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METHODS OF CHEMICAL REGENERATION OF POLYMERIC MEMBRANES

Key words

Membrane filtration, fouling, regeneration of membranes, CIP station.

Abstract

The study addresses problems concerning reducing the effects of fouling, accompanying cross flow filtration. Mechanisms of fouling production depend on the properties of the fluids being filtered, the characteristics of the membranes, and the conditions of the filtration processes. This mechanism relies upon the accumulation of particles and colloids, microorganisms, and salts on the surface and in the pores of the membrane. This results in a dramatic flux decline and retention of the membrane. One of the most effective and significant way to reduce fouling is by choosing an appropriate membrane and the optimal process conditions adjusted for the fluid characteristics. However, this does not solve the problem entirely. Fouling may be either reversible or irreversible. In some cases, depending on the structure of membrane, reversible fouling can be removed by backwashing. In the other cases, it is required to use chemical purification of the membranes. Its efficiency depends on the cleaning reagent

activity, ionic strength, concentration, and pH, as well as temperature, pressure, time, and the flow rate of cleaning solution. The introduction of the reactants is performed in order to loosen the structure and dissolve the deposit, to maintain the foulant in the solution and to prevent its re-embedding on the membrane surface. Better results of cleaning can be achieved by improving the conditions for the transport of the reaction products from the membrane into the solution. It is mostly controlled by the flow rate of the cleaning solution, but it must also take into account the temperature and time of cleaning, which affect the mass transfer and chemical reaction. This is achieved by means of a suitably designed cleaning-in-Place (CIP). Mobile pilot installation of CIP was prepared by the Institute for Sustainable Technologies - National Research Institute in Radom. It is designed to develop, verify and optimize the CIP procedures in terms of pilot and test membrane systems.

Introduction

The monograph [1] highlighted the growing importance of nanostructured materials and nanostructures in technics, particularly in solving ecological problems and environmental issues. Reducing industrial nuisance for an environment is associated with a reduction in water consumption and the amount of wastewater discharged into the environment. This can be achieved through the wider use of modern methods of the separation and purification of liquids. Some membrane techniques have a great potential in this field. They enable treatment and purification of seawater and its replacement with drinking water, the purification of technological liquids, and the extension of their operation in industrial circuits, as well as the treatment of industrial and municipal waste [2]. Membrane techniques make it possible to close the water circuits and to reduce water consumption. They do not require the use of chemicals for support, and they do not cause transformation components to be separated. A particular feature is that they do not cause a chemical transformation of substances, thus enabling their recovery in the process of wastewater treatment. In the process of purification, some of the components in the wastewater can be recovered. This allows saving raw materials, energy, and labour. However, a serious problem in the management of water concerns the deposition of biological components and organic components of treated liquid on the membranes as well as precipitation of minerals on them (Fig. 1).

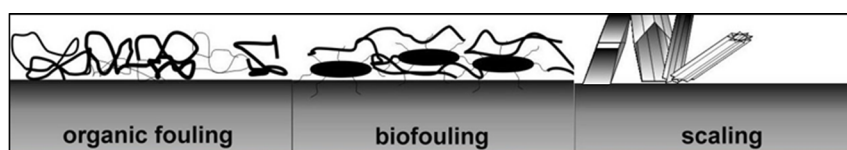


Fig. 1. Schematic representation of fouling structure layers resulting from the deposition of organic substances, microorganisms, and mineral substances

Usually, however, all processes take place simultaneously and the effect is defined as a common fouling. One of the following phenomena aids fouling [3]: concentration polarization and the resulting concentration of substances dissolved in the water at the surface of the membrane, adsorption of the substance on the membrane, and structural changes in the polarization layer. The most adverse effect of these phenomena is the formation on the membrane surface so called „filter cake”. This causes membrane blocking, resulting in a dramatic decrease in filtration flow and the selection ability of membranes.

Depending on the requirements for the purification of liquids, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or reverse osmosis (RO) may be used. The comparative characteristics are shown in this paper [4]. The main driving force of these processes is the transmembrane pressure. These techniques vary in the pressure at which the process is carried out and in the transport mechanism of permeate components through the membrane. Generally, it can be assumed that, in the case of porous membranes (MF, UF), separation proceeds by the sieving mechanism. Components smaller than the pores pass through the membrane into the permeate, while larger ones undergo condensing in the retentate (Fig. 2). Significantly, the sieving mechanism in NF and RO membranes is in decline. The separation of components of the liquid to be filtered is carried out through the diffusion. The determinant for this process is not only pressure, but also the molecular mass of a molecule and its physicochemical state (charge, polarity, bipolarity, the shape, the diameter of the replacement).

