PP surface to yield the final hydrophilic surface.

1. E. Ruckenstein, D. B. Chung. *J. Colloid Interf. Sci.*. 1988 (123): 170-185.

SL F10

THEORETICAL STUDIES ON CARBON DIOXIDE REMOVAL FROM A GAS STREAM IN HOLLOW FIBER MEMBRANE CONTACTORS

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This paper presents theoretical studies and modeling investigations on the reactive absorption of carbon dioxide in alkanolamine solutions, specially the monoethanolamine, in a hollow fiber membrane contactor device. The absorption mechanism was built based on mass transport conservation laws in all three regions involved in the process, i.e. the gas phase, the membrane barrier and the liquid region. The gas is flown in the fiber bore in which the velocity is assumed to obey a fully developed laminar flow, and the liquid solution is circulated counter-currently to the gas flow in the shell side where the velocity is characterized by the Happel's free surface model. The rigorous model consisting of a set of highly non-linear partial differential equations is rewritten in dimensionless form and numerically solved. The outlet gas and liquid concentrations, the reactive absorption rates, and the gas removal efficiencies are parametrically simulated with the Graetz and Sherwood numbers, and the gas to liquid flowrates.

SL F11

MODELLING THE TRANSPORT ACROSS NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES IN CASE OF HEAVY METAL CONTAINING SOLUTIONS

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When designing membrane units, it is necessary to know the transport characteristic of the membrane. The most important parameters of the transport characteristic are the permeate flux and rejection and several models are developed to model them.

Experiments are carried out using a test membrane apparatus in batch mode. The test solutions are heavy metal containing solutions. The effects of initial concentration and transmembrane pressure on permeate flux are studied. The heavy metal concentration of the permeate is analysed. In this work the “resistance in series model” is applied to model the permeate fluxes. The model states that not only the membrane resistance but other resistances (extended resistance) arise due to concentration polarization, gel formation, adsorption, fouling, etc. The novelty in this work is to use a contracted resistance term R_f , called fouling resistance beside membrane resistance, which contains all the other resistances. Based on our investigations a new equation is established for the calculation of fouling resistance. The derivation of equation is based on dimensional analysis and engineering considerations.

The extended “resistance in series model” is applied to model the experiments. Since the experiments are carried out in a batch way, all the significant parameters change in time and also in yield. (Yield is defined as the ratio of permeate volume and initial feed volume.) In order to perform direct information about the state of the filtration at different experiments, the modelling is carried out in the function of the yield. The use of the estimated parameters of the model, based on experimental data, the osmotic pressure difference and fouling resistance can be calculated and implemented into the flux-model.

The comparison of the measured and modelled fluxes shows good agreement, which verifies, that the resistances can be merged into one term. It also proves that the equation established for the calculation of fouling resistance is correct.

SL F12

NUMERICAL STUDY OF THE EFFECT OF A CHARGED MEMBRANE IN THE FRACTIONATION OF TWO PROTEINS WITH OPPOSITE CHARGES

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The efficiency of protein fractionation by ultrafiltration is reduced by concentration polarization, which indirectly reduces the apparent selectivity of the membrane. The complete understanding of this phenomenon requires the modelization of the electrical interaction between the membrane and the proteins. This interaction can also influence solute transmission, selectivity and fouling [1]. In this work, the fractionation of a solution of two proteins with opposite charges by a charged membrane is studied by numerical methods. A numerical code, based on the finite difference method, is developed to study protein fractionation by solving the Poisson-Boltzmann, the Navier-Stokes and the Nernst-Planck equations. The code developed is used to study the effect of the electric charge of the membrane and of the ionic composition of the solution in the electric field, flow field, concentration fields, permeate velocity, protein transmission and selectivity.

[1] R. van Reis, J. M. Brake, J. Charkoudian, D. B. Burns and A. L. Zydney, 1999. High-performance tangential flow filtration using charged membranes, *Journal of Membrane Science*, 159 (1999), 133-142.

SL F13

MATHEMATICAL MODEL OF MASS TRANSFER IN AN ELECTRODIALYZER WITH NET-LIKE SPACERS

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A mathematical model of mass transport in an electro dialyzer has been proposed and validated by comparison with experimental data obtained with EDR-III single-pass electro dialysis stack. The model is based on Nernst-Planck equation and local balances. It assumes existence of the hydrodynamic boundary layer at the liquid – membrane interface and uniform flow distribution in the bulk solution with complete mixing in cross direction by effect of turbulence promoter used. The model also uses parameters which take the properties of turbulence promoters into account.

The model has been implemented in „EDR Design Studio 1.00“ software tool for projection of EDR applications. This software tool is used to analyse incoming inquiries in MEGA a.s. It allows to calculate flow rates and compositions of all hydraulic streams in the system, DC voltage and current, salt removal, current efficiency, polarisation and power consumption.

Stack performance such as salt removal in one hydraulic stage depends on the concentration of ions present in feed water, flowrate, voltage, temperature and water recovery. It has been also shown both theoretically and experimentally that stack performance is strongly affected by the nature of ions present in feed water. In the treatment of feeds with the same conductivity but composed of different electrolytes, different salt removals are obtained. In addition to temperature, conductivity cannot be used as an only input parameter characterizing the water or solution to be treated, but a good feed water analysis is required. This is of a great importance when designing an EDR technology. Water composition varies from case to case. The most significant ions present in natural waters are Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- and NO_3^- ions.

SL F14

INVESTIGATION AND MODEL BASED QUANTIFICATION OF THE INFLUENCE OF MEMBRANE MODULES ON PROTEIN SEPARATION PERFORMANCE WITH POROUS MEMBRANE ADSORBERS

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Membrane adsorbers have successfully been applied in antibody production for trace contaminant removal and virus clearance [1]. So far much research for improvement of membrane adsorber performance has been focussed on more suitable and efficient base membranes and improved surface chemistries [2], as well as on novel membrane module design to optimize flow distribution of membrane devices [3].

In the first part of this work, a new generation of membrane adsorbers was prepared via UV-initiated heterogeneous grafting polymerization on suited macroporous regenerated cellulose membranes. Their dynamic separation performance was investigated in detail with respect to target proteins, pore size distribution of the base membranes and architecture of the functional layers using two different membrane modules, commercial CIM[®] disc holder and a custom-made flat-sheet membrane module from Sartorius (Scell). It was shown that the average utilization of binding capacity of the membranes was improved by over 50% for both maximum dynamic binding capacity and breakthrough capacity when using the Scell in comparison with the CIM module. The internal flow distribution of the membrane modules was further quantified based on a novel radial zone rate model, which is characterized by the number of radial zones and the fractional volumetric flows through these zones. Model parameters were estimated by fitting the breakthrough curves under non-binding conditions. The evaluation showed that the utilization of peripheral regions of the membranes was more effective for Scell than for CIM module. The latter was dominated by the preferential flow through the central region of membrane module. This novel model can also be coupled with different kinetic and isotherm models for the characterization of membrane adsorber stacks for various zone geometries.

References

- [1] J. Zhou, T. Tressel, *Biotechnol. Prog.* 22 (2006) 341.
- [2] M. Ulbricht, *Polymer*, 47 (2006) 2217.
- [3] R. Ghosh, T. Wong, *J. Membr. Sci.* 281 (2006) 532.

SL F15

WHEY TREATMENT: CURRENT STATUS AND PERSPECTIVES OF MARKET DEVELOPMENT IN THE REPUBLIC OF BELARUS

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Whey treatment is the key problem for the task solution on decrease in an environmental load of dairy processing enterprises, for expansion of a forage reserve, for production of a group of high-valuable milk concentrates. Manufacturing of whey grows rapidly in Byelorussia so if 1,02 mln. t were produced in 2004., 1,36 mln. t in 2005., 1,49 mln. t in 2006, 1,54 mln. t in 2007, 1,86 mln. t in 2008, in 2010 it is being planned to be processed up to 2,0 mln. t of whey.

The program of “Whey treatment and dried dairy product manufacturing in the Republic of Belarus for the 2008-2010” was accepted by regulation of Council of Ministers with the purpose of maximal use of the dairy resource, which is treated in the Republic of Belarus. Special purpose capacity for whey treatment and production of wide range of products on its base is being planned to be created in the framework of this program. As a basis for realization of the program the following scheme of accommodation of capacities is accepted: some small plants prepare whey for transportation and they transfer it for its processing to the central enterprise. The main direction of processing dairy manufacturing is planned to produce the range of dry food and fodder products.

The structure of whey processing is being planned in the following way: 10-15 % of the whole whey resource will be used in the liquid or concentrated form in dairy, baking and confectionery branches, up to 15 % will be used in manufacturing of a fatty concentrate, up to 10 % in lactose production, others will be produced into WPC by UF and various types of whey powder. Realization of the whey treatment program is directed to satisfy intrarepublican demand for products of whey treatment. Such orientation will allow stopping import of products on these positions, strengthening an export potential of the country, having possibility to created maneuver at variation of a conjuncture of the world market.

SL F16

MODELLING ASYMMETRY OF TRANSPORT PROPERTIES OF MODIFIED ULTRAFILTRATION MEMBRANES

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Chemical volumetric or surficial modification of commercially available membranes is a new direction in membrane technology. So, using accessible ultra- or nanofiltration membranes and modifying agents it is possible to improve membrane selective properties and productivity in the respect of low-molecular electrolytes solution. Such filters possess high permeability under low pressure drop (<1.5 MPa), and this is their undeniable advantage in comparison with reverse osmosis membranes.

In the present work the theory of ions transport through charged homogeneous membrane basing on Nernst-Planck equations [1] is applied to describe ultra- and nanofiltration of electrolyte solution using bi-layer membrane with one chargeable layer. Concentration and electric potential profiles as well as rejection coefficient and difference of electric potentials across the system are found as functions of physico-chemical and geometrical parameters. The asymmetry of transport characteristics which has been found and described previously for diffusion through charged bi-layer membranes [2] is sustained also for the rejection coefficient and the difference of electric potential across the membrane in spite of orientation of the bi-layer membrane towards the salt flux. At the moment qualitative agreement between theoretical and experimental results is revealed.

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References

1. V.G. Gorsky, V.M. Starov, A.N. Filippov, M.T. Bryk, R.R. Nigmatulin, *Soviet Journal Water Chemistry and Technology*, 14(2) (1992). 93.
2. A.N. Filippov, V.M. Starov, N.A. Kononenko, N.P. Berezina, *Special issue of Advances in Colloid and Interface Science*, 139 (2008). 29.

SL F17

PROGRESS IN THE MATHEMATICAL MODELING OF THE FLOW HYDRODYNAMICS IN THE SPACER FILLED CHANNEL

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The uniform flow hydrodynamics represents a guarantee of the reliable operation of many chemical technologies. The working chamber (active zone in between membranes) of the electro dialysis unit represents a typical example. In regions with locally increased residence time of the solution, its excessive local depletion occurs. In an extreme case the reduced process efficiency and deteriorated life time of the membrane are the direct negative consequences. Uniform residence time distribution is in this particular case supported by the application of the net-like spacer in the space between membranes. Also suitable geometry of the distribution channels contributes to the uniform distribution of the solution into the working chamber. The optimization of the distribution channels and spacer geometry thus lead to an improvement of the unit performance. Mathematical modeling represents a promising approach to accomplish this task.

From the mathematical point of view net-like spacer represents the most challenging issue. It is because the description of the flow hydrodynamics in this spatially structured system requires three-dimensional (3D) model. When considering dimensions of an industrial system, this is not a feasible task. In this work a novel approach is presented solving the outlined problem by reduction of the model dimensions from 3D to 2D. This is possible because of the structure of the net-like spacer used. It consists of two layers of fibers. In each layer the orientation of the fibers is identical. Due to this the model domain may be separated into two individual hydraulic sub-layers, which can be mathematically treated as 2D. In order to preserve the 3D character of the flow corresponding to the real equipment, exchange of the liquid between the layers is allowed. The model results of laminar and turbulent flow regimes are subsequently compared with the experimental data. The model equations (based on Navier-Stokes eq., anisotropic Darcy's law and continuity eq.) were solved by means of the Finite Elements Method in the COMSOL MultiphysicsTM environment.

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SL F19

EVALUATION ON ECONOMICS OF ASH REMOVAL FROM WHEY PROTEIN BY ION EXCHANGE MEMBRANE

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The myth on achievement of more than 93% demineralization through single process by an Ion Exchange Membrane Unit (Electrodialysis equipment) is removed by setting up the highest performance of the first commercial equipment in India on Acid Whey.

When we have well satisfied on the performance of the Ion Exchange Resin Unit (Filling Columns) and ease of manufacturing operation does not force for us to look for further improvement of production economics. The international demand on the dropping down of Lactose price is forcing the industry to look really on the numbers. Who will believe in the numbers projected by the equipment supplier without having an experience on the Acid Whey? Our experience of more than ten years in this product, plant operation and all together with new experience on the Electrodialysis Unit changed the economics and it is proved now that it is worth putting the Electrodialysis Unit by scraping the Ion Exchange Resin Unit for the production of demineralized whey powder. One can do wonder and various permutation & combination on different range of mineral profile to meet the customer demand. We have the actual industrial plant data and maintenance issues Lets not believe what others say since they can't achieve it since they have not improved for decades as nobody has been asked for.

We will discuss an Electrodialysis Unit operating data, maintenance issues and challenges in this report. The overview on flexibility and demand of complex product and huge reduction of waste water generation makes the Electrodialysis Unit more economical equipment. Presentation will be focused on advantages and inconveniences of electrodialysis technology in comparison with ion exchange resin technology, particularly mass balance results (main yields and losses - proteins, lactose, acids and salts) and energy consumption and other requirements (electricity, water, chemicals, effluent volumes, dimensional specifications).

SL F20

ACTUAL POSITION OF ELECTROMEMBRANE PROCESSES ON THE WORLD DESALINATION MARKET AND FUTURE RESEARCH AND DEVELOPMENT POTENTIAL IN THIS FIELD

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Although all water desalination technologies remain an expensive alternatives to existing water sources, world installed capacity has grown rapidly in recent years. Largest growth contribution lies in rising water demand caused by population growth in scarce water regions (Gulf, Spain, southwest of the USA).

Pressure membrane processes, thermal processes and electromembrane processes are used today for water desalination. Pressure membrane processes (reverse osmosis and nanofiltration) are the most universal technology applied on more than one half of the market. Advantage of reverse osmosis inheres in high rejection, nanofiltration is chosen for its low energy demand. Thermal processes (multi stage flash, multiple effect distribution and vapour compression) gain their position in the desalination of highly salted wastewaters and seawaters of the Gulf region, because of low dependence of thermal process economy on rising salt concentration. Market share of electromembrane processes is relatively small in compare with pressure and thermal ones. Electrodialysis is successful in low salinity brackish water, river water and wastewater desalination and treatment of difficult to treat waters like nitrates removal from wastewater or fluorides from groundwater. Advantage of electrodialysis is high water recovery, caused by higher salt supersaturation, and lower fouling susceptibility, which allow using simpler water pre-treatment. Electrodialysis is also very important process for separation of ionic and non-ionic molecules with large applications in food industry (dairy, wine), electroplating industry and pharmacy. Electrodeionization is gaining its position in pure water market being and alternative to reverse osmosis and ion exchange without any chemical needs. Electrophoresis is used for regeneration of paint coating baths.

Advantages of all desalination technologies are pulled together in hybrid processes. Water treatment process with the recovery of electrodialysis, rejection of reverse osmosis, product quality of electrodeionization and concentrate salinity of thermal process can be realized by combination of all desalination processes. The way leads us through complex mathematical models of joint technology, thorough laboratory and pilot scale experimentation and economical evaluation of every alternative design of hybrid technology. High level of knowledge of hybrid technology is necessary to be able to design desalination plants today, when sizes and capital costs of new desalination project are rising sharply to cut operating costs.

PC 01

THE OSCILLATION OF CONCENTRATION FIELD AT THE MEMBRANE-SOLUTION INTERFACE AND TRANSPORT MECHANISMS UNDER OVERLIMITING CURRENT DENSITY

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Application of laser interferometry allowed visualization the process of formation and development of the diffusion layers in a solution near the surface of a cation-exchange membrane in a wide range of current densities.

The experiments were made in the seven-compartment electro dialysis cell. Central investigated compartment consisted of single-type cation-exchange membranes MC-40, that allowed to consider a membrane relative to cathode as an individual one. The experiment was performed at constant current intensities and the continuous feed of solutions ($Re = 2$). Rotating compartment it was possible to assign any angle between the investigated membrane and the direction of the Earth gravity field. In the work membrane was in two horizontal positions.

Application of laser interferometry allowed to reveal two stages in the development of concentration field. 1 stage: if the current exceeds the limiting diffusion current density within the range from one and a half up to five times then the following facts are observed: laminar character of convective flows in the diffusion boundary layer, oscillation stability of the concentrations profiles; the main transfer mechanism is migration and diffusion. 2 stage: for 5-6 fold exceeding of the limiting current value the following is characteristic: turbulent pulsations of hydrodynamic flow rate towards the surface of membrane; concentration profiles loose their oscillation stability; transfer mechanism is convective (substance towards membrane transported due to pulsations of hydrodynamic flow rate that are normal to the surface of membrane). There are two effects of convection destroying the diffusion boundary layer: gravitational free convection and electroconvection. The fact that development of oscillation does not depended on the membrane position in the gravity field approves that the most probable mechanism of oscillation is electroconvection. It is obtained that in the high-intensive current modes the values of the normal components of the flow rate for hydrodynamic pulsations supplying substance from the bulk of solution to the surface of membrane and intensifying mass transfer were comparable with supply flow rate of solution into membrane passage flow.

PC 02

CURRENT VOLTAGE CURVES AND THE LIMITING CURRENT FOR THE SYSTEM: ANION EXCHANGE MEMBRANE - ACID AND SALT SOLUTIONS

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The electro dialysis is one of the large scale usage method for separation where the driving force is an electric potential difference applied across the membrane stack. The ED finds many applications, e.g. in the desalination of waters, in the industrial waste water treatment, in the food industry, in the recovery of acids, salts and bases, etc. [1].

The efficiency of electro-membrane process depends on many factors. One of the most important is the quality of ion exchange membranes and the hydrodynamic conditions in the membrane module. The hydrodynamic conditions strongly influence the concentration polarization (CP) at the membrane surface, which is caused due to the difference of ion transport numbers in the solution and in the membrane. CP limits the upper value of current density which can be applied. The current density for which the concentration of electrolyte at the membrane surface reaches zero is called the limiting current density, j_{lim} . It is determined from the current-voltage curves.

In this paper the current voltage curves are shown for anion exchange membrane Neosepta ACM (Tokuyama Co., Japan) in dilute aqueous solutions of sulfuric, nitric and phosphoric acid and of their salts (Na_2SO_4 , NaNO_3 and NaH_2PO_4) in the same hydrodynamic conditions. From these curves the limiting current density, j_{lim} , has been determined. For each type of electrolyte the equation relating j_{lim} and the thickness of polarization layer, l_{pol} , has been presented, from which l_{pol} has been calculated. Regarding H_2SO_4 it has been assumed that both HSO_4^- and SO_4^{2-} anions can cross the membrane, whereas the phosphoric acid has been treated as monoprotic acid. The differences in the calculated l_{pol} for each electrolyte has been discussed and the possible explanation has been given.

