

MAŁGORZATA KABSCH-KORBUTOWICZ*

APPLICATION OF HYBRID MEMBRANE PROCESSES IN NATURAL ORGANIC MATTER REMOVAL FROM WATER

Natural organic matter (NOM) is a diverse mixture of organic compounds that are widespread in both surface and ground waters. NOM is not of direct concern in drinking water, but it may affect its quality and influence the course of water-treatment processes, and that is the reason for removing those substances. As either conventional or membrane-based processes have many disadvantages in the case of NOM removal, combination of those processes must be applied to reach the main goal, i.e. potable water of the highest quality. Hybrid processes based on coagulation or activated carbon adsorption and micro-filtration or ultrafiltration are very effective in NOM removal during water treatment.

1. NATURAL ORGANIC MATTER CHARACTERISTICS

Natural organic matter (NOM) is a diverse mixture of organic compounds that are widespread in both surface and ground waters. Those substances range from macromolecules to low-molecular weight compounds, such as simple organic acids and short-chained hydrocarbons.

Based on filtration procedure organic matter in waters can be divided into dissolved (DOC) and particulate (POC) organic carbon substances, but there is no strict boundary between these fractions. The dissolved and particulate fractions overlap the colloidal fraction, which consists of suspended solids that are operationally considered solutes. Generally, DOC occurs in greater abundance than POC, accounting for approximately 90% of the total organic carbon of most waters.

DOC fraction consists of multiple components such as amino acids, proteins, humic substances (HS), etc. Fractionation of DOC matter into different groups is given in figure 1.

Aquatic humic substances generally comprise one-third up to one-half of carbon dissolved in water, thus are the dominant fraction of NOM in waters. Taking into

* Wrocław University of Technology, Institute of Environment Protection Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, e-mail: malgorzata.kabsch-korbutowicz@pwr.wroc.pl

consideration solubility of different fractions of humic matter and their molecular weight, three main groups of those substances were established [2], [3]:

- Humic acids (HA) – the fraction of humic substances insoluble in water in acidic medium (pH < 2) but soluble at higher pH values; the major extractable component of soil humic substances; dark brown to black in colour; in their chemical structure, phenol groups and long-chain fatty acids prevail; average molecular weight > 2000 Da.

- Fulvic acids (FA) – the fraction of humic substances soluble in water at all pH values; they remain in solution after removal of humic acid by acidification; light yellow to yellow-brown in colour; average molecular weight < 2000 Da; the average length and diameter of molecules is 60 and 2 nm, respectively.

- Humins – the fraction of humic substances neither soluble in water at any pH value nor in alkali; humins are black in colour; they consist of bitumen, coupled with fatty acids and humic acids.

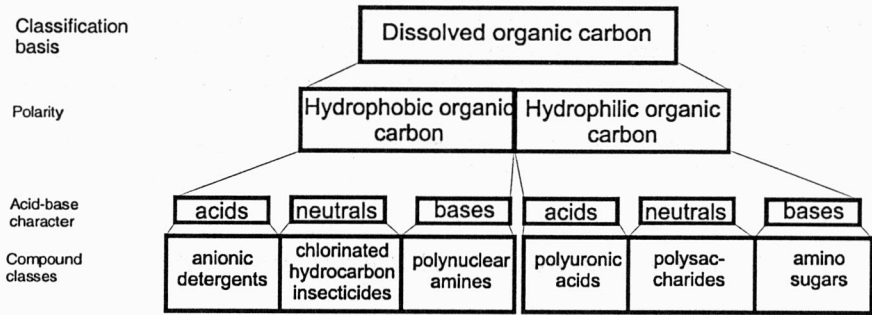


Fig. 1. Fractions of DOC matter [1]

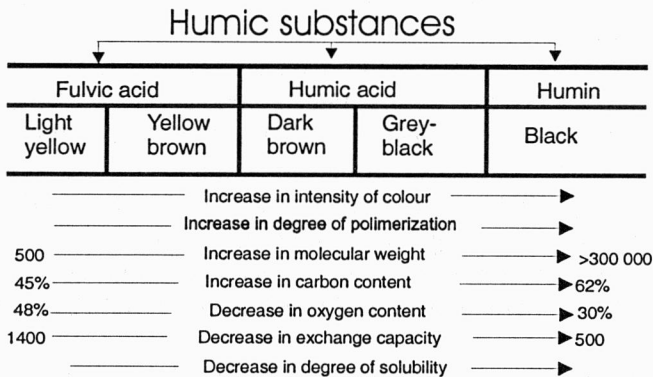


Fig. 2. Chemical properties of humic substances [4]

Comparison of chemical properties of the fractions of humic substances is presented in figure 2.

