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MEMBRANE REACTORS AND INTEGRATED SYSTEMS IN THE CHEMICAL PROCESS INTENSIFICATION

It is well known that the chemical process intensification is novel design philosophy where significant reductions in plant scale can be achieved by matching the chemical, biological and/or physical requirements with the fluid dynamics of a process. Resultant benefice can include reductions in capital and operating cost, and/or significant improvements in efficiency process yield, waste production and inherent safety. Applications include implementation of continuous processes, compact heat exchangers and separators, modification of chemistry and improved plant layout and control.

Process intensification include:
- Compact reactors;
- Continuous processing;
- Compact separation methods;
- Reactors and separation systems optimisation;
- Novel chemistry;
- Combined use of equipment;
- Improved plant design and process development;
- Improved control systems (particularly for continuous processing);
- Achievement of significant process improvements through process intensification.

One would expect, that membrane reactor with chemical active and permselectivity walls, and/or circulate active career could play a great role in the chemical and biochemical process intensification.

In Russia carried out to investigations to the prospects for use different type membrane reactor in chemical industry, biotechnology and environment. The emphasis is on the evolution of the new energetic- and resource save, safe and little waste production.

This lecture aims to discuss basic principles and potential application membrane reactors, MR, membrane integrated systems (permabsorber and permstractor), IMS, the adsorption or chemical active filters, MAF, with use the planar sorbents or catalysts and combine MR+IMS or MAF+IMS equipment was proposed. I shall consider of joint research completed in several organisations including Chemistry and Biological departments of Moscow State University and Membrane Centry of Institute of Petrochemical Synthesis RAS.

1. ADSORPTION- OR CHEMICAL ACTIVE FILTERS AND THE REGULAR STRUCTURE APPARATUS

Traditional adsorption apparatus using granulated sorbents are not efficient enough for the treatment of gases in order to separate the toxic components from the gaseous waste. Therefore chemical active filters have been used to this propose using mineral tissue (web) in the planar form. The advantages planar sorbent in comparison with the traditional (granular) sorbents:
- higher efficiency sorption;
- possibility of differential design of the sorption ensuring high technological flexibility;
- optimisation of the mass transfer and heat transfer in the sorption units (the chemisorption is connected with the release of heat which should be transferred out of the system).

Aim of our research was investigation of potential use of the new sorbents (adsorption or catalytic active filters) for cleaning industrial gases from hazardous pollutants (radioactive gases, organic contamination's and heavy metals).

Materials:

- Acids treatment basaltic fibres, tissue and felt;
- Active coal fibres, tissue and felt;
- catalytic active basaltic fibres.

Basalt planar sorbents were used for separated acid gases, organically vapours and vapours and water from polluted air or natural gas. Coal planar sorption of organic vapours, radionuclides and vapours of volatile metals. Composite units containing planar sorbents made from different materials (coal and basalt).

We have made studies into regular structures apparatus with planar adsorbents uses for next aims:

- Treatment of gaseous multicomponent waste streams;
- Removal H_2O, CO_2, SO_2, H_2S from air;
- Volatile organic compounds (chlorinated micropollutants like furanes, volatile ketone (MEK, MIBK), dioxins (PCDD sterioisomers) etc. recovery from gaseous waste;
- Monitoring of pollutants (benzene, xylol, dichlormethan, toluene, butanol, methanol) in workplace air;
- Cleaning air from volatile hazardous elements (I, Ag, Sb, As, Cr etc.) and their separation form polluted air resulting during incineration of municipal waste and in fire accidents;
- Removal from gaseous phases and storage of volatile heavy metals.

We have considered the potentiality of regular structures apparatus with planar catalysators uses for the performance of the next processes:

- conversion of dioxins stereoisomers obtained in various incineration process to simple gases;
- transformation of organic compounds to gases may be important for energetic.
- thermo- and photodegradation of halogenated hydrocarbons
- production of methane and ethylene from agricultural and industrial wastes

Pollutants removal from fluegas with active filters compared with conventional techniques the granular adsorbents has a main advantaged: high removal efficiency, small volume, simple operation, excellent scale-up ability, no entertainment, flooding or channelling. Filtration through the adsorption or catalytic active filters is a new, very selective separation process which combines adsorption, catalysis and filtration technology to produce an optimized hybrid process.