References

1. K.Scott, Handbook of Industrial Membranes, Elsevier Advanced Technology, Oxford, 1995.

PC 03

CHARACTERIZATION OF THE VARIOUS MODIFICATIONS OF PERFLUORINATED SULPHOCATIONIC MF-4SC MEMBRANES FOR FUEL CELLS

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The membranes materials for fuel cells should have the stable hydrophilicity and high proton conductivity. Samples of perfluorinated sulphocationic MF-4SC membranes, modified by various additives, are prepared. Polyvinyl alcohol, polyvinyl butyral, sulphonated polysulphon and hydrogen zirconium phosphate are used as modifying agents. Water content, exchange capacity, specific conductivity, diffusion permeability and current-voltage curves of modified and hybrid membranes in the HCl solutions were investigated [1]. The structural characteristics membranes are investigated by method of standard porosimetry. The obtained results confirmed the efficiency of modifying.

The experimental data on concentration dependences of conductivity and diffusion permeability are used for calculation of the transport-structural parameters of membranes according to the model approach. These parameters were used for the estimation of the transport numbers of ions in membranes. It was shown that the selectivity of modified membranes does not change.

The water immobilization in the membrane structure due to modifying additives was confirmed by voltammetry method. The effect of a longer plateau of the limiting current was observed in the current-voltage curves of the modified membranes. The slope of the ohmic portion of curve is the same because the membrane contribution in the general resistance of system is not essential. Hybrid materials on the base of perfluorinated sulphocationic MF-4SC membrane and hydrogen zirconium phosphate are more perspective for the application at high temperatures.

The analysis of experimental data permits to propose membranes materials with optimal set of electrochemical characteristics to improve the performance of fuel cells.

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References

1. N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin, *Advances Colloid Interface Sci.*, 139 (2008) 3.

PC 04

VOLTAMMETRIC CHARACTERISTICS OF MF-4SC MEMBRANE, MODIFIED BY POLYANILINE

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The composite membranes on the base of perfluorinated MF-4SC membrane and polyaniline are prepared. The polymerization of aniline proceeded in the membrane matrix (bulk modification) and on the membrane surface (surface modification). The current-voltage characteristics of composites in the “free standing” state are investigated. The parameters of current-voltage curves to be used for testing of membrane are as follows: the slope of the ohmic portion, the limiting current value, the length of limiting current plateau, and the potentials of the transitions into limiting and overlimiting state [1]. The effect of stabilization of limiting current density is observed for MF-4SC membrane after bulk modification [2]. The potential of transition to the overlimiting state for the composite membranes is above 3 V, whereas for the original membrane this value is 0.85 V. It has been shown that the plateau length depends on the type and concentration of solution, characteristics of the original membrane and polyaniline oxidation degree. We assumed that the water energy state in the composite membrane is a key factor determining the potential of transition to the overlimiting state. The effect of current-voltage curves asymmetry is observed for different orientation of the polyaniline layer towards the current direction for an anisotropic composite membrane after surface modification [3]. This effect is investigated in the different conditions of experiment: depending on the speed of current increase in a range from $1 \cdot 10^{-5}$ up to $1 \cdot 10^{-3}$ A/s, and also from an electrolyte type in 0.05 M solutions HCl, NaCl and NaOH. The thickness of the polyaniline layer was defined on the basis of analysis of micro cut photos. The asymmetry effect is discussed taking into account the concentration profile formed inside the composite membrane in the course of polarization.

The present work is supported by the Russian Foundation for Basic Research (project № 08-08-00609).

References

1. N.V. Loza., N.P. Berezina, N.A. Kononenko, S.A. Shkirskaia, *Elektrokhimiya (Rus.J. Electrochemistry)*, 42 (2006) 907.
2. N.P. Berezina, N.A. Kononenko, N.V. Loza., A.A.-R. Sytcheva, *Elektrokhimiya (Rus.J. Electrochemistry)*, 43 (2007) 1417.
3. N.P. Berezina, N.A. Kononenko, A.A.-R. Sytcheva, N.V. Loza, S.A. Shkirskaia, N. Hegman, A. Pungor, *Electrochimica Acta* (in press).

PC 05

MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES OF HETEROGENEOUS ION EXCHANGE MEMBRANES

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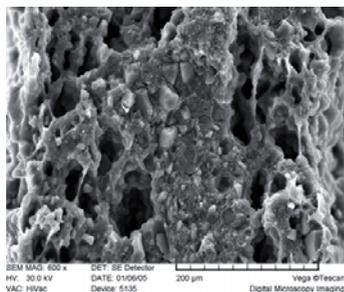
Heterogeneous ion exchange membranes are used in many applications, such as electrodialysis (ED), electrophoresis (EF), electrodeionization (EDI) and low temperature fuel cells (FC). They must be chemically stable and exhibit good mechanical and electrochemical properties.

Heterogeneous ion exchange membranes usually consist of three components: ion exchange resin (cationic or anionic), binder and reinforcing textile.

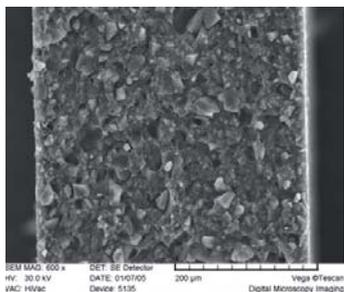
Preparation of heterogeneous ion exchange membranes can be divided into three main steps: ion exchange resin grinding, the preparation of a heterogeneous ion exchange mixture, the preparation of ion exchange membranes by extrusion.

Technology process influences final morphology of the membranes and accompanying mechanical and electrochemical properties which are very important for membrane application. Methods of membrane characterization allow disclosing optimize and solve problems which could occur on a technology scale.

Methods of membrane characterization involved: study of morphology, determination of ion exchange capacity, electrochemical properties (R_A , R_S , permselectivity, and transport numbers), water sorption, gas permeability and porosity measurement.



Extruded membrane



Pressed membrane

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PC 06

CHARACTERISTICS OF ION EXCHANGE AND FILTRATION PROCESS IN THE ZEOLITE-ENHANCED MEMBRANE MICROFILTRATION

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Ion exchange between the sodium ions from zeolite A and calcium ions from solution was studied as a part of planned water cleaning and softening process which combines zeolite ion exchange with constant flux membrane microfiltration. In the process the membrane provides a positive barrier to high concentrations of both natural solids and zeolite, while the added zeolite simultaneously assists in the removal of dissolved compounds such calcium divalent ions.

Both the kinetics and the equilibrium were determined by measuring concentrations of Ca^{2+} ions in the liquid phase during the exchange process. The capacity of the zeolite studied (synthetic zeolite ZP-4A (SILKEM, Kidričevo, Slovenia)) was around 100mg/g as Ca^{2+} . The ion exchange process was rapid and non-linear. The equilibrium was well described by UNILAN model and the kinetics by Ho-McKey's model.

The specific resistance of zeolite filtration cake which was created on the membrane surface decreased significantly from 5.5×10^{10} m/kg to 1×10^{10} m/kg with the increasing amount of calcium ions loaded inside the zeolite particles. Measurements of ζ -potential and the size of zeolite particles have been carried out to examine the reason for the decrease of specific filtration cake resistance. ζ -potential of zeolite particles increased from $-60 \mu\text{V}$ for fresh sodium loaded zeolite to nearly zero for fully calcium loaded particles. The decrease of the particles surface charge resulted in agglomeration into large clusters. The size of the original zeolite particles was in interval from $2 \mu\text{m}$ to $10 \mu\text{m}$ while agglomerates were larger than $100 \mu\text{m}$. Filtration cake formed from these agglomerates was more permeable and the specific filtration cake resistance decreased.

NOVEL ALKALINE POLYMER ELECTROLYTE FOR ELECTROLYTIC SPLITTING OF WATER

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Hydrogen economy represents one of the generally accepted concepts of the future human society supply by the energy. Hydrogen can be used both as a source of the energy as well as the energy carrier for the storage of the peak energy production (especially in the case of the renewable energy source) to be used during the high energy demand. In the first case fossil fuels are the typical raw material for the hydrogen production. In the second case water electrolysis is a typical choice.

Water electrolysis is a well established industrial process. Nowadays it is based on the electrolysis of 20 to 30 % KOH solution. Alkaline environment is used because of the lower corrosive aggressiveness when compared to the acidic one. Liquid electrolyte has to be used because sufficiently stable polymer electrolyte is not available yet. Replacement of the liquid electrolyte by a polymeric membrane and design of corresponding electrode would result in a significant simplification and intensification of the technology. Therefore an important endeavour is invested during the last decades into the development of suitable polymer material and related membrane. This is also the aim of the present study. Several polymers bearing various functional groups based on the quaternary ammonium and phosphonium were selected. Their stability in the alkaline environment was evaluated. On the base of these experiments trialkylbenzylammonium and alkylpyridinium groups have been selected for the further tests. Ion exchange phase has been incorporated into the heterogeneous membranes. Therefore also matrix polymers influence on the properties of the resulting membrane has been studied. Mechanical as well as electrochemical properties of the prepared membranes were determined, including ion exchange capacity and ionic conductivity. Selected membranes showing promising properties were tested in a laboratory electrolyser utilising Pt modified nickel electrodes. Tokuyama A006 anion selective membrane was used as a reference material.

Acknowledgement

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PC 08

THE APPLICATION OF ELECTROCHEMICAL MEMBRANE REACTOR FOR HYDROGENATION OF RAPE OILS

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The increase in the saturation degree of fatty acids present in edible oils by hydrogenation is a major fat modification process in the fats and oils industry used since its development at the beginning of the 1900s. It is carried out to improve oxidative and thermal stability of the oil and to convert normally liquid oil to a semisolid or solid product. The conventional hydrogenation is generally performed in a three-phase semi batch reactor: hydrogen gas is bubbled in hot liquid oil (150-225°C), usually under pressure (10-60 psig), in the presence of a catalyst, typically powdered nickel. Unfortunately, a high reaction temperature favors the production of trans fatty acids isomers, which are harmful to human health. Therefore, the development of low temperature technologies for the hydrogenation of edible oils is of current interest. Several alternatives to conventional hydrogenation processes have been proposed in the past few years. In the last decade Pintauro et al. [1,2] described a low temperature electrochemical method, employing a proton-exchange membrane reactor, for edible oil hydrogenation (soybean, canola and cottonseed oils). Their analysis of the oil indicated satisfactory yields and the lower trans fatty acid formation than obtained by gaseous hydrogenation processes.

In this work we present our results on the hydrogenation of rape oil in the PEM reactor. The preliminary results have shown that it is possible to obtain a partially hydrogenated product with *trans* fatty acids content about 0.5% or even below detectable limit at temperature range 50-60°C. Two membranes have been chosen for detailed testing – Nafion[®] (DuPont, USA) and Fumapem[®] (FuMA-Tech GmbH, Germany). The influence of operating conditions (temperature, current density, flow of oil) on the content of *trans* fatty acids and the efficiency of process is discussed.

References

1. W. An, J.-K. Hong, P. N. Pintauro, J. Appl. Electrochem. 28 (1998) 947.
2. W. An, J.-K. Hong, P. N. Pintauro, K. Warner, W. Neff, J. Am. Oil Chem. Soc. 75(1998)917.

PC 09

ELECTRODIALYSIS FOR THE PRODUCTION OF BUILDING BLOCKS FOR CHEMICALS FROM PROTEIN SOURCES

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Keywords: Electrodialysis, amino acids, zwitterions, iso-electric point, functionalized specialty and bulk chemicals

The conventional route to obtain functionalized chemicals is from hydrocarbon feedstocks. However, the depletion in fossil feedstocks, the increasing oil prices and the ecological problems associated with CO₂ emissions, urges the chemical industry to find novel alternative routes. The aim of the present work is the development of an energy efficient method for the production of functionalized specialty and bulk chemicals from cheap protein sources.

Amino acids, obtained in a mixture (20 amino acids) from hydrolysis of cheap protein sources (e.g. side streams from the production of biotransportation fuels from rapeseed oil) can serve as biomass based precursors, as a source for chemicals. A promising technology to fractionate the amino acid mixture is electrodialysis (ED).

Electrodialysis (ED) is applied for the selective extraction of ions from solutions and can also be used to separate amino acids (zwitterions) based on the differences in their iso-electric points (pI's). Amino acids can become positively or negatively charged due to the loss or gain of protons (H⁺) depending on their surrounding pH. ED should be able to isolate every single amino acid as long as there is a difference in their corresponding iso-electric points. However, the successful fractionation of each amino acid requires the modification thereof to obtain pronounced differences in their pI's.

The research approach consists of four main stages: 1. Proof of principle; 2. Membrane development; 3. Module and dynamics; and 4. Reaction and separation.

This work is performed in close collaboration with Wageningen University (NL).

PC 10

ELECTRODIALYSIS IN WHEY DESALTING PROCESS

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The utilization of whey is limited by its high content of salts. We used electro dialysis unit ED-Z mini (Mega, a.s.) to remove ions from sweet liquid whey and whey with added salt (1 % w/w of NaCl) and observed conductivity changes during the process. Samples were taken every 10 minutes and the drop in K^+ , Na^+ , Ca^{2+} , Mg^{2+} was measured by capillary electrophoresis PrinCE-C750 (Prince Technologies B. V.). Ions were detected with DAD detector at 206 nm and the quantity was determined according to calibration. The negative detection with imidazole in the basic electrolyte was used. Liquid whey was desalted in 50 minutes from the initial conductivity of 4.83 mS.cm^{-1} to 0.32 mS.cm^{-1} . Whey with added salt was desalted in 65 minutes from 18.41 mS.cm^{-1} to 0.34 mS.cm^{-1} . During electro dialysis, priority is given to monovalent ions removal. In whey with no added salts the concentration of K^+ decreased from 1.667 g.L^{-1} to 0.017 g.L^{-1} , Na^+ from 0.425 g.L^{-1} to 0.018 g.L^{-1} , Ca^{2+} from 0.363 g.L^{-1} to 0.018 g.L^{-1} and Mg^{2+} from 0.122 g.L^{-1} to 0.025 g.L^{-1} . In whey with added salt the K^+ concentration decreased from 1.540 g.L^{-1} to 0.043 g.L^{-1} , Na^+ from 3.922 g.L^{-1} to 0.084 g.L^{-1} , Ca^{2+} from 0.325 g.L^{-1} to 0.029 g.L^{-1} and Mg^{2+} from 0.116 g.L^{-1} to 0.015 g.L^{-1} . These results demonstrate that electro dialysis is an effective way of elimination of salts from whey.

PC 11

TRANSPORT OF SULPHURIC ACID AND CUPRIC SULPHATE IN CONTINUOUS DIALYZER

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The simultaneous transport of sulphuric acid and cupric sulphate through an anion-exchange membrane Neosepta-AFN was investigated in a counter-current continuous dialyzer for various acid/salt concentration ratios and volumetric liquid flow rates. The basic transport characteristics – the acid recovery, the rejection coefficient of salt and the overall dialysis coefficient – were evaluated from the measurements at steady state. Under the experimental conditions given, the acid recovery was found to be in the limits from 67% to 91% and the rejection coefficient was in the range from 74% to 96%. The maximum acid recovery can be reached at low volumetric liquid flow rates of the feed and low initial salt concentrations. On the contrary, the maximum rejection of salt can be observed at high volumetric liquid flow rates of the feed and high initial acid and salt concentrations. Nevertheless the results obtained showed that for $\text{H}_2\text{SO}_4/\text{CuSO}_4$ mixture the Neosepta-AFN membrane can be considered a good separator.

PC 12

CURRENT EFFICIENCY OF REMOVAL OF INORGANIC ACIDS IN AN ELECTROLYZER WITH ANION EXCHANGE MEMBRANE

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The industry expansion and economical development require the production cost limitation. Concurrently the strong pressure on environmental protection necessitates the exploration of new ways that fulfill those criteria. The metal plating and finishing industry consumes large amount of inorganic acids used for etching in preparatory processes. The inorganic acids like H_2SO_4 , HCl , HF , HNO_3 , H_3PO_4 are used for this purpose. The acids can be recovered from etching effluents or rinsing water in technological line in electroplating plant by the membrane techniques like diffusion dialysis and electro-dialysis. Therefore for the optimization of these processes it is necessary to understand the membrane transport of ions. The transport of HNO_3 and H_2SO_4 through the anion-exchange membranes (AEM) in diffusion dialysis was described in detail by Palatý and Žáková [1]. The electrotransport of H_2SO_4 in AEM was discussed by Pourcelly et al. [2]. The transport mechanism of multivalent anions in the electro-electrodialysis was described qualitatively by Jörissen et al. [3]. The separation possibility of mixture H_3PO_4 and H_2SO_4 using AEM was investigated in [4].

In this work the electrolysis results of the mixture of HCl and H_2SO_4 with anion exchange membrane ACM (Tokuyama Co., Japan) have been presented. The current efficiencies of pure acids as well as that of the mixture have been determined. The influence of presence of one acid on the transport of another acid has been described. The influence of current density and electrolyte concentration on the current efficiency of acids has been shown.

References

- [1] Z. Palatý, A. Žáková, J. Coll. Interf. Sci. 268 (2003) 188.
- [2] G. Pourcelly, I. Tugan, C. Gavach, J. Membr. Sci. 97 (1994) 99.
- [3] J. Jörissen, S. M. Breiter, C. Funk, J. Membr. Sci. 213 (2003) 247.
- [4] S. Koter, M. Kultys, Electric transport of sulfuric and phosphoric acids through anion-exchange membranes in aqueous solutions, Permea 2009, Prague, 7-11 June, 2009.

PC 13

CHARACTERISTICS OF EDR-III ELECTRODIALYSIS STACK

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Electrodialysis (ED) is a membrane process used for the solution desalination. By this method, it is possible to get two main streams: diluate, a solution with lower salt content than feed, and concentrate, a solution with higher salt content than feed. The driving force for the transport of ions is the gradient of electric potential and the selectivity of the ion transport is assured by ion exchange membranes. Cation exchange membranes are permeable for the cations and anion exchange membranes for the anions. Using the right combination of ion exchange membranes and spacers we can separate the feed into the diluate and the concentrate.

The electrodialysis stack EDR-III, manufactured by MEGA a.s., is composed of two tightening boards containing electrodes, ion exchange membranes and spacers. The electrodes are made from Ti/Pt. It is possible to reverse polarity which helps to protect against fouling and scaling. The stack contains up to 600 cell pairs. Operating conditions are: flow rate 30 – 60 m³/h and voltage max. 500 V. The stacks are used for desalination of water solution with a salt content is in the range 1000 – 8000 mg/L. Depending on the variations of operating conditions and salt content, cut is between 20 – 75 %. The typical cut is 50 % for one hydraulic and electrical stage of ED, higher cuts (up 75 %) can be accomplished in two hydraulic and electrical stages.

