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WASTEWATER TREATMENT BY MEANS OF CHARGED MEMBRANE PROCESSES

The paper presents highlights of charged membrane processes and their major applications to wastewater treatment. No detailed designs were included.

A role of separation processes in the modern environmental engineering was discussed by listing main scenarios of environmental strategies and documenting an important position of membranes among those processes. The 'idea' of 'Low- and No-Waste Technology' was presented to show a specific role of membranes in both basic manufacturing technology as well as recycling and abatement of harmful components.

The most common operations using charged membranes were described as potential separation tools in various environmental applications. Four factors responsible for efficiency and economy of any technology were listed and discussed in a view of charged membranes application.

Brackish water (treated as a specific wastewater) desalination was described and a role of charged membranes in this process presented on a wider background of water desalination.

1. INTRODUCTION

The conventional wastewater technology, traditionally creating the wider area of sanitary (civil) engineering activities, took a minimum advantage of separation processes. The most common was such an approach which allowed neutralization of various sewage streams by mixing different categories of wastewater – municipal with industrial or inorganic with organic. Even the main objective – internal neutralization – was not satisfied, the procedure was implemented just to convert sewage to sludge, no matter what secondary effects it will cause in the natural environment. The most common result following mixing of industrial (inorganic) wastewater with municipal (organic) sewage was a distinguished presence of heavy metals in the final deposit, which secondarily affected water and soil resources.

A modern environmental law, including rigorous standards and restricted execution, caused that mixing malpractice became too expensive for two main reasons:

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(1) direct cost of allowances and penalties for discharge of toxic components, as well as (2) a real market value of these components. To avoid presence of harmful and precious components in sludge it became necessary to separate those elements from various wastewater streams before their mixing.

Almost parallel to the wastewater technology transition from mixing to separating, a new attractive 'ideology' appeared among approaches competing in solving several waste streams problem – 'Low- and No-Waste Technology'. Just < an ideology> not a tool, since it appeared very soon, that such a technology can't 'live its own life' and could be only a part of a basic technology of manufacturing of a certain product, causing environmental hazard. In practice <Low- and No-Waste Technology> means introducing of separation processes as soon as possible to each individual basic technology stream before it becomes a waste and recycling any valuable component already within the basic technology line.

The process engineering, which is serving the greatest number of unit operations to the environmental engineering, is offering a long list of separation tools, which should fulfill several requirements to be successfully implemented in modern technology, forced to discharge minimum waste. Among those tools membrane separation processes appeared to be the best, satisfying such important requirements as:

- possibility to select optimum membrane material for required separation task;
- possibility to make use of various physical gradients to achieve minimum cost;
- long live-time and recoverable activity in heavy conditions of multi-cycle service;
- possibility to compose modular systems working in various sequences (parallel, in series, mixed), allowing us to built an installation able to complete adequate tasks on required scale;
- easy to create a modern hybrid system linking various membrane operations among them or membrane process with other separation tools;
- significant reduction of surface required for installation compared to traditional methods;
- high selectivity in separating solute components of a close affinity or dimensions;
- possibility to avoid a troublesome and expensive phase-change, creating a chance to avoid also thermal stresses causing very often serious structural changes in a treated substance.

Membrane operations allow implementing effectively the most important scenarios of solving crucial environmental problems:

- *initial prophylactic separation,* allowing for early elimination of those components, which could potentially pass to waste streams, as well as enrichment of some required components;
- *integration of separation with a basic manufacturing technology,* allowing us to recycle some components, which were formerly treated as spent products, such as energy and water;
- *separative reduction of a discharge at a technology exit,* by eliminating either substrates or products by the so-called 'end-of-the-pipe'process;

• *remediation activities using separation,* eliminating man-made changes in the natural environment – excess of secondary pollutants;

• *alternative solutions using separation,* which allow us to substitute environmentally conflict process for neutral or at least for less harmful.

Charged membranes could satisfy a majority of the above demands.

2. CHARGED MEMBRANE PROCESSES IN GENERAL

Charged, permselective, membranes implemented in the operation of *electrodialysis*, driven by electrical potential, entered water and wastewater technology the first time and on the biggest scale as a mean for water desalination. This process was dislodged from its position by development of pressure driven membrane operation – reverse osmosis, which became the first non-thermal process competing on water desalination market. After about two decades of regression elctrodialysis, operating with modern ion-exchange membranes, found a new wide area of applications just in wastewater treatment, fulfilling also the requirements of 'Low- and No-Waste Technology'.

