Microfiltration in Water Treatment for Removal of Suspended Solids and Natural Organic Matter

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Abstract. At this article are presented membrane separate processes – microfiltration, ultrafiltration, nanofiltration in water treatment and materials and modules used in application of various membrane technologies. Theoretical part is completed with results from pilot plant experiments realised in water treatment plant Klenovec, where was used the microfiltration technology for removal of insoluble substances (expressed by a number of particles) from water. Over the last years water quality has deteriorated in water-supply reservoir Klenovec and this technology was tested for the purposes of modernization of the inefficient technology in water treatment plant. The pilot-plant tests for membrane filtration examination were carried out by using the microfiltration unit AMAYA 5 with a performance of 5 m³/h. Coagulation and flocculation run in two stages. At the first stage, the coagulant is dosing into a static mixer, which led the mixture to the second stage from. The second stage represents the tubular flocculator. In the membrane module, there is placed one ceramic element with a membrane surface of 25 m², pores size of 0.1 µm, and consisting of 2000 tubules with a diameter of 2.5 mm. The results obtained from pilot plant experiments in WTP Klenovec supported theory, that this process with high efficiency of treatment surface water is suitable for this kind quality of water to obtain water for drinking purposes.

1. Introduction

Membrane separation processes are increasingly being used not only for water treatment of sea water during last years, but in the treatment of ground, surface and waste water as well. In consideration with a classic treatment (such as coagulation and classic filtration) the reason of increasing popularity of use of membrane processes in a treatment of drinking water is mainly in a perfect water quality of a treated water that is being achieved by using membrane technologies.

Membrane processes solve a lot of requirements connected to tighter specifications for various undesirable substances. These substances are presented in water which makes them a reasonable issue in obtaining a quality drinking water. The biggest advantage of these processes represents their ability to remove completely the pathogenic organisms resistible to the disinfection based on using chlorine. Membrane technologies are very efficient also in combination with a proper pre-treatment of water in removal of presented natural organic matter (NOM) whose presence is responsible for an ineligible colouring of the water, the stink and taste of the water. These substances mainly act as the pre-cursors for formation of the disinfection by-products.
1.1. Membrane processes

A thin, semipermeable membranes in water separation into two separate flows caused by the action of pressure are used in membrane processes.

Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) are among the membrane processes based on separation of particles of a certain size from water by using the impact of pressure difference. A typical feature common for all these methods is a semipermeable membrane (0.05 – 2.0 mm), which catches (holds) or passes required components. Towards the classic mechanical filtration, these processes are able to separate the particles of the size of microns above all. The macromolecules and particles up to the size of the ions may be separated eventually by these processes.

1.2. Membranes

Membrane has to be as so much thin as possible, because of its resistance to pass-by of the components would be as low as possible. The membrane has to resist the effect of big pressure differences. Because of that it is being usually manufactured as a thin layer on a porous solid base making a low resistance against the passing-by component – so called asymmetry membrane or the membrane may consist of more than a one layer – a composite membrane formed by a combination of several inorganic and organic layers in order to improve its mechanic attributes.

The requirements given to a membrane are these:
1. high selectivity,
2. high permeability,
3. long lifetime.

Selectivity influences the separation efficiency, the regeneration of membrane and purity of the product. The selectivity is inversely proportional to the dimension of membrane area. It is the most important factor in assessment of membrane quality, since an insufficient selectivity requires a multistage equipment which is usually less economically profitable than a conventional separation process.

Permeability has an impact on the velocity of filtration process and also it affects the dimension of membrane area necessary for a proper separation and therefore it increases the capital costs to the process.

Lifetime of the membrane depends on its stability to the mechanical, thermal and chemical impacts and has an impact on maintenance costs or on eventual membrane exchange.

Membranes are being manufactured from modified natural polymers (acetate, acetylbutyrate and a nitrate of cellulose), from synthetic polymers (polyamides, polyethylene, polypropylene) and from other various materials (ceramic, metal membranes).

There is a disadvantage in using these materials:
• a natural affinity to the organic substances,
• sensibility towards the strong oxidizers,
• sensibility towards the formation of microbial biofilms.

These factors are decreasing the lifetime of polymeric membranes and it is necessary to perform the membrane exchange after some time.

The ceramic membranes whose pores are regular (equidistant), with a good thermal and mechanical properties are perspective. These membranes are manufactured by laying a ceramic layer containing
pores of a diameter of 0.05 μm on the bearing stratum consisting of SiC or Al₂O₃ with pores of a diameter of 8-10 μm.

In consideration to polymeric membranes, the advantage in using the ceramic membranes rests in:
• almost no (or minimal at least) affinity towards the organic substances
• the endurance towards the aggressive chemical substances (strong oxidizers, strong acid solutions)
• a short time of washing (by compressed air or power water)

Based on the factors that are mentioned above, the opinion on the lifetime of ceramic membranes is much longer than it is in case of polymeric. Because of that the operation costs are decreasing in the process of water treatment.