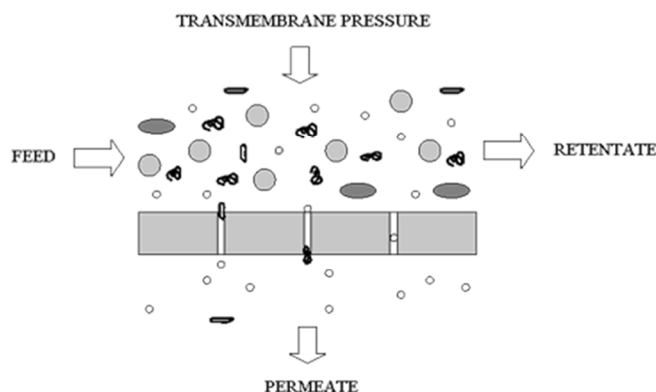


Fig. 2. Directions of mass flow during the selective separation process [5]

Both the sieving and the diffusion mechanism aid fouling accumulation on the membrane. At the surface of the membrane, condensing of separated components and the loss from the feed as well as the "compression" to the membrane surface occurs. This process involves complex physical and chemical interactions between the surface of the membrane and the constituents of the

filtered liquid. These phenomena depend on both the nature of filtered liquid and the membrane. The most significant issues are membrane structure (porous or solid), its charge, hydrophilicity or hydrophobicity, and surface roughness [6]. Eventually, fouling leads to increased hydraulic resistance of the membrane [2, 7] and increased transmembrane pressure, where the process is carried out at a constant stream flow [8, 9] It also leads to a decrease in the permeate flow at a constant transmembrane pressure [10–12].

An effective manner of elimination of the effects of fouling is the periodic removal of filter cake, e.g., through the use of back flushing [13]. Nevertheless, this procedure cannot be used in every case (solid and composite membranes) and is not always effective. In many cases, molecular forces between foulants and the surface of the membranes preclude the back flush. The only way to avoid these problems is membrane stripping (called Clean in place – CIP) using a variety of substances reducing or eliminating these effects. This procedure should enable the removal of various foulants while maintaining the original characteristics of the membrane [14]. However, one of the side effects of improperly performed membrane cleaning is an adverse change in the properties of the membrane surface, retention capabilities, and filtration stream. Therefore, a single universal CIP procedure is not possible, but each case requires individual approach and solution.

1. Chemical cleaning of membranes

In the process of "deep" water purification, the most important techniques are NF and RO. Due to the water environment, membranes are particularly susceptible to fouling. Treatment of NF and RO membranes is practically possible only through the use of CIP procedures. The use of this procedure reduces the efficiency of the process [15]. Chemical cleaning of the membranes has a great impact on the manufacturing process and its costs due to the time needed to perform all the operations, the consumption of water and chemicals, the danger of corrosion and degradation of the membrane system, the need for recycling or reclamation, washing baths, and new waste management.

The selection of the CIP reagent is a function of the membrane material and the type of foulants. Some parameters, such as the concentration, the speed and flow rate, temperature, pH, pressure, and time of the process should be met. In practice, it is thought that NF membranes also require different cleaning procedures even working under identical conditions [16]. This is because the characteristics of the membrane affect the composition and fouling structure layer. Certain combinations of reactants and membranes are incompatible and may result in irreversible loss of flow or the retention capacity of the membrane. Thus, the selection of a proper cleaning procedure is crucial to the exploitation of membrane systems. The activity of reagents should be confined to the removal of foulants from the membrane surface and, if necessary, from its pores.

However, it is common that the reagents affect the structure of the membrane itself, changing the surface or porosity of the membrane. This may result in the recovery of the filtration stream higher than of the native membrane, which is sometimes associated with deterioration in its retention characteristics [17, 18]. The selection of the appropriate reagent is crucial for the effectiveness of the CIP.