PC 14

STUDY OF ELECTRO-MEMBRANE FILTRATION IN ENZYME FRACTIONATION USING AMINO ACID

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Generally, separation of the desired enzyme from other enzymes produced by the cell is attempted using a combination of different chromatography techniques in order to achieve adequate purity or using membrane filtration. However, membrane filtration has low selectivity because of different enzyme with similar size in the complex feeds while chromatography is expensive. Electro-membrane filtration (EMF) seems to be a promising technology for the fractionation of enzyme. The principle of EMF is that it combines the separation mechanisms of membrane filtration on the basis of molecule size and electrophoresis based on the migration of charged molecule when applying an electric field. In order to investigate the potential application of EMF for enzyme fractionation, amino acids are chosen as the model solution mainly for two reasons: firstly, both amino acid and protein have amphoteric character meaning they can be positively or negatively charged depending on the pH of the solution; secondly, amino acids provide a simpler comparison between experimental and theoretical trends: they have hardly any effect on membrane fouling as compared to enzymes, which shows complex behavior on membrane. It is therefore expected that the studies on the separation of amino acids mixture will be beneficial to the further research on enzyme separation.

In this study, EMF of NaCl was firstly carried out in order to understand the basic mechanism of electrophoresis. Results show the conductivity change is dependent on the electric current and electrode polarity. This is in line with the expectation that the transport is governed by electric current and electrode polarity as in conventional electrodialysis; Secondly, EMF of single amino acids, the negatively charged glutamic acid and positively charged lysine was studied. The concentration enrichment of these amino acids in either feed compartment or permeate compartment indicates EMF has the potential to fractionate amino acids with different charge condition. Results show that electric current and the conductivity of the initial permeate solution have effect on the transport rate of amino acids. Finally, the separation of the binary mixture, negatively charged glutamic acid and neutral leucine was successfully carried out. The experiment results show that an enriched fraction of leucine in the permeate compartment can be produced from a model solution. Thus EMF has the potential to become an attractive separation technology.

Furthermore, the studies of amino acid separation are beneficial to the further research of enzyme separation.

PC 15

RECYCLING MEMBRANE CONTACTOR SYSTEM FOR BIOHYDROGEN PURIFICATION

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The search of alternative energy sources becomes more and more important in recent time. Biogenic destruction of organic wastes by certain bacteria community is prospective technology of hydrogen production. Such a way of “biohydrogen” production also is environmental friendly process since it repeats one of the processes of natural organic waste destruction. However, biohydrogen always contains from 20 to 50% of CO₂ as typical by-product. Therefore the recovery of CO₂ from biohydrogen is required to improve the quality of product. Low energy consumption, lower losses of components and high recovery degree of components should be achieved during separation in order to make competitive this technology of hydrogen production. A system based on gas-liquid membrane contactors (GLMCs) is proposed for biohydrogen separation. GLMCs unite advantages of absorption separation methods (high selectivity, wide list of commonly used absorbents) with advantages of membrane separation methods (high, determined and constant area of mass exchange, relatively low energy consumption).

GLMC is a device where gas and liquid phases are separated by a membrane. Suggested separation system consists of two GLMC-modules. First module works as absorber and second one works as desorber. Biohydrogen enters into the absorber where CO₂ is absorbed by a liquid absorbent which constantly circulates between absorber and desorber. The desorber serves for the regeneration of liquid absorbent.

Experimental investigation of mass transfer and hydrodynamics in laboratory GLMC-modules has been carried out. A mathematical model has been developed and used for the investigation of the separation properties and potential of the separation system based on two GLMC-modules. Modelling was carried out in wide range of parameters such as composition of biohydrogen, gas and liquid flow rates.

Obtained results show that suggested system looks very prospective due to high separation characteristics and possibility of separation properties adjustment that is especially important since productivity of bioreactors and/or biohydrogen composition can vary during the time.

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PC 16

CATALYTIC MEMBRANE CONTACTOR/REACTOR (CMCR) FOR WATER TREATMENT

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Introduction

Catalytic membranes form an upcoming area of R&D in the membrane technology field. A new type of catalytic membrane is a hydrophobic polymeric membrane coated with palladium nano-particles - a joint development by TIPS (Russia) and TNO [1]. The working of the CMCR was demonstrated for the hydrogenation of in water dissolved oxygen, and for the combined chemical and biological oxygen and nitrate reduction in water.

Results

Dissolved oxygen reduction in water.

Nanoclusters of Pd particles were deposited on the fibres in Liqui-Cell, Celgard X50 modules. Dissolved oxygen concentrations in water were reduced to the sub-ppb level. Calculations showed that Pd costs are about 5 Euro per 0.4 l. module (with 1.4 m² of membrane).

Combined chemical and biological oxygen and nitrate reduction in water.

Bacterial populations capable of growth with H₂, NO₃⁻ and CO₂ as the sole sources for energy and carbon were obtained from field samples, which formed pink biofilms on virgin membranes. Biofilm formation on Pd-coated membranes was barely visible.

Indications for synergy between chemical and biological catalysis, in the reactor with Pd-coated membranes were:

- A 28% higher maximum nitrate reduction rate,
- A 44% higher maximum bromate reduction rate,
- The up to 20-fold lower effluent nitrate concentrations.

References

[1] J. Membrane Science, 299, pp. 38-44 (August 2007).

THE INFLUENCE OF TYPES OF DUAL MODIFIED STARCHES ON THE ENZYMATIC HYDROLYSIS IN THE CONTINUOUS RECYCLE MEMBRANE REACTOR

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Starches modified doubly by oxidation and acetylation are commonly used and applied in the food industry as stabilizers, thickeners, binding agents and emulsifiers.

The aim of work was to study the influence of the degree of substitution of acetylated oxidized starch (E-1451) on the process of enzymatic hydrolysis in a continuous recycle membrane reactor (CRMR).

Three kinds of E-1451 starch preparations with different degrees of carboxyl group substitution (0.04, 0.11 and 0.5%) and with different degrees of acetylation: 0.5 and 3% were examined.

Hydrolyses were performed in a continuous recycle membrane reactor equipped with an ultrafiltration module containing a ceramic membrane of tubular configuration. The membranes used were characterised by the following parameters: a length of 0.3 meters, external diameter of 10 mm, three channels, and a molecular weight cut-off of 50, 15 or 8 kDa. During the process the membranes were working in four variants: 50 kDa, 15 kDa, set of 50 and 15 kDa, set of 15 and 8 kDa. The hydrolysis process was performed over a period of 150 minutes at a temperature of 60°C, at the transmembrane pressure of 0.5 MPa and with a 0.3 ml of enzyme preparation BAN 480 L per 1 kg of dry starch.

Permeate as well as retentate fractions were collected and dried. The viscosity measurements were performed with the Haake Viscotester VT 550, Thermo Electro Corporation (Germany) at the a temperature of 60°C.

It has been found that different degrees of substitution caused considerably unlike rheological properties of modified starch solutions (starch gruel).

The obtained results of permeate flux and membrane permeability showed that for the sake of quite big viscosity of starch solutions at the beginning of hydrolyse process it was better to apply two different membranes working one after another. The kit consisting of 50 and 15 kDa membranes seemed to be the best solution.

The effectiveness of hydrolysis process was affected by the type of modification as well as the degree of substitution of acetyl groups in the macromolecules of starch.

PC 18

UTILIZATION OF THE PRODUCTS FROM CONCENTRATION OF RED WINE BY NANOFILTRATION

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In the wine there are several components, which have beneficial effect on human organism such as anthocyanidins, their glycosides, the anthocyanins, resveratrol, condensed polyamids etc. They have antioxidant effect and provide protection against cardiovascular system's diseases and different cancers.

The mild concentration of the valuable substances of the red wine can be solved by cross flow nanofiltration (NF) using flat sheet membrane ($R_{NaCl}=75\%$, $A=0.046\text{ m}^2$). Two operating parameters were changed during the concentrations: the temperature (20-40 °C) and transmembrane pressure difference (10-20 bar). The product is the wine-concentrate which contains the valuable components in great amount. The by-product, the nanofiltration permeate can be utilized by distillation due to its alcohol content. Monomer anthocyanin content, total phenolic content, resveratrol content and total acid content were determined in the samples using spectrophotometric, titrimetric and HPLC methods.

The nanofiltration was suitable for the red wine concentration, because in the concentrated wine samples the concentrations of the active compounds were two or three times higher than in the initial red wine. On higher transmembrane pressure difference higher retention was observed but rising the temperature the retentions were decreased. The retentate, the final product had similar alcoholic content as the original wine. If water is added to the retentate, the product will be similar to the wine but with decreased alcohol content. Using distillation the permeate can be utilized as strong alcoholic drink "pálinka" because of its alcohol content. We compared the second distillate of red wine and NF permeate using a descriptive sensory method, the profile analysis. Between the two samples there was no significant differences, which means that the by-product of the wine concentration is a consumable product – "pálinka".

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PC 19

EXPERIMENTAL AND MODELING STUDY OF FRUCTOOLIGOSACCHARIDES FORMATION IN CONTINUOUS MEMBRANE REACTORS

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Fructooligosaccharides (FOS) are considered to be physiologically favourable functional food ingredients. FOS can be produced from sucrose by enzymatic catalysis with free enzymes compartmentalized in continuous membrane bioreactors (CMBR). The synthesis is a complex process involving a multitude of sequential reactions leading to the final products. The resulting FOS structures are mainly 1-kestose (GF₂), nystose (GF₃) and 1^f-fructofuranosyl nystose (GF₄), where, G and F mean glucosyl and fructosyl moieties of the sucrose molecule, respectively. The by-product of the conversion is glucose that has been reported to be the main factor lowering yield during FOS synthesis. Moreover, hydrolysis reactions of FOS also occur resulting lower grades of polymerisation. The amount and nature of FOS formed in the CMBR depends upon several factors including the enzyme source, the concentration and nature of the substrate, the degree of conversion of the substrate and the operation conditions. In this study, a mathematical frame for modeling CMBR processes is provided. The approach followed in this work uses the design equations of the membrane reactor configuration and the coupled equations describing the enzyme kinetics as a basis for calculations. The kinetic parameters are obtained from data in the literature and through well-designed experimentation using various enzyme sources. The simultaneous numerical solution of the proposed set of ordinary differential equations allows the prediction of the dynamic behaviour of FOS production in CMBR systems. The presented simulation technique is a useful tool for obtaining high yield and high purity of FOS by evaluating the optimal system design, operation, and control.

PC 20

CONTINUOUS ORGANIC ACID PRODUCTION IN A MEMBRANE BIOREACTOR WITH SUBMERGED CERAMIC FLAT MEMBRANES

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Most of the organic acids, such as citric and lactic acid, are commercially produced by fermentation in bioreactors. A major objective of fermentation in industry and research is to maximize the volumetric productivity. Membrane bioreactors (MBR) give the possibility for continuous process with cell recycle to obtain high cell concentration and therefore high volumetric productivity. In this device the biocatalyst, enzymes or whole cells are retained by means of membrane. Recycle systems normally used are installed in an external loop including tubular polymeric membranes. In this work, ceramic flat membranes were submerged in the reactor for achieving a high cell concentration with low product inhibition (Fig. 1). The active layer of the membrane is directly faced with the fermentation broth. Minimizing clogging and biofouling effects, fluid dynamic impacts, back-flushing and potential bubble input were investigated in this aqueous-two-phase-system and compared to an external cell recycle configuration (tubular ceramic membrane).

The efficiency of this continuous process using two different bacillus strains regarding to the biomass concentration, medium properties and the control of biofouling was examined.

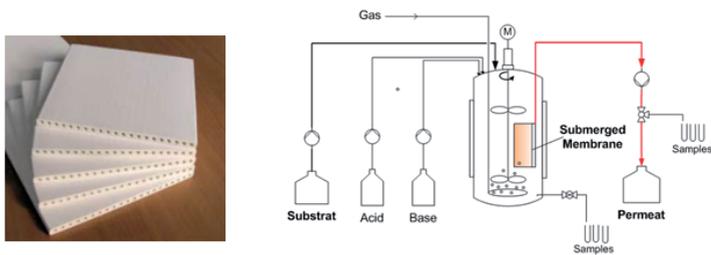


Figure 1 left: ceramic flat membranes; right: flow sheet

PC 21

APPLICATION OF ELECTRODIALYSIS FOR GALACTURONIC ACID RECOVERY FROM AGRO-WASTES

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Pectin rich agro-wastes can be utilised for manufacture of galacturonic acid. Galacturonic acid and derivatives are valuable raw materials in food and cosmetic industries as acidifying agents and for production of vitamin C.

Backbone of pectin molecules is composed of galacturonic acid as a monomer. Sugar beet pulp, apple pomace and other wastes (e.g. press cakes) from fruit juice industry are pectin rich raw materials. To obtain galacturonic acid, pectin is extracted from various raw materials then its enzymatic hydrolysis results in galacturonic acid (GA) in diluted aqueous solution.

In this work the aim was to manufacture galacturonic acid from pectin of press cakes of various berries. For this purpose firstly pectin was extracted with hot water from the press cake then enzymatic hydrolysis was carried out using Pectinex 100L enzyme preparation. The hydrolysate contains mainly carbohydrates (oligo- and monosaccharides) and galacturonic acid. To recover galacturonic acid, electro dialysis (ED) seems a suitable process, because only galacturonic acid is present as a charged compound in the solution.

To obtain galacturonic acid from hydrolysate of pectin a 2 step electro dialysis was used, where in the first step galacturonate was removed from the hydrolysate by using an asymmetric ED cell containing 3 cation and 2 anion selective membranes. Then in the second step galacturonic acid was recovered from the galacturonate by a bipolar ED stack.

EXTRACTION AND SEPARATION OF VALUABLE COMPONENTS FROM TANGERINE PEELS USING MEMBRANE FILTRATION

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Membrane separation processes such as ultrafiltration and reverse osmosis can be used for concentrating solutions and removing solvent not only from fruit juices and similar water solutions but also from extraction solutions.

In the present work ultrafiltration (UF) and reverse osmosis (RO) were used for concentrating and separating solvent from four solutions prepared by extraction of tangerine peels with 50 % aqueous ethanol solution. Extraction was performed by a conventional method for 2 h at room temperature and in three stages. Extract solutions were collected separately after each stage, these being the first three samples to be analyzed. A fourth sample was obtained by collecting together all solutions obtained during the three extraction stages.

For concentrating the extraction solutions a Millipore laboratory scale membrane filtration apparatus was used, with a cross flow mode, and a polysulphone spiral wound for UF and polyamide flat sheet membrane for RO. The concentration of samples by UF was performed at a permeate flux of 18 – 23 L/(m²h) and 7.5 bar transmembrane pressure and recirculation flow rate of 200 L/h. The concentration by RO was performed at a permeate flux of 10 – 14 L/(m²h) and 38.5 bar transmembrane pressure and recirculation flow rate of 400 L/h.

Antioxidant activity, solid content and composition of flavonoids in retentate (R) and permeate (P) were determined by spectrophotometric, gravimetric and HPLC method.

High antioxidant activity was determined for the samples from the first stage of extraction at different membrane processes. The highest antioxidant activity was established for retentate samples following RO. The highest solid content was found in the samples of the first stage of extraction and in the retentate of RO for most samples.

PC 23

A RESEARCH ON MEMBRANE PROCESS OF THERMALLY STABLE SALT REMOVAL FROM ALKANOLAMINE ABSORBENT

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Industrial amine absorbents used for purifying natural and industrial gases from acidic impurities (CO₂, H₂S etc.) gradually lose their absorptive properties because of thermally stable salt (TSS) accumulation. Growing concentrations of these salts lead to a considerable increase in amine solution corrosiveness.

This research focuses on developing an electromembrane-based technology of TSS removal from aqueous alkanolamine solutions. A product of diethanolamine (DEA) reaction with acetic acid was used as TSS model. Electroconductivity of DEA solutions in water was studied. It was shown that electroconductivity dependence on DEA concentration reached the maximum in the range of 15-20% by weight, while DEA solution electroconductivity in the studied acetate concentration range (0 – 2% by weight) increased linearly as acetate concentration grew. The kinetics of DEA acetate removal from the solution (direct electro dialysis) was studied using a laboratory electromembrane apparatus with sequential desalination and concentration chambers. Besides, similar experiments were performed on the same solution treated with NaOH in the amount equivalent to DEA acetate content.

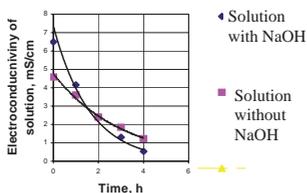


Fig. Electro dialysis process kinetics

As shown in the figure, converting DEA acetate into sodium acetate accelerates the process during its initial stage and reduces energy consumption. Industrial tests of pilot plant with the capacity of 100 l/h confirmed that the research results obtained by modelling were correct.

PC 24

APPLICATION OF CERAMIC ULTRAFILTRATION MEMBRANE IN WATER TREATMENT

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Potable water treatment requires particular commitment in natural organic matter removal. Those substances act as precursors of harmful disinfection by-products, and thus should be removed from water intended for human consumption. Ultrafiltration using ceramic membranes can be a suitable process for natural substances removal. Ceramic membranes are resistant to chemical, physical, thermal, biological and mechanical factors, can be utilized for several years, kept in dry state and disposed, after usage, as ceramic material.

Reported experiments were dedicated to evaluate the suitability of ultrafiltration ceramic membrane for water treatment with remarkable focus on natural organic matter separation. Effect of membrane working time and linear flow velocity on transport and separation properties was also investigated. In the experiments 7 channel 300 kDa MWCO ceramic membrane (Tami) was used. Experiments were carried out on model solutions and surface water (Odra River, Poland) at transmembrane pressure 0.2-0.5 MPa.

On the basis of the results obtained it might be stated that loose UF ceramic membrane can successfully eliminate natural organic matter from water. The colour and absorbance 254 nm retention coefficients exceeded respectively 90 and 70 %,. The increase of transmembrane pressure resulted in slight decrease of separation properties. However the increase of driving force brought about the increase of permeate flux. Analyzing the influence of process duration on transport properties of membrane, the decrease of hydraulic efficiency, due to membrane blocking, was observed. Experimental data clearly suggests that concentration of organic substances in treated water affects the influence of membrane fouling: the increase of organic matter results in higher membrane blocking. The increase of linear flow velocity upgraded the transport and separation properties of membranes. With the increase of flow rate, the decrease of fouling intensity was observed.

PC 25

GASES HIGH PURIFICATION BY MEMBRANE MODULE WITH FEEDING RESERVOIR ON UNSTEADY CONDITION

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Nowadays the membrane gas separation is one of intensively developing fields of gas separation technology. New apparatus are being designed with more and more effective construction and industrial engineering.

In the present work gas purification from low- and high penetrating impurities was offered to be carried out by membrane module with feeding reservoir. In this apparatus purified gas mixture is placed in feeding reservoir from where it is passing to membrane module for separation. Low penetrating impurity is isolated and purified mixture is pumping by compressor to feeding reservoir again then it is recycling.

The math simulation of investigated separation process was created. The calculation was suggested for the case of low concentration impurity and countercurrent flow regime of membrane module operating. Purification degree of gas mixture was defined as the ration of impurity concentration in feeding reservoir before and after purification. It depends on ration of quantity of purified mixture in feeding reservoir before and after purification as power function. It is shown that in investigated apparatus the infinite purification from low penetrable impurity might be carried out fundamentally since impurity is continuously sampling from membrane module.