1.3. Membrane modules
In a membrane technology, the membranes are used in a form of membrane modules, so called structural elements containing a proper arrangement of the membranes for a certain process. The requirements on the module are: a large surface of the membrane on the unit volume of the module, a cheap production, an easy access during the treatment and an easy exchange of the membrane.

In terms of shape and arrangement the modules are:
a) tubular  d) plate-and-frame
b) capillary  e) spiral wound
c) with a hollow fibres

1.4. Comparison of the membrane processes
Microfiltration
In contrary to the classic filtration, when the smaller particles that are being removed from water are about the dimension of micrometres, the particles of the size of 10⁴ to 10⁵ nm of an order are being retained when using the microfiltration. The pressure requirement on microfiltration is up to 2 bars. This process is being used in removal of particularly suspended substances, bacteria, algae and protosoa such as Gardia and Cryptosporidium from the water. Most frequent is the application of microfiltration in a treatment of drinking water. Microfiltration membrane modules are usually plate-and-frame or with a hollow fibres made from polymers and tubular or capillary, unless the material which are they made from is ceramic. Microfiltration can be carried out in two ways, the dead-end-filtration (DEF) and cross-flow-filtration (CFF). The DEF method represents a parallel to the classic filtration while the filtration mixture is flowing upright towards the membrane and the filtrate is passing through the membrane. But other much more method of filtration is getting more popular currently – the much more effective method of filtration with a cross-arrangement of the permeate and retentate flow (cross flow filtration) Figure 1.
Ultrafiltration
Macromolecules may be separated by using the Ultrafiltration (molecular weight range 2-200 kDa). So as the particles of 0.002 \( \mu \text{m} \) diameter about and bigger particles of a diameter about 102 up to 100 nm, such are viruses, proteins, polysaccharides or colloid particles may be separated. A required difference in pressure in front of the membrane and behind the membrane is just a bit higher than the difference at MF. But still we deal with the units of several bars. Ultrafiltration modules are similar to the microfiltration, mostly used are the spiral-wound membrane modules.

Nanofiltration
Organic substances of low molecular weight are separated by this type of membrane process. The size of separated substances is rather being mentioned in units of molecular weight than in size units. Nanofiltration is capable to separate the substances up to 20 kDa approx., which corresponds to the molecules of pesticides and herbicides. The pressures are higher than as it is for Ultrafiltration and they ranged in tenths of bars. Most frequent are the applications of water softening and pesticides removing from the water. Only the spiral-wound modules are used and the hollow fibres are rare. But the material they are made from is always the same, the polymeric material [1-6].

| Parameter                          | Microfiltration     | Ultrafiltration | Nanofiltration         |
|------------------------------------|---------------------|-----------------|------------------------|
| Pore size                          | 0,1 - 10 \( \mu \text{m} \) | 1 - 100 nm      | < 2 nm                 |
| Applied pressure [bar]             | 0,2 - 2             | 1 - 5           | 5 - 20                 |
| Membrane thickness [\( \mu \text{m} \)] | 10 - 150           | 150             | carrier layer about 150 \( \mu \text{m} \), active layer about 1 \( \mu \text{m} \) |
| Transmembrane pressure [bar]       | < 4                 | 1 - 10          | 10 - 25                |
| membrane material                  | polymer, ceramic    | polymer, ceramic| polyamide              |

Humic substances (mainly humic acids and fulvic acids) are present in almost all natural waters and often represent a major proportion of organic pollution (known in the literature as “natural organic matter” or NOM) [7].

The negative effect of humic substances on water quality and its treatment can be summarized in that they:
- increase the intensity of the color of water,
- increase the acidity of water,
- affect the biochemical stability of water,
- influence the formation of metal complexes and increase the heavy metal content in water,
- influence the formation of THM in water chlorination,
- decrease the removability of the low molecular weight of fulvic acids that have coagulated,
- increase the consumption of coagulants and disinfectants.

Important precursors of organohalogen compounds in water are mainly fulvic acids and humic acids. Experimentally, it was confirmed that fulvic acids occur in approximately 60% more organochlorine compounds in comparison with humic acids [8-11]. To prevent the formation of chlorinated hydrocarbons, it is necessary to reduce the content of humic substances in water or change the method of disinfection.

In practice, NOM is usually characterized by the measurement of its TOC, DOC, adsorption of UV light (UV254), or COD. NOM is also a major contributor to the brownish-yellow color in water; thus, measurement of color can provide some indication of the amount of NOM that the water contains [12].
2. Experimental part
The objective of the experiments in the locality of Klenovec (a water treatment plant) was to study of microfiltration with ceramic membrane using different coagulant (a ferric sulphate PIX113 or polyaluminium chloride PAX-XL19) and performance (overflow) of Amaya 5 on efficiency removal of turbidity, colour, organic substances, solid substances, living organisms, residual coagulant, etc. from surface water in a water tank Klenovec.