The prior analysis demonstrated that regular structures apparatus with planar adsorbents and/or catalysts hold the greatest promise for next application:

- environmental protection;
- energetic;
- chemical and petrochemical industry.

ADSORPTION ACTIVE FILTERS: THEIR SYNTHESIS AND USE IN THE AIR CLEANING FROM HAZARDOUS SUBSTANCES

Project of bilateral WTZ Wissenschaftlich-technische Zusammenarbeit co-ordinated by DLR and auspices of BMBF

Short title: **Adsorption filters for air cleaning**

Objectives of the Project :

l. Design of the adsorption active filters based on the chemically treated basalt fibres, leached glass fibres and active coal.

2. Testing sorption properties of the tailored active sorbents for sorption of organic volatile compounds (chlor-organic compounds, dioxines, acid gases, etc).
3. Preparation of planar sorbents to be used for cleaning air containing hazardous compounds).
Duration of the project 3 years.
Working program:
Task sharing between the partner institutions:
1. Chemical faculty of the Moscow State University:
Design and preparation of the tailored sorbents, intermediate products and planar sorbents (tissue, based on various fibbers).
2. GSF - Institute of environmental chemistry:
Testing active sorbents for sorption of hazardous organic compounds by means of gas chromatography, thermal desorption with Mass spectroscopic detection.
3. Nuclear Research Institute Rez (Balek):
Characterisation of porosity and surface area and thermal stability and chemical durability using Diffusion structural analysis; porosity and surface area determination by sorptometer.

Travel of Russian scientists to GSF

l998	1 travel	3 weeks	1 travel	10 days
1999	1 travel	1 month	1 travel	2 weeks
2000	1 travel	1 month	1 travel	2 weeks

Equipment's and chemicals : 8000 DEM for chemicals and parts Laser printer for PC and software upgrading.

2. INTEGRATED MEMBRANE SYSTEMS

2.1 Membrane methods

1. Porous or non-porous (dense)
2. Active (membrane catalyst or ion- conductor) or chemical passive
3. Materials:
   Inorganic membranes: Metal, alloy, ceramic, glass
   Polymeric membranes: non-porous gas separation asymmetric composite membranes
4. Geometry of membrane: flat sheet or hollow fibber.

The dense polymeric membranes meet the criteria of high selectivity, but satisfying the criteria of high permeability is limited by the thickness of the membrane, which again is constrained by the mechanical strength and durability of the membrane. To meet the dual challenge of selectivity and permeability, there has been a recent thrust to support thin layers of highly selective membrane material on a porous support with high permeability. The advantages of a dense polymeric membranes are high gas permeability and selectivity and absolutely microbe non permeability. Disadvantage to this membranes are poor chemical, mechanical and radiation stability and low resistance to temperature.

As opposed to polymeric membranes, the inorganic membranes are characterized by high resistance to temperature and corrosive environments, and good mechanical stability. There is increasing interest utilising inorganic membranes to separate gas mixtures at high temperatures. One of their most promising applications is in membrane reactors where chemical conversion and product purification by separation take place in the same device. These applications are involved with chemical synthesis, but membrane reactors also have potential used in high temperature gas cleanup operations.

2.2 Permabsorbers

Recovery, purification and concentration of gases, treatment and control of the gas mixtures compositions are the key processes of modern chemical technology and ecology. At the moment the separation of gases is carried out by different methods which are cryogenic, sorption and membrane ones. Each of them has own benefits and disadvantages. For the real technological systems the combined application of the different treatment methods is of interest. The next stage of the different gas separation methods combination is the creation of integrated systems of the membrane technology.

Integrated membrane systems in gas separation: membrane-absorption systems included:

Separation modules of liquid- membrane contactor:

1) Membrane permabsorber;

2) Selective membrane valve.

Condition of operation:

1) Flowing;

2) Circulating;

Selective flowing-liquid absorbent:

1) Non-specific in relation to the components of gas-separation mixture;

2) Solubility's of the gaseous components in a liquid could differ considerably;

3) Liquid could react with one or several of the gas components.