The variety of available membrane types and the fouling mechanisms and types of foulants forces one to search for the most suitable reagent for each case. Taking into account the chemical nature and mechanism of action, the reactants can be divided into several groups [19]:

1. Alkali (NaOH, KOH, NH_4OH);
2. Acids (HCl, H_2SO_4 , HNO_3 , H_3PO_4 , citric acid, oxalic acid);
3. Salts (NaCl, KCl, NaNO_2 , NaNO_3 , Na_2SO_4 , NH_4Cl);
4. Surfactants (SDS – anionic, CTAB – cationic);
5. Chelating agents: ethylenediaminetetraacetic acid (EDTA) and the sodium salt of ethylene diamine tetraacetic acid (Na_2EDTA , Na_4EDTA);
6. Enzymes (peptidases, proteolytic, hydrolytic); and,
7. Disinfectants (oxidants) NaClO , H_2O_2 , KMnO_4 .

Commercially available preparations are usually a mixture of the above mentioned groups of the reactants.

Alkaline reagents cause hydrolysis of the organic foulants and make inorganic ones dissolved [19]. The presence of hydroxyl ions in the baths leads to an increase in the ionic strength and the masking of the surface charge on the membrane [17]. High pH also results in the negative charge of an organic matter as a result of the deprotonation of the functional groups such as carboxyl, hydroxyl, and amine groups [20]. It also results in dissolving the foulant and removing it from the membrane [18]. As a consequence, alkaline solutions appear to be more effective than the acidic ones in the removing of organic foulants. Thus, alkali with acidic reagents is used to remove organic fouling. This dominates in the processes of filtration of surface water and the recovery and regeneration of the technological water solutions and wastewater.

Acid baths are able to effectively remove precipitated salts (scaling) from the surface and from the pores of the membrane. Interactions between acids and foulants consist in the dissolving and chelating of inorganic substances as well as in the hydrolysis and saponification of organic substances [19]. In the study [21], in order to clean NF membranes, HCl, NaOH and Na_4EDTA were used as chelating agents. As a result, the removal of scaling and organic fouling as well as biofouling was obtained. It was also found that the chelating agent played a key role in this process. This enables the exchange of metals forming scaling between the ligands. However, the complete removal of scaling required periodic use of the acid baths. Alkaline and chelating reagents improved the flow, but deteriorated the retention capacity of the membrane.

The mechanism of the action of the **salt solutions** is associated with the structural changes in the bonds of the gel layer and ion exchange. The salt solution prevents the structural integrity of the deposit layer by reducing the cohesion forces between the foulant molecules. Changes in the structure and a deformation of the gel layer are the result of a difference in osmotic pressure between the solution stream and the inside of the gel layer. Salt solutions (e.g., NaCl) make the deposit layer of hydrophilic gel swell and become porous, and sodium ions diffuse into it and displace Ca^{2+} [22]. This process aids the breaking of the bonds between calcium and organic compounds such as alginates. In the study [22], it was found that NaCl removes hydrophilic deposits (alginate in the presence of Ca^{2+}) from the surface of the RO membrane with a negative surface charge used for the desalination of water, and it is less effective with respect to hydrophobic gels (humic substances).

Surfactants reduce the surface tension and dissolve aggregates of macromolecules by forming a micelle around them, thereby detaching it from the surface of the membrane. They also display the chelating agent's activity [19]. In the research [23], it was found that the surfactants in alkaline solutions (NaOH) produce synergies and facilitates the removal of the organic foulants from the membrane. The surfactants contribute to the contact of alkali with an organic matter and cause a negative charge of the organic matter and the weakening impact of similarly charged membrane surface.

Chelating agents are able to remove both organic and inorganic foulants [22–24]. They allow the removal of the metal ions from the gel layer and weaken its integrity (e.g., alginate in the presence of Ca^{2+} on the surface of the membrane forms a very stable gel layer). In the experiment [24], a fouling organic layer with effectively stabilized Ca^{2+} was removed from the RO membrane surface using the surfactant (SDS) and chelating agent (Na_2EDTA). The addition of NaOH had no effect on the properties of the cleaned membrane. That is, SDS mixed with chelating agents is sufficiently effective in removing organic fouling. Thus, the composition is safer for both the membrane and installation that do not contain NaOH.

