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THE IMPORTANCE OF MEMBRANES TO MODERN TECHNOLOGIES

The paper points out that membranes play increasingly important role in different branches of *human friendly technologies*. Membrane processes are implemented in industry, in energetic and environmental protection, where the formerly used *cleaning technologies* are recently replaced by modern *clean technologies*. Effective separation of different components from industrial sewage or wastes makes it possible to recover raw materials or to recycle chemicals, cleaning agents, etc. This enables us to improve environment and to reduce total costs simultaneously. However, membranes are still used in cleaning technologies for wastewater treatment, remediation of contaminated soils, purification of ground waters, cleaning of industrial gases and sewage. Besides membranes are also used for the improvement of human health, e.g. artificial organs (kidney, lunch, pancreas and skin), pyrogens removal, blood processing and controlled release of medicines. Membranes are successfully used in the production of healthful and tasteful food. Agriculture uses membranes in hydroponics or for controlled release of fertilisers, herbicides, pesticides, insecticides, and pheromones. This way of delivery protects soils and ground waters against penetration of chemicals. The above-mentioned membrane applications are reviewed.

1. MEMBRANE PROCESSES

Membrane processes have appeared in many technologies in the last two decades, however they were known for nearly over two centuries. The first research on osmosis and gas separation was performed on natural plants or animal membranes in the XIX century. These early studies were very intensive and attracted attention of famous scientists, i.e. Fick, Graham, van Hoff, etc., who formulated the basic laws and prepared background to further development of *membranology*. In these times, the membranes were considered as interesting but completely useless curiosity without any links with practical application. This was due to low permeability and poor separation selectivity of those membranes. The invention of asymmetric membranes caused the break-up in membrane technology thirty years ago. This enabled the membrane technologies to be introduced on a commercial scale and it was the first step in creating membrane market. The further stimuli of this development were achievements in ma-

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terial sciences and new technologies of membrane manufacturing. The newest composite membranes have multilayer structure which allows us to meet requirements of high permeability with controlled cut-off.

Membrane applications can be classified within four categories, i.e. separation of homogeneous and heterogeneous mixtures, contacting of species or components, controlled release of species and inclusion of components.

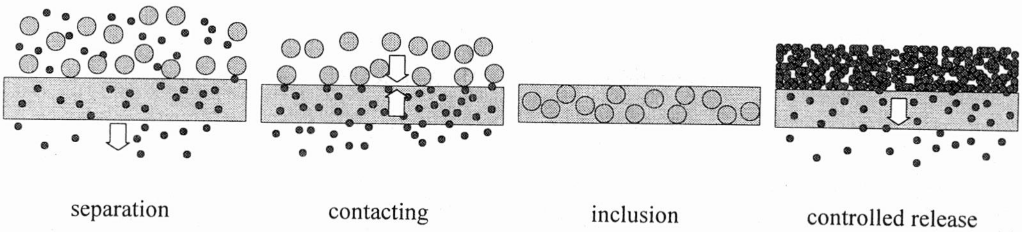

Fig. 1. Membrane's functions

Separation processes prevail among industrial applications of membranes, especially in chemistry, pharmaceutical and food industry as well as biotechnology. Membrane separation processes are carried out either in order to fractionate the mixtures into the given products, by-products and wastes or to purify and finally concentrate the products. In contactors the membranes may be used as artificial interfaces that ensure improvement of classical unit processes. Controlled release is the newest membrane application that allows us dosing precisely some species to given environment. Immobilisation of enzymes, antibodies or microorganisms within membranes is recently applied in biotechnology.

