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# Membrane separation processes – Quo vadis?

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**ABSTRACT**

This paper is a voice in the discussion about future development of membrane technologies. The development of membrane technology on the example of artificial kidney has been presented. The authors try to answer the question: where are membrane technologies going now and what is the future of membrane processes?

*Keywords:* Membrane processes; Development; Technology

## 1. Introduction

According to the definition, a breakthrough design/technology is an idea that at the time of its conception, in the opinion of specialists, proposes a solution to an unresolved problem. In 1911, Prof. Abel's proposal to use a membrane for the construction of an artificial kidney was undoubtedly a breakthrough concept. Life experience shows that generally at the time of the conception of a breakthrough solution expectations and prospects are more optimistic than reality.

The conception of an idea is the initiating moment. The horizontal dark-gray line (Fig. 1) is the expected level, while the dotted dark-gray line shows the attainable level. From the point of view of the general market rules, it is a signal that the design/technology has reached its peak, and further investment in the concept is unfounded. There comes the waiting time for a new breakthrough idea.

## 2. Overview of the technical development of dialysis in the historical perspective

### 2.1. Devices

Considering the above, it is advisable to trace at which point of the development of membrane technology we are today. This article is an attempt to trace the development of membrane technology based on the analysis of progress in the area of artificial kidney. It is worth noting that quantitatively more than half of the produced membranes are output targeted at hemodialyzers. Therefore, in 1913 Prof. Abel announced in *The Times* that he was working on the construction of an "artificial kidney" and, more specifically, on the construction of a membrane device – a dialyzer (Fig. 2).

Unfortunately, ex vivo research could not be called a success – problems connected with blood clotting did not allow the author of the idea to celebrate success. The lack of idea concept of how to deal with the clotting of blood in the dialyzer hampered the progress in building an artificial kidney for many years.

The invention of heparin resulted in a breakthrough. In 1923, German scientist Georg Haas developed a prototype that contained all the necessary components of the apparatus, and used cellophane sausage coating as a dialysis membrane. It was a progenitor of capillary dialyzers. The experiment performed on a dog was a success. Unfortunately, it was not him to be declared the "father of an artificial kidney".

The work on the artificial kidney slowed down. It was only in 1945 when a young Dutch doctor W. Kolff conducted a successful procedure of cleansing the blood of a young girl

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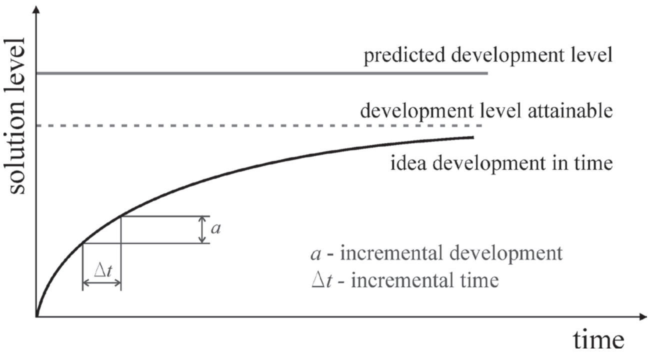


Fig. 1. Chart showing the development of the design/technology over time.

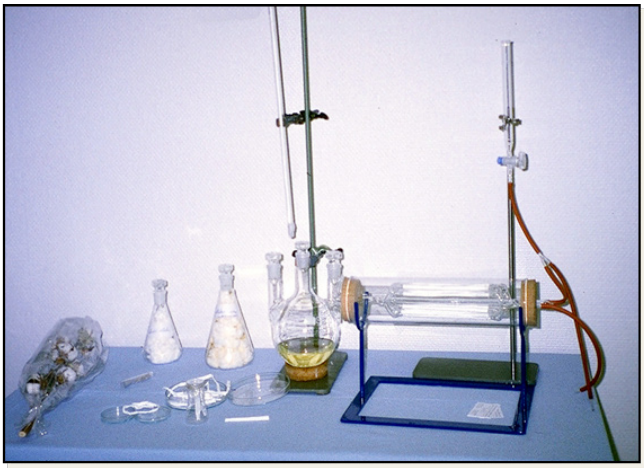

Fig. 2. Prototype of an artificial kidney according to Prof. Abel's idea [1].

suffering from acute renal failure. This time, the design of the dialyzer was made of a juice can and sausage coating. It was a prototype of a spiral dialyzer (this type of dialyzer was widely used in clinical practice, even in the 1970s) – Fig. 3.

