

Defining the effect of the chemical concentration and solution pH on membrane chemical cleaning process

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Abstract. In the process of treating natural water from surface sources, precipitated substances are tend to be deposited on the ultrafiltration membrane, either as suspended solids or as gel structures, formed by humic substances with metal salts. Hydraulic washes are unable to remove gelled structures from the surface of the membranes. Consequently, the phenomenon of gelation on the surface of the membrane causes gradual decrease in productivity, which is a negative factor. Chemical washing of membranes is generally used to remove the gel layer from the membrane surface. In this paper, the range of compositions which effectively remove complex contaminants is proposed, and also the efficacy of both pH and changes in the concentration of active substances on the process of washing the membrane are analyzed.

1 Introduction

There are recommended schemes that allow uninterrupted operation of the system during the treatment of water from surface sources with the use of ultrafiltration treatment. Typically, these consist of a feed pump, coarse filter, ultrafiltration module, disinfectant and deodorizing agent dosing pumps, backwash tank, backwash pump, membrane cleaning and chemical disinfection system, clean water tank, coagulant and flocculant supply system.

In the process of ultrafiltration water treatment, precipitates are formed on the membrane surface, consisting of: humic and fulvic acids [1], as well as their complexes (iron, aluminum deposits, hardness salts) [2, 3]; biological sediments (biofouling, fungi and molds); colloidal substances of natural and man-made origin; proteins [4]; petroleum products.

Chemical Clean in Place (CIP) technology and hydraulic washes [5, 6] are used to remove deposits that form on the surface of an ultrafiltration membrane. Periodic hydraulic flushings are carried out every 20-40 minutes, depending on membrane fouling, thus allowing to wash away suspended substances, those which do not exhibit high adhesion to the surface, from the membrane surface. CIP washings are carried out when the membrane capacity drops by more than 20-30 % of the initial capacity, in the case when the hydraulic

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washes are no more capable of restoring the efficiency of the filter sheet. In the process of treating waters containing high concentration of organic substances, chemical cleanouts are carried out every 5-10 days, depending on the level of contamination of the membrane elements, which in turn depends on the condition of the water supply source.

In the practice of membrane usage, acid and alkaline detergents are most commonly used [7, 8]. The basis for such substances is hydrochloric or citric acid, as well as caustic soda and various detergents. The heterogeneous nature of pollution in the water supply source requires a careful approach to determining the composition of chemical reagents for washing and the conditions for their implementation. The choice of the optimal solution for washing the membranes is complicated by unstable water quality, which varies greatly depending on seasonal and anthropogenic factors.

One of the main factors determining the durability and operation life of ultrafiltration membranes before replacement is both membrane sheet and modifying layer resistance to the cleanout solutions. Cleanout solutions should not cause deterioration of the membrane performance. This principle is fundamental when defining the composition of the washing solution, its pH and dosage.

2 Methods

To ensure the sameness of membrane contamination condition during the experiment, the following method was developed.

Water obtained as a permeate on a reverse osmosis system was used as a solvent in a modular solution. To increase the content of organic substances in the water, to make it similar in composition to the Dnipro River during the flowering period, especially in terms of chromaticity and permanganate oxidation, a peat extract, which is based on humic and fulvic acids, was used. Calcium and magnesium chloride, calcium and magnesium sulfate were used to impart hardness to water. They were mixed in equal mass proportions to give the water a total hardness not exceeding 4 mg-eq/l. Sodium chloride solution was added to the water to remove the salt balance. This solution was defined as modular.

The usage of this modular solution guarantees that the membranes receive the same portions of contamination in all cases.

To ensure the convergence of concentrations, in addition to the weight method, the determination of the masses of pollutants the following measurements were carried out:

- total salt content was measured by the conductometric method;
- the stiffness of the modular solution was measured by the titrimetric method [9];
- the color of water was measured by a photometric method using a spectrophotometer

Expert 003, following the method [10].

The quality of the modular solution corresponded to the following indicators: total turbidity in the flow up to 5 NTU, total hardness 4 mg-eq/l.; pH = 8.1 ± 0.5 , total mineralization 450 mg/l $\pm 2\%$ permanganate oxidation 18.7 mg/l O₂, temperature 20.0 ± 0.5 °C.

The modular solution was introduced into the water by dosing pumps equipped with pulse output water meters to conduct water flow measurement. This made it possible to maintain the concentration of pollutants at the same level while the flow rate was changing due to membrane permeability decreasing in the process of water treatment.

The conditions for conducting ultrafiltration membrane cleanout experiments: the duration of cleanout is between 5 and 15 minutes, the temperature is 20.0-40.0 ± 0.5 °C, the specific consumption of the washing agent is 160-220 ± 5 l/m²hr.

