FACTORS LEADING TO A DECREASE IN MEMBRANE PERMEABILITY FOR WATER FILTRATION AND WASTEWATER

V.N. Derevjanko, PhD, Dr.Sc., N.P. Nechitaylo, PhD
Pridneprovskaya State Academy of Civil Engineering and Architecture, Ukraine

INTRODUCTION

Liquid separation with membranes is the perspective method in terms of ecology and economy. These methods make it possible not only to concentrate and fractionate fouling in wastewaters, but also to extract valuable components. However, the main factor to slow development of the processes of membrane treatment of water and wastewater is sharp productivity slowdown of membrane with irrational methods of water pre-processing or its absence.

Choice of proper method of separation with membranes and condition of preliminary water preparation makes it possible to prolong filter run and thereby to secure necessary technical and economic performance and ecological specifications. It is necessary to identify factors affecting membrane fouling in order to select appropriate technology of preliminary water preparation. In the previous article the author in details studied the biological fouling of membranes and its properties conditioning tendency to biological fouling. The main factors to affect the fouling rate of membranes are the following:

- nature and concentration of solutes and solvents,
- membrane type,
- pores distribution within size of membrane,
- characteristics of the membrane surface and its material,
- hydrodynamics of a membrane module.

Three main types of resistance are encountered in general case of mass transfer through a membrane: water solution resistance to mass transfer, membrane resistance and resistance of permeate. Resistance of permeate can be neglected in ordinary conditions of membrane separation process and then only two components of resistance remain to consider: water solution resistance (external resistance to diffusion) membrane phase resistance (internal resistance to diffusion). It is exactly the concentration polarization that creates external diffusion resistance. During treatment of natural water and wastewaters with ultrafiltration methods concentration of solutes increases on the membrane surface in comparison with its content in base solution due to transfer of solvent – water through a membrane. This phenomenon is called concentration polarization. Selectivity and specific duty of a membrane decrease due to concentration of soluble substances on the membrane surface. As correlation of concentration of soluble substances on the membrane surface and in the volume of treated solution exponentially rises with increase of specific duty, concentration polarization can be the factor to limit membrane permeability. With elevated concentration of soluble substances by separating surface of a membrane, the latter can partially deteriorate or modify. [1]

1. HUMIC AND FULVIC ACIDS SLUDGING ABILITY

Humic and fulvic acids are organic products, commonly found in water, readily soluble, impart a yellowish to red-brown colour to water. Fouling with humic and fulvic acids is primarily connected with its ability to fix multivalent salts. In the study [2] it is described that the most susceptible membranes to fouling are the ones with positive charge of material. Humic acids form chelates with polyvalent metals that leads to gel layer formation on the membrane surface.

In the study Schafer A.I.with co-authors [3] described the role of humic acids in the process of gel and concentration polarization. Using any kind of materials for membranes gave no opportunity to avoid irreversible consequences of sludge formation within high concentration of hardness salts. The key factor of formation of gel layer on the membrane surface is humic acids presence in solution. These researches are well correlated with the ones in the study [2].Schafer A.I. with co-authors discovered that complexes of calcium and humic acids form thick sludge on the membrane surface that also results in considerable flux decline of treated water

.Gel layer formation speeds up with rise of pH. At the same time concentration of humic acids increases in premembrane layer. Humic and fulvic acids have high molecular weight that promotes gel formation on the membrane surface due to low diffusion rate. Formation of layers of organic and inorganic fouling one above the other on the membrane surface has been studied in the research [4]. It was discovered that during formation of sludge layer conditioned with Fe-Si the main role is played by the reduction of membrane hydrophobic properties due to humic acids. In the study [4] it is showed that hydrophilic membranes are less susceptible to sludge formation including with colloids of humic acids. In the study [3]it is showed that hydrophobic membranes are susceptible to the heaviest formation of sediment of different kind on its surface. Also authors [5] compared sludge formation on the membrane surface in the conditions with and without sediment formative mineral salts. These researches led to the conclusion that with salts presence sludge formation is more rapid. These researches show that during the membrane treatment with the presence of humic acids water must be with minimal amount of hardness salts and low pH.

All these conclusions are corroborated in the study Tu S-C. [6] , that reaffirm membranes with negative surface charges and greater hydrophilicity are less susceptible to sludge formation due to fewer interaction between polar groups on the membrane surface and chemical substances of organic compounds.

2. EFECT OF INORGANIC COMPONENTS ON INCREMENT IN MEMBRANE RESISTANCE

Sahachaiyunta P. and colleagues [7] examined the influence of silicate solutions on the fouling of the reverse osmosis membranes in the presence of minute amounts of various metal cations such as barium, manganese, nickel and iron that are present in industrial circulating water and wastewaters. Experimental results showed that iron is the most active from the view of sludge forming.