After the end of World War II, W. Kolff emigrated to the United States, where he tried (initially without much success) to interest the medical world in his solution. It was only in 1954 during the Korean War, at the time, when a great number of the marines suffering from acute renal failure were returning to the United States, that Kolff was recalled. W. Kolff and his colleagues rapidly developed a design, which resulted in making the first dialysis in Cleveland Clinic (Ohio, USA) (Fig. 4). Interestingly, the artificial kidney developed by Kolff and his colleagues was a modification/alteration of a washing machine available at that time in the US market. The theme of a washing machine appeared more than once in the following designs of an artificial kidney.

Organization of hemodialysis stations in the United States was a strong market signal that stimulated companies to join the movement in order to occupy an appropriate market position. Therefore, Niels and Alvall's design showed up in the market (Sweden) soon. It was an acid-proof steel structure, which was upgraded in engineering terms. In 1964, France introduced a new type of hemodialyzer called Kill's dialyzer (Fig. 5).

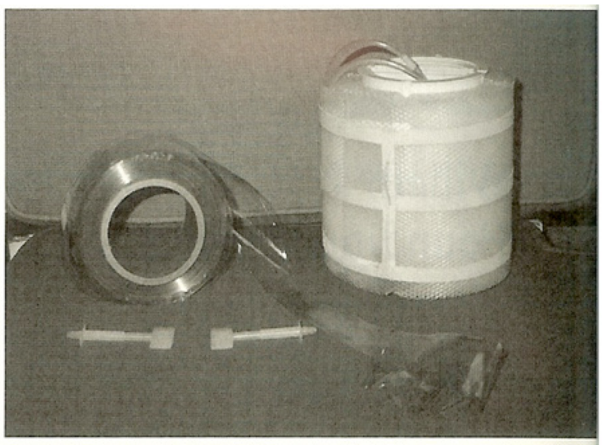

Fig. 3. Dialyzer made by Dr. W. Kolff used in 1945 to conduct the world's first – and also successful – hemodialysis in a teenage girl [2].

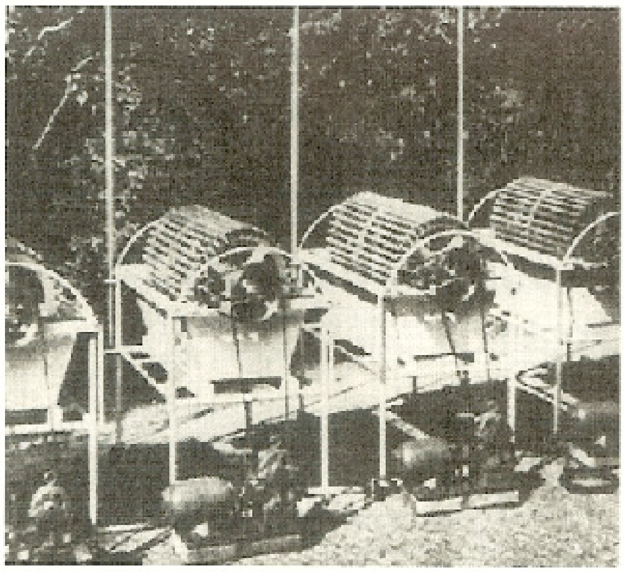

Fig. 4. Apparatuses of an artificial kidney made in the United States (according to the concept of Prof. Kolff). The units shown in the picture were intended as an aid to the war-torn Europe. One of those units went to Poland (to Cracow) [3].