At the last time it was proposed to use non-porous gas separation membranes in membrane-absorption systems combining the membrane and sorption methods. Two types of gas separating modules (***membrane permabsorber and selective membrane valve)*** are suggested which are the membrane absorber and the membrane valve operating in the both flowing and circulating condition.

The main reasons for the application on non-porous polymeric membrane systems are the flexibility, selectivity, good productivity and the sterile properties of these systems.

Membrane absorber

The ***membrane absorber*** (Fig.7a) consists of the two cells which are absorption and desorption ones and the liquid specifically selected as an agent for extraction is circulated between them. The gas mixture is passing over the polymeric membrane in the absorption cell. The most permeable component of gas mixture diffuses selectively through non-porous polymeric membrane into the flowing liquid under it, is absorbed by this liquid and transfer to desorption module. The degassing of liquid occurs in the desorption membrane module through the non-porous polymeric membrane with obtaining of the high concentrated gaseous products. There are two operating conditions of the membrane device which are flowing one when the liquid is taken out of gas separating device, and when the liquid is continuously circulated in system.

The liquid absorbent can be non-specific in relation to the components of the gas-separation mixture. The solubility's of the gaseous components in a liquid could differ considerably. Also, a liquid could react with one or several of the gas components. The productivity and selectivity of the membrane permabsorber depend on the gas-transport properties of the polymeric membranes, on the temperature of the liquid absorbent in stripper, on the flow rate of liquid absorbents, on the concentration of a selective carrier in a liquid, etc.

We are use a hybrid process for separation of ethylene/ethane mixtures using a membrane permabsorber comprising hydrocarbon-stable composite asymmetric non-porous gas-separation flat-sheet membranes made from co-polymer: polydimethylsiloxane/polyphenylsilsesquioxane with a high permeability for hydrocarbons and flowing solution of silver nitrate used as a selective absorbent for ethylene.

Membrane valve

A membrane valve consist of two modules: a permeator and desorber (Fig.7b). The permeator is divided by two polymeric gas-separation membranes, M1 and M2, between which a thin layer of absorbent liquid is moving. The investigated gas mixture and gas-carrier are passing under the surface of sandwich. The components of the gas mixture are dissolved in the liquid absorbent and are driven out of the permeator to the desorber (membrane M3 and M4). The selective membrane valve has one inlet for the initial gas mixture and three outlets for the product leaving the separation device. The plant can be used to separate a three-component gas mixture: the gas insoluble in the absorbent passes above the membrane, the fast component of the gas mixture passes through the composite membrane, and the third component, dissolving well in the absorbent, is entailed by the liquid into the desorber.

The proposed methods has been tested by separating a three-component gas mixture carbon dioxide-methane-hydrogen using the membrane valve operating in the circulation mode with desorber. Asymmetric membranes produced from poly(vinyltrimethyl silane) and aqueous solutions monoethanolamine of different concentrations served as the carrier of carbon dioxide.

Emission of volatile (halogenated) organic compounds (VOC) to the atmospheric are a serious problem, particulary due to large volume flows and low concentration levels. For the recovery of VOC's a new membrane based process is proposed: selective membrane absorption. selective membrane absorption is a new, very selective separation process which combines absorption and membrane technology to produce an optimized hubrid process.

Absorption is very selective process for recovering VOC's from air. With the combination of membranes and absorption, it is possible to recover VOC's at very low level (<1 mg/m^{-3}) and to concentrate them in the absorption liquid. Recycling the process gas (e.g. air) is then possible. By regenerating the absorption medium. the absorbed VOC's can be recovered and reutilized.

Selectivy membrane absorption combines the advantages of these short diffusion pathways:
- compact hollow-fibre membranes with short diffusion path ways
- phase separation by the membrane
- recovery of VOC's, even at low concentrations, by high affinity absorbents

After the modelling of mass transfer in the membrane module the optimal composition of the absorption mixtures was calculated with vapour-liquid thermodynamics system options.

2.3 Permsractors

Membrane based extraction are emerging contacting technologies which have several advantages over conventional contactors, such as, high mass transfer, compactness and no fluid mixing.

We explored the possibility of perstractors in next liquid/liquid extraction processes:
- Removal of toxic organic compound from waste water
- Removal of heavy metals from industrial waste or natural water.