In this apparatus purification from high penetration impurity might be also realized. In this case purified gas mixture from feeding reservoir is passing to membrane module from where purified gas is sampling. Impurity is concentrating in low pressure cavity of membrane module and pumping by compressor into feeding reservoir where its concentration is increasing. There are two possibilities of purified gas isolating. First is operating at continuous sampling rate and second – at constant product composition (purity level). In the first case the separation degree is constant, while the concentration of impurity is increasing in purified mixture. Therefore, the impurity level in sample products is also increasing over time. In the second case it necessary to carry the process at constant impurity concentration in sampling product which is possible at separation degree increasing in membrane module. It was shown that the second case of purification process (on unsteady condition) is more efficient than the first one, due to losing of energy.

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PC 26

PERFORMANCE EVALUATION OF A SEQUENCING BATCH MEMBRANE BIOREACTOR WITH NUTRIENT REMOVAL AND BACTERIAL DIVERSITY

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This paper is utilized a sequencing batch membrane bioreactor (SBMBR) with intermittent aeration to perform nutrient remove and a partial nitrification process. Several batch experiments were carried out to investigate the nutrient removal characteristics. The removal efficiencies of SS, COD, TN and TP for the SBMBR process were 96.7, 95.5, 73.6 and 98.1%, respectively. It was also found that all the organic- and ammonia-nitrogen was nitrified into nitrite rather than nitrate form, showing partial nitrification. The results of the batch experiments showed that heterotrophic nitrification occurred and that nitrite was still the predominant oxidized nitrogen species. It was also observed that autotrophic denitrification occurred during the denitrification batch experiments, although the autotrophic denitrification rate was only 34% of the heterotrophic denitrification rate. In addition, there was no significant difference in the phosphate uptake rate observed between using nitrite and nitrate as electron acceptors. Finally, 5 and 3 nutrient removal related bacteria were identified in the SBMBR reactor using the pure cultured and cloning methods, respectively.

KEYWORDS

Nitrogen, phosphorus, membrane, cloning, activated sludge.

PC 27

EMULSION PERTRACTION FOR TREATMENT OF PASSIVATING BATH

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Introduction

Passivating is an operation frequently used in galvanic industry to improve corrosion resistance of galvanized objects. Selective removal of accumulated heavy metals with an emulsion pertraction installation will extend the life time of the passivating bath.

Emulsion Pertraction principle

The heavy metal ions to be removed are bound by an acidic extractant present in the pores and lumen of hollow fibre membranes. At the inside of the hollow fibre membranes a dispersed strip liquid continuously regenerates the extractant. In this way an optimal driving force for transport is maintained in the membrane contactor. There is no selectivity needed of the membrane itself; the selectivity of the process is provided by the extractant.

Project Towards an Innovative Galvanic Industry

During the EC Life project Empereur two full scale, fully automated emulsion pertraction installations were successfully demonstrated at the sites of two Dutch galvanic firms. The pay back time is estimated at < 2 years.

In the framework of the EC/FP7 research for SME Associations the emulsion pertraction technology will be adapted to the new generation of Cr(VI)-free passivating baths, which have a factor 20 higher Cr(III) content. Full-scale demonstrations on production lines of 9 SMEs will be performed in Spain, Sweden and the Netherlands.

Acknowledgement

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PC 28

INFLUENCE OF IONIC STRENGTH AND pH OF DISPERSED SYSTEMS ON MICROFILTRATION

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The influence of particle shape, ζ -potential and size with change of pH and ionic strength on permeate flux during the microfiltration of model dispersions (two different china clays with mean particle sizes of 3.5 μm and 1.5 μm) on flat sheet ceramic membranes (ZrO_2 , mean size of pores 0.2 μm) have been studied. The experiments include measurement of the basic characteristics of model dispersions. The description of the experimental system is also presented.

The results of the experiments show that ζ -potential of particles have indispensable impact on the permeate flux. This phenomenon is especially pronounced during the microfiltration of dispersion in the area close to isoelectric point of dispersion, when the value of permeate flux increased to double value of non-treated dispersion (see Fig. 1). This phenomenon has caused the particle interaction. In the area close to isoelectric point the dispersion had tendency to instability, particles tend to aggregate. It resulted in a higher porosity of filter cake and thereby to a higher value of the permeate flux and lower value of the filter cake resistance.

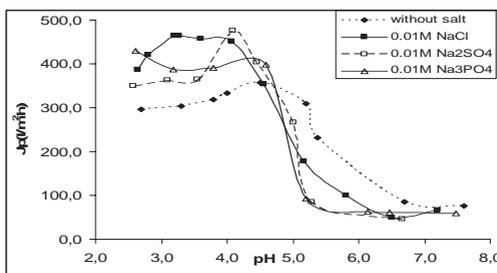


Figure 1: Steady state value of the permeate flux as a function of pH and different ionic strengths of NaCl , Na_2SO_4 and Na_3PO_4

Acknowledgements

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OPTIMIZATION OF THE PROCESS OF REMOVAL OF Co^{2+} IONS FROM WATER SOLUTIONS BY APPLICATION OF SOLUBLE POLYMERS AS THE COMPLEXING AGENTS

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The paper presents the possibility of removing of Co^{2+} ions by application of hybrid complexation-ultrafiltration process. The method of design of experiments has been proved to be an effective tool for optimization of ultrafiltration enhanced by soluble polymers.

In the literature, different treatment technologies for the effective removal of heavy metals such as: chemical precipitation, ion exchange and adsorption on activated carbon, metal oxides, biomass and fungi were reported. However, these techniques are either incapable of reducing the concentrations to the required levels or generate high volumes of sludge or solid wastes.

Alternatively, polymer enhanced ultrafiltration (PEUF) becomes a very attractive method because of high removal efficiency and low energy consumption. PEUF is the process based on the complexation of water soluble polymers with heavy metals in combination with ultrafiltration (UF).

In the process of separation of metals by using of UF method, the influence of different variables such as; pH, polymer-metal contact time, initial metal concentration, polymer loading ratio, ionic strength and temperature should be quantified. Mathematical models can help to obtain a better understanding of the whole process and predict results of untested conditions.

In this study, the optimal conditions of cobalt (II) rejection in PEUF process by using of two different polymers : non-sulfonated PVA and sulfonated PVA were investigated. The optimal conditions of complexation established by response surface model for non-sulfonated PVA polymer are found as follows: initial concentration of $\text{Co}^{2+} = 5.70 \text{ mg L}^{-1}$, the ratio between polymer and metal ions, $r_{(\text{polymer}/\text{metal})} = 8.58$ and $\text{pH} = 5.93$. The retention coefficient in these conditions was 31.94%.

For sulfonated PVA polymer, the optimal conditions were as follows: initial concentration of $\text{Co}^{2+} = 10 \text{ mg L}^{-1}$, $r_{(\text{polymer}/\text{metal})} = 1.2$ and $\text{pH} 6.5$ and the retention coefficient - 99.98%. As it can be clearly seen from this optimal point, Co^{2+} removal ability of sulfonated PVA was quite higher than the non-sulfonated one. Although the polymer concentrations used in the tests with sulfonated PVA were approximately ten times lower than the non-sulfonated one, the removal efficiency of cobalt ions was significantly higher.

PC 30

ZINC RECOVERY USING POLYMER FILTRATION

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The treatment of wastewater containing metallic ions at a relatively low concentration but in a large volume is a problem. Traditional separation techniques such as membrane filtration and/or liquid-liquid extraction are not efficient and evaporation is too expensive. This situation is common and the chemical Nitrate reduction process is a good example. In this case, Nitrates are converted into Nitrogen into a two steps reaction. They are quickly converted into Nitrites using Zinc pellets, and then Sulfamic Acid turns Nitrites into Nitrogen. This operation leaves Zinc cation (Zn^{2+}) at a concentration close to the norm (50 ppm). Therefore, it becomes complex and expensive to recover Zinc by electro-winning because the solution is too diluted.

An alternative is to use water soluble and/or insoluble metal binding chemicals in combination with filtration. This technique is based on size exclusion with retention of the metal ions bound to a chelating agent. Therefore, smaller unbound species in solution are able to freely pass through the pores of the filtration membrane while chelated species remain trapped. Three trial chemicals have been selected, namely: D-Gluconic Acid, Polyacrylic Polymers (low and high molecular weight M_w 15 000 and 100 000) and finally Diethyl Aminoethyl Cellulose (DEAC). This choice covers the main situations encountered in polymer filtration. D-Gluconic Acid forms low molecular weight complexes retained by the filter, but when unbound, it passes through the membrane. The interactions between Zn^{2+} and the two Acrylic Polymers give large moieties retained by membrane. Finally, with DEAC, the chelated ion becomes insoluble and may be separated from the solution by using a standard filtration. The behaviors of the complexed and free zinc were determined by measuring the metal ion retention on stirred dead-end cell at room temperature using a Polyethersulfone 3K membrane (pores size ca. 0,005 micron). The experimental results indicate that at a basic pH (8-9) Zn^{2+} is strongly bound to D-Gluconic Acid, Polyacrylic Polymers and DEAC. In acidic pHs, all these complexes are destroyed. Zn^{2+} release has been carried out at pH 4.70 (with DEAC) and below the pKa of the compounds (3.86 D-Gluconic Acid; 4.25 Acrylic Acid). Zinc retention percentages using an average chelating agent concentration of 0.5-0.2 g/L are respectively equal to 92 % (DEAC), 85 % (D-Gluconic Acid) and ca. 96 % (Acrylic Acid Polymers, low and high molecular weight).

PC 31

INFLUENCE OF PERCENTAGE SHARE OF MUNICIPAL LANDFILL LEACHATE IN A MIXTURE WITH SYNTHETIC WASTEWATER ON THE EFFECTIVENESS OF A TREATMENT PROCESS WITH USE OF MEMBRANE BIOREACTOR

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The investigations covered the determination of the most favourable amount of leachate treated along with synthetic sewage in a membrane bioreactor. Its percentage was changed over a range of 3-40% vol. COD and BOD₅ of the leachate ranged from 3000 to 3500 mg/dm³ and 170 to 280 mg/dm³ respectively. The leachate was characterized by a high concentration of ammonia nitrogen (over 1000 mg/dm³) and low BOD₅/COD ratio (0.06 on average), which indicated its negligible susceptibility to biodegradation.

The concentration of activated sludge in the membrane bioreactor was maintained within 3.5 – 4 g/dm³, the sludge loading with contaminants reached the level of 0.1 gCOD/gTSD while the oxygen concentration in the aeration tank was 4 mgO₂/dm³. The system operated in a 12-h cycle.

The degree of contaminant removal was assessed, analyzing changes in the following indicators: COD, BOD₅, TOC, N-NO₃, N-NH₄, P_{og}.

The results revealed that the volume of leachate in the treated mixture of sewage should not exceed 10%. All the tests showed a decrease in COD and BOD₅ by about 90%. The only indicator which exceeded the standard was nitrate nitrogen. Thus, the leachate purified by activated sludge was additionally treated by reverse osmosis.

Effectiveness of wastewater treatment through reverse osmosis after it was pre-treated applying the membrane bioreactor

Pollution indices	COD	BOD ₅	TOC	N-NH ₄	N-NO ₃	N _{tot}	P _{tot}
Raw wastewater [g/m ³]	800	250	170	180	7,0	640	17
Wastewater after BM [g/m ³]	71	2,0	22	2,5	94	220	2,0
Wastewater after RO process [g/m ³]	1,5	1,0	1,0	0,5	3,5	5,0	0,0

The wastewater thus treated meets the requirements of the Regulations of the Ministry of Environmental Protection dated 28 January 2009 and can be discharged into receiving water.

BROMINATION AND CROSSLINKING OF POLY(VINYLTRIMETHYLSILANE)

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The investigations of polymeric membranes on the base of high permeable glassy vinylic and acetylenic polymers take special place in membrane technology. It is connected with unique gas and vapor separation properties and high gas permeabilities of these polymers [1,2]. However in some cases for the effective use of these polymers it is necessary to increase the separation selectivity for some pairs of gases. Also the improvement of membrane stability to organic components containing in real industrial mixtures is required for some industrial using of polymers. The crosslinking of polymers can be one of methods of the decision of these problems.

This work is dedicated to obtaining of crosslinked polymeric films based on poly(vinyltrimethylsilane) (PVTMS). PVTMS is the representative of high permeable glassy polymers. The method of obtaining of crosslinked polymeric membranes is developed on the basis of brominated PVTMS. We developed the method of insertion of bromine into PVTMS with various agents of bromination (Br₂, N-bromosuccinimide). The use of N-bromosuccinimide as bromination agent allows to perform selective bromination of PVTMS into the trimethylsilyl group (up to 60% wt. of bromine) without any destruction. For crosslinking brominated PVTMS is treated by diamines (ethylenediamine, 1,12 - diaminododecane, 2,2-(ethylenedioxy)-bis-(ethylamine)). Obtained crosslinked samples of PVTMS combine high gas separation selectivity parameters with the resistance to organic solvents.

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[1] N.A. Plate, S.G. Durgaryan, V.S. Khotimsky, V.V. Teplyakov, Yu.P. Yampol'skii. Novel polysiliconolefins for gas separation, *J. Membr. Sci.*, 52, 289 (1990).

[2] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau. Poly[1-(trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and functions, *Prog. Polym. Sci.* 26 (2001) 721-798.

PC 33

STRUCTURE AND PROPERTIES OF MEMBRANES «POLYCON

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Composite chemosorptional fibrous materials are often used as ion-exchange membranes. One of the most perspective methods for making ion-exchange membranes is polycondensational filling when synthesis and formation of ionite matrix occurs on a surface and within the structure of fibrous fillers. Combination of different fibrous fillers and ion-exchange matrices makes possible to produce materials with a wide range of properties (1,2). The process exhibits mutual influence of the binder with fibrous filler, formation of transit layer, interdiffusion of the fiber into the binder and the binder into the fiber and as a result – formation of monolithic structure. Investigation of physicochemical processes running during reinforcement of polymeric binder with chemical fibers shows that fibrous fillers change rate and depth of the binder curing within the composition, structure in the transit layer and within the volume of the polymer, stability of properties of the obtained composite material under the influence of external factors, that is they exhibit chemical activity. Components of polymeric matrix, in their turn, have an influence on the fibers: during diffusion of the low-molecular components of the binder into reinforcing fibers they plasticate and their properties change to some extent.

Membranes «Polycon» can be widely used for several purposes: in sorptional and ultrafiltrational processes as intercanal fillers of electro dialysis units. The advantage of «Polycon» materials is their high sorptional rate, especially at the initial stages, thus providing sorption without additional consumption of energy. They have highly developed surface, that allows to reduce resistance of filtrating layer, to increase stability of purifying, to make filters' design simpler, to reduce energy and water consumption. They have three-dimensional structure with high hydrolytic stability enabling their multiple application in sorptional processes.

POLYMER MEMBRANES MODIFIED BY FULLERENE C₆₀ FOR PERVAPORATION OF ORGANIC MIXTURES

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Inclusion of carbon nanoadditives in polymer matrix can lead to compositions which physico-chemical properties differ from that of parent polymers. Two polymers – poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(phenylene-*iso*-phthalamide) (PA) were modified by fullerene C₆₀ and some other carbon nanostructures. These novel materials were developed by our research team for the use in membrane technology: gas separation, ultrafiltration and pervaporation [1, 2]. The aim of the report is to present transport properties of fullerene-containing materials in pervaporation of (a) the reacting mixture: ethanol – acetic acid – water – ethyl acetate by fullerene-containing PPO membranes and (b) the methanol/cyclohexane mixture with azeotropic point by fullerene-containing PA membranes. The experimental study of thermodynamic and transport properties: dependence of sorption parameters, selectivity and fluxes on the contents of carbon additives in PPO and PA was under the question.

In the case of quaternary reactive system ethanol – acetic acid – water – ethyl acetate, the selectivity of fullerene-containing PPO membranes depends not only on binary interactions between component and the membrane polymer, but also on more complex competitive interplay between all species of the reacting system. The optimal content of fullerene additives in homogeneous membranes should be about 2 wt%: in this case the main component of permeate becomes ethyl acetate. As a result the ethyl acetate removal promotes shifting of the reaction equilibrium and the subsequent accelerating of esterification.

Transport properties of membranes based on pure PA and its composites containing 2, 5, and 10 wt% C₆₀ were studied in pervaporation of methanol/cyclohexane mixture. All membranes were essentially permeable with respect to methanol. As compared with pure PA, the flux and so-called inverse selective separation properties were improving for membranes containing 2 and 5 wt% C₆₀, whereas these transport parameters were all out of this proportion for membrane containing 10% C₆₀.

To give an exhaustive characterization of the transport processes, membrane swelling or sorption toward individual components of liquid mixtures was studied. Transport properties were analyzed by using some physical properties: intrinsic viscosity, density, and contact angles that characterize surface tension of homogeneous membranes.

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1. Polotskaya G.A., Penkova A.V., Toikka A.M., Pientka Z., Brozova L., Bleha M. *Separation Science and Technology*. 2007 42 (2) 333.
2. Penkova A., Toikka A., Kostereva T., Polotskaya G. *Nanotubes, and Carbon Nanostructures*. 2008 16 398.

CHITIN WHISKER-REINFORCED CHITOSAN FILMS FORMED UNDER APPLIED ELECTRIC FIELD

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Chitosan membranes and films are usually prepared from high-molecular-weight (HMW) chitosan, which exhibits good film-forming properties owing to multiple intra- and intermolecular hydrogen bonding. It was reported that the tensile strength of chitosan films in an aqueous environment increases and their affinity to water decreases with incorporation of α -chitin whiskers. These slender chitin rods with nano dimensions (width \times length 5-70 \times 150-800 nm) reinforce the chitosan phase.

In this study the chitin whisker-reinforced chitosan films were prepared under the applied homogeneous electric field by the solution casting technique. In films preparation, two fractions of commercial chitosan (Aldrich) with the average weight molecular weight (Mw) 536 and 789 kDa with deacetylation degree (DD) 82.6 and 79.0%, respectively, were used. Chitosan was dissolved in 1 % aqueous solution of acetic acid, mixed with concentrated aqueous solution of α -chitin whiskers (MaviSud Ltd, Italy), cast on a glass plate, which was finally placed between two metal plate electrodes. The electric field (6 kV) was created by means of a soft power supply PBK4 (Information Unlimited, Inc, USA). At fixed experimental conditions above mentioned, the only variable was the content of chitin whiskers (0.75 - 30 %) in chitosan films. The films with the same compositions were prepared by the tradition casting technique, i.e. without the applied electric field for evaluating its contribution to the composite chitosan film properties.

It was shown that there is the limit of the α -chitin whisker content, higher which the properties of the composite chitosan films become worse independently whether the electric field was applied during their formation or not. The effects of the applied electric field on structural, mechanical and gas permeable properties of the chitin whiskers-reinforced chitosan films were analyzed and discussed.

Acknowledgements

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PC 36

REFRIGERATION SYSTEM FOR PILOT SCALE MEMBRANE APPARATUSES AND ITS APPLICATION FOR JUICE CONCENTRATION

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One of the main advantages of the membrane separation of foodstuffs is the low temperature procedure. In many cases the membrane separation can be carried out at room temperature or below room temperature, therefore the valuable components are not damaged by thermal decomposition. During the filtration of viscous juices an application of recycle is necessary to decrease the fouling. This recycle flow rate causes friction and step by step increases the temperature of the juice. In the Hungarian climate at summer time the cooling down of the juice can not be solved by cooling water circulation, the available juice temperature is 35 °C, or more.