Osmotic water (permeate), anionic surfactant solution (surfactant), Trilon B solution in combination with caustic soda (NaOH), Trilon B solution in combination with NaOH and surfactant were used as washing solutions for ultrafiltration membranes cleanout.

While using the abovementioned types of chemical reagents, ultrafiltration membranes cleaning efficiency was evaluated, as well as changing the pH of the washing solution and the concentration of chemicals in the washing solution.

3 Results and discussion

As a point of reference, demineralized water was used to test the effectiveness of membrane cleanness after chemical cleanout, which was fed through the membrane for 30 minutes at an operating pressure in front of the membrane of 10^5 Pa. These rinses were performed in automatic mode 1 time per day, every 24 hours. Such a condition was necessary, as showing the final result of ultrafiltration membrane washing.

Since the contaminants are multi-layered, leaching of the interlayer space is possible – thus structural gulls are formed. At the same time, when the working pressure is applied, within 30 minutes there is a gradual decrease in the performance of the membrane, caused by the compaction of the loosened gel layer caused in its turn by the action of chemicals used in chemical cleanouts. Accordingly, after 30 minutes the actual performance of the membrane sheet is obtained.

3.1 The effect of solution pH on the process of membrane chemical cleaning

The analysis of the effect of solution pH on the process of chemical cleaning of ultrafiltration membranes has been carried out. Anionic surfactants (surfactants) solution, Trilon B solution in combination with caustic soda, Trilon B solution in combination with NaOH and surfactants were used as cleanout solutions. To increase the pH of the solution, caustic soda was used. The pH was kept at 11.

The effect of pH of the washing solutions on the degree of washing of ultrafiltration membranes is displayed in Table 1 and Figure 1.

Table 1. Decrease in the performance of ultrafiltration membranes and the degree of cleanout using CIP-K technology while keeping pH = 11.

| Reference point | Osmotic water cleanout, $\text{dm}^3/\text{m}^2\text{hr}$ | Surfactant cleanout (pH=11), $\text{dm}^3/\text{m}^2\text{hr}$ | Trilon B +NaOH cleanout (pH=11), $\text{dm}^3/\text{m}^2\text{hr}$ | Trilon B +surfactant +NaOH cleanout (pH=11), $\text{dm}^3/\text{m}^2\text{hr}$ |
|-----------------|---|--|--|--|
| 0 | 130 | 130 | 130 | 130 |
| 1 | 125 | 125 | 125 | 125 |
| 1.1 | 127 | 130 | 130 | 130 |
| 2 | 110 | 117 | 119 | 123 |
| 2.1 | 115 | 120 | 122 | 125 |
| 3 | 103 | 108.5 | 112 | 117 |
| 3.1 | 106 | 112.5 | 116 | 122 |
| 4 | 98 | 107 | 108.5 | 114 |
| 4.1 | 101 | 109 | 112 | 120 |
| 5 | 95 | 105 | 106 | 113 |
| 5.1 | 100 | 109 | 111 | 118 |
| 6 | 93 | 103 | 105 | 111 |
| 6.1 | 99 | 106 | 110 | 116 |
| 7 | 93 | 102 | 105 | 108 |

Comparative analysis of indicators of cleanout degrees is made by the help of osmotic water rinse. Combinations of the Trilon B + surfactant + NaOH cleanout solution (pH = 11)

show the highest degree of purification. It can be seen that the cleaning efficiency of Trilon B increased significantly along with an increase in pH from 4.9 to 11.0. Whereas, in the case of surfactants there was only a slight increase at a higher pH. At pH = 11, all the carboxyl functional groups of Trilon B become deprotonated [11], the values of the pKa dissociation constant constitute: 1.99; 2.67; 6.16 and 10.26. At pH = 11, Trilon B chelate ability increase resulted in a more efficient ligand exchange reaction between Trilon B and the complex formed by humic acids with iron and aluminum. Consequently, the gel layer collapsed more easily compared to a lower pH value and, thus, cleanout was more efficient. The pH of the surfactant solution had practically no effect on purification, since the pKa of the sulfate functional group of the surfactant is 2.12 [12].

We can conclude from the above, that the pH of the Trilon B cleanout solution is the determining factor affecting the chemical reaction between the cleaning agent and the gel layer of the ultrafiltration membrane, while the chemical reaction between surfactants and pollutants is less susceptible to a change in the pH of the solution.