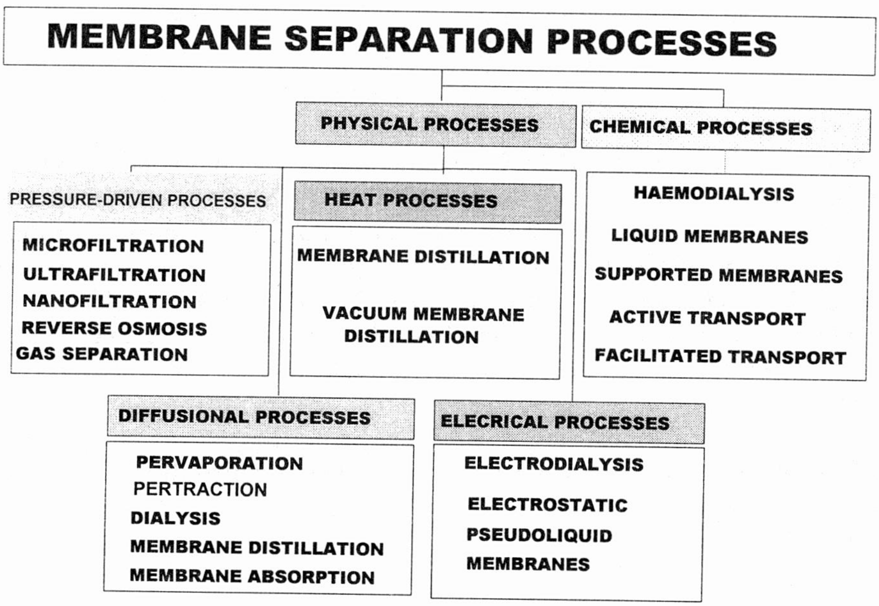

Fig. 2. Membrane's separation processes

Actually a number of membrane separation processes approach 20. They base on several driving forces such as pressure, concentration, temperature or electric potential gradient. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and gas separation (GS) are called the pressure-driven membrane processes. The microfiltration is used to separate the suspensions, colloids, emulsions, bacteria and viruses basing on the particle to pore size ratio, i.e. sieving (screening) mechanism. Ultrafiltration allows macromolecules such as proteins, dextranes to be separated from solution and is commonly used in biotechnology. Nanofiltration is used to separate medium-sized molecules, sugars, detergents and during softening of the water for removal of some salts that make water hardness. Reverse osmosis enables removal of micromolecules and ions from the water. This enables practically indefinite purity of the water to be achieved.

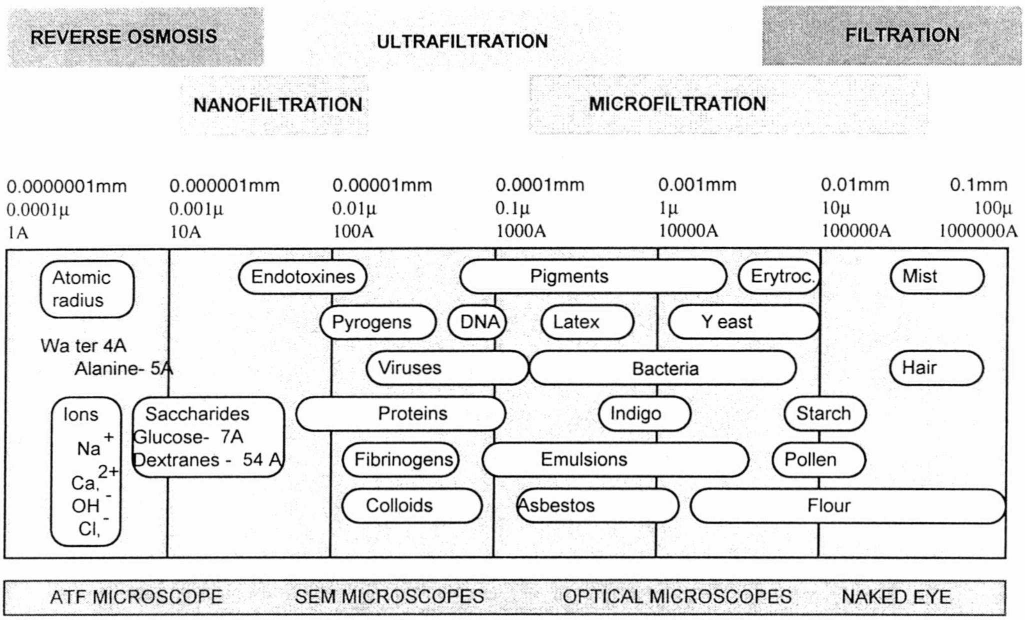

Fig. 3. Pressure-driven membrane's separation processes

The competitive processes with reverse osmosis are the dialysis (DL), haemodialysis (HD) and elecrodialysis (ED) with ion-selective membranes. Pervaporation (PV) is one of the newest membrane processes that is very selective in separation of specific components from the solution. Separation mechanism in pervaporation membranes bases on the solubility difference between various components in membranes. Then organic components may be separated from the water or, on the contrary, they may be dewatered. Separation of different organic components, i.e. alkenes, alkanes, alkynes, alcohols, ketones, esters and organic acids, etc, from the mixture may also be achieved by means of pervaporation. Membrane distillation (MD) enables us to separate volatile components basing on small temperature gradients and may utilise the waste heat. Membrane distillation (MD), extraction (ME) and absorption (MA) are much more effective than classic unit processes. In the examples, these membranes play the role of artificial interfaces and they are called the membrane contactors. Liquid membranes (LM) or their newer version, i.e. supported membranes (SM), are one of the most selective separation processes enabling us to separate any given component from very diluted multicomponent solution. The membranes play the role of semipermeable but passive barrier in all of the above-mentioned processes. During active and facilitated transport the included carriers react with given component on one side of the membrane and then they are transported onto the opposite side where this is eventually released. It is worth mentioning that not a very long time ago the active transport has been considered only as a domain of living organisms. In this case, the direction of mass transport is opposite to intrinsic transport resulting from chemical potential gradient. Moreover, some of the membranes can also simulate multifunctional performance of cells.