Perstractors with suppoted liquid membrane technique

The membrane extraction technique is based on selective extraction of metal or organical compounds from liquids using Supported Liquid Membrane technique (SLM-technique) and enrichment of one component using compact membrane elements, followed by component analysis in enriched pure re-extraction solution by known mode.

We was used Supported Liquid Membrane technique (SLM-technique) for monitoring of mercury and antimony in natural water sources and biological solutions with the determination limit 10^3-10^4 mg/l.

There is a need in convenient and simple method of mercury and antimony analysis in natural water sources and biological solutions, with the sensitivity corresponding to concentration limits for these toxic metals in water. Simple photometric, ionometric and strip methods adapted to field use often don't correspond to this sensitivity level and are under the hindering influence of many other ions. More sencitive device methods like spectroscopy of different types are too complicated for permanent use in field conditions, and often remain sensitive to excess of hindering metals.

The main features of a new method are:

1. Elaboration of the kinetic model for membrane extraction of heavy metals in cationic and anionic forms through SLM conjugated with co- and counter-current transport.
2. Achieving high extraction selectivity of the metal analysed (up to 10^2-10^3) due to proper choice of selective chelating agent and re-extraction phase content.
3. Concentrating of metal analysed in re-extraction solution by a factor of 10^2-10^4 due to "active" counter-current transport.
4. Volume of the probe analysed can be as small as 20-30 ml.

In future the method can be extended for environmental analysis of many other toxic metals, e.g. Ni, Cr, Cd, Zn, etc.

Scientific and technical description included:

1. Collection and analysis of the data on discription and migration of mercury and antimony together with accompanying metals in natural water sources, biological solutions and soils.
2. Testig of SLM loaded with lipophylic metal-selective extragents selected from the classes of polyalkylaroylthyoureas, alkylthyoethers, etc.
3. Investigation the kinetics of "active" metal transport coupled with proton or hydroxyl counter-current transport from the re-extraction phase.
4. Development of the cassette element design with thin channels for source and reextraction solutions that are separated by a porous hydrophobic support soaked with the solution of lipophylic chelating agent. The element measures not more than 6x12x2 cm; the volume of extraction solution for loading the reusable SLM in the cassette is 0.5-1 ml.
5. Field testing of the method on real natural sources, wasters and biological solutions. Development of procedure recomendations for using the method in monitoring and biological investigations.

Membrane extraction discs.

In Russia the continuous environmental monitoring of dissolved toxic metals using membrane extraction discs was be developed.

Method is based on using of new simple units - membrane extraction discs (MED) - macrocapsules measuring a coin or a tablet, that are a micro-vessel with walls being metalselective impregneted liquid membrane. Hydrophobic pores of this membrane are soaked with hydrocarbon lipophylic chelatng agent, that is selective to the metal analysed. The micro-vessel contains re-extraction solution impregnating a tablet-like porous spacer and, if necessary, an indicator that forms a colored complex with metal ions. MED being placed in a flow of analysed water selectively extracts the metal which is accumulated in the inner re-extraction solution. The analysis of metal absorbed in this solution can be carried out by traditional methods after MED opening (strontium can be determined through the complex with ethylene diamine tetraacetic acid or using atomic absorption spectroscopy). Another method is the spectrophotometry or visual estimating the intensity of comlex or deposit colour directly through transparent membrane compared with standarts, without destroying the MED and with the possibility of its further using (nikel determination in form red precipitated dimethylglyoxyme complex).

If the process of metal ion transport is attended by the process of counter-current transport of eny component from the internal re-extraction solution (e.g., hydrogen cations), this will allow to attain multiple concentrating of the metal analysed inside the MED. In this case the concentration degree can reach 10^4.

In properly made MED the metal absorption rate is directly proportional to the metal's concentration in the external solution, i.e. the resulting value corresponds to averaged metal concentration in water source during MED's exposition time. MED's are the simpliest and extremely cheap analytic units for durable quantitative accumulation of toxic metals. Using of them permits to develop a simple method of continuous environmental control of them in different water sources and wasters.