To keep a lower temperature in the membrane apparatuses a pilot size refrigeration system was designed and constructed, which can serve three parallel membrane units. The base of the design was a systematic measurement series with different juices (black-current, raspberry, must and apricot) [1,2], different membranes (MF or UF for clearing and NF or RO for concentration) and different recycle flow rates to find out the relation among the temperature increase in the different apparatuses, at changed raw materials and various operation parameters. The cooling of the juices was strongly influenced by the intermediary liquid (water or glycol-water solution) as well.

On the base of the measured data it was calculated the maximal and the average heat capacity, the surface of the heat exchangers, pipes and valves etc. and the control system. The precision of the temperature is ± 0.5 °C in the three parallel apparatuses during the concentration of different juices.

[1] Sz. Banvolgyi, Sz. Horvath, E. Bekassy-Molnar, G. Vatai: Concentration of blackcurrant (*Ribes nigrum* L.) juice with nanofiltration, *Desalination* 200 (2006) 535–536

[2] A. Kozak, Sz. Banvolgyi, I. Vincze, I. Kiss, E. Bekassy-Molnar, Gy. Vatai: Comparison of integrated large scale and laboratory scale membrane processes for the production of black currant juice concentrate, *Chemical Engineering and Processing: Process Intensification*, Volume 47 (2008) 1171-1177

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THE DEVELOPMENT OF SILICA-FILLED THIN FILM POLY(1-TRIMETHYLSILYL-1-PROPYLENE) MEMBRANES FOR ORGANOPHILIC PERVAPORATION

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Poly(1-trimethylsilyl-1-propyne) (PTMSP) is a substituted polyacetylene that exhibits the highest oxygen permeability of all known synthetic polymers. The high permeability can be attributed to the extremely high free volume of the polymer matrix, which can be further increased by incorporation of silica nano-particles [K. De Sitter et al., PhD thesis K.U. Leuven, 2007]. In this work the potential of PTMSP based membranes in organophilic/hydrophobic pervaporation (PV) and solvent-resistant nanofiltration (SRNF) will be discussed.

A thin PTMSP/silica film is coated onto a support membrane, which has to be highly porous, may not negatively influence the selectivity and should provide mechanical stability to the silica-filled PTMSP layer.

A first part of this work consisted of the characterization of two different support membranes: polyacrylonitril (PAN) and polyvinylidene fluoride (PVDF). Clean water flux, molecular weight cut-off, contact angle, surface roughness, scanning electron microscopy and capillary flow analysis are some of the tests that were performed. PVDF displayed superior properties and was therefore used in this work.

A second part in this study focused on the characterization of the polymer and to define the desired membrane properties for PV and SRNF. Different polymer batches were characterized for molecular weight, structure, dope rheology and purity. Positron annihilation lifetime spectroscopy (PALS) measurements were performed to quantify the free volume of the different batches.

Initial PV tests on a 10/90 wt% ethanol/water feed resulted in fluxes up to $3,7 \pm 1,3$ kg/m².h and selectivities of 12 ± 2 for the thin film silica-filled composite PTMSP/PVDF membranes. Due to PTMSP's poor chemical stability in a wide range of solvents, the membranes need to be crosslinked. By heat treating the final membrane, 3,3'-diazidodiphenylsulfone will decompose and the resulting nitrenes will insert into a carbon-hydrogen bond in PTMSP to form a substituted amine [S.D.Kelman et al., *Polymer* 48 (2007), 6881-6892]. The influence of the crosslinks on the membrane characteristics in PV and SRNF will be investigated.

COMPOSITE MEMBRANE MATERIAL WITH SELECTIVE NaA ZEOLITE LAYER ON FLEXIBLE SUPPORT

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Dehydration of organic solvents and reagents is the problem of permanent importance. Among existing technological solutions for these processes pervaporation is the most promising method in terms of energy and resource saving. Zeolite NaA membranes are already used for water removal in industry and surpass numerous polymeric membranes. Usually the tubular alumina supports with thin layer of zeolite are applied. In the frame of this work the new type of composite membrane material with selective NaA zeolite layer was developed. The support consists of stainless steel net coated with ceramic layer of TiO₂. This material is very flexible and can be easily installed into various housings. Pervaporation tests of these membranes were carried out in specific regime with constant feed composition of water/alcohol mixture from one side of membrane. Separation characteristics were calculated from the weight of permeate and its composition (Fig. 1).

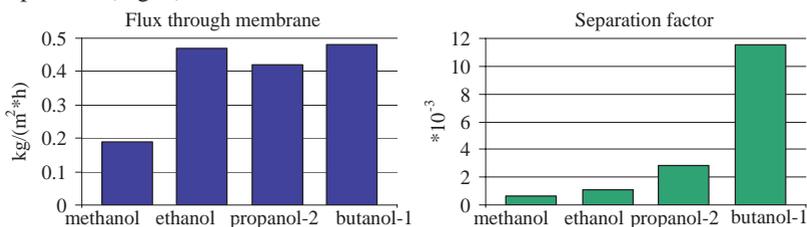


Fig. 1. Separation characteristics for alcohol/water mixtures at 75 °C, water content in the feed of 10 wt. %.

Sufficiently high separation factor and permeability in combination with flexibility and installation simplicity into compact modules are significant advantage of this composite membrane.

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PERVAPORATION MEMBRANES BASED ON COMPOSITES OF POLYIMIDE WITH POLYANILINE OR ITS COPOLYMER

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Modern application of membrane technologies for solving environmental problems and for separation of chemically aggressive mixtures in industry promotes the search of new membrane materials. Polyaniline (PANI) is a electroconductive polymer with properties, which may be of great practical interest for membrane use because of its high selectivity in separation of small molecules and high chemical stability to the most solvents. However, low mechanical properties and high melting point of PANI restrict the formation of free-standing membranes. To maintain the required mechanical properties in the present work, PANI was involved in matrix of aromatic polyimide poly{[4,4'-bis(4''-N-phenoxy)diphenylsulfone]imide-1,3-bis(3,4-dicarboxyphenoxy)benzene] (PI). PI-PANI composites were prepared by mixing PI and PANI solutions in N- methylpyrrolidone with ultrasonic treatment. In this work, besides of PANI homopolymer, copolymer of aniline with anthranilic acid was used. Poly(anthranilic acid) can be transformed into PANI after membrane formation by decarboxylation at 250⁰C.

The membranes were characterized by thermogravimetric analysis, transmission electron microscopy, and surface tension measurements. It was established that contact angles of water and methanol on membrane surfaces increase, whereas contact angle of toluene decreases with increasing PANI content in the composite. It is evidenced that membrane surfaces became more hydrophobic due to the inclusion of PANI into the PI matrix.

Transport properties of membranes were studied in pervaporation and sorption experiments. Pervaporation of two organic mixtures: methanol/toluene and methanol/cyclohexane was researched at 50⁰C. Membranes based on PI-PANI composites were selective with respect to methanol in pervaporation of both organic mixtures. It was shown that values of equilibrium sorption for methanol and toluene decrease upon inclusion of rigid PANI centers into the PI matrix which leads to increasing Flory-Huggins interaction parameters χ .

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PC 40

MICRORELIEF AND ROUGHNESS OF ION EXCHANGE MEMBRANES STUDIED BY THE TAPPING MODE ATOMIC FORCE MICROSCOPE

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Ion exchange membranes have an inhomogeneous and rough surface that influences on their operational electrochemical and mass-exchange characteristics. The roughness of the surface, i.e. the set of fine irregularities forming the surface micro-relief with a rather small step, is the reason for that the real membrane area available for mass-exchange, S , is larger than the visible geometric surface area, S_g . The exchange area relates to the visible geometrical area of the membrane by the factor of roughness $f_r = S/S_g$.

The purpose of the work is to study the true area of ion exchange membrane surfaces and, in particular, to find the surface roughness caused by factors of different nature, by applying the AFM method providing quantitative measurements.

Microscopic researches was carried out by means of the scanning probe microscope produced by the NT-MDT corporation, Solver P47 Pro model (Russia, Zelenograd) in the semi-contact mode on the dry samples. According to the international standards, the phenomenological parameters of homogeneous and heterogeneous ion exchange membrane surface were measured. Scale properties of the surface amplitude characteristics (roughness, asymmetry, excess) were revealed. It was found that in the dry state, the surface of ion exchange membranes is morphologically macro-heterogeneous; however, the micro-roughness is insignificant. For heterogeneous membranes, the height of the macro-heterogeneous relief is 1 to 2 microns.

The effect of membrane conditioning in solutions and current/heating application on the morphology and the microrelief of several ion exchange membranes was examined. It was established that the commercial membrane samples are characterized by relatively small values of the roughness factor. After application of an electric current and/or elevated temperature, the value of f_r was found increased.

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PC 41

GYROID MEMBRANES MADE FROM NANOPOROUS BLOCK COPOLYMERS.

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Block copolymers have an amazing possibility to self-organize into specific structures in the nanoscale. Chemical incompatibility between the copolymer blocks is the main driving force for the self-organization. We can control the copolymer morphology by controlling the total molecular weight and the composition of the block copolymer during the polymerization. Nanoporous material can be obtained by removing (etching) the minority block from the matrix of the majority block. Such a nanoporous material with well defined pore size can find many applications. Ultrafiltration membrane is one of them.

Here we present a nanoporous material with gyroid morphology from 1,2-polybutadiene-polydimethylsiloxane (PB-PDMS) crosslinked by dicumyl peroxide (DCP). The PDMS block was etched by tetrabutylammonium fluoride (TBAF) or by hydrogen fluoride (HF) after the crosslinking of the PB block.

During testing gases permeability and separation properties it was concluded, that a skin layer is formed on at least one surface of a sample, which was confirmed by atomic force microscopy (AFM) results. An effort to remove this skin layer was put and results of differently treated samples are compared.

In order to test the separation properties of the membranes a solution of different polyethylene glycols (PEG) was filtered. Different molecular weights of PEG (56, 12, 8, 3 and 1 kg/mol) were dissolved in methanol/water mixture with 80/20 volume ratio. Figure 1 shows results of three permeates and feed as characterized by size exclusion chromatography (SEC).

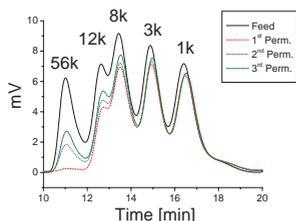


Figure 1 Comparison of SEC data obtained from the feed and permeates of the PEG solution in methanol/water mixture.

The following permeates unfortunately showed 56k peak. The reason is probably concentration polarization caused by insufficient stirring. New set up to avoid this problem is designed. Finally some techniques to prepare thin nanoporous film are found.

PC 42

SURFACE MODIFICATION OF VBC-S-DVB MICROSOPHERES IN PREPARATION OF SORBENTS FOR AMF PROCESS

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In many regions, water shortage forces to use saline resources that endangers present and future social and economic development. Boron seems to be one of the problematic ingredient due to its difficulties to remove from water. If it is present in larger amount it becomes toxic. For that reason WHO recommends 0.3 µg/L as the critical value for tap water. There are several methods used for removal of boron but the conventional separation processes could not match the actual challenges of environmental control. So, it strong need to find more economically efficient method for B removal. Adsorption membrane filtration, AMF, process is a relatively new separation technique that integrates sorption with membrane separation. This hybrid can be successfully applied either to water treatment and recovery of any valuable component. The paper deals with studies on preparation of polymeric microspheres with N-methyl-D-glucamine (NMDG) ligands. The efficiency of prepared resins in boron removal was investigated and was compared to the efficiency of commercial sorbent. New polymeric resins were synthesized by reacting NMDG with vinylbenzyl chloride-styrene-divinylbenzene (VBC/S/DVB) copolymer at the reflux temperature, 1,4-dioxane as solvent, and in microwave reactor, dimethyl sulfide (DMSO) as solvent. VBC/S/DVB copolymer with gel structure, containing 6 wt % DVB was obtained using membrane emulsification and suspension polymerization. After selection of emulsification and polymerization parameters it was possible to obtain particles with 25 µm diameter and narrow size distribution. The obtained resins were characterized using FTIR, XPS and elemental analysis. These polymeric materials were evaluated for removal of boron from solution containing 2 ppm of B, pH = 8.2, in AMF process. It was shown that among the synthesized resins that one obtained by microwave modification showed the best sorption property towards B. It was comparable to commercially available resin Dowex XUS 4359.00.

MEMBRANE EMULSIFICATION AS THE METHOD FOR PREPARATION OF MOLECULAR IMPRINTED POLYMER MICROSPHERES

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A new method for syntheses of uniform poly(styrene-co-divinylbenzene) microspheres containing template dibutyl phthalate with high specific surface areas was designed by combining membrane emulsification technique and suspension polymerization. In the first step the oil in water emulsion was prepared. Membrane emulsification is relatively new membrane technique that allows production of emulsion droplets under controlled conditions and with a narrow droplet size distribution. The formation of droplets is a superposition of the following process parameters: pore size and the wetting properties of membranes, transmembrane pressure, the viscosity of both phases, presence of emulsifier, temperature, and so on.

After emulsification the o/w emulsion was poured into the round-bottom flask and the suspension polymerization was carried out. In the presented studies such parameters as ratio of monomers, kind and amount of porogens, amount of template, amount of organic phase and composition of water phase were altered to investigate their effect on geometry of obtained microspheres. The studies were supplemented by the effect of time and temperature of polymerization. The research was focused on selection of such process parameters that guaranteed preparation of monodisperse microspheres with template foot-prints and high surface areas. It was found that physicochemical properties of porogens had essential effect on the size distribution and porous features of obtained particles. The uniform (SPAN < 0.6) microspheres with high yields was obtained using porogen with the low aqueous solubility. It was noted that the concentration of organic phase did not affect the properties of P(St-co-DVB) particles even when higher concentration of dispersion phase was applied. The proper adjustment of other parameters can cancel such influence. Concentration of PVA modifies the diameter distribution of obtained spheres however the differences are not so large. The molecular weight of PVA has a great influence of the properties of emulsions and polymeric particles. The obtained imprinted microspheres showed higher sorption capacity towards dibutyl phthalate than their off-template analogues. It was shown that membrane emulsification is the useful method for formation of monodispersed particles with foot-prints of separated species.

THE MODIFIED ULTRAFILTRATION MEMBRANES AND ASYMMETRY OF THEIR TRANSPORT PROPERTIES

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Modified ultrafiltration membranes on the base of aromatic polyamide and polysulfone membrane matrix are prepared. Dilute solutions of polyelectrolytes are used as modifying agents. Transport properties of the modified membranes are investigated. The water permeability (at pressure 0.2 MPa) decreases essentially, and rejection of polyethyleneglycol ($M_w=1000$) grows sharply. Thus the efficiency of modifying is confirmed. The diffusion permeability of modified ultrafiltration membranes is also measured. The diffusion of NaCl solution through a membrane to the "pure" water side is studied. The effect of asymmetry of diffusive characteristics is found for some samples. A membrane on the base of aromatic polyamide after two-layer modifying by the polyelectrolyte is most perspective for research of asymmetry effects of transport properties.

The theory of "fine porous membrane" is applied for an estimation of experimentally observable asymmetry effect of the diffusion permeability [1]. The mathematical model describing a filtration process of electrolyte solutions of various types using bi-layer membranes is developed and the analytical solution is obtained. The algorithm and program for calculation of concentration profiles and rejection ability of a membrane system is created depending on the given difference of pressure and initial concentration, as well as a density of the fixed charges of membrane layers. As a result the qualitative conformity between theoretical and experimental results is obtained and the asymmetry effect of the rejection ability of the bi-layer system is confirmed for various orientations of a membrane to a salt flow.

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References

1. A.N. Filippov, V.M. Starov, N.A. Kononenko, N.P. Berezina, *Advances Colloid Interface Sci.*, 139 (2008). 29.

PC 45

A MODEL FOR THE MICROFILTRATION OF WHEY WITH CERAMIC TUBE MEMBRANES

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Sweet whey is a by-product of cheese production, it takes 90 volume % of the fresh milk. Not long ago it was considered as a useless by-product, and was released to sewage, causing an auxiliary load to the wastewater treatment plants. Nowadays application of whey became important topic, because it contains valuable materials for the human organism. In some cases, for example in soft drink production, application of whey may require a reduction of water and salts. In our earlier researches we proved that the nanofiltration combined with diafiltration can be used for concentration of proteins and lactose in whey. With this process we may reduce the water and monovalent ions (sodium, potassium, chloride), but lactose, proteins and bivalent ions (calcium, magnesium) will be retained by the membrane and concentrated. For using a spiral wound nanofiltration membrane module for this concentration-diafiltration, the removal suspended solids from the whey is necessary, otherwise they would foul the spacer of the membrane.

Microfiltration can be an effective pre-filtration process, the lipids and bacteria can be removed from the whey before the next operation, while the proteins and lactose will not be retained by the membrane. In our current research, we were analyzing the effect of the different operating parameters and the static mixer to the flux and to the rejection properties of the ceramic tubular microfiltration membrane.

As a result of our experiments, we can tell that microfiltration is an effective filtration process, where different suspended solid materials could be removed from whey before the next operation. At the same time most of the lactose and proteins passed through the membrane into the permeate. The microfiltration process was modeled on the basis of the experimental data using the models from literature. With this model we can express the effect of different operating parameters and the effect of static mixer to the flux and to the retention of some whey components, using microfiltration membrane.

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PC 47

EVALUATION OF NANOFILTRATION FOR DIAFILTRATION OF DYES SOLUTIONS: EXPERIMENTAL OBSERVATIONS AND MODEL VERIFICATION

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In the manufacture of liquid dyes, almost complete desalting, which helps to improve the stability of the product, enhances the solubility of the dye. Diafiltration is used to allow a high level of desalting to be achieved. However, the success of the application of NF for the desalting is related, among other factors, with magnitude of the permeate fluxes decline. Here we show that the dye and salt concentration, the salt rejection and pressure applied are responsible for the decrease of flux values as well as for desalting purposes. We found in the process of desalination of aqueous dye-salt solutions by polymeric NF membranes (Esna 1, Desal 5DK, NF 70, NF 90, NF 270 and TR 60) that cake layer formation of dye molecules on membrane surface, especially at low salt concentrations, was the principal cause of flux decline. Furthermore, we found that from the solution-diffusion model, the intrinsic rejection coefficient can be predicted as function of feed dye concentration.

Our results demonstrate how the mathematical modelling of NF and description of discontinuous diafiltration by periodically adding solvent at constant pressure difference can be important for prediction of the diafiltration process in the manufacture of liquid dyes. We anticipate our results to be a starting point for more precise models of desalination process.

Acknowledgements

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PC 48

APPLICATION OF THE TRACER TECHNIQUE FOR EVALUATION OF THE FLOW STRUCTURE IN MEMBRANE MODULES

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Residence time distribution (RTD) technique for diagnosing hydrodynamic conditions in the ultrafiltration module with movable part creating helical Taylor-Couette flow (CTF) inside the tubular, membrane apparatus and the module with cross flow, was applied. The possibility of application of fluorescein and radioactive ^{99m}Tc in the form of pertechnetate ion ($^{99m}\text{TcO}_4^-$) as the tracers for this purpose was tested.