Enzymes are used in the cleaning processes concerning the membranes that are sensitive to chemicals, pH and temperature, thus it must be conducted under mild conditions. Enzymatic baths can improve the quality of cleaning while reducing the consumption of chemicals and energy costs, due to the lower temperatures in enzymatic baths than in chemical ones. Enzymes are biodegradable and can be produced for the specific demands. There are commercially available formulations for specific applications on the market [25] with additions to enzymes, e.g., endopeptidases (Subtilisin) or a mixture of proteases containing other active ingredients, e.g., anionic surfactants. They are particularly effective in the cleaning process of proteins and carbohydrates (e.g., starch), which are hydrolysed by their action. In many cases, the use of enzymes allows for a greater stream of permeate cleaning chemical, but it is typically

expensive, although in some cases inevitable. The chemical state of the membrane after the enzymatic treatment varies from that after the chemical treatment. This is more expensive, but generally inevitable, which is the reason for reducing in the hydraulic resistance against the native membrane. Nevertheless, there is a risk that the deposit of deactivated enzymes or the products of destruction accumulate on the membranes changing the selectivity.

Commercial reagents are usually a mixture of several components selected for chemical parameters of the different categories of wastewater, but, in most cases, the composition is not given by manufacturers. In some cases, information is available on the qualitative formula [18], e.g., it may contain an amphoteric surfactant and EDTA – high pH = 11 indicates the presence of the alkali or a mixture of detergents, buffers, EDTA and sodium tripolyphosphate, trisodium phosphate, which raises the pH to over 11.

The efficacy of the agents used in the CIP procedure depends largely on the state of fouling layer that determines access of cleaning deposit layer. The effectiveness of chemical cleaning depends on the chemical reactivity of the agents that are supposed to weaken foulant-foulant and foulant-membrane interfaces. Effective detergent eliminates or reduces the cohesive forces between the foulant molecules which maintain the integrity and strength of the foulant layer or cohesive and adhesive forces between the foulant molecules and the membrane that maintain the foulant layer on the membrane surface.

Certain reagents significantly increase the flow of permeates relative to the native membrane. This may be due to pore cleansing using material that remains during their preparation or the adsorption of the reagent onto the membrane surface and thereby increasing its hydrophilicity [26]. The increase in hydrophilicity makes the interaction stronger between water molecules and polar groups on the membrane surface, limiting water conversion on the surface of the membrane. The increase in charges on the membrane causes an increase in the electrostatic repulsion forces between the active points of the membrane and causes the membrane to become more open. The increase in the membrane charge also increases the repulsion forces between the membrane and the foulant. Significant savings can be achieved by the proper selection of reagent from the productivity of the membrane and its retention capacity point of view. For example, washing with a solution of Na_4EDTA and $\text{Na}_5\text{P}_3\text{O}_{10}$ provided a sufficient stream recovery after one cleaning cycle, while the other reagents combination required two or three cleaning cycles to obtain the same results [21]. It is worth noting that the high stream recovery is not always a total removal of foulant. Particularly, it is needed to select proper cleaning reagents for NF and RO membranes that are required to stop ions.

For an effective and safe CIP process, appropriate cleaning baths are used. The CIP process is based on selecting a cleaning reagent and some chemical and physical parameters of the liquid to be filtered. A known composition of the filtered liquid enables the prediction of the foulant type and the selection of an

appropriate method of its disposal. In practice, the most commonly used concentration of acids (citric, phosphoric acid, nitric acid) or hydroxides ranges between 0.5 and 2.0%. However, the selection of a detergent for the CIP should be preceded by consultation with the membrane manufacturer and the manufacturer or supplier of cleaning agents. The wash solution should be prepared with deionized water so that the ions do not weaken the action of the reactants. The volume of the prepared cleaning bath depends on the volume of the filling installations, and it is usually a ratio of 1 to 2–3. It should also adjust the pH, temperature, time, the conditions of flow, and other parameters to the expected effects of a CIP process.

A complex issue is the stripping of the membranes of petroleum products [27]. This problem occurs during the microfiltration process prior to RO seawater desalination. Hydroxides are not very effective in this application, and even 1% concentration give the recovery of a stream of 36%. Much more effective is oxalic acid, which provided 80% recovery flow filtration at 0.5% concentration, but after subsequent wash cycles, the time of membranes work reduced. The best results of sequence cleaning was as follows: first, 0.5% NaOH supplemented with oxidant (NaOCl), and then with 1% oxalic acid, which enabled ~95% stream "recovery", and ~96% time "recovery" [27]. Reducing the stream and work time in subsequent cleaning cycles did not exceed a few percent. In the case of ceramic membranes, procedure CIP is used only at the moment in which the flow filtration is smaller than the initial 30% after completion of backwash cycle (back flush or back pulse).