Authors of the work dispose of an method of hydrophobic macrocapsules' production, and of all necessary components for MED production:
- Hydrophoic membranes based on fluoropolymers and polyolefines, self-carrying and composite ones;
- Acid-resistant macroporous spacers based on polyolefines of foam, sintered and non-wooven types;
- Delective lyophilic extragents for strontium and nicel extraction, of two classes: bis-(alkylcycloalkyl)-crownether and alkylene-bis-diphenylphosphine oxide with pendant aliphatic arm. Lyophilic alkylated hydroxyoximes for selective nikel extraction.

Long-term selective toxic metal (e.g. water dissolved nikel and strontium salts at concentration 10^{-2}-10^{4} mg/l) accumulation method from a wastes, potable water or natural water reservoir for its subsequent analysis was be developed.

Perstractors with flowing liquids.

There is a growing need separation techniques which selectively recover metal ions from industrial process streams. The newly developed membrane-absorption or extraction process is abble to recover metal-free water and a concentrated metal solution from above streams. Membrane extraction processes can be used for concentrating metal solutions from ppm-level to g/l-level with recycling of the concentrated metal solution and of the metal-free water as interesting possibility.

The permstractor was used also for separation of multicomponents liquid mixture.

The permstractor (Fig.8) consists of the three cells. The liquid mixture (L1) is passing over the polymeric membrane in the extraction cell. The most permeable components of liquid mixture diffuses selectively through porous polymeric membrane (M1) into the flowing liquid (L2) under it, is absorbed by this liquid and transfer to reextraction module. The reextraction of liquid occurs in the reextraction membrane module. Components of liquid mixture difuses selectively into the flowing liquid (L3) under it through the porous polymeric membrane (M2) with obtaining of the high concentrated products. Products cleaned with help different liquids L4 and L5 and membranes M4 and M5. There are two operating conditions of the membrane device which are flowing one when the liquid is taken out of liquid separating device, and when the liquid is continuously circulated in system.

3. MEMBRANE CHEMICAL REACTORS

The used of membranes in chemical reactors is motivated by the equilibrium shift coursed by selective or preferential permeation of reaction products, leading to higher conversion in single pass. By selectively permeating one or more reaction products through the membrane wall, it is possible to achieve significant enhancement over the equilibrium conversion of the reactor feed stream. The equilibrium shift also allows attaining a given conversion at less severe conditions of temperature and pressure. As reaction and permeation proceed simultaneously, the separation of product can be accomplished in the reactor unit itself, or at least the down stream separation load is reduced. Selective or preferential permeation may prevent further reaction of a product and this may improve the yield of a desired component in a multiple reaction system. On the other hand, the ability to introduce a reactant in a controlled manner through a permeating membrane may allow the regulation of the reaction leading to better yield and selectivity and improved control. In addition, the membrane may allow hot separation of products and eliminate the need for quenching a reaction to prevent back reaction. The membrane itself may act as a catalyst or catalyst may be impregnated on the membrane. The membrane reactor may be bifunctional and two complementary reactions may take place on either side of the membrane, the product of reaction on one side acting as a reactant on the other side, while the endothermicity of one reaction is compensated by the exothermicity of the other.

In the Chemical Department of Moscow State University and in the Institute of Petrochemical Synthesis we are working in next direction:
- Construction of various new types of membrane reactors;
- Transport mechanism of fluids through active or passive membranes;
- Separation of mixed wastes;
- Steam reforming of methane;
- Water gas shift reaction;
- Dehidratation of various hydrocarbons;
- Purification of tritium for thermomolecular energy installation;
- Radioactive waste management of nuclear power;
- Eir and water pollutants monitoring.

There are basically two types of membranes which can be used for membrane reactors: dense (non porous) and porous. The former is called the inert membrane packed bed reactor while the latter is called inert membrane fluidized bed reactor. When the membrane itself act as a catalyst or catalyst is impregnated in the membrane and the reactants pass through the empty tube having the catalytic membrane wall, it is called a catalytic membrane reactor. When a CMR is also packed with catalysts, it is called a packed bed or fluidized bed catalytic membrane reactor. In industrial reactors, shell and tube configuration with an assembly of single tubes or multichannel monoliths may be incorporated into a large shell. The membrane reactors are usually operated in parallel or cross-flow mode, with the reactants on one side and vacuum or a sweep gas.