Based on the properties of charged membranes several operations, driven not only by electrical gradient, were developed in parallel with electrodialysis. The most common systems are:

• *electrodialysis (ED)* – in the conventional system of alternating cation- and anion-exchange membranes placed between cathode and anode, which allows us to concentrate solute in one chamber, while diluting it in the neighbouring;

• *electrodialysis reversed (EDR)* – differing from the conventional one by operating in such a way that poles of the direct current are changing, causing a change of ions flow direction, which prevents scaling of membrane surface as a result of concentration polarization phenomenon;

• *electrosorption (ES)* – applying a combination of charged with neutral membranes to complete some specific separation tasks;

• *electrodecantation (DE)* – introducing membrane systems to support precipitation and sedimentation of a certain component from a system difficult to separate;

• *piezodialysis (PD)* – using the so-called mosaic membranes (composed of microfragments of cation- and anion-exchange properties), which are usually listed among charged-membranes in spite of the fact that the driving force is pressure.

A few more operations using charged membranes at gradient other than electrical are driven by the *chemical activity*, among them:

• *diffusion dialysis (DDI)* – applying systems of ion-exchange membranes to force a 'preferential transport' of certain ions taking advantage of existing gradient of concentration;

• *Donnan dialysis (DD)* – acting on a similar principle of excluding one ions, while preferring transport across membrane of others;

• some other more specific forms of the so-called *preferential* or *facilitated transport*.

3. CHARGED MEMBRANE PROCESSES IN WASTEWATER TECHNOLOGY

Comparing a variety of operations engaged in water treatment with those used for wastewater technology it soon appears that the latter are much more complicated, especially in that which concerns industrial wastewater. Complex composition, very often consisting of inorganic and organic matter, different concentration of solute, quite often extreme values of temperature and other physical parameters, causes demand for perfect separation tool. As it was mentioned in the introduction, membranes are close to an ideal picture, satisfying numerous of listed requirements.

Two competing criteria have to be considered choosing any optimal technology – efficiency (or yield) and expenses (investment and operation costs). Using membrane operation as a part of any technology – in basic manufacturing or controlling waste – such important factors must be considered in terms of yield and cost: (1) choice of a *driving force* and related (2) selection of *membrane process*, which implies (3) *type of membrane*, as well as (4) some specific *features of basic manufacturing and local conditions*, especially if membrane operation is to be additionally introduced into an existing system.

- Among driving forces *electrical potential* (ΔV) is located on the second position just after *pressure gradient* (ΔP) and before *chemical potential (activity)* ($\Delta\mu$) and *temperature gradient* (ΔT).
- A choice of membrane process *should primarily depend on wastewater composition*, but very often such factors as life-time of membrane, easier and cheaper operating, as well as availability of know-how are deciding about a selection of system to be implemented, no matter which solution is objectively optimal.
- A selection of the type of membrane *is due to the process chosen*, but within a certain membrane type there exist again a number of choices depending on size, form, flux, and such specific parameters for charged membranes as type of active groups, ion-exchange capacity, electrical resistance, durability at higher temperature and others.

In this factor, a number of different options could occur. A situation differs significantly if manufacturing process is already existing or just designed. In the first option, a freedom of technology changes and introduction of membrane operation is usually very limited. In the second case, a wide choice of options is possible to design new hybrid technology including a single membrane process or sometimes even intermembrane hybrid process.

Electrodialysis became a valuable tool for a selective separation in all those cases where ionic system is present. Selectivity of membranes and proper selection of process parameters allow us to separate various solute components such as ions of opposite pole or of different valency and even of a close affinity as ions of the same valency from the same systematic group or isotopes.

ED became one of those operations which found application in both: manufacturing technologies as well as auxiliary processes developed in order to recycle or abate valuable or spent by-products. These applications are most widely exploited in processes protecting metal products: plating and preparation of surface by etching, especially effective when precious and highly toxic metals as chromium, cadmium, nickel, zinc and some others are in use and could be recycled. Less common, but of the same environmental importance is application of ED to radioactive wastewater carrying ionic species.

Ion-exchange membrane stacks are assembled not only in described conventional manner of electrodialysis (altering cation- and anion-exchange sheets), but also in other combinations, e.g.: composition of membranes of the same charge in *electrosoption* or *electrodecantation*. In some of those operations, most often in *diffusion dialysis*, complicated (and expensive) bipolar and multipolar membranes are applied. Some of them are not available on a market in a form of sheets or modules, since few manufacturers (chiefly Japanese) have a position of monopolist and prefer to purchase an expensive total installation with adequate know-how instead of lower complicity cheaper components.

The environmental engineering is quite often dealing with wastewater carrying components of a very low value but at the same time very harmful or troublesome. Such cases require application of available less expensive separation process, which means making use of the cheapest driving force. To satisfy these difficult requirements charged membranes in various *preferential and facilitated transport* processes have been used. Apart from the above mentioned service of DDI, also *Donnan dialisysis*, usually applying weakly-basic or weakly-acidic ion-exchange membranes, was successfully implemented.

Either DDI or DD is very often merged with ED in an *inter-membrane hybrid separation system*. Such systems were already applied to utilize low-value or useless but very troublesome acidic spent liquors remaining after etching of ferric-metal tin-plates. Already classic is another example of linking ED with column-ion-exchange for recycling of zinc in rayon manufacturing, taken from the author's lab. This system illustrates the second option of a *hybrid separation system attended by membrane process.*

Already mentioned mosaic membranes belong also to these with ion-exchange centers. *Piezodialysis* based on that type of charged membranes drew a great attention as a potential tool for economic desalination process, but failed due to imperfection of mosaic structure. That promising process never left laboratories.