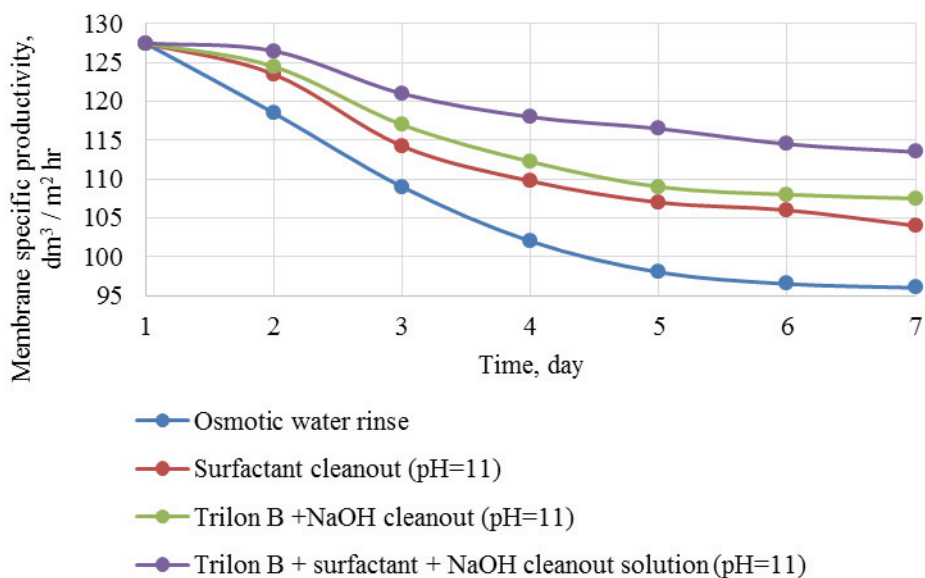


Fig. 1. Influence of the solution type used for ultrafiltration membrane surface modular contamination CIP-K cleanout at pH = 11.

According to data shown in Figure 1, the combination Trilon B + surfactant + NaOH shows the greatest cleaning effect and the performance drop of the ultrafiltration membrane was minimal. This can be explained by the mutually reinforcing effect, as well as by the complex effect of the components of the cleanout solution on the process of washing the impurities off the membrane surface. Surfactants acted as a detergent, which has a high surface activity and is able to enhance deprotonation and wash-off effect while removing membrane surface contamination. Caustic soda softens the contaminants; Trilon B contributes to the leaching of metal ions from the gel layer.

Thus, we achieved the greater stability of the water treatment system functioning, guaranteeing the higher stability for heavily loaded filter sheet.

The conditions of the experiment were the same for all experiments. It is also worth noting that the surfactant concentration was kept at 2.2 mmol/dm³, and Trilon B was kept within 2 mmol/dm³.

3.2 The relation between the efficiency CIP-K cleanout membrane regeneration and the concentration of the chemical substance

Researching of the effect of chemical concentration on the process of chemical cleanout of ultrafiltration membranes has been carried out. The experiments were carried out using wash solutions that contained different dosage of Trilon B and Trilon B and caustic soda combination while keeping the pH of the solution at 11 ± 0.1 . The process of keeping the pH of the solution was carried out using a metering pump with an electrode controlling the pH in circulating water. At the moment when the pH value fell below 10.9, a concentrate containing sodium hydroxide and the base substance Trilon B or Trilon B + surfactant was introduced into the water. The temperature of the solution was kept at 30 °C and the volume flow rate of 220 l/m²hr.

The results of the research of the effect of Trilon B concentration on the efficiency of ultrafiltration membrane surface CIP-K cleanout are shown in Figure 2. The percentage effectiveness of CIP-K cleanout is displayed along the horizontal axis.

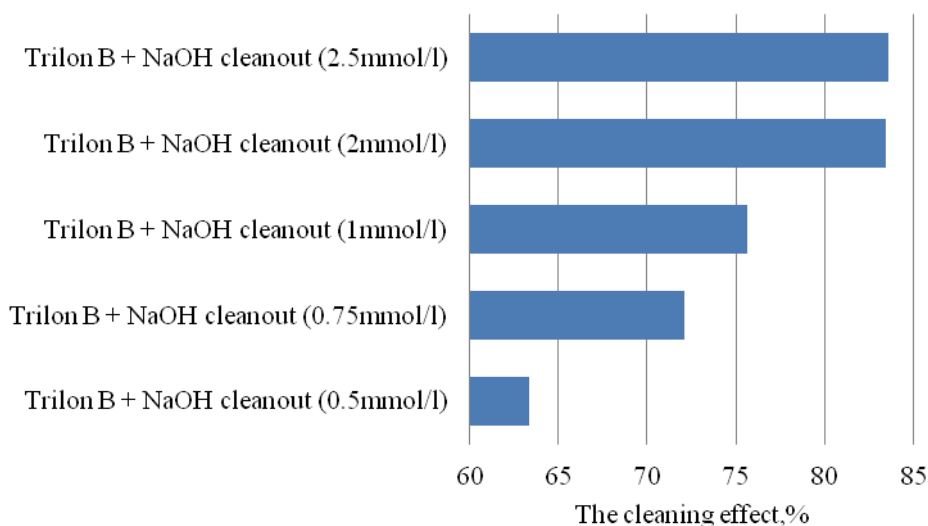


Fig. 2. The effect of Trilon B concentration on the efficiency of ultrafiltration membrane surface CIP-K cleanout.