Application of the CIP procedures for membranes becomes a necessity in the following cases:

- a) Approximately 30% decrease in the speed (yield) filtration,
- b) Approximately 10% increase in the inlet pressure,
- c) Approximately 30% of the increase in transmembrane pressure,
- d) A decrease in retention factor, and
- e) A longer than the two-hour delay in the process of filtration.

There are other requirements, e.g., sanitary specifying the frequency of cleaning filter system (in the food industry, some installations membrane is subjected to a CIP procedure once per shift or once a day).

CIP efficacy depends not only on the reactants used, but also on the process parameters and its implementation. The CIP procedure consists of several unit operations, during which the membrane is treated with various reagents. The use of the subsequent types of reactants must be separated by cleaning the membrane with high purity water (DEMI or RO). In a typical CIP procedure, the membrane is treated with acids (or bases), rinsed with bases (acid), and again washed, and sometimes it is essential to use additional enzymatic treatment. Often, the cycle is repeated several times in order to obtain the desired characteristics of the membranes. Important factors to be taken into account when applying the CIP are the conditions in which membrane will go after

installation. The natural state is to come back to normal operation. However, if the installation is in a resting state (e.g., production break), the procedure CIP must be subjected to the maintenance procedure of the membranes. The purpose is to protect membranes from drying out (after drying, membranes enduringly lose their properties) and microbial attack. Restarting the system requires the maintenance of membranes.

The efficiency of cleaning depends on the temperature of the bath, which should be maintained at a constant level. At too low a temperature (below 15°C), the chemical reactions are slower, and cleaning time is prolonged. It may decrease the efficacy of the process, which, in the long term, leads to the rapid exploitation of the membrane. On the other hand, too high a temperature (above 45°C) may cause damage to the polymer membrane or deactivate the enzymes (over 55°C) on enzyme baths. Cleaning should be introduced at low shear rates (free flow). For example, the flow rate of the washing bath for an eight-inch membrane module should range from $5.5 \pm 2.5 \text{ m}^3\text{h}^{-1}$ at a pressure of 3–4 bars. High values of flow rate and pressure may cause mechanical failure of the membrane fragments while removing a fouling layer, which can be embedded again in the membrane and cause damage to the surface and shorten vitality. For all these reasons, the completion of the CIP processes requires the use of a suitably designed system to ensure its effective implementation.

2. The equipment for membranes cleaning

Overview of substances used for the cleaning of membranes coated with fouling (scaling) and the mechanisms and consequences of their actions, as well as the ways and the conditions to counteract them, shows that this is not a trivial issue from a technical point of view. The key problem is to define foulants and mechanism of their interaction with the membrane. The determination of these factors allows for selection of the best cleaner composition and the conditions of its use. It is also necessary to use an appropriate technological system that will enable the efficient process of the cleaning of the membranes and ensure the maintenance of its conditions [28]. The technological system must also ensure the cleaning process in the shortest time. As a result, in some cases, the CIP is equipped with an "intelligent" measurement and control systems to optimize the CIP process in real time. For economic reasons, it is recommended to avoid oversizing of the CIP system. Practice has shown [13] that the minimal solution is a system comprising two service tanks of appropriate capacity, provided that the individual operations will be precisely planned and carried out in a strict time regime. The easiest way to achieve this is to introduce the fully automated control of the process. The design of CIP requires a thorough study to determine the most favourable conditions and the best system structure for this CIP process. The Institute for Sustainable Technologies – National Research Institute in Radom has developed and built pilot systems such as MF, UF and NF-RO.

The MF system is equipped with tubular ceramic membranes and other systems are in helical polymer membranes. Maintaining their efficiency requires periodic removal of all possible forms of fouling. Because of the necessity to move a CIP, a mobile system has been planned. This mobile system is designed in such a way as to obtain the smallest mass with the centre of gravity located at the intersection of simple connecting points of support (wheels) as low as possible. The virtual model of the designed mobile CIP is presented in Fig. 3. The capacity of the tank and the other elements were chosen to ensure the maintenance of the purity of the MF, UF, and NF-RO systems. Because the system must operate autonomously, it was also equipped with a control system for temperature regulation of the working solution. This system aims to enable the development and implementation of any procedure for CIP in order to clean and sanitize membranes and utility systems.