If such a water is exposed to air or is chlorinated, Fe^{2+}, Mn^{2+} and sulfide are oxydized to $Fe^{3+,}$ Mn^{3+} and elemental sulfur, respectively, which form insoluble colloidal hydroxides and elemental sulfur as shown in the following equations :

$$4Fe(HCO_3)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 + 8CO_2$$

$$4Mn(HCO_3)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_2 + 8CO_2$$

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

Iron fouling occurs more frequently than manganese fouling, since iron is present in the raw waters more abundantly than manganese and the oxidation of iron occurs at a much lower pH

3. EEFFECT OF PROTEINS AND COLLOIDS

Surface processes occurring during removing of the proteins are similar to film-formation processes described in the study [3]. For example, when filtering bovine serum albumin clogging of channels takes place with the formation of layer on the membrane surface. Further simple non-aggregated protein affiliates to film-formation process with forming of disulfide linkages that results in increase in membrane resistance. The researchers developed a mathematical model describing this dual mode process. In the study Yiantsios S. G. and Karabelas S. investigated the role of formation of stable aggregate films on the membrane surface with formation of colloids. Yiantsios S. G. and Karabelas S. showed that in the process of film-formation on the surface of the reverse osmosis and ultrafiltration membranes not only water velocity above a membrane, transmembrane pressure, size of particles and its quantity play an important role, but also colloids'resistanceto mechanical impact. The authors proved that standard tests carried out to determine fouling rate of membranes and also most used mathematical models do not allow defining the necessary parameters to a high precision. One of the main conclusions of this study showed that use of acids in order to prevent sludging of mineral impurities can result in formation of colloid film on the membrane surface. The explanation for this is to be that lowering of pH reduces the negative charge of colloids, causing more sludge formation on the membrane surface.

Colloidal fouling has also been modelled in the study [8]. Authors of the study [9] compared ultrafiltration and nanofiltration membranes fouling with interaction with various organic substances. This way colloids cause pore blockage of hydrophobic membrane dueto its hydrophobic properties. In particular, it was defined that ions of polysaccharides and amino sugars were found to play an important role in film formation.

Such dissolved natural polymer substances as proteins and polysaccharides are among the heaviest contaminants of ultrafiltration and nanofiltration and reverse osmosis membranes. They are found in natural waters and wastewaters and are the waste

product of microorganisms. These substances have considerable capacity to block the membrane surface as they can accumulate not only on the membrane surface but also enter the membrane pores. This was found by the authors during the tests of membrane bioreactors [10]. Proteins, polysaccharides and polysaccharide-like compounds were found to be the main cause of fouling formation on the membrane during filtration of biologically treated wastewaters [11]. Polysaccharides and proteins in water are found as high-molecular soluble compounds and also as colloidal forms.

As film-forming material, polysaccharides are neutral in character, they interact with the membrane surface either through hydrogen bonding or as colloids, so that results in the formation of multi-level gellayer.

Due to its amphoteric property protein interact with the membrane surface by forming a layer of colloidal gel [12]. Characteristics of soluble polymers and the degree of microbial adhesion to the membrane surface vary with species, the phase of sludge formation on the membrane surface, water chemistry, pH and temperature.

CONCLUSIONS

Membranes fouling is one of the factor that brings down appeal of this method of water and wastewater filtration.

For successful membrane ultrafiltration technology performance periodic sanitation or pretreatment is required.

One of perspective development path is using membranes, that have bactericidal properties and their design should prevent biofilm formation.

The most perspective development path is adding modifying components to membranes material or inoculating of modifying material with antifouling properties.

REFERENCES

1. ***Kocharov P.G.*** *Teoreticheskie osnovy obratnogo osmosa. Uchebnoe posobie. M: RXTU im. D.I. Mendeleeva, 2007, 143 s.*

2. ***Nystrom M., Ruohomaki K., Kaipa L.,*** *Humic acid as a fouling agent in filtration. Desalination. 106, p.78-86, 1996.*

3. ***Schafer A.I., Martrup M., Lund Jensen R.*** *Particle interactions and removal of tracecontaminants from water and wastewaters Desalination 147, p. 243-250, 2002.*

4. ***Khatib K., Rose J., Barres O., Stone W., Bottero J-Y., Anselme C.*** *Physicochemical study of fouling mechanisms of ultrafiltration membrane on Biwa Lake (Japan), J. Membrane Science 130, p. 53-62, 1997.*

5. ***Kabsch-Korbutowicz M., Majewska-Nowak K., Winnicki T.*** *Analysis of membrane fouling in the treatment of water solutions containing humic acids and mineral salts. Desalination 126, p. 179-185, 1999.*

6. ***Tu S-C., Ravindran V., Den W., Pirbazari M.*** *Predictive membrane transport model for nanofiltration processes in water treatment, AIChE Journal 47(6), p.1346-1362, 2001.*

7. ***Sahachaiyunta P., Koo T., Sheikholeslami R.*** *Effect of several inorganic species on silica fouling in RO membranes. Desalination 144, p.373-378, 2002.*

8. ***Bacchin P., Aimar P., Sanches V.,*** *Model of Colloidal Fouling of Membranes. AIChE Journal 41(2), p.368-376, 1995.*

9. ***Jarusutthirak C., Amy G., Croue J-P.*** *Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. Desalination 145, p. 247-255, 2002.*

10. ***Meng, F.; Chae, S.-R.; Drews, A.; Kraumer, M.; Shin, H.-S.*** *Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane materials. Water Res. 43, p. 1489–1512, 2009.*

11. ***Nguyen, T., Fan, L., Roddick, F.A., Harris, J.L.*** *A comparative study of microfiltration and ultrafiltration of activated sludge-lagoon effluent. Desalination, 236, p. 208–215, 2009.*

12. ***Amy, G.*** *Fundamental understanding of organic matter fouling of membranes. Desalination, 231, p. 44–51, 2008.*

Recommended for publication: 18.09.2014.