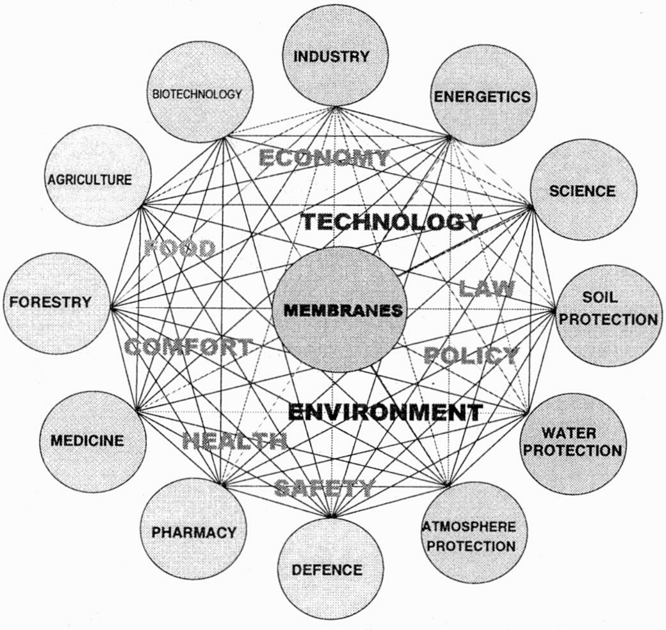

Fig. 4. Relations between several membrane applications that affect human life-standard

The aim of the paper is to review these membranes' applications that may be considered as human friendly. In this broad sense, almost all categories of human activity can influence our comfort, health and satisfaction of the life. The most spectacular factor that affects our comfort is our environment shaped by industry, energetic and agriculture. The condition of our environment depends on policy of authorities, law regulations, economical constrains and available technologies. Our health also depends on knowledge and potential in medicine, pharmacy, as well as on healthful and tasteful food.

2. INDUSTRY

Nowadays membrane processes enable practically unlimited selectivity of separation to be reached with arbitrary efficiency. Membrane processes are very effective, energy-safe and environmentally friendly. The only barrier to some of their implementations is the cost. One way of the capital cost's reduction is the newest idea of integrated systems. This bases on the concept that each of the competitive separation processes is always more expensive than the system composed of integrated processes. Therefore membrane processes do not need to be used as unique separation techniques but rather should be combined with other unit processes to reduce the costs and improve the effectiveness. The second way to enhance the economy of modern technologies is recycling and recovery of raw materials. The rational usage of raw materials, by-products and energy makes that the hope for wasteless (Fig. 5) and clean technology with complete recycling becomes true. It can be anticipated that in modern industry emphasis should be put on clean rather than on cleaning technologies. There are several profits that will be gained from rationalisation of technologies throughout application of selective membrane separation techniques, i.e.: recovery of by-products and recycling of materials, reduction of disposal problems, reduction of expenditures on raw materials and energy, improvement in environment conditions

Table 1

Some selected applications of the membranes in industry

Branch	Examples of matured implementations	Process
Chemistry	Concentration and recovery of substrates, catalyst's recycling, removal of organic components from water solutions, fractionation of hydrocarbons, crystal cleaning, recovery of cleaning agents, emulsion break-up, recovery and concentration of polymers, filtration of amines and glycols, purification and concentration of acids, purification of glycerine	RO, NF, UF, MF, PV, ED, DL
Petrochemistry	Fractionation of hydrocarbons, wastewater treatment, fuel dewatering, separation of azeotropes	PV, DM
Paper industry	Recovery of chemicals and reagents: pigments, chelating agents, emulsifiers, latex, defoaming agents, neutralisation of wastewater	RO, NF, UF, MF
Textile industry	Recovery of oil finish, polyvinyl alcohol, latex, dyes and detergents	RO, NF, UF, MF
Leather industry	Recovery of tannin agents and chemicals from unhairing baths	RO, NF, UF, MF
Electronics	Preparing of ultrapure water for flushing of integrated circuits, air filtration, water recycling	RO, NF, UF, MF
Metal industry	Regeneration of cooling emulsions for cutting, rolling drilling, etc, separation of condensates from compressors, neutralisation of galvanic wastes, recovery of oils and greases from degreasing baths, concentration of washings with diluted electrophoretic paints	RO, NF, UF, MF
Transport	Removal of oil from washings after cleaning of transportation means and tanks	UF, MF