Charged membranes present the biggest group among membranes with active centers. Other active centers such as: catalytic (including enzymatic), red-ox, semiconductors, chelating and others have already been built into a membrane structure. Importance of these new types of membranes is difficult to overestimate. On a long list of potential membrane applications a high place take their direct and indirect implementations in environmental engineering, such as artificial systems for biodegradation and bioregulation or for non-conventional energy generation.

4. CHARGED MEMBRANES IN BRACKISH WATER DESALINATION

Brackish water creates a specific category of industrial wastewater. Natural underground water of a wide range of mineralization is during mining activities pumped out and converted into wastewater which is being discharged to retention reservoirs or directly and indirectly to surface water resources.

It is well known that in sea water desalination the membrane technology is successfully competing with distillation. The environmental acceptance of any of these options depends on the economic utilization of the concentrate remaining after the desalination of brackish water. Brackish water desalination creates much more difficult technological task compared with the sea water treatment, not only because the concentrate must be brought to dry products but also due to a complicated solute composition in the underground water. Brackish water varies not only in its total solute concentration but also in its composition, whereas in the sea water the ratio of separate components is constant and only the total concentration changes.

The first global attempt to implement membrane process for water desalination was linked with gold-mine brackish water in the Republic of South Africa already in the '50s. Probably the largest design ever made applying ED was that of Yuma plant, located on USA–Mexico border, also very interesting as an environmental policy case. The aim of this installation was to treat underground water getting permeate used to dissolve the Colorado River highly mineralized by American agriculture, just to meet conditions of the international treaty between two neighbouring countries. The concentrate is to be send by 80 km canal to the Bay of California. The original concept planned to use ED, but development of RO created a big competition, growing every day. The first attack was defended by substituting standard ion-exchange membranes for ones better resistant to high temperature to improve their conductivity and reduce the cost of electric current. The second attempt to survive current driven process was a change of the ED system for EDR.

Each water desalination process has its optimum solute concentration range. While column-ion-exchange is applicable up to 500 mg/dm^3 and in some special methods to 2–3 g/dm^3, ED has the optimum range between 5 and 10 g/dm^3, which could be slightly extended. The higher concentration is the domain of RO/NO processes competing up to about 40–50 g/dm^3 with distillation, which finally has no competition in the upper range. The author's team suggested already in the late 70's the hybrid desalination system composed of a series of separation processes providing that each could work in its optimum concentration of solute, which is at the same time the most economic.

Since 1975 the Central Mining Institute has been exploiting its own design of the Debiensko pilot distillation plant for mean-salinity water of 100 g/m^3. The system based on the MSF process includes pretreatment to remove calcium and magnesium. The installation is yielding 2400 m^3/d of demineralized water (50 mg/dm^3) and two sorts of salt (99.6 and 99.0% NaCl), as well as anhydrite and post-crystallization liquors as by-products easy to utilize. Only this small plant has already eliminated over a million tons of salt from mining water being discharged to the surface water.

In 1994 the thermal part and a year later the membrane stage of Dembiensko II were completed to eliminate brackish water totally from coal mines. These multinational undertakings (GIG and ENERGOTECHNIKA, Poland; RCC, VBB and

NORDCAP, Sweden, based on US technology) attained expected efficiency. Dembiensko (8000 m^3/d, 23 g/dm^3) and Budryk (3500 m^3/d, 12 g/dm^3) brackish water of mid-salinity is pretreated and separated by reverse osmosis (RO). Parallelly high salinity water from Budryk (1800 m^3/d, 114 g/dm^3) is being distilled. The process consists of four stages: (1) pretreatment, (2) RO, (3) further thickening of RO concentrate by distillation, and (4) crystallization with the utilization of by-products. The target capacity of Debiensko II is to treat over 14 thousand m^3/d of brackish water of the above salinity, producing daily: 9 thousand cubic meters of potable water, 4 thousand cubic meters of condensate, 300 tons of salt (>99.8% NaCl) and 30 tons of calcium sulfate. It is easy to observe that this example does not include ED, but was described as modern hybrid process.

Concluding, it has to be clearly stated that charge membrane processes are relatively expensive due to a complicity of membrane structure and higher cost of their preparation, as well as relatively higher cost of operation referred to use of the electric current. Also running of current driven process is more complicated at least for concentration polarization phenomenon effecting scaling of membranes.

On the other hand, there are numerous cases in which optimum separation or separation at all is possible only by taking advantage of ionic selectivity of charged membranes. These cases occur both in basic manufacturing technologies as well as in spent components recycling or abatement. They are the most attractive and effective tools to be composed in hybrid processes and to be included in 'Low- and No-Waste Technology'.

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