At the WTP Klenovec, the pilot-plant tests for membrane filtration examination were carried out by using the microfiltration unit AMAYA 5 with a performance of 5 m$^3$/h. Coagulation and flocculation run in two stages. At the first stage, the coagulant is dosing into a static mixer, which led the mixture to the second stage from. The second stage represents the tubular flocculator. In the membrane module, there is placed one ceramic element with a membrane surface of 25 m$^2$, pores size of 0.1 µm, and consisting of 2000 tubules with a diameter of 2.5 mm. At first, the reverse washing (physical washing) is carried out by filtered water from the reverse washing reservoir at the pressure of 5 bars. Then the aeration follows at the pressure of 2 bars. The time needed for a washing and aeration is very short, just 20 seconds. Sludge is led into the reservoir of waste water. We performed membrane washing each 2 hours in the beginning of the tests and each 4 hours later over the tests [13-17].

The equipment itself performs the chemical washing (CEB) automatically within the mentioned time intervals. The CEB can be oxidative or acidic. Sulphur acid concentrate is used in ACID CEB which was performed once a day. Sodium hypochlorite is used in OXID CEB, once a day in the beginning and 3 times a day in the later period of experiments. This interval we prolonged in order to avoid the increase in transmembrane pressure – TMP and therefore it would not had been necessary to perform the oxidative washing so often.

3. Results and discussions
The aim of the performed tests was the evaluation of the possibility of using the microfiltration technology on ceramic membranes with preliminary coagulation in one-step water treatment process at the WTP Klenovec during the seasons when the water is tolerably pure in terms of physical-chemical properties of the water. But a relatively high activation (biological) is typical for the water over that season as well. In Figure 2 is shown the progress of activation and insoluble substances (expressed by a number of particles) in a raw after at the influx to the WTP Klenovec during the whole testing period.

![Figure 2](image.png)

**Figure 2.** Number of living organisms and insoluble substances particles in a raw water at the influx to WTP Klenovec during a testing period.

There was no activation, after using the microfiltration with a ferric sulphate PIX113 as a coagulant or polyaluminium chloride PAX-XL19. This is illustrated in Figure 3 regarding the different performances of the equipment.
The results of water after the treatment testing show that the water met the criteria of Government Regulation no. 247/2017 Coll. of the Slovak Republic (Figures 3, 4) whether that the coagulant (on the basis of iron or aluminium) was used or not within the tests. In case we did not use the coagulant, plugging of the pores was faster and by that the transmembrane pressure was increasing – TMP. Thereby the general consequence in a filtration process shortening and therefore the need for more frequent membrane washing occurred as well. Applying this into the operation would mean a moderate increasing of the operational costs.

![Figure 3](image1.png)

**Figure 3.** Number of living organisms before and after microfiltration with preliminary coagulation

In Figure 4 there is shown the plot describing the coagulant Fe PIX 113 traces which was dosing during the first four days and AL PAX- XL19 which was dosing during the next 8 days. After dosing of coagulant Fe PIX the values for Fe ranged between 0.47-1.59 mg/L, in case of coagulant Al PAL- XL19 the values of Al ranged between 0.02-0.294 mg/L and were close to 0 after the filtration.

![Figure 4](image2.png)

**Figure 4.** Fe content (in the left) and Al content (in the right) in raw water and water after microfiltration

Figure 5 (left) shows the values of turbidity in raw water (ranged between 2.14-3.89 NTU) and values of turbidity after dosing of coagulant Fe PIX and after microfiltration (ranged between 0.09-0.16 NTU). In case of second experiment with coagulant Al PAL-XL19, the values of turbidity in raw water ranged between 2.36-5.16 NTU, after dosing of coagulant and after microfiltration values were between 0.08-0.19 NTU (Figure 5 right).

![Figure 5](image3.png)

**Figure 5.** Turbidity in raw water and water after microfiltration

Figure 6 (left) shows the values of pH in raw water (ranged between 7.65-8.34) and values of pH in filtrate after dosing of coagulant Fe PIX and after microfiltration (ranged between 7.11-7.49). In case of second experiment with coagulant Al PAL-XL19, the values of pH in raw water and filtrate ranged between 7.65-7.89 and 7.22-7.85, respectively (Figure 6 right).
Figure 5. Turbidity progress in a raw water and in filtrate during the microfiltration tests

Figure 6. Progress of pH value in a raw water and in filtrate during the microfiltration tests

Figure 7. COD\textsubscript{Mn} progress in a raw water and in filtrate during the microfiltration tests

Limit value for COD\textsubscript{Mn} of a treated water originating from a surface water reservoir is 3.0 mg/L at the outflow from the WTP. COD\textsubscript{Mn} ranged between 2.3-3.6 mg/L during the tests at the WTP Klenovec and was 1.5 mg/L after the treatment (Figure 7).

4. Conclusions
All obtained results from pilot-plant tests at the WTP Klenovec confirm the possibility of ceramic microfiltration membrane to treat surface water excellently and to make it a drinking water. Several factors refer this technology is a prospective treating technology and for obtaining a drinking water of high quality. These processes are among the low-pressure membrane processes and are highly chemically endurable. In every WTP using where these processes were installed, the processes are
designed of ceramic microfiltration elements. The oldest WTP with microfiltration is in Kyoto and it comes from 1998

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