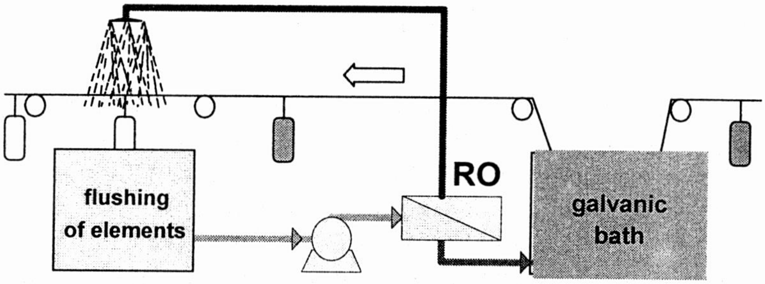

Fig. 5. An example of waste-free electroplating plant with purification of the recycling water by means of RO

3. ENERGY AND FUELS' PRODUCTION

Direct importance of membrane process to energetics concerns boiler-water purification and softening, wastewater and waste-gas treatment. Membrane technologies do not need additional chemicals and agents since they are competitive with ion-exchange process of water softening. This enables us to reduce outflow of wastewater, disposal costs and environmental problems. The another aspect of membrane significance to energetics is reduction of power consumption in these technologies where membranes were applied. The osmotic engine is very interesting contribution to new sources of energy involving membranes, but its application is very limited. Much more promising seems to be production of new environmentally-friendly fuels. Hydrogen may easily be separated from natural and coke-oven gases on the appropriate membrane. Biotechnology offers a cheap technology of fuel (ethanol) manufacturing basing on hydrolysis of polysaccharides such as starch or cellulose in membrane enzymatic bioreactor. Membrane is essential because very expensive enzymes must not be wasted and should be immobilised within reaction space. The costs of production are low because raw materials are cheap based mainly on renewable sources such as plants or wastes. The only obstacle is the content of water (due to water ethanol azeotropes) in ethanol that can cause corrosion of the engines. The water can easily be removed on hydrophilic pervaporation membranes (Fig. 6).

Table 2

Applications of the membranes in energy and fuels' production

Branches	Examples of matured implementations	Process
Energetic	Water softening, decarbonization, removal of radioisotopes, sulphur removal from gas	NF, RO, UF
Fuel	Manufacturing of ethanol from cellulose and starch, methane from agricultural and municipal wastes, hydrogen and hydrocarbons	UF, GS

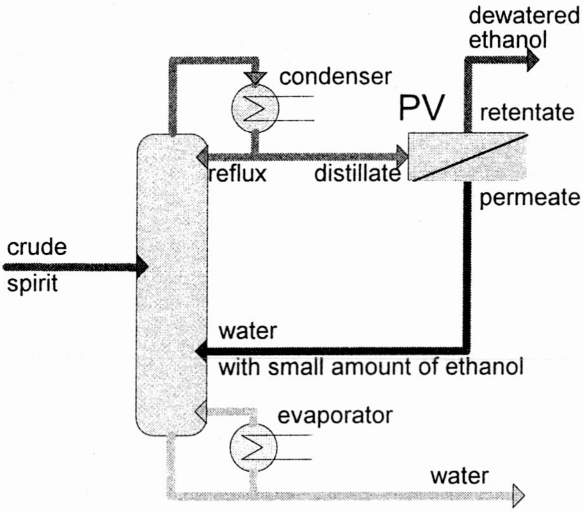

Fig. 6. Production of fuel (dewatered alcohol)
by means of membrane-based hybrid process

4. FOOD AND BEVERAGE PRODUCTION

The importance of membrane technologies to food production can be also partially deduced from their agricultural applications. This can be summarised in conclusion that controlled delivery of chemicals via membrane-controlled release enable us to produce health food.