The tracer studies were supplemented by modelling. The model of retentate flow consisting of two axial – dispersion models open-open and open-closed connected in series was developed. The influence of process parameters: transmembrane pressure (P), retentate flow (Q_R) and rotation frequency of the inner cylinder (Ω) on mean residence time (MRT) and dimensionless variance of residence time (vard) has been evaluated.

The results obtained have shown strong reduction of vard with the rise of all considered process parameters. With the rise of retentate flow and transmembrane pressure the MRT decreased. The retentate flow structure for open-open model was close to the plug flow and it was expressed by high value of Peclet number. There was no significant change of Peclet number for the open-closed model.

Response surface methodology with central composite orthogonal design for modelling of hydrodynamic conditions in the apparatus and for studying the interactions of the process variables was applied. The optimal process parameters were as follows: $P=0.81$ bar, $Q_R=105.37$ l/h, $\Omega=2661.25$ rpm. Under these conditions the retentate flow structure was very close to the plug flow.

Another membrane module with cross-flow “static” configuration was studied by RTD method combined with the tracer technique. In that case 1-meter long tubular module was divided into two sections to observe more precisely different hydrodynamic conditions in particular sections. For each section the model consisting of two units with axial dispersion open-open channel type, connected in series was applied. Very small value of Peclet number in the initial zone of the first section was obtained from the data of experiments. It might be due to the inlet effect, because of velocity profile equalization in small distance from the inlet to the module.

PC 49

DO THE MOLECULAR DESCRIPTORS CAN BE USED FOR THE PREDICTION OF RETENTION IN NONAQUEOUS NANOFILTRATION ?

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The molecular descriptions have been applied for the characterization of retention data in organic solvent nanofiltration. The descriptors of solute molecules were calculated using the program Dragon ver. 5.5 enabling the calculation of 1664 descriptors divided into 20 groups. Before that the geometry of molecules has been optimized using Gaussian®. Two linear model equations relating the retention coefficient, R , with one ($R = a_0 + a_d d$) and with two descriptors ($R = a_0 + a_{d1} d_1 + a_{d2} d_2$) have been tested using the literature data for two sets of solutes. The first one (“soft” set) consisted of saturated and aromatic hydrocarbons (White’s data), the second one (“hard” set) contained the substituted aromatic hydrocarbons with heteroatoms (data of Geens et al.). The “hard” set was tested in 14 membrane-solvent systems.

It has been found that the “soft” set of compounds is described reasonably well by both equations; the 1-descriptor equation has yielded the cross-validation coefficient $Q_{cv}^2 > 0.95$, for the 2-descriptors equation Q_{cv}^2 was significantly higher (> 0.995). The best descriptors belong to GETAWAY descriptors and Burden eigenvalues.

Regarding the “hard” set of compounds the 1-descriptor equation fails, whereas for the 2-descriptors equation for each membrane-solvent system a pair of descriptors yielding $Q_{cv}^2 > 0.99$ has been found. However, that equation is still not satisfactory when applied with the same descriptors to the couples of systems even with the same membrane or solvent. No dominant group of descriptors regarding all 14 membrane-solvent systems for that set of solutes has been found. Taking the 1- or 2-descriptors equation and seeking the common descriptors for a couple of systems it automatically involves the assumption that the change of solvent or membrane will affect only the coefficients of these equations. However, the situation is more complicated and more sophisticated models should be taken into consideration.

PC 50

MODELLING OF FACILITATED DIFFUSION OF AMINO ACIDS IN THE SOLUTION/ ION EXCHANGE MEMBRANE SYSTEM WITH NON-CONDUCTING SPACER

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The term of "facilitated" diffusion describes the anomaly high rate of substance transfer in membranes (biological, liquid, ion-exchange) due to a carrier within the membrane. In the case of amino acid and a cation-exchange membrane in H^+ form, a bipolar ion A^\pm form a cation AH^+ with H^+ at one side of the membrane, then this cation diffuses through the membrane to release A^\pm at the other side. The concentration and, hence, the diffusion flux of AH^+ are generally much higher than those of A^\pm .

A mathematical model of the "facilitated" amino acid transport in a membrane system of cylindrical geometry was developed. A hollow fibre membrane was located within an impermeable coaxial cylinder. We considered the cases of presence or absence of a rectangular non-conducting spacer adjacent to the membrane surface on the side of the cylinder. The equations of hydrodynamics, convective diffusion and the boundary conditions, connecting the convective-diffusion transfer of a substance in the feed / receiving solution and in the membrane phase were used. The influence of hydrodynamic, geometric and concentration parameters on the "facilitated" transport of amino acids with or without the spacer was analyzed. The equations were reduced to a dimensionless form. Using a numerical solution based on the control volume approach, the local and mean characteristics of the process (concentration profiles, distribution of local surface concentration, amino acid flow and factor of facilitation) at different flow rates in the internal and external compartments were calculated.

Comparison of theoretical and experimental results has shown a good model adequacy. Theoretical optimization of the spacer size was carried out.

The work was performed under financial support of the Russian Foundation for Basic Research (project *09-03-97567-r_centre_a*).

PC 51

COMPARISON OF TRANSPORT PROPERTIES OF HYPERBRANCHED AND LINEAR POLYIMIDES

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Polyimides exhibit very good overall stability at temperatures from -150 to 250 °C. These rigid polymers with a high glass transition temperature are mostly used in (micro)electronics, aircraft (space) industry and as separation membranes [1]. Non-porous, flat polyimide membranes show high separation factors (selectivities) in separation of selected gas mixtures but low permeability both of gases with larger molecules and organic vapours. The permeability in a polymer depends on the solubility and the diffusivity of the permeating species in that polymer. When the difference in the solubilities is low mostly glassy polymers are used and the separation is more based on the difference in diffusivity which is also governed by the free volume of polymer. From the point of view of a controllable free volume, hyperbranched polymers are very attractive candidates to the membranes with convenient transport properties. It is reported that according to the results of computer simulation there are many accessible cavities of atomic and slightly larger size in the rigid hyperbranched polymers, i.e. also in hyperbranched polyimides [2]. In our contribution we will namely present the transport properties of membranes made of hyperbranched polyimides based on 4,4',4''-triaminotriphenylmethane and 4,4'-oxydiphthalic anhydride for hydrogen, nitrogen, oxygen, carbon dioxide and methane. The comparison with transport properties of the linear polyimide based on 4,4'-methylenedianiline and 4,4'-oxydiphthalic anhydride will be made.

Acknowledgement: The grants of GA CR 104/09/1357 and MSM 6046137302 and 6046137307 are gratefully acknowledged.

[1] Hergenrother P.M.: High Perform. Polym. **15**, 3(2003).

[2] Fang J., Kita H., Okamoto K.: J. Membr. Sci. **182**, 245 (2001).

PC 52

COUPLING EFFECT DURING VAPOUR PERMEATION OF ORGANIC MIXTURES THROUGH POLYMERIC MEMBRANES

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A mass transport of organic compounds and their binary mixtures at wide activity range through dense semicrystalline low density polyethylene membranes is presented. Single and binary vapour permeation measurements were performed at 25°C by the differential flow permeation apparatus connected with GC-MS device^{1,2}. Determined values of the steady-state molar fluxes revealed the differences between single and binary permeation as well as the mutual coupling effect of second component in mixture on permeation flux of the first one² at different concentrations of both penetrants. Due to different penetrant-polymer interactions in each system the resulting coupling effect contributes positively or negatively onto molar fluxes of compounds in binary mixture².

Reference

1. K. Friess, M. Šípek, V. Hynek, P. Sysel, K. Bohatá and P. Izák, Comparison of permeability coefficients of organic vapors through non-porous polymer membranes by two different experimental techniques, *J. Membrane. Sci.*, 240 (2004) 179
2. K. Friess, J. C. Jansen, O. Vopička, A. Randová, V. Hynek, M. Šípek, L. Bartovská, P. Izák, M. Dingemans, Jo Dewulf, H. Van Langenhove, E. Drápli, Comparative study of sorption and permeation techniques for the determination of heptane and toluene transport in polyethylene membranes. (Submitted into *J. Membrane Sci.* in November 2008)

Acknowledgements

The authors are grateful for the financial support from the Ministry of Education, Youth and Sports MSM (Grant No. 6046137307) and the Grant Agency of the Czech Republic (Grant No. 104/09/1357).

PC 53

SORPTION AND PERMEATION PROPERTIES OF IONIC LIQUID-SILICONE BLENDS FOR BUTANOL VAPOURS

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Transport properties of butan-1-ol vapours in polydimethylsiloxane membrane and in its blends containing 10, 20 and 30 wt.% of ionic liquid benzyl-3-butylimidazolium tetrafluoroborate ([BBIM][BF₄])¹ were determined using the gravimetric sorption apparatus² and the differential flow permeameter². Measurements were performed at 37°C and the values of diffusion and permeability coefficients and the equilibrium sorption were determined over whole range of vapours activity. Determined anomalous behavior of the diffusion coefficients at higher vapour activities are discussed in details³.

Reference

1. M. Kohoutová, A. Sikora, Š. Hovorka, A. Randová, J. Schauer, M. Tišma, K. Setníčková, R. Petříčkovič, S. Guernik, N. Greenspoon, P. Izák, Influence of ionic liquid content on properties of dense polymer membranes, *European Polymer Journal*, (in press)
2. K. Friess, M. Šípek, V. Hynek, P. Sysel, K. Bohatá and P. Izák, Comparison of permeability coefficients of organic vapors through non-porous polymer membranes by two different experimental techniques, *J. Membrane. Sci.*, 240 (2004) 179
3. P. Izák, K. Schwarz, W. Ruth, H. Bahl, P. J. Dyson, U. Kragl, Increased productivity of *Clostridium acetobutylicum* fermentation of acetone, butanol, and ethanol by pervaporation through supported ionic liquid membrane, *Applied Microbiology and Biotechnology*, 78 (2008) 597

Acknowledgements

The authors are grateful for the financial support from the Ministry of Education, Youth and Sports MSM (Grant No. 6046137307) and the Grant Agency of the Czech Republic (Grant No. 104/08/0600).

PC 54

HYBRID MEMBRANE PROCESSES AT WATER TREATMENT

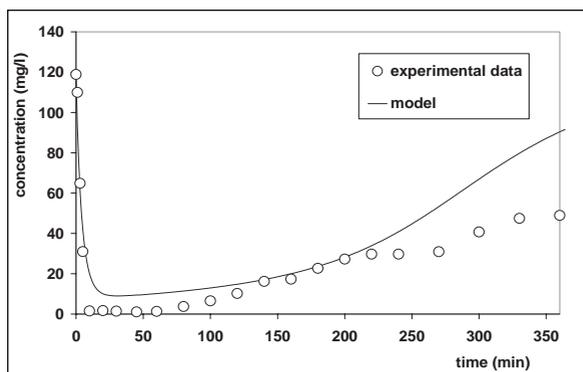
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Wastewater reuse is one of the principal tasks of nowadays epoch. During the last years, for this purpose several physical, chemical and combined methods have been used. This contribution deals with the study of combined adsorption (or ionic-exchange) membrane separation processes in water treatment.

This paper summarizes the results of studies dealing with combined hollow fiber membrane microfiltration operated at dead-end configuration. The processes combine membrane microfiltration and ionic exchange on zeolites or adsorption of DOC on powdered activated carbon, respectively.

In comparison with classical processes, the hybrid membrane microfiltration offers more effective way of water treatment.



Sorptive ability of PAC for Egacid Red in combined process, $c_o=119$ mg/L,
 $c_{PAC}=1$ g/L, permeate flux= 10 L(m².hr)⁻¹

APPLICATION OF MEMBRANE SEPARATION PROCESSES IN THE PRODUCTION OF BIOETHANOL

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Bioethanol is well known as an octane number enhancer. The addition of ethanol to a conventional fuel leads to a decreased emission of gaseous pollutants, such as carbon monoxide (CO) and carcinogenic volatile organic compounds. The European Union, in an attempt to reduce emissions of greenhouses gases, in line with the obligations of the Kyoto Protocol, set a target that fuels for transport should contain 5.75 of biofuels in 2010 [1].

Ethanol is obtained by fermenting any biomass high in carbohydrates (e.g. starches, sugars or celluloses), so its combustion does not increase the greenhouse effect (zero carbon dioxide emission) [2]. The scheme of the bioethanol production process is presented in Fig. 1. Contribution will review possibilities of the application of various membrane processes (e.g. enzymatic membrane reactors, micro-, ultra- and nanofiltration, gas separation and pervaporation) in the production of bioethanol and by-products management. Special attention will be given to pervaporation for the removal of ethanol from the fermented broth and dehydration of ethanol and fusel oils [3].

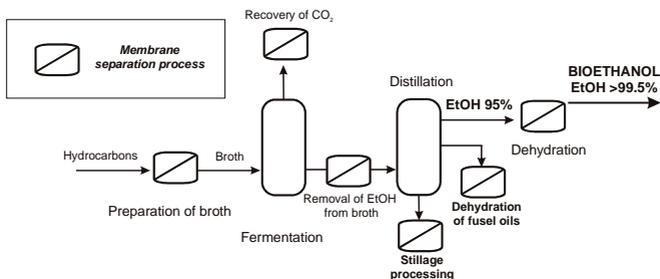


Fig. 1. Implementation of membrane separation processes in the production of bioethanol.

References

- [1] W.Kujawski, Ł.Zieliński, Bioethanol - one of the renewable energy sources, *Env. Protection Eng.*, 32 (2006) 143-149.
- [2] M. Lewandowska, W. Kujawski, Ethanol production from lactose in a fermentation/pervaporation system, *J. Food Eng.* 79 (2007) 430-437.
- [3] W.Kujawski, Application of membrane separation processes for the production of biofuels and reuse of side-streams, *Chemia Przemysłowa* 356 (2007) 24-28 (in Polish).

MODELING OF THE KINETICS OF PERVAPORATIVE RECOVERY OF ETHANOL FROM FERMENTED BROTH WITH THE USE OF THE SOLUTION-DIFFUSION THEORY

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The aim of this study was a mathematical description of the kinetics of ethanol separation from fermentation broth of *S. cerevisiae* yeast by the vacuum pervaporation technique. Model equations were developed on basis of the solution-diffusion theory[1]. The finite differences method has been used to calculate the concentration profiles of permeants within the membrane[2]. The optimal number of grid points and their distances were found by numerical tests. The formulated model describes the transport of feed components under the non-stationary conditions. Model equations were solved with the use of the backward differentiation method[2]. Model parameters were estimated by fitting of experimental data with the use of the Nelder-Mead method[3]. Calculations were performed for separation experiments with broths containing 3-6 wt % of ethanol. Very good agreement with the experimental data has been obtained (Fig. 1).

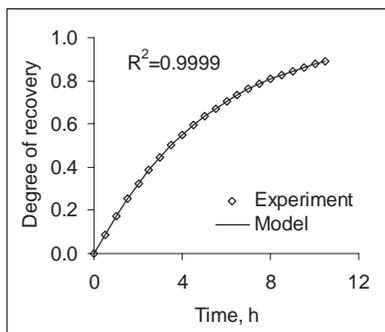


Fig. 1. Ethanol recovery from a broth containing 4.97 wt % ethanol.

References

1. Lonsdale, H.K., Merten U., Riley, R.L. (1965). Transport properties of cellulose acetate osmotic membranes, *J. Appl. Polym. Sci.* 9, 1341–1362.
2. Ceynowa, J., Adamczak, P., Staniszewski, M. (1997). Kinetics of olive oil hydrolysis in enzyme membrane reactor. Bond graph network model of reactor performance (Part 1). *Acta Biotechnol.*, 17, 161–169.
3. Kręglewski, T., Rogowski, T., Ruszczynski, A., Szymanowski, J. (1984). Optimization methods in FORTRAN. PWN, Warszawa (in Polish).

DEVELOPMENT & COMPARISON OF NON-PARAMETER REGRESSION METHODS FOR PREDICTION OF CELL VOLTAGE AND CURRENT EFFICIENCY IN A LAB SCALE CHLORINE-ALKALI MEMBRANE CELL

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This paper presents the development & comparison of Non-parameter Regression Methods such as Artificial Neural Network (ANN), Genetic Algorithm Optimization (GA) and Support Vector Machine (SVM) models for the prediction of cell voltage and caustic current efficiency (CCE) versus various operating parameters in a lab scale chlorine-alkali membrane cell. In order to validate the model predictions, the effects of various operating parameters on the cell voltage and CCE of the membrane cell were experimentally investigated. Each of six process parameters including anolyte pH (2-5), operating temperature (25-90 °C), electrolyte velocity (1.3-5.9 cm/s), brine concentration (200-300 g/L), current density (1-4 kA/m²), and run time (up to 150 min) were thoroughly studied.

The new ANN, GA & SVM models yielded the accurate prediction of experimental data with the lowest standard deviation error (SD). It was found that the developed models are not only capable to predict the voltage and CCE but also to reflect the impacts of process parameters on the same functions. The predicted cell voltages and current efficiencies using these models were found to be close to the measured values. According to the obtained results, SVM model is suitable for the prediction of current efficiency with an average deviation (for test validation data) of 1.53% while GA & ANN models are suitable for the prediction of cell voltage with an average deviation of 1.21% & 1.27%, respectively. This study was done by financial support of National Elites Foundation.

Keywords: Chlor-Alkali, Membrane Cell, Electrolysis, Artificial Neural Network, Genetic Algorithm, Support Vector Machine

INVESTIGATION OF THE EFFECT OF TRANSMEMBRANE PRESSURE ON SEPARATION OF SWEET WHEY BY NANOFILTRATION

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In this study sweet whey was concentrated by nanofiltration. In the recent past whey hasn't been only considered as polluting by-product of the dairy industry but also a source of various components of high value, such as lactose, proteins, vitamins and minerals. Functional properties of whey proteins and peptides were verified in some earlier studies. In whey appears almost all of the lactose content of milk, and this sweetening capacity makes whey concentrate suitable for utilization in ice creams, drinks or in cooked products.

Experiments were carried out in batch-mode, permeate was divided from the feed off while the volume of the feed was reaching the final volume desired. In order to investigate the effect of transmembrane pressure on the behaviour of whey components, concentration test was repeated at several pressures up to 60 bar. Transmembrane pressure was kept constant during the tests. For the analysis samples were taken from permeate and retentate as well. Total soluble solid content, lactose content and protein content of the samples was determined using infrared measurements. Ion concentrations were measured by ICAP equipment.

The effect of transmembrane pressure on concentration polarization and total resistance of the process was also examined. To describe the process, resistance in series model and the van't Hoff law were used. Concentration near to the membrane surface is by order of magnitude was higher than concentration in the permeate, therefore concentration of the permeate in the van't Hoff law was neglected. The van't Hoff law was substituted into the resistance in series model and the permeate flux was plotted in the function of lactose content and TSS content as well. A linear relation was obtained, from the intercept of the line the average value of the total resistance and from the slope the concentration polarization was estimated. The experimental and calculated data of permeate fluxes were compared at several transmembrane pressures.