It was an innovative design, to the extent, that for the first time it introduced a plate-type module for use. Despite the rapid technological progress, the existing solutions had very serious drawbacks in use, such as high volume of the filling system of patient – artificial kidney. In practice, it was a very arduous, manual installation of the entire system, immediately prior to connecting it to the patient, a very large area of the membrane, a very long duration of the process, a cumbersome and painful as well as at the same time traumatic way of connecting the patient's circulatory system to the cardiopulmonary bypass. In 1968, an American company introduced the capillary design to the market. It was a real breakthrough in hemodialysis. The exchange surface was reduced from a dozen or so square meters to maximum 2 $m^2$. Let us appreciate also Polish scientists – in 1964 Zbylut Twardowski published an article in Acta Med. Pol. entitled "On the advantages and possibility of constructing a capillary artificial kidney" and also patented the idea in Poland. Unfortunately, this idea was not appreciated in Poland. A dozen or so years later, Prof. Twardowski emigrated from Poland to Canada. The launch of capillary dialyzers in the market radically changed the situation. Currently, the volume of filling the system ranges from about 200 ml, while the volume of filling the hemodialyzer itself was about 80–120 ml (depending on its size). The procedure time was reduced from over 10 h to 4–6 h. Today's solutions no longer require two insertions into the circulatory system – a "single needle" system was developed. In principle, all the disadvantages of the first solution have been removed.

The contemporary set of apparatus for hemodialysis (Fig. 6) is controlled by a computer system having in its memory several programs allowing the attending physician to choose the appropriate procedure, which is the best for a given patient.

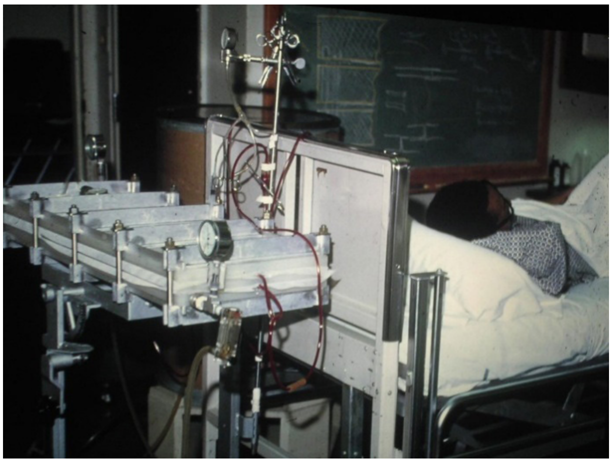

Fig. 5. The process of Kill's dialyzer haemodialysis in a clinic [2].

Fig. 6. Contemporary artificial kidney [4].

*2.2. Materials*

The matter called "collodium" was used to build the first in the history artificial kidney apparatus proposed by Prof. Abel in 1911. The first successful "ex vivo" experiment on dog was performed by G. Haas in 1923. He applied cellulosic sausage sleeves to separate the whole blood from dialysate. In 1945, young doctor W.J. Kolff saved Sophia Schafstaat's life, the first artificial kidney patient in the history of medicine. Dialysis was continued for 11.5 h in hospital in Kampen [2]. The first, more/less professional hemodialyzers, had a membrane surface area in the range of 12 $m^2$, and the time of dialysis session lasted approximately 12–16 h, and blood channel priming volume required approximately 1.5 $dm^3$ of blood. On the long range, such performance was unacceptable. The membrane surface area of contemporary hemodialyzers for adults is in the range of 0.8–1.8 $m^2$, and priming volume varies between 80 and 180 ml. Such progress was achieved by optimization of geometry of the blood channels (capillary ID 200 microns and membrane wall thickness varies between 7 and 14 microns). There are a lot of technical requirements for the contemporary hemodialyzers such as: hemocompatibility, efficient mass transfer, properly adjusted membrane sieving characteristic, hydrophilic membrane material – a must. Dialyzers must be provided as sterile, dry and properly packed units. At the moment, the majority of hemodialyzers are sterilized using ethylene oxide; however, the so-called first-use syndrome forces engineers to work in order to reduce this phenomenon. Dialyzers sterilized by means of steam are free of such disadvantages, but at the same time they do create new difficulties. Membranes sterilized by radiation are at the moment practically not acceptable by the medical world due to polymer degradation.

Since 1945 till now, many polymers like cellulose, cellulose diacetate, polyacrylonitrile, polysulfone and other have been tested and modified.

The need for a membrane with additional functionalities has been recognized and intensively evaluated. In order to increase dialyzer clearance, at the end of the 1970s, Enka Company (Germany) introduced an experimental line of cellulosic membranes saturated with activated charcoal. To prevent blood clotting and, what is even more important, to reduce heparin administration, at the end of the twentieth century, Carmeda (Sweden) introduced hemodialyzers containing membranes with implanted heparin on the surface.