The another aspect of membrane application in food production is the possibility of the quality improvement. Several kinds of beverages and juices are microfiltered just before their racking or bottling which enables us to remove all microorganisms that spoil the quality and durability of the products without adding any preservatives. This so-called cold sterilisation does not deteriorate in any extent the taste or smell of the product and keeps its full natural flavour and content with all desired components as vitamins, sugars, esters, acids, etc. The improvement of the product quality is made due to clarification of wines, beer, liquors, and juices by means of membranes. The removal of undesired components, e.g. pectin, salts or acids from juices or sugars from egg protein before drying, also improves the natural product quality. In some cases, the removal of alcohol from wine or beer is also desired and this can be achieved by means of pervaporation without any changes in taste or flavour.

Application of membranes has also its economical aspect if we take into account the concentration of liquid substrates before drying or any other processing. The removal of water from juices, milk, coffee, tea and cocoa before drying gives substantial savings in energy consumption.

In diary industry (Fig. 7) membranes offer almost all steps of separation. Initially milk is dewatered to reduce its volume by 30%. By the way a new kind of products appeared on the market such as cheese "Feta" whose composition of proteins and sugars was better.

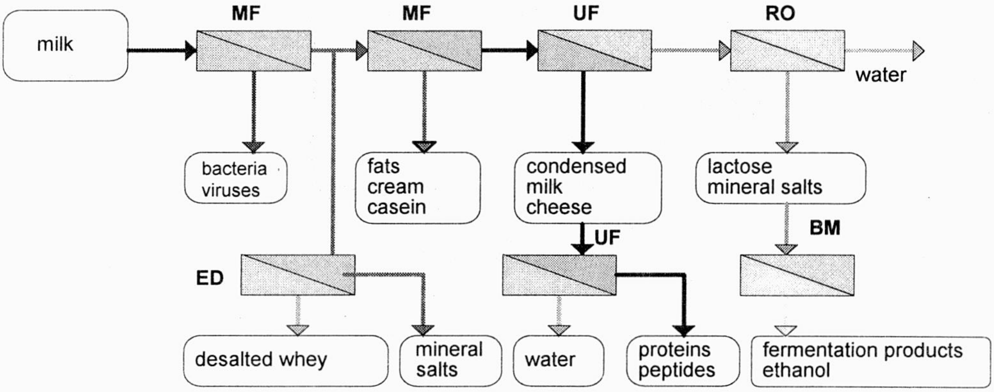

Fig. 7. Flow sheet of milk processing basing on membrane processes

Membrane processes enabled us also to get a new source of substrates. The proteins can be separated by means of ultrafiltration from plant and animal by-products.

Table 3

Some selected applications of the membranes in industry

Branches	Examples of matured implementations	Process
Food industry	Recovery of proteins from animal and plant by-products, recovery of proteins from plants, Soya beans, potato juice during starch manufacturing, desalting of vegetable dye, concentration of pectin and gelatine, cold sterilisation of products	UF, MF
Sugar industry	Sugar refining, molasses removal, purification and concentration of bat and cane juice	RO, NF, UF
Beverages	Clarification of juices, syrups, wines spirits and liquors. Concentration of fruit and vegetable juices, purification of organic acids, glucose and fructose. Cold sterilisation of beer, wine and spirits	RO, NF, UF
Diary industry	Sterilisation of milk, concentration of skim milk and whole milk during cheese making and powdered milk production, milk desalting, concentration of sweet and sour whey, manufacturing of protein concentrates from milk, recovery of lactose from whey	MF, UF, ED

The mass production of proteins from Soya beans is well known, but getting proteins from vegetables, herbs, grass and leaves sounds strange, however now it is a fact. The hydrolysis of such polysaccharides as cellulose or starch gives monosaccharides that can directly be consumed or connverted to alcohol. This may be produced in membrane bioreactors with contribution of enzymes. The enzymes must be immobilised in the reaction system on the ultrafiltration membranes, whereas the product passes through the membrane. This technology is also used to produce cheap and non-toxic fuel (ethanol) that can be added to petrol.

To sum up: the profits coming from application of the membranes to food processing are the following: the new products, the better quality, elimination of undesired components without chemicals and preservatives, saving the sensitive natural components, the new sources of substrates, the utilisation of wastes or by-products, saving energy and production costs, reduction of waste disposal costs and reduction of wastes at all.

5. AGRICULTURE

Application of the membranes in agriculture consist principally in precise dosing of various remedies by means of controlled release. The fertilisers, pesticides, herbicides and insecticides are continuously delivered to the soil with controlled rate using special granules and capsules with membranes on their surfaces. The rate of chemical delivery is balanced with the rate of its consumption or degradation. Thus the concentration may always be maintained on the desired constant level. The advantage of controlled release is obvious because this reduces consumption of chemicals, their costs, and contamination of the soil. The concentration of the species in the soil is under control that ensures optimal growth of plants.