Let us examine the different constructions of membrane reactors. Schematic layouts for the membrane reactor systems are presented in Fig.9. The walls of reaction vessel are made from the gas selectively materials. We are suggested that in the reactor occurs a second-order reversible chemical reaction involving four gases. The each walls of reactor have different selectivity with respect to component of reaction mixture. Certain of the membrane walls are used for the initial reaction components supplied in reaction vessel, other walls is removed of reaction products from reaction vessel). Fig.8 show membrane reactor which allows to carry out the removal of both of reaction products. It is possible to operate the system as a catalytic membrane reactor by replacing the membrane with a catalyst-impregnated membrane or a membrane which itself acts as a catalyst. The packed bed catalytic membrane reactor can be prepared by packing the catalytic membrane reactor with catalyst).

Experiments with membrane reactors included study of gas diffusion in solids with simultaneous diagnostics of membrane material.

Membrane materials: metals (Pd, Pt, Ag, Fe, Ni, Cu), alloys, materials with coats and welds, ceramics, glasses (porous or dense)

Diffusants: hydrogen isotopes (protium, deuterium, tritium), air components, inert gases (stable and radioactive)

Diffusion methods: permeability method, sorption and desorption methods, thermodesorption spectroscopic analysis, frequency probing method, autoradiography method

Methods of membrane diagnostics: 1) Gas Diffusion Probe Method. 2)Auger Electron Spectroscopy. 3) Nuclear Gamma-Ray Resonance Spectroscopy Method (Mossbauer effect).

There is increasing interest utilising inorganic membranes to separate gas mistures at high temperatures. One of their most promising applications is in membrane reactors where chemical conversion and product purification by separation take place in the same device. These applications are involved with chemical synthesis, but membrane reactors also have potential used in high temperature gas cleanup operations.

Porous and dense ceramic membranes for the application in high temperature reaction processes and separation. Composite ceramic membranes are investigated for the application in selective gas separation membrane reactors. The type of nanostructure of those composite membranes determines the application possibility.

Dense mixed-conducting oxide membranes offer a large potential in the separating oxygen from air or for selective feeding of oxygen into chemical reactors. Oxygen is transported through the membranes in the form of anions, being charge compensated by the transport of electronic charge carriers. Promising candidates are stabilized zirconia or bismuth oxide, doped with multivalent metal ions, and perovskitetype oxides $(La,A)(Co,B)O_{3-\delta}$ (A= Sr, Ba; B= Fe, Mn). The permeability occurs above 600^{o}C, reaching values that may be comparable to those axhibited by micro-porous membranes.

Microporous membranes based on silica or silica-composite systems transport preferably He, H_2 and CO_2 in comparison with all other gases. The permeability is relatively high (H_2 300 m^3/m^2.bar.day at 200^{o}C) and for the system H_2/C_3H_6 the separation factor is over 200 at 200^{o}C. In this case the selective toplayer is very thin (<100 nm) and is partly present in the support.

Dense and microporous membranes can be furthermore used in high temperature reactors as passive membranes to remove selectively one of the reaction products at reaction temperature. A special case of microporous membranes are zeolite membranes. The ordered cavities and channels can be considered as micropores. Mesopores and macroporous membranes (pores >3 nm) are at high temperature less selective but have a high permeability. These types of materials can however be made very suitable as actives membranes in high temperature reactors. The internal surface of the membranes (or membrane toplayers) are then provided with catalytically active components. With these active membranes reactions can be carried out with a feed from both sides of the membrane and process conditions can be optimized for high conversion and selectivity. A special case is air polution control through the removal of NO_x with NH_3.

Palladium and its alloys with ruthenium, nikel or other metals from groups V1 to V111, silver and zirconia are examples of dense membranes. Palladium-based membranes are permeable only to hydrogen while silver and zirconia are permeable only to oxygen. These membranes have high selectivity, but low permeability. Zirconia membranes are solid oxide electrolytes and their permeability depends on ionic conductivity. Examples of commercial porous inorganic membranes are ceramic membranes, silica and titania, glass and porous metals, such as stainless steel and silver. These membranes are characterized by high permeability, but low selectivity. Recently attempts are being made to combine the selectivity of the dense membranes and the permeability of porous supports using various techniques, new materials are being developed and preparation techniques devised to produce thinner membranes and/or smaller pore-sized membranes. Methods are also being developed to modify the pore structure, producing smaller pores and increasing the stability of the membrane.