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ADSORPTION OF Cu(II) ON CHITOSAN MEMBRANES FUNCTIONALIZED WITH D2HEPA

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Chitosan is the deacetylated form of chitin, which is the most abundant biopolymer in nature (Figure 1). This polymer has both reactive amino and hydroxyl groups that can be used for chemical reactions and salt formation. The regeneration of saturated chitosan for non-covalent adsorption can be easily achieved by using an acid solution as desorbing agent. Chelation ion exchange in contrast to simple ion exchange uses the three-dimensional structure of molecules to remove ions of specific size [1] (figure 1).

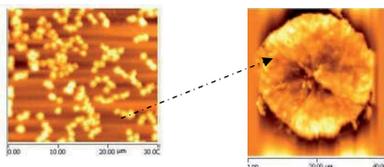


Figure 1-AFM analysis of self-assembly chitosan-Cu(II) (b), zoom) from [2].

In this work, for the first time, di-2-ethylhexyl phosphoric acid (D2HEPA) microcapsules are prepared by emulsion coupled to phase inversion technique [3, 4] with chitosan as shell material. The preparation conditions for well-controlled microcapsule size (Figure 2) and its distribution are investigated.



Figure 2- SEM analysis of chitosan-D2HEPA microcapsule cross-section

The effect of different crosslinking degree has been correlated with extraction capability. The size of the prepared microcapsules and their morphology are characterized. The extraction equilibrium, kinetic characteristics and stability of microcapsules for recovering Cu(II) are studied.

References

- [1] G.C. Steenkamp, K. Keizer, H.W.J.P. Neomagus, H.M. Krieg, Copper (II) removal from polluted water with alumina/chitosan composite membrane, *J. Membrane Sci.* 197 (2002) 147.
- [2] Y. Hu, Y. Wu, Jiye Cai, Y. Ma, B. Wan, K. Xia and X. He, Self-assembly and Fractal Feature of Chitosan and Its Conjugate with Metal Ions: Cu (II) / Ag (I), *Int. J. Mol. Sci.* 8 (2007) 1.
- [3] A. Figoli, G. De Luca, E. Longavita, E. Drioli, *Sep. Sci. Technol.* 42 (2007) 2809.
- [4] M.G. Buonomenna, A. Figoli, I. Spezzano, R. Morelli, E. Drioli, Combined Emulsion and Phase Inversion Techniques for the Preparation of Catalytic PVDF Microcapsules, *J. Phys. Chem. B.* 112 (2008) 11764

RECOVERY AND RECYCLING OF SF₆ GASES IN MICROFILTRATION MEMBRANES

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Sulfur hexafluoride (SF₆) is being widely used in a variety of industrial processes such as electric, magnesium and semiconductor industries which emit significant quantities of high global-warming potential (GWP) gases. Following its exposure into environment, the compound almost resides in the atmosphere for a very long time and is a high radioactively-active gas with high fugacity and low solubility in water. Therefore, SF₆ has been selected as one of six target green house gases under the Kyoto Protocol of the UN's Framework Convention on Climate Change in 1997. Under limitations, SF₆ mixtures from industry should be handled to be used reused on-site. In the rare case that collecting recovered gases are not appropriate for reuse on-site, it might be further treated off-site. In this research, the membrane separation method was preliminary evaluated in order to handle the SF₆ mixtures emitted from various industries.

A series of microfiltration (MF) membrane filtration experiments was performed in order to investigate the effect of various parameters on the recovery of SF₆ from N₂/SF₆ gas mixtures. The effective membrane surface area was 1.2m². In this experiment, polysulfone hollow fiber membrane for gas separation was applied to obtain the high recovered SF₆. Recovery and recycling experiments resulted that hollow fiber membrane could efficiently separate SF₆ from N₂/SF₆ gas mixtures, and the recovery of SF₆ increased with a decrease of feed pressure and an increase of gas flow rate. In addition, the effect of original N₂/SF₆ mixture ratio on recovery rate was significantly observed and the recovery loss is examined at any conditions. The maximum recovery of SF₆ by using MF membranes showed over 90%. From the experimental results, their relationship with the separation properties of the membranes is examined systematically.

Key words: Greenhouse Gas, Hollow fiber membrane, Sulfur hexafluoride, Recovery

PC 61

LONG AND SHORT TERM PERFORMANCE TESTS FOR SWRO DESALINATION PLANT AT URLA BAY, IZMIR

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A mini pilot-scale seawater reverse osmosis (SWRO) system was installed at Urla Bay, Izmir, Turkey. The complete system consists of sand filters, a 5 micron filter, a high pressure pump accomodated by a low pressure pump, two parallel mounted reverse osmosis membranes (spiral wound FilmTec SW30 2540) having 2.8 m² active area. A flow diagram of SWRO plant was shown in Figure 1. In this study, short-term and long-term operational data obtained from this mini pilot-scale SWRO plant were presented and analysed. A comparison was performed between a single-membrane and a two-membrane systems for short and long term operations. It was shown that over 36 hours of continuous operation, the permeate flux decreased by about 4% of its initial value but salt rejection stayed nearly constant for two-membrane operation. Surprisingly, boron rejection increased slightly when two membranes were used in the system. For single-membrane operation, permeate flux declined by 3% while salt and boron rejections did not change substantially.

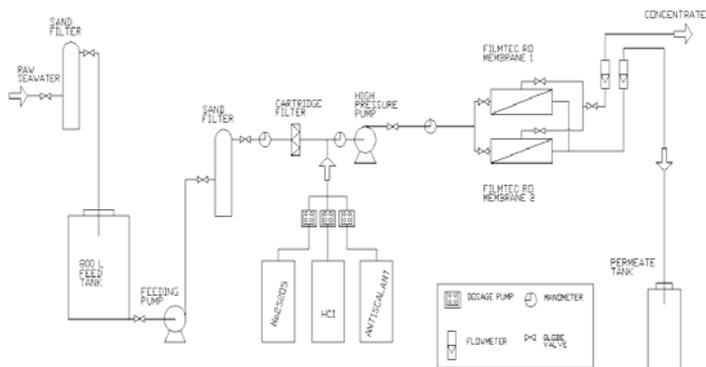


Fig. 1. Flow diagram of SWRO system at Urla Bay

PC 62

CONCENTRATION OF TOMATO EXTRACT BY NANOFILTRATION

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Consumption of tomato (*Lycopersicon esculentum*) and its products has beneficial effects on human health. This effect has been attributed to carotenoids: lycopene, β -carotene, phytoene, phytofluene, lutein, γ -carotene, ζ -carotene and neurosporene. Lycopene, which constitutes more than 80% of the total tomato carotenoids, has attracted considerable attention in recent years. It is an acyclic, hydrocarbon compound with 11 conjugated double bonds, molecular formula $C_{40}H_{56}$ and molecular weight of 537. With regard to its antioxidative activity lycopene may play an important role in the reduction of oxidative stress linked to some degenerative diseases. Indeed, lycopene has been reported to possess protective effects on some types of cancer, e.g. prostate cancer, cardiovascular diseases and age-related macular degeneration [1]. The benefits to human health of other carotenoids present in tomato in a much smaller amount are also well documented [2]. Obtaining carotenoids from tomatoes can be performed using extraction with solvents. Because tomato carotenoids are liposolubles, organic solvents are usually used.

In the present work, we have used petroleum ether, acetone and a mixture of these solvents in the extraction of carotenoids from a commercial tomato puree. Then, nanofiltration with two commercial membranes (SolSep BV, the Netherlands) has been carried out to obtain carotenoid-rich extract. The total pigment content has analyzed in the permeate and retentate. The influence of the type of solvent on the retention properties of membranes has been discussed.

References

1. A. O. Omoni, Aluko R. E., Trends Food Sci. Tech. 16 (2005) 344.
2. A. V. Rao, L. G. Rao, Pharm. Res. 55 (2007) 207.

PC 63

PERVAPORATION ASSISTED SYNTHESIS OF VARIOUS FLAVOUR ESTERS IN IONIC LIQUIDS

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The demand for natural, pure and high quality flavours is gradually increasing nowadays. The esterification of short chain alcohols by free or immobilised lipase enzymes is a proper route to produce these flavouring compounds in different reaction media (e.g. organic solvents, solvent-free system). Recently it has been found that ionic liquids are suitable media, as well.

In our laboratory synthesis of ethyl acetate isoamil acetate and ethyl lactate (all of them naturally occurring flavouring compounds) was tested in ionic liquids using *Candida antarctica* lipase B enzyme. Since esterification is an equilibrium reaction the concentration of the side product water influenced the product yield, therefore the water content of the reaction mixtures was controlled by pervaporation (Fig. 1). In the first two cases the removal of the produced water increased the ester yield as expected [1, 2]. In contrast to these reactions in the synthesis of ethyl lactate from lactic acid and ethanol a lower yield was obtained using pervaporative water removal. The reason of the peculiar behaviour is probably the decomposition rate of lactoyllactic acid (the open chain dimer of lactic acid, present in concentrated lactic acid solutions) which was slowed down by the lower amount of water available.

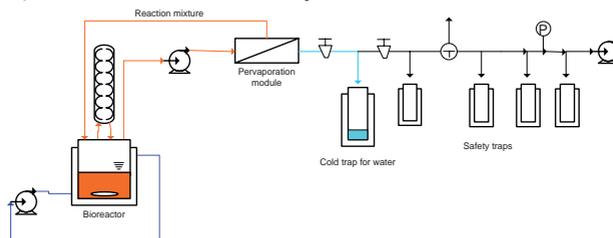


Fig. 1: Schematic diagram of pervaporation system

[1] L. Gubicza, K. Bélafi-Bakó, E. Fehér: Waste-free process for continuous flow enzymatic esterification in ionic liquid medium. *Green Chem.* 10 (2008) 1284 -1287

[2] L. Gubicza, N. Nemestothy, T. Fráter, K. Belafi-Bako: Enzymatic esterification in ionic liquids integrated with pervaporation for water removal, *Green Chem.* 5 (2) 236-239 (2003)

PC 64

VACUUM SUBLIMATION DEHYDRATION AND MEMBRANE TECHNOLOGIES

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Technology of preserving food products, medications and ferments by sublimation dehydration presupposes the absence of high-temperature processes on all stages. This creates a serious problem of guaranteeing sanitary welfare of food products, and in pharmaceutical preparation of their sterility. In this case membrane processes can be successfully applied and act as an item to improvement and reduction in price of the technology.

Traditionally applied technologies of vacuum evaporation negatively effect the product quality. Therefore membrane concentrating and sterilization of such kind of raw substances as juices, extraction of medical plants and bacterial concentrate have good prospects.

By the end of vacuum sublimation dehydration cycle drying chamber should be devacuumized, i.e. filled with air or nitrogen. Incoming gas should be cleaned from extraneous substances, dewatered and disinfected. Membrane sterilization of gases is implemented in pharmaceutical industry, but in food technologies of sublimation products air is dewatered and ran through filters with sorbents.

Our university is one of the leading centers in Russia in the sphere of sublimation dehydration and low-temperature food technologies. We have approved some baromembranous processes for preconcentration (ultrafiltration) and membranous sterilizing of liquids (microfiltration) in low-temperature food technologies. This permitted to reduce expenditure of energy in 1.5 - 1.6 times, even so the quality of finished product was higher than with the use of traditional processes (filtration, vacuum evaporation).

PC 65

NANOFILTRATION AND REVERSE OSMOSIS OF PIG MANURE: COMPARISON OF RESULTS FROM VIBRATORY AND CLASSICAL MODULES

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The use of membrane technology is a good possibility for the concentration of manure into a small volume that can be transported to the fields. The disposal of manure often requires pre- or post-treatment with respect to environmental legislation. Membrane processes would be a good way to achieve these requirements. In pressure-driven membrane processes, microfiltration and ultrafiltration are usually efficient in concentrating the nutrients associated with particles, such as phosphorus, but for other constituents, e.g. ammonia and potassium, the retention requires nanofiltration (NF) or reverse osmosis (RO).

In this study, two different membrane processes, a classical cross-flow (3DTA) and a vibratory shear-enhanced process (VSEP) were compared as regards the reduction of the total volume and the dry matter from pig manure. Two NF and two RO membranes were used. The fluxes were compared during the tests of pretreated manure concentration. Each composite membrane was tested with regard to the membrane, gel layer and porous resistances. It was found that the gel layer was much lower in the case of the VSEP, because of the high shear-enhanced forces on the membrane surface during the experiments. Our results indicated that NF and RO were suitable for pig manure treatment.

Keywords: Manure, Nanofiltration, Reverse osmosis, VSEP, Fouling, Membrane resistance, Gel-layer resistance, Total resistance

COPPER RECOVERY BY POLYMER SUPPORTED ULTRAFILTRATION (PSU) AT PILOT SCALE

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Polymer supported ultrafiltration (PSU) is a membrane separation process, successfully applied in the treatment of industrial wastewater effluents with metal ions [1]. In this technique, the first step consists of the selective reaction between a water-soluble polymer and a target metal ion. Next, the macromolecular complex previously formed can be separated from the rest of non-target ions in an ultrafiltration stage, in which the former is retained by the membrane (retentate stream) meanwhile the latter pass through the membrane surface (permeate stream).

In the present work, a complete PSU study has been carried out at pilot scale. The selected metal and polymer were copper and partially ethoxylated polyethylenimine (PEPEI), respectively. The whole work presented here has been carried out with a closed-loop ultrafiltration pilot plant. It works with a stainless steel module and ceramic multi-channel membranes, Kerasep® from Novasep®, with 19 channels and membrane areas from 0.082 to 0.25 m².

The first step consisted of checking the membrane hydrodynamic behaviour when polymer solutions, with a concentration of 0.06 % wt. and at pH 6, were filtered. These operating conditions were selected based on previous studies of our research group [2]. The influence of transmembrane pressure (from 0 to 5 bar), temperature (from 28 to 50 °C) and tangential velocity (from 0 to 6 m s⁻¹) on both, permeate fluxes and rejection coefficients was studied. With these studies, carried out at total recirculation mode, the optimal working conditions were selected.

Next, the polymer ability to bind copper was checked working at the optimal working conditions selected in the previous step, obtaining copper rejections always higher than 0.97. Finally, the installation set-up was made to work at both, feed & bleed and discontinuous modes to simulate different processes configuration and to obtain raw data to carry out a subsequent economical study.

Furthermore, the polymer stability to several cycles of PSU was checked as all the experimental runs were carried out with the same polymer solution.

References

- [1] Cañizares, P.; Pérez, Á.; Camarillo, R.; Linares, J. J.; *J. Membrane Sci.*, 240 (2004) 197-209.
- [2] J. Llanos, Á. Pérez, P. Cañizares, Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration, *J. Membr. Sci.*, 323 (2008) 28-36.

PC 67

SUPPORTED LIQUID MEMBRANES FOR REMOVAL OF Cr(VI) IONS

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Removal of chromium VI ion from aqueous solution by means of supported liquid membranes (SLMs) was evaluated. As a membrane phase Aliquat 336 was employed while hydrophobized filtered paper (Whatmann) served as a porous support. To improve stability of liquid membranes they were coated by polyethyleneimine, PEI crosslinked by means of glutaraldehyde. The obtained membranes were tested in the Donnan dialysis process and the flux of Cr(VI) was calculated. It was shown that the uncoated membranes were not stable for the long time of service. They broke after 24 hour service. Much more stable appeared membranes coated with crosslinked PEI. The PEI/Aliquat 336 and PEI membranes were in service for seven days while the feeding and receiving solutions were changed every 24 hrs. One difference between evaluated membranes was observed - the flux of chromium VI was significantly larger through PEI membrane than through PEI/Aliquat 336 one. After the first run of separation process, a decrease of Cr(VI) flux was noted for both evaluated membranes. The next runs were stable and the flux did not decrease dramatically.

Using the approach for solvent impregnated resins it was concluded that transport process was facilitated by formation of bounds between chromium ions and nitrogen atoms of amine functional groups. In the case of Aliquat 336 the N/C atomic ratio is worse than for neat PEI. Hence, the Aliquat can reduce the transport when SLM is coated with polyethyleneimine. It seems that PEI membrane can be used for efficient separation of Cr(VI) ions.

PC 68

NEW GENERATION OF POLYMER SEPARATORS IN Ni-Cd HIGH POWER BATTERIES

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The poster presents method for manufacturing of new generation of polymer separators for the use in high power Ni-Cd batteries. The separator is the weakest part of the battery and the life-service of the battery is mainly limited by the separator failure. The ideal separator should show the following features: i) be a strong spacer between electrodes, ii) be as thin as possible to offer the compact structuring of the cell, iii) be chemically resistant, iv) be available at low cost, v) be conductive in electrolyte. It seems that porous polymer membranes can meet these requests. However, the use of porous polypropylene membranes is restricted due to material hydrophobicity. Hence, the manufacturers' interest is shifted to hydrophilization of the spacer surfaces.

The contribution shows the efficient method for polymer modification: grafting of poly(acrylic acid) on Ar plasma activated Celgard 2500 membranes. Two kinds of plasma processes were investigated: microwave plasma and barrier plasma. When the first one is well known and widely used (2.45GHz plasma acting at vacuum) the second one seems to enter new method for surface modification. It is based on generation of high voltage difference on the polymer surface at acts for a very short time. The important benefit of the barrier plasma is possibility to use it at normal pressure. After activation of membrane surfaces, the pieces of membranes were immersed in monomer solution to allow grafting of polyacid chains. AFM and SEM studies showed the effect of activation parameters to the grafting yield. The prepared spacers exhibit very good surface resistance (usually less than 50 mΩ/cm²) and good stability (withstand 1000 charging-discharging cycles). The obtained separators are characterized by better operational properties in Ni-Cd battery than commercial spacers.

PC 69

COMPOSITE POLYMERIC MEMBRANES SYNTHESIS BY PLASMA POLYMERIZATION FOR GAS SEPARATION

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Commercial gas separation applying membranes is a dynamic and rapidly growing field. In the last 20 years; the study of gas permeability and permselectivity of polymer membranes has increasingly become a subject of intense, world wide research both in academia and industry. In order to develop new polymers with improved properties it is required to use new manufacture techniques and understand the structure-properties relationship of polymer structure and gas permeation. Plasma polymerization for membrane preparation is a very promising field. This plasma technique is a very versatile method to produce polymeric films with tuneable chemical compositions and properties different from those produced from the same precursors (monomers) by conventional polymerization methods.

Among the different plasma polymer precursors reported in the literature, the organosilicon monomers allow to deposit plasma polysiloxane layers which seem to be promising materials for gas separation processes. These polymers also exhibit high chain packing density, this characteristic provides interesting permselectivity.

In this work, the Ion Gun Inverse Magnetron (IGIM) plasma polymerization technique has been used to produce composite polymeric flat sheet membranes for the separation of H₂/CH₄, H₂/CO₂, CO₂/CH₄, CH₄/N₂, and O₂/N₂ gas mixtures. Plasma polymer films from hexamethyldisiloxane (HMDSO) have been deposited on different polymeric porous supports, such as polyamide, PTFE, cellulose acetate and polysulfone. The gas separation membranes have been prepared using different plasma conditions: power (30W, 40W and 50W) and exposures (3 hours and 5 hours). The developed gas separation membranes have been characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-ray Spectroscopy (EDS). Gas separation and permeation properties for H₂, CH₄, CO₂, O₂ and N₂ gases through the plasma polymerized membranes have been investigated in detail as a function of pressure and support type using a time-lag method, and related to the morphology of the membranes.