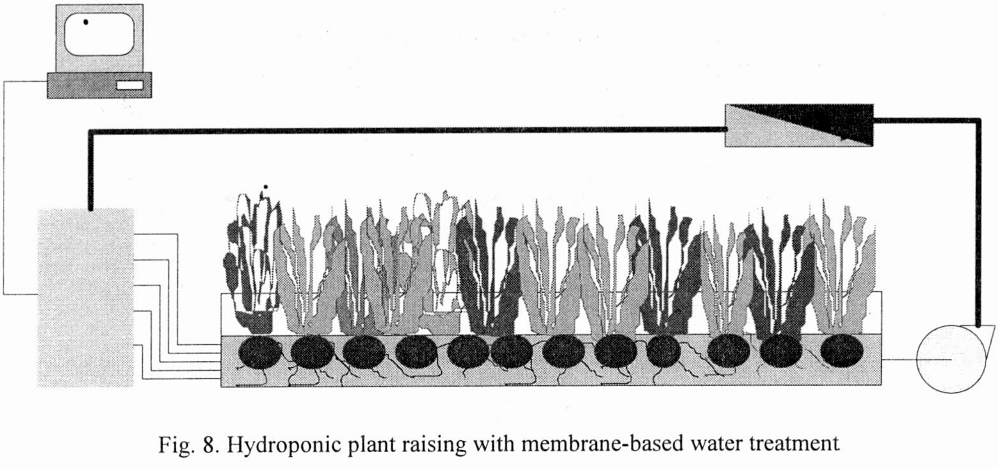

Fig. 8. Hydroponic plant raising with membrane-based water treatment

The membranes are also used in modern stock farming for controlled release of pheromones that frighten the insects from the cattle. To this end special earmarks with pheromones that repel insects are attached to cattle's ears. It was noted that cows, which were not annoyed by the insects, gave even by 40% milk more. Pheromones are also used in forestry to attract insects to special traps.

Traditional usage of the chemicals in agriculture usually leads to overdosing. The plants frequently accumulate some of the chemicals in their cells, and animals or we consume these chemicals subsequently. The usage of the membranes for controlled release benefits by limited usage of the components that can be dangerous for peoples, animals and ecosystems. This is connected with health protection accompanied by cost's reduction and improvement of environment conditions.

The hydroponics is plant cultivation in closed systems under complete control. In this case, the water purification and dosage of fertilisers is carried out by means of the membranes.

6. ENVIRONMENTAL PROTECTION

Nowadays the attitude of people towards the environmental problems is gradually changing according to urbanisation and technology development. This has been stimulated by visible degradation of ecosystems due to antropogenic activity in industry and agriculture. On the other hand, the technology development offers new opportunities to find various remedies. The balance between sources of wastes and waste-treatment technologies is the key contributing factor to the condition of our environment (Fig. 9).

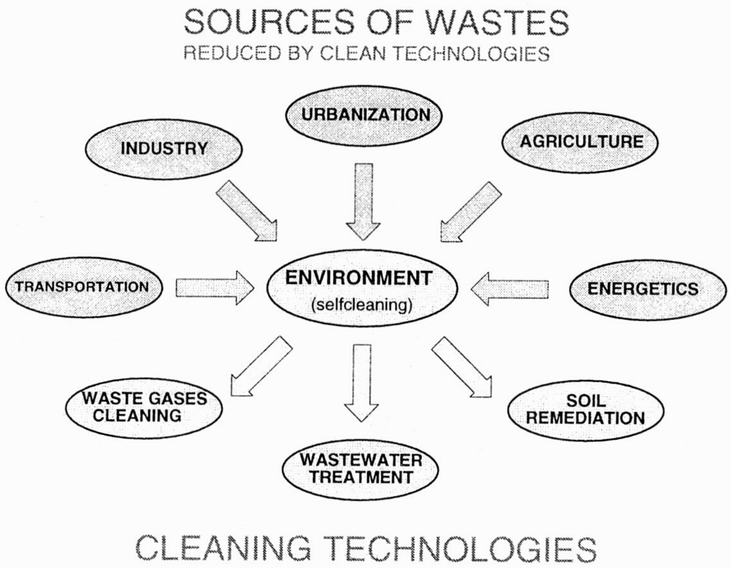

Fig. 9. The balance between sources of wastes and cleaning technologies

Table 4

Some selected applications of the membranes in environmental protection

Branches	Examples of matured implementations	Process
Water treatment	Water desalting, softening, decarbonizations, disinfection, and removal of metals, organic components and odours	RO, NF, UF, MF, ED, PV
Wastewater treatment	Recovery of detergents and oils from emulsions, removal of metals, organic components, radioactive materials, poisons, surfactants, purification of landfill leachates, ground waters, industrial and municipal wastes	MF, UF, RO, LM