The results of the research show that the effectiveness of cleaning using Trilon B increases simultaneously with cleaning agent dosage increase. In the case of Trilon B, the cleaning efficiency increased proportionally to the concentration of the substance and reached the threshold effect at 2.0 mmol/dm³. Note that Trilon B concentration of 2 mmol/dm³ and 2.5 mmol/dm³ gave almost the same effect of restoring the filtering ability of the membrane: 83.43 % and 83.58 %, respectively. Thus, increasing the concentration of Trilon B above 2.0 mmol/dm³ does not have a practical effect and this value can be considered as a threshold.

In the case of surfactants, a noticeable increase in the cleaning efficiency was observed with an increase in the concentration of surfactants from 2 to 9 mmol/dm³. The results of the research are displayed in Figure 3. The percentage effectiveness of CIP-K cleanout is presented along the horizontal axis.

It is also worth noting that the surfactant concentration at the level of 9 mmol/dm³ slightly exceeds the critical concentration of the surfactant micelle concentration, the level of which is usually considered to be 8.36 mmol/dm³ in deionized water [13]. Therefore, it was concluded that purification using surfactants with a level above the critical

concentration of micelle formation is the most important factor which defines the efficiency of chemical regeneration of the membrane when removing humic contaminants. A similar mechanism for surfactant cleanout of nanofilter membranes contaminated with humic acid in the presence of calcium ions was discussed in [14]. However, it is worth noting that an increase in the surfactant concentration above 2 mmol/dm³ causes significant foaming and complication of cleanout process. Increasing the surfactant concentration can be performed only in the presence of service personnel, which significantly complicates the CIP-K cleanout process.

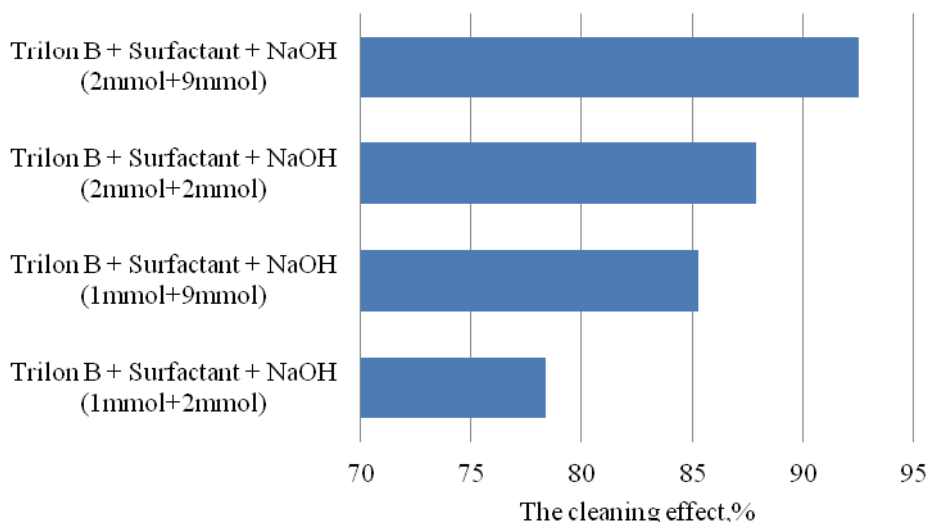


Fig. 3. The effect of Trilon B and surfactant concentration on the efficiency of ultrafiltration membrane surface CIP-K cleanout.

Conclusions

In the course of the research, it was made clear that the degree and speed of cleanout is significantly influenced by such indicators as the pH of the solution and the concentration of basic substances.

This study showed the possibility of increasing the performance of ultrafiltration membranes due to usage of CIP-K technology by 20 %. It was also found that the optimal pH for complex removal of pollution equals 11 pH units. It was also found that increasing of Trilon B concentration causes the increasing effectiveness of contamination cleanout. The optimum concentration of Trilon B is 2 mmol/dm³.

Also, during the research experiments of surfactant usage were conducted. The optimal concentration for CIP-K is established experimentally and equals 9 mmol/dm³.

Thus, the combination of Trilon B and surfactant at pH =11 allows to obtain an optimal cleanout effect and to increase the efficiency of the water purification system fed by surface water sources using modified ultrafiltration membranes. Accordingly, operating parameters for the CIP-K technology were defined and thus this technology is recommended for industrial use.

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