MICROWAVE PLASMA SURFACE TREATMENTS ON POLYSULFONE GAS SEPARATION MEMBRANES

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Gas separation membrane systems have received a lot of attention from both industry and academia. This is due to the fact that there is a belief that membrane separation processes may offer more capital and energy efficiency when compared to the conventional separation processes in some applications. In order to accomplish this objective, membrane materials with superior permeability and selectivity and advanced fabrication technologies to yield membranes with high permeability and selectivity, are the primary focuses for most membrane scientists in the last two decades.

Casting by phase inversion and surface modification using plasma techniques has attracted interest in polymeric membrane-based separation of gases or vapors. Plasma crosslinked polymer selective layers offer advantages as membranes, particularly in terms of stability. Without crosslinking the material will tend to swell when exposed to certain gas mixtures, and hence separation properties are affected.

In this work, phase inversion technique has been used for producing asymmetric polymeric flat sheet membranes for the separation of H₂/CH₄, H₂/CO₂, CO₂/CH₄, CO₂/N₂ and O₂/N₂ gas mixtures. Different thicknesses of polymeric gas separation membranes were prepared by the wet-phase separation method using different polysulfone content in *N,N*-dimethylacetamide. After casting, the synthesized membranes have been surface modified by using microwave plasma reactor using different process conditions (plasma power, gasses, time duration, and pressure).

The manufactured membranes have been characterized by Scanning Electron Microscopy (SEM) (morphology), Fourier Transform Infrared Spectroscopy (FTIR) (chemical structure), and Energy Dispersive X-ray Spectroscopy (EDS) (chemical analysis). Permeability of H₂, CO₂, CH₄, N₂, O₂, and ideal selectivity of different pair of gasses has been investigated before and after the plasma treatment using a time-lag method. The correlations between the final membrane structure/permeation properties and the process conditions used (casting and plasma surface treatment) are discussed extensively.

CONTINUOUS RECYCLE MEMBRANE REACTOR FOR ENZYMATIC HYDROLYSIS OF DUAL MODIFIED POTATO STARCH

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An alternative method for a conventional unit operation for the saccharification of liquefied starch is introduction the membrane processing as a relatively new method of performance of enzymatic hydrolysis. The recycle membrane reactor (CRMR) is a specific mode for running continuous processes, in which enzymes are separated from products with the help of a selective membrane. CRMR compared to the traditional batch reactor brings possibility of continuous operation in lower volume reactor in shorter reaction time, with higher productivity and with lower operating cost.

In our laboratory the processes of enzymatic hydrolysis were led on the continous recycle membrane reactor consisting of a reaction container, an outer ultrafiltration module and a rotary lobe pump. Membrane separation were carried out in the ultrafiltration unit containing a tubular ceramic membrane (Tami Industries, France, molecular weight cut off 50, 15 and 8 kDa).

Materials for investigations were dual modified potato starches (by degrees oxidation and acetylation). BAN 480 L containing amylase obtained from a selected strain of bacteria was used as hydrolytic enzyme.

The hydrolysis processes lasted for 150 minutes and filtrate fractions were collected to determined the efficiency of hydrolysis by estimation of content of dry substance and the amounts of reducing groups in the permeate fractions. The magnitude of permeate flux was the measure of the effectiveness of separation process. Two different variants of courses of hydrolysis process were investigated. According to *variant I*: realizing hydrolize, for the first 30 minutes the process was led without simultaneous separation. The reaction mixture has been circulated in a reactor just by baypass. Then for next 120 minutes it has been put in the filtering system with two different membranes. In *variant II* the membrane reactor was used in a classic version.

It was found that the manner of conduct process had influence the effectiveness of hydrolysis. The obtained results indicated that the hydrolysis in *variant I* led to obtain higher productivity. The effectiveness of the membrane processes is strongly influenced by fouling phenomena in the reaction system.

MECHANISM OF PERTRACTION OF BUTYRIC ACID THROUGH LIQUID MEMBRANE WITH PHOSPHONIUM IONIC LIQUID

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In pertraction of butyric acid (BA) through the liquid membrane containing phosphonium ionic liquid (IL) tetradecyl(trihexyl)phosphonium bis-(2,4,4-trimethyl)pentylphosphinate (Cyphos IL-104) and diluent *n*-dodecane two mechanisms of transport of are proposed. The first is related to physical solubility of BA in diluent in form of BA monomer and dimer. The second mechanisms is reactive extraction of BA by IL. From this follows that the flux (J) and mass-transfer coefficient (K_p) are sum of individual ones related to these modes of transport

$$J = J_{\text{phys}} + J_{\text{react}} \quad K_p = \frac{J_{\text{phys}} + J_{\text{react}}}{c_{F, \text{ls}}} = K_{p, \text{phys}} + K_{p, \text{react}}$$

The distribution coefficient of physical extraction of BA by *n*-dodecane is linearly dependent on concentration of BA in the aqueous phase according to the equation

$$D_{\text{phys}} = K_m + 2K_m^2 K_d c_F$$

where K_m and K_d are the extraction constants of monomer and dimer of BA. Since the mass-transfer coefficient is proportional to the distribution coefficient $K_{p, \text{phys}}$ should increase with the increase in $c_{F, \text{ls}}$. Contrary to this Fig. 1 shows that the overall mass-transfer coefficient decreases. This is connected with decreasing value of the overall distribution coefficient of BA with concentration.

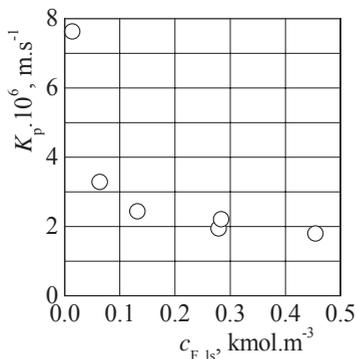


Fig. 1. Concentration dependence of overall mass-transfer coefficient in pertraction of BA through supported liquid membrane containing 0.7 kmol.m^{-3} Cyphos IL-104 in *n*-dodecane. Temperature: 25°C .

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IONIC TRANSPORT IN COMPOSITE MEMBRANES BASED ON MF-4SC AND POLYANILINE

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In some cases transport properties of membranes can be improved by modification with finely dispersed compounds. The main reason for property change is the ion sorption at the phase boundary which results in the defect concentration and conductivity increase. From this point of view, polyaniline (PANI) can be considered as perspective additive because of its nitrogen atoms able to act as the proton acceptor. The main aim of this work was synthesis and study of transport properties of composite materials based on perfluorated sulfonic cation-exchange membranes MF-4SC (Russian analog of Nafion membranes) and PANI.

MF-4SC/polyaniline composite membranes were obtained by the matrix polymerization of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the hydrogen form of MF-4SC solution. Membranes with anisotropic distribution of PANI were obtained by the sequential diffusion of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and aniline solutions through the membrane from its one face or by coating the commercial membrane with modifying solution (a mixture of MF-4SC solution and PANI). The ANI:MF-4SC ratio was changed from 0.05 to 1. The kinetics of aniline polymerization was monitored by UV-visible spectroscopy. The influence of concentration and type of oxidant on polymerization rate was studied.

Proton and electron conductivity of MF-4SC-PANI composite membranes was studied by impedance spectroscopy in the wide temperature range. The maximal composite effect was observed for the membranes with the PANI:MF-4SC ratio equal to 0.1. Their proton conductivity consists about 0.18 S/cm. For all studied materials electron conductivity does not exceed 0.05% of total conductivity.

Diffusion permeability of NaCl and HCl solutions and H^+/Na^+ interdiffusion was studied for composite membranes with anisotropic distribution of PANI in different directions. The difference between interdiffusion coefficients and diffusion permeability of HCl solutions in different directions consists 8 - 79% and 12 - 87% respectively. The diffusion permeability is higher when the modified surface is placed facing the compartment containing water. The interdiffusion coefficients decrease with the PANI content increase as well as with the salt concentration growth.

PC 74

COMPOSITE MEMBRANES BASED ON MF-4SC INCORPORATING INORGANIC NANOPARTICLES

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Perfluorosulfonic cation-exchange membranes, such as Nafion (DuPont, USA) and MF-4SC (Plastpolymer, Russia), are widely used for electrochemical synthesis, water purification and fuel cells. But these membranes have several disadvantages such as low conductivity at low humidity, relatively low mechanical strength at high temperatures. The incorporation of inorganic species can assist in improving membrane properties. Silica and zirconia with high sorption ability can be considered as perspective additives.

In this work the synthesis and transport properties of composite membranes based on MF-4SC incorporating nanoparticles zirconia, silica and silica with phosphotungstic acid (PWA) were studied. Composite membranes were obtained by two different methods: synthesis of inorganic nanoparticles in membrane pores (*in situ*) and membrane casting using polymer solution and precursor of ZrO₂ and SiO₂ (ZrOCl₂ and Si(OC₂H₅)₄ respectively). Materials have been characterized using thermogravimetric analysis, impedance and NMR spectroscopy in the wide temperature range and at different relative humidity.

It was shown that in most cases composite membranes had higher proton conductivity than the polymer-only system measured under the same conditions. Materials containing 3% SiO₂ and 5% ZrO₂ have the higher conductivity. At low relative humidity, MF-4SC – SiO₂ and MF-4SC – SiO₂ – PWA composite membranes are characterized by conductivity more than one order of magnitude higher than that for MF-4SC.

NMR data show that self-diffusion coefficients of water increase after MF-4SC membrane modification. At low relative humidity, self-diffusion coefficients of water for MF-4SC – SiO₂ composite membranes are considerable higher than those for initial MF-4SC membranes.

PC 75

POROUS CERAMIC MEMBRANES DESIGNED FOR SEPARATION OF CO₂

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Keywords: CO₂, ceramic membrane, grafting, hydrophobic

Membrane properties can be roughly defined by two parameters that are permeability and selectivity. Gas separation is possible by both dense and porous membranes. Gas separation in dense membrane depends on the differences of solubility of gaseous species into the membrane defined by the Fick's law. Their selectivity can be very high but their permeability is highly dependent on their thickness and preparation of defect-free ultrathin dense membranes is still a challenging program in many areas. On the other side, ceramic membranes offer very good performances toward permeability because they are porous but their selectivity is usually based on Knudsen flow model that is correlated with the square root of the molar mass of gaseous species.

A way to overcome the limits imposed by the Knudsen law is to apply another diffusion mechanism by sticking on the surface of the ceramic, chemical functions that will induce specific diffusion mechanism based on differential solubility of gaseous species in the additional layer. We report how we could achieve it through a grafting process where one build a true chemical bond between organic molecules and the membrane surface (made of a metal oxide). To achieve this operation, the molecules must then exhibit a bi-functional structure including one head group that allows it to react with the oxide surface (silanol Si(OR)₃, phosphonate (PO(OH)₂),...) and a chain that will confer the surface properties (amine, alkyle or fluorinated tail...).

We validated this approach by successfully grafting hydrophobic perfluorinated siloxanes on porous zirconia membranes deposited onto commercial tubular supports. The first effect of this operation is to switch the initially hydrophilic oxide surface toward a superhydrophobic one (wetting angle above 140°) with keeping the ceramic porous. These membranes were first characterized by the determination of the liquid entry pressure of water, LEP_w, to evidence their hydrophobic feature. LEP_w was measured at 11, 13 and >15 bars for membranes with cut-off of 300, 15 and 5 kD, respectively.

Gas permeation tests were performed for both pure gases and N₂/CO₂ mixtures. Experiments conducted yield to an average selectivity of CO₂ over N₂ of 2.8, which is higher than the selectivity predicted by Knudsen's mechanism.

PC 76

MASS TRANSPORT OF BINARY MIXTURE THROUGH INORGANIC, MULTI-LAYERED MEMBRANE

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The classic problem in diffusion theory is limited to linear systems with constant diffusivity. This condition is often not fulfilled for diffusion in polymeric membranes and especially in inorganic (zeolite, silicalite-1, etc.) membrane in which equilibrium isotherm is generally non-linear and the diffusion of components may be strongly coupled. The mass transport can be further altered by several support layers applied that allow both the diffusive and the viscous flows. The Maxwell-Stefan equations provide an adequate basis for the description of multi-component mass transfer in porous media. A single compound mass transport through multi-layered membrane and binary mass transport through a membrane layer and the separation of these components will be discussed applying the extended Langmuir adsorption isotherm and the Maxwell-Stefan approach as well as the Vignes equation, in two cases:

- a) the friction between the diffusion species (the coupling effect) can be neglected (the so-called single-file diffusion),
- b) the general case, if the friction between components may not be neglected;

General mathematical models were developed to describe the mass transport in such nonlinear system taking into account the external mass transfer resistances as well. The essential of this method is that the membrane layer is divided into number of thin sub-layers with constant parameters (see e.g.[1, 2]). The obtained differential equation system was solved analytically. The concentration distribution and the mass transfer rates are defined by rather simple, closed, explicit mathematical expressions for binary mass transfer. The predicted data are verified with experimental data of de Graaf et al. [3] for ethane/methane separation on zeolite membrane and with data of van den Broeke [4] for CO₂/CH₄ on silicalite-1 membrane as well as with data of Thomas et al. [5] for gas transport on multi-layered membrane.

The mass transfer rate should be replaced into the differential mass balance equation given for the tube (or shell) side of the membrane layer and the effect of the concentration dependency on the outlet concentration will be shown taking into account the external mass transfer resistances as well.

References

- [1] Nagy E., *Ind. Eng. Chem. Res.*, **46** (2007) 2295-2306
- [2] Nagy, E.: *J. Membrane Sci.*, **274** (2006) 159-168.
- [3] de Graaf, J.M., Kapteijn, F., Moulijn, J.A., *AIChE Journal*, **45** (1999) 497-511.
- [4] van den Broeke, L.J.P., Bakker, W.J.W., Kapteijn, F., Moulijn, J.A., *AIChE Journal*, **45**, (1999) 976-985
- [5] Thomas, S., Schafer, R., Caro, j., Seidel-Morgenstern, A., *Catalysis Today*, **67** (2001) 205-216.

CONVERSION OF BIOFERMENTATION PRODUCTS USING POROUS MEMBRANE-CATALYTIC SYSTEMS

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Using of biofermentation products as feed for the processes of hydrogen generation and other valuable substances is great of interest for the moment. Currently an attention is paying on gas-phase heterogeneous catalytic reactions by using microreactors with the aim of the process intensification. In this case several general advantages of microreactors can be noted: compactness of industrial installations, easy scaling up of membrane unit, good control of the process operation. The most prospective trends in this field are the processes of methane conversion into syngas and light olefins as well as the steam reforming of bioproducts such as ethanol, acetic acid, etc. into hydrogen. For this purpose several types of catalytic ceramic membranes, which are active in this reaction were synthesized. Set of experiments showed that methane conversion occurred intensively already at 600°C and reaction of above steam reforming runs about 450-500°C (about 300°C lower then in traditional catalytic reactor). This difference can be because of heat and mass transfer, which are better in microporous membrane as well as intensification of molecule collisions in membrane channels. All studied membranes had different compositions. Practical interest for dry reforming of methane represented Ni-Al membranes modified by La-Ce and Pd-Mn catalysts. Membranes modified by Pd-based catalysts were promising for steam reforming. It was shown that La-Ce on Ni-Al has higher activity in dry methane reforming than Ni-Al/Pd-Mn. In the same time the H₂/CO ratio in product is also different (at T=600°C it is 1.25 on Ni-Al/Pd-Mn, it is 0.63 on Ni-Al/La-Ce). As to steam reforming the highest productivity during conversion of acetic acid was obtained for Pd/Ni-Al membrane (up to 600 l/dm³·h), but the highest conversion was observed for Pd-Co/Ni-Al (up to 100%) membrane. It was shown that the highest conversion of ethanol was also up to 100% on Pd-Co and Pd-Zn membranes. The conditions of all steam reforming experiments were following: W_{liquid feed}=0,5 ml/min, W_{carrier gas}=10 l/h, composition of liquid feed was 1:13 ethanol (or acetic acid respectively):water. Particularities and prospects of catalytic membrane microreactors studied are considered.

Acknowledgements

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GAS PERMEABILITY PROPERTIES OF MODIFIED MEMBRANES BASED ON EXFOLIATED GRAPHITE

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Inorganic porous membranes including carbon based materials have been attracting more and more attention due to high thermal, chemical and mechanical stability [1]. They also demonstrate good permeability and reasonable selectivity in relation to gases. This paper presents the results of the study of foils based on exfoliated graphite, which was developed at Moscow State University. Electroconductivity and gas permeability of H₂, N₂, O₂, CO₂ of graphite were obtained for graphites of different density. For gas permeability measurements differential and integral permeability methods were used. Electroconductivity was estimated by double-contact method. It was shown that membranes demonstrate low ideal O₂/N₂ selectivity but high H₂/CO₂ selectivity.

The modification of the foil was carried out by two methods. First modification was done by removing of dense boundary layers in order to increase the permeability and examine the influence of boundary properties on gas permeability and selectivity. It was shown that the selectivity of the foil is determined by central high-porous layer.

Second type of modification was made using fluorine. Gas phase fluorination is usually applied to change the surface properties of materials. Depending on the type of virgin materials and used techniques, the improved properties may concern wettability, chemical stability, permeability, conductivity etc. [2]. We made surface fluorination of the foils based on exfoliated graphite of different densities under variation of temperature of the treatment. After fluorination membranes demonstrate increasing of permeability, they also have good conductivity and selectivity.

Obtained results can be used for further development of new carbon membranes for gas separation.

[1]G.Q. Lu, J.C. Diniz da Costa, M. Duk, S. Giessler, R. Socolow, R.H. Williams, T. Kreutz. *Journal of Colloid and Interface Science* 314(2007)589-603

[2]A. Tressaud, E. Durand, C. Labrugère, A.P. Kharitonov, L.N. Kharitonova. *Journal of Fluorine Chemistry* 128(2007)378-391

PC 79

THE QUALITY CONTROL OF ION EXCHANGE MEMBRANES RALEX

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Quality of ion exchange membranes RALEX is checked by interoperable and check-out control. The control consists of the measurement of physical, chemical and electrochemical properties. It is focused on characteristics of materials and membranes. An identical system of control is used for characterization of membranes from industrial application for research and troubleshooting purposes. Standard properties of commercially sold membranes are given and statistic evaluation of membrane properties is carried out monthly.

PC 80

ION EXCHANGE MEMBRANES RALEX IN THE PROCESS OF DEMINERALIZATION OF WHEY

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Ion exchange membranes RALEX are used in demineralization of whey by electrodialysis. Demineralization of whey is a batch process. Due to fouling of membranes (especially protein fouling in diluate chambers), regeneration is carried out after demineralization period. Regeneration process consists of rinsing with solutions of acids and hydroxides. High frequency of regeneration and the usage of aggressive chemicals put high demands on resistance of membranes. Because of it the attention is paid to control of quality of membranes. Results from industrial operation confirm high resistance of RALEX membranes. In spite of that, research works which should increase the lifetime of membranes are in progress.