The membranes in two ways contribute to environmental protection improvement. The first one concerns the recultivation of already destroyed ecosystems, and the second one is based on hindering or even eliminating the further contamination of our environment by the design of clean technologies. The older technologies cannot be ceased instantly, especially in the countries of lower development level. The membrane separation processes offer the non-invasive, less expensive and effective method of purification of waste-gases, wastewaters as well as recultivation of contaminated ground waters and soils. The *cleaning technologies* should progressively be replaced by *clean technologies* that will be completely safe for our environment. Basing on modern membrane separation processes the *clean technologies* became reality. The membrane processes enable us to fractionate and recycle several components of such wastes as chemicals, detergents, oils, dyes, etc. This reduces disposal costs simultaneously with the extra-income earned sometimes from by-products. The additional profit comes from the energy consumption that is coupled with lower emission of waste gases in power stations. Improvement of human and animal health is incommensurable but substantial.

7. BIOTECHNOLOGY

Biotechnology is a new method of processing, conversion or producing desired products from raw materials or wastes by means of biological elements such as enzymes, microorganisms and tissues in bioreactors under controlled conditions and environment. Biotechnology is the newest achievement of interdisciplinary cooperation of engineers and biologists enabling us to manufacture natural products without contribution of animals or plants. Biotechnology is applied in a broad range of human activities including these above mentioned in previous part of the paper.

The main areas of biotechnology applications are:

Production of fuels: ethanol from organic wastes and cellulose, methane from rural wastes, hydrogen and hydrocarbon due to photosynthesis by plant tissues.

Production of foods: protein production from inorganic substrates such as crude oil and natural gas is above 20 times faster than in natural plants. Production of aminoacids, sugars, organic acids, chemical compounds for taste, smell and colour improvement.

Production of chemicals: butanol, acetic acid, acetone, alcohols, dioles, enzymes, higher organic acids, aminoacids, polysaccharides, dextranes, xantan, and alginian.

Production of means for health protection, diagnostics and therapy, i.e.: antibiotics, vitamins, aminoacids, hormones, sterrides, immunoproteins (vaccines, interferones, antibodies), insulin, human growth hormone, monoclonal antibodies.

Production of means for agriculture: nutritive additives for feeds, fodder, biological fertilisers, herbicides, pesticides, veterinary drugs.

Production of metals (biohydrometallurgy): copper (10%), uranium (10%), nickel, and cobalt, silver, gold.

Environmental protection: desulfuration of flue gases, treatment of industrial and municipal wastewater, neutralisation of toxic contaminants in soil and ground waters.

The main advantage of biotechnology is the possibility of synthesis or conversion of the substrates that cannot be produced or synthesised artificially. The second advantage are the moderate operating conditions that correspond to narrow ranges of temperatures and pressures and concentrations in living organisms. Therefore the production costs are also moderate. Biotechnological processes require the precise monitoring and control of a large number of parameters that is usually done by computers. One of disadvantages is the necessity of precise separation of desired products from multicomponent and usually very diluted systems. Thus the separation problems are essential for biotechnology. Membrane processes are used in biotechnology in *up-stream processing*, *bioreactors* and *down-stream processing*.

Table 5

Some selected applications of the membranes in biotechnology

Area	Examples of matured implementations	Process
Upstream	Water purification, sterilisation of products	RO, NF, UF, MF, ED, PV
Bioreactor	Immobilisation of enzymes or microorganisms in membrane bioreactors, culture of animal or plant tissues within membranes, oxygenation of fermentation "broth", removal of inhibitors and products in steady-state bioreactor, gauges for monitoring	MB, MF, UF
Downstream	Cell harvesting, recovery of products, fractionation, purification and concentration of final products and by-products	MF, UF, RO, PV

In up-stream processing, raw materials are prepared before bioreactor. The membranes are used for water purification and sterilisation of substrates.

In bioreactor, membranes are mainly used for immobilisation of enzymes or microorganisms in reaction space that is essential for the process economy. Another role of the membrane within bioreactor is to remove the by-products that may enhance the reaction kinetics. Removal of bioproduct may also shift the constant of reaction equilibrium that leads to higher conversion of substrates. Some additional functions of membranes in bioreactor are delivery of gas and liquid substrates, purification of the air vents and in gauges that control the bioprocess.