## 3. Summary of the state of affairs

*3.1. Technological aspects*

With reference to the definition of a breakthrough design/technology described above, in a nutshell, the question at which point of the development of dialysis we are today comes up. In principle, the duration of the procedure cannot be reduced – this is due to a limited speed of transport of toxic substances within the body. The survival time of people undergoing regular haemodialysis increases, but the average survival is still not impressive, and it is about 8–9 years. The longest survival time is about 20 years. Hemodialysis is the chance to significantly prolong life, but at the same time, it slowly devastates the organism. People, who undergo hemodialysis, after a few years have clear signs of progressive degradation of the body. The effectiveness of hemodialysis in its current version seems to have reached its apogee. Among the specialists, a controversy is growing. The medical world demands superior membranes, but it does not specify what exactly this "superiority" should consist in. The circles representing the world of technology ask for a precise definition of the expectations. So far, there has been no agreement. However, it seems that the currently available technologies have already exhausted their potential.

### 3.2. Economic aspects

The issue concerned has yet an economic dimension. Providing patients with appropriate benefits under the general insurance seems impossible. Perhaps, only the United States provides all those in need with free and immediate access to dialysis. Nevertheless, also in that country, it is said that if the annual amount of hemodialysis grows at the current pace, it will be necessary to decide what to do next. The average cost of hemodialysis is approximately 120–150 USD. Statistically, 50 new incidences of becoming ill occur per million people. The population growth in the world (natural and prolongation of the average survival rate) as well as the systematic lengthening of the average survival rate result in a systematic increase in the demand for hemodialysis. As shown by market research, the global production growth of hemodialyzers is constant and ranges from 8% to 10%. Stocks capacity in this regard is above 50%. It is easy to calculate the annual cost of hemodialysis for a country with a population of 40 million, assuming that everyone in need receive the necessary help. Assuming that the average survival rate time is 8 years, and considering that the hemodialysis treatment is performed three times a week, the annual cost of satisfying the needs in this area will amount to approximately 400,000,000 USD. It is noteworthy that the increase in the average survival rate by 1 year will increase expenditure by about 49,000,000 USD.

### 3.3. Water

Another emerging problem is the consumption of and access to water. The cost of water permanently shows the rising tendency and its availability decreases (Fig. 7). Water is the basis of today's hemodialysis. During the 5-h dialysis, consumption of dialysate (water + minerals) is approximately 150 $dm^3$, which means that every year (12,000 patients) the consumption of highly treated water will be approximately 291,600 $m^3$ for hemodialysis only in Poland. In the mid-1970s, a prototype of an artificial kidney apparatus was developed (mainly for military purposes), wherein the dialysate was circulating in a closed circuit. Removal of the toxic substances from the circulatory system took place in the column performing the enzymatic process and sorption. Given the growing crisis of water (defined as high shrinkage of relatively easily available resources of drinking water), work on a significant reduction in water consumption for a single treatment should be started.

The lack of drinkable water or a limited access to it might cause severe problems including a war. Water is a strategic matter [7–9]. Unfortunately, till today, there is no rational solution on how to deal with it. The suggested guidelines can be summarized as the following points:

(1) Rational and thrifty water use.
(2) Wastewater recovery.
(3) Closed industrial water-wastewater loops.
(4) Low water consumption industrial technology.
(5) Rational use of gray water.
(6) Restrictive geological regulation in respect to deep mining.

### 3.4. Intelligent membranes

The term of "intelligent" membranes, sometimes called "smart" membranes, is referred to the membranes reacting automatically or on an external stimulus to the unwanted situation in order to prevent it [10]. A good example of such an intelligent membrane is a membrane covered by heparin. The heparin dipoles, properly attached to the membrane surface, are able to prevent RBC clotting on its surface. It is believed that by implanting active species on the membrane surface, we can take control over unwanted processes taking place on the membrane surface.

Figs. 8 and 9 show membranes developed in Poland by our team. They illustrate the surface of modified membranes, with extra functionalities assigned to them at the same time.