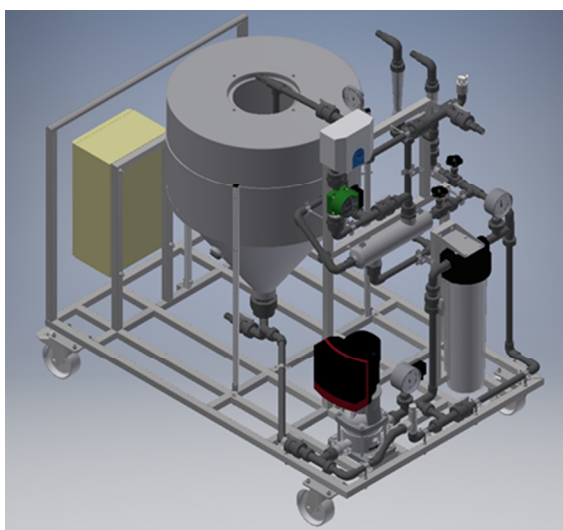


Fig. 3. The virtual model of the designed pilot mobile CIP system

Summary

It can be assumed that fouling is a complex phenomenon that creates considerable difficulties in the implementation of industrial membrane processes by lowering their efficacy. With the current state of the technology, it is not inevitable. In order to reduce its negative effects, some techniques might be used. Currently, the crucial significance for the fouling problem is the chemical cleaning of the membranes (CIP), implemented directly in the phase of membrane system exclusion from the active phase of the filtration process. In order to increase the efficiency of the process and to obtain synergy, while cleaning the membranes, several different reagents with different mechanisms of

action and interacting with various foulants are used. For the cleaning of the membranes loaded with organic and biological fouling in the surface and in pores, alkali solutions are used. Contamination of the membranes, due to scaling, is most commonly removed by acids, often supplemented with chelating agents. In contrast, organic fouling caused by peptides is typically removed by enzymes. Effective execution of CIP procedures requires the use of proper systems, which should be optimized in terms of functionality and the cost-effectiveness of the implemented process.

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Metody i sposoby chemicznej regeneracji membran polimerowych

Słowa kluczowe

Filtracja membranowa, fouling, regeneracja membran, stacja CIP.

Streszczenie

W artykule omówiono podstawowe problemy związane z usuwaniem skutków foulingu, towarzyszącego procesom filtracji membranowej techniką „cross flow”. Mechanizm powstawiania foulingu zależy od charakterystyki filtrowanej cieczy, charakterystyki membrany oraz warunków realizacji procesu filtracji i polega na akumulacji cząstek, koloidów, mikroorganizmów oraz soli na powierzchni i w porach membrany. Jego skutkiem jest zmniejszenie strumienia filtracji, a także pogorszenie charakterystyki retencyjnej membrany. Jednym z najskuteczniejszych, a zarazem kluczowych sposobów ograniczenia foulingu jest optymalne dobranie membrany i warunków procesu do charakterystyki filtrowanej cieczy. Nie rozwiązuje to jednak problemu w całości. Fouling może mieć charakter odwracalny lub nieodwracalny. W niektórych przypadkach, zależnych od rodzaju membran, fouling odwracalny może być usuwany poprzez płukanie zwrotne. W pozostałych niezbędne jest zastosowanie chemicznego oczyszczania membran. Jego efektywność zależy od sposobu działania reagenta myjącego, jego siły jonowej, stężenia oraz pH roztworu myjącego, a także temperatury, ciśnienia oraz czasu i szybkości przepływu cieczy myjącej. Wprowadzenie reagentów ma na celu rozluźnienie struktury i rozpuszczenie depozytu, utrzymanie foulanta w roztworze oraz zapobieganie ponownemu jego osadzeniu na powierzchni membrany. Usprawnienie oczyszczania można uzyskać poprzez poprawę warunków transportu masy produktów reakcji od membrany do roztworu. Najczęściej jest to kontrolowane przez prędkość przepływu kąpieli myjącej, jednakże należy brać także pod uwagę temperaturę i czas mycia, które wpływają na transport masy i szybkość reakcji chemicznych. Wymagane parametry procesu uzyskuje

się dzięki zastosowaniu odpowiednio zaprojektowanej instalacji CIP. Mobilną pilotową instalację CIP opracowano w Instytucie Technologii Eksploatacji – PIB w Radomiu. Jest ona przeznaczona do opracowywania, weryfikacji i optymalizacji procedury CIP w odniesieniu do pilotowych i testowych instalacji membranowych.