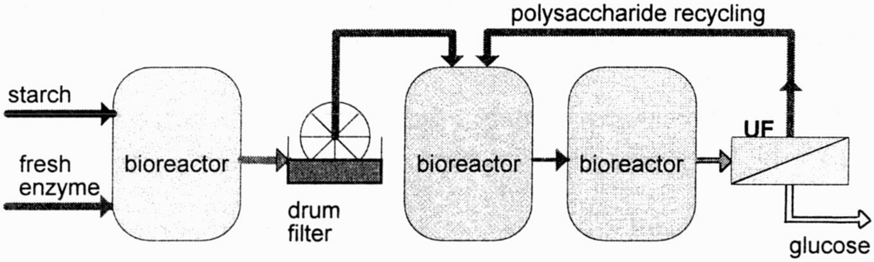

Fig. 10. The application of membranes in glucose production based on starch hydrolysis

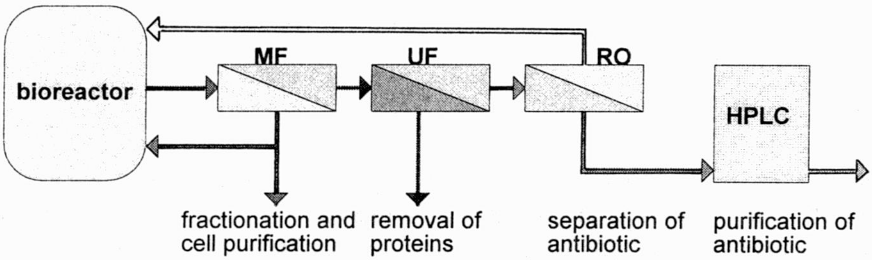

Fig. 11. The application of membranes in antibiotic production based on microbial bioreactor

In down-stream processing, the final products are in multicomponent and diluted fermentation broth. The products must precisely be fractionated, purified and concentrated to the desired levels by means of several membrane processes.

8. MEDICAL APPLICATIONS

In medical treatment, membranes find several kinds of application such as artificial organs, controlled release of medicaments, medicine manufacturing, water and air purification, diagnosis and research (Table 6). However, Graham in 1866 and Abel in 1926 studied dialysis, and Kolff implemented the artificial kidney in 1944. This first attempt was unsatisfactory and now artificial kidney is a complex device where blood is decomposed and its content is corrected in several separation steps such as dialysis, ultrafiltration and microfiltration. In 1955, Kolff also invented the artificial lung for blood oxygenation during surgical operations. This membrane device originated with the new process called 'membrane absorption' that is intensively developed in environmental protection. Esato and Eisemann improved the artificial lung in 1975, and in the same year Chick invented the artificial pancreas. The semipermeable membranes are also used as artificial skin. Recently the membranes with active transport are intensively studied in the context of artificial liver.

The controlled release enables us to maintain the required constant level of the medicine in the patient's body and to avoid overdosing, hence such a procedure is more safe and convenient for patients than injections. The hormones, enzymes, antibiotics and psychotherapeutic drugs are delivered in this way.

Table 6

Medical applications of membranes

Branches	Examples of matured implementations	Process
Medicine	Artificial organs: kidney, pancreas, lung, liver, skin, water and air purification, delivery of medicines by controlled release, blood processing	DM, UF, MF
Pharmacy	Sterilisation of substrates, products, water depyrogenation, water for dialysis, manufacturing of monoclonal antibodies, hormones, vaccines, antibiotics, enzymes and organic acids	MF, UF, RO, ED, BM

Membranes are used to purify the water for injections, especially for the removal of pyrogens. They are also used in numerous pharmaceutical technologies for fractionation, purification and concentration of proteins, vaccines, antibiotics, dextranes, and sugars.

One of the most spectacular examples of membrane application is cultivation of microorganisms or even tissues to obtain the natural products in membrane bioreactors (MB). The monoclonal antibodies, vaccines, hormones, enzymes and antibiotics are produced using these biotechnological methods. The air in hospitals, especially during surgical operation, is cleaned on microfiltration membranes. Membranes are also used in diagnostic, especially for microbial analysis and as an element of detectors for analysers.

9. CONCLUSIONS

The aim of the paper was to emphasize the important role of membrane processes in several branches of human activity. As it was shown the application of these modern technologies of separation enables us to achieve the coupling effects of energy reduction and substrate consumption during production. The recovery of raw materials and by-products reduces the emission of wastes to our environment. These positive effects bring innumerable benefits allowing the improvement of process economy, environment protection, health and comfort of human beings and all living creatures on Earth.