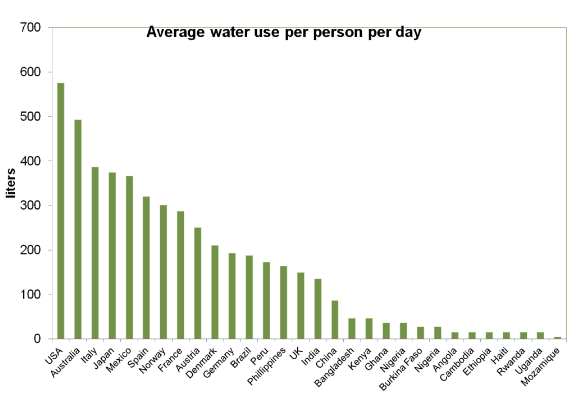


Fig. 7. Daily water consumption per capita per day in various countries (based on [5,6]).

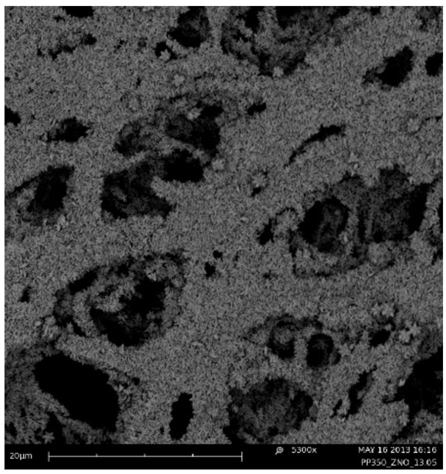


Fig. 8. Zinc oxide nanorods on the surface of the membrane polypropylene (PP) [11].

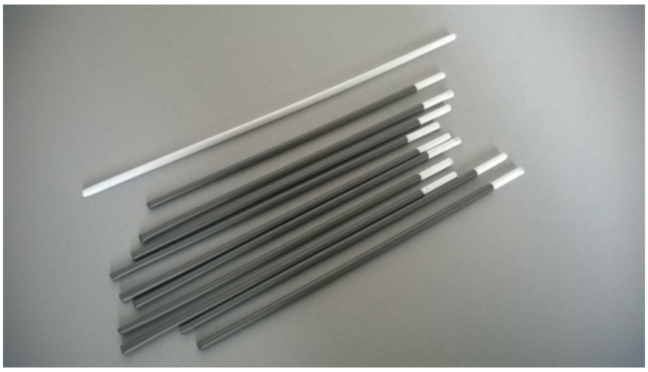

Fig. 9. Membranes made of polypropylene coated with titanium [12].

Currently, membrane technologies in use do not basically resolve problems of water management completely. Current solutions significantly reduce the volume of wastewater, without reducing its load at the same time. Concentrated wastewater remains in a liquid form, which from the point of view of the environment is a serious threat. Both the evaporation of the concentrated wastewater and (which would be more desirable) its separation into constituent parts are not always possible, and even if it is possible, it is unacceptable for financial reasons.

In order to modify membranes with ZnO nanorods, the chemical bath deposition was used. According to the authors' knowledge, it is one of the first times when porous polypropylene material was modified with ZnO nanowires using this method, which is typically used for modification of glass plates. Membranes modified with ZnO nanorods (Fig. 8) have good photocatalytic and antibacterial properties. Such membranes are able to degrade organic pollutants like methylene blue in 90%. They are also able to reduce, for example, the amount of B. subtilis (cfu $ml^{-1}$) in LB (lysogeny broth) medium by five orders of magnitude and in minimal medium to sterilize the broth completely [11].

As far as membranes with titanium are concerned, after their surface oxidation, membranes with $TiO_2$ can be obtained. Such membranes, lit by UV, have very good deep oxidation properties. This kind of membranes can be used in integrated processes, where filtration and photo-Fenton oxidation are run simultaneously in one apparatus.

## 4. Conclusions

(1) By analyzing an individual case of an artificial kidney, nevertheless, representing approximately 50% of the global membrane market (in monetary terms), one should try to answer the question "Quo vadis?". Perhaps, this is the right time to seek new breakthrough technologies; perhaps, it is the right time to devote more attention to the concept of "intelligent membranes".
(2) Investment and operation costs as well as costs of disposal of waste membranes seem to be too high – it is necessary to develop more cost-effective solutions. The problem of disposal of exploited membranes is of particular concern.
(3) Given the increasing "water crisis", it is advisable to pay more attention to recycling water circuits and to the use of water-saving technology.
(4) It is time to search for new solutions.

## Acknowledgment

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