THURMAN [5] reported that surface water DOC contains about 45% of FA, 5% of HA, 25% of low-molecular weight acids, 5% of neutral compounds, 5% of bases and contaminants; however, the quantitative amount of each fraction is case specific.

According to MAYBACK [6] the mean content of NOM in streams of the world is 5.75 g C/m^3 . Its highest content is found in the sub-arctic zone (10 g C/m^3), and the lowest – in the temperate and arid zones (3 g C/m^3). In the last decades, due to acid rains and variations in climate, a constant increase of NOM concentration in waters is observed.

NOM is not of a direct concern in drinking water, but it may affect its quality because it increases the disinfectant and coagulant demand, providing substrates for disinfection by-products (DBP) formation, forms complexes with heavy metals and organic micropollutants, and enhances microbial regrowth in distribution system. Figure 3 shows the influence of NOM on various aspects of water quality.

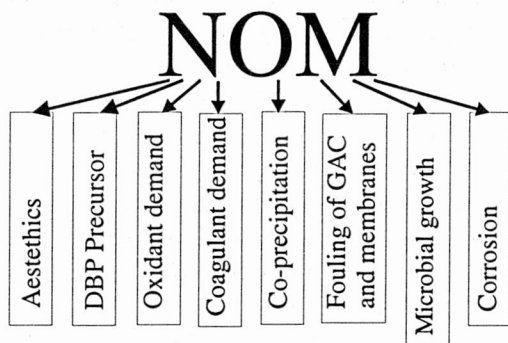


Fig. 3. The influence of NOM on water quality issues [7]

In the EU Directive No. 98/83/EEC related to the quality of water intended for the human consumption, three global parameters characterising organic matter amount are defined: colour, TOC and permanganate oxidability. No limit was fixed for colour; it must be acceptable to consumer and no anomalous change must occur. For TOC, no anomalous change must occur. The value of permanganate oxidability must not exceed $5 \text{ g O}_2/\text{m}^3$. According to Polish regulations (Directive of Minister of Health of 19.11.2002) colour and permanganate oxidability of drinking water may not exceed 15 g Pt/m^3 and $5 \text{ g O}_2/\text{m}^3$, respectively.

2. NATURAL ORGANIC MATTER REMOVAL

Due to unprofitable influence of NOM on water quality, it must be removed from potable water. Among different physicochemical processes applied in water treatment, coagulation, activated carbon adsorption and membrane separation are considered to be most effective.

Chemical coagulation with aluminium or iron salts has traditionally been used in water treatment for turbidity removal. This process is also, to a certain extent, effective in NOM elimination. Aluminium or iron coagulation has been shown to remove certain fractions preferentially – humic (hydrophobic) NOM and higher-molecular weight NOM are more effectively removed than their counterpart fractions [8]. Some waters with a dominance of nonhumic or low-molecular weight NOM (or both) are unsusceptible to coagulation allowing NOM removal [9]. Certain researchers [10] reported that a decrease in the value of ultraviolet absorbance (UVA) was more significant than a decrease in the concentration of dissolved organic carbon, which indicated that aromatic (humic) NOM was preferentially removed. Coagulation efficiency can be influenced by the type of coagulant used, the coagulant dosage, pH, ionic strength, temperature and other factors. Moreover, a portion of the alum added to water is not removed during treatment and remains as residual aluminium in the treated water [11]. The presence of aluminium in treated water has been considered for many years to be undesirable, because we have grounds to suspect that it is one of the causes of neurological diseases (i.e. Alzheimer's disease).

Activated carbon adsorption is commonly used in water treatment when dissolved organics must be removed. The process is very effective in taste and odour control as well as in pesticide separation. LAINÉ et al. [12] reported that powdered activated carbon was most effective in separation of humic substances of MW < 1000 D. The experiments performed by de WALLE and CHIAN [13] revealed that activated carbon efficiently separated organic substances of MW ranging from 100 to 10000 D. In the same time, hydrophilic substances were removed in 30%, while hydrophobic – in 80%. Generally, smaller NOM molecules are adsorbed more readily than larger ones because pore blockage of large molecules can limit the sites accessible to adsorption [14]. Adsorption of NOM on activated carbon is strongly influenced by pH, water quality, carbon properties and process parameters.

Pressure-driven membrane processes are more frequently used in drinking water treatment. This can be attributed to more stringent water quality regulations, a decrease