The high permeability of the inorganic membranes can be combined with the good selectivity of the organic membranes. The concept of liquid-immobilized membranes can be adapted in the field of inorganic membranes with molten salts incorporated in their porous matrix.

4. MEMBRANE MICROFOTOREACTORS FOR TOTAL ORGANIC CARBON ANALYSIS

New analytical device for determination the value of Total Organic Carbons (TOC) in water solution is based on exhaustive photooxydation of water-dissolved organics in microreactors using TiO_2 semiconductive photocatalyst in a plain or turbular membrane form. In this case photochemical reaction is provided on membrane photocatalyst's surface while UV-irradiating and at the same time removing the reaction products through the pores to the oposite membrane side. Using of membranes having a developed porous structure with open submicron pores and transmembrane permeability to liquids and gases permits to simplify the construction of a photooxidizing unit used, to make it usable repeated many times and to increase the completeness of photooxidation, that is, accuracy of the analysis. Earlier, during the preliminary research, the russian scientists have already prepared the composit membrane photocatalysts from TiO_2 (by sol-gel method from alxoxide precursors) and have investigated them regarding their activity during the oxidative destruction of chlorinated aliphatics, phenols, aromatic acids, many phosphorus, nitrogen and sulfur containing compounds, for example, surfactants, in water solution.

It was established that in appropriate conditions (excess of oxidixing agent, Pt- and Ru-doped membranes) the end products are H_2O, CO_2 and Cl. Releasing CO_2 can be separated through gas permeable membrane (teflon, silicon, that are at authors disposal) and analysed by any known methods, like condumetric detector.

The using of membrane microphotoreactor for total organic carbon analysis with TiO_2 -based membranes permits to reach high sensitivity (determination limit corresponds some ppm of TOC in water by using condumetric detector), long-term stabiliy and high selectivity, associated with the selectivity of gas permeable membrane.

5. MEMBRANE BIOREACTORS.

Biological water denitrification is a proven process to remediate the increasing nitrate pollution of drincen water. In anioic conditions denitrifying bacteria are able to use nitrogen oxides as electron acceptors consequently nitrate may be sequentially reduced to molecular nitrogen. To achieve biological denitrification rates reactors with cell retention or cell immobilization must be used.

The uses of non-porous asymmetric polymeric gas-separation membranes in membrane bioreactors appears to have considerable promise. The thin dense work layer of membrane offer sterile of processes by reason of total absence of micro-organisms permeability from one compartment of reactor to another. In this case, the high aim gas membrane productivity obtain.

The membrane reactor construction is similar to Integrated membrane systems construction. However, there are circulate water suspending of micro-organisms (bacterium's, algae). The equipment incorporates light source for controls of micro-organisms life.

We have made studies into membrane bioreactors with circulate suspended micro-organisms uses for next aims:

- the production of as gases as hydrogen and oxygen;
- recovery of gases to biomass;
- conversion of one gasses in another.

Examples are provided by conversion of carbon dioxide in hydrogen. Carbonic acid gas is an extreme environmental hazard, whereas hydrogen is important for energetic.

The prior analysis demonstrated that membrane bioreactors with circulate suspended micro-organisms substance hold the greatest promise for next application

- apparatus for life provision
- hydrogen energetic
- environmental protection
- production of artificial protein.

6. COMBINE EQUIPMENT

In our laboratory, new construction of combine integrated membrane systems was proposed. Equipment integrates in one module different methods of processing and separation of gas mixtures: absorption, adsorption, extraction and liquid catalyse. For regeneration of liquid carrier can be put to use desorption and reexstraction processes. Equipment is dedicated to the cleaning of the liquid nuclear plant wastes from radionuclides. Its make possible remove from waste the organic volatile matter, two radioactive metals and two gasses. Integrated system have one input and six output for remove the cleansed streams.

In summary it may be said that in Russia carried out to investigations to the prospects for use different type membrane reactor in chemical industry, biotechnology and environment. The emphasis is on the evolution of the new energetic- and resource save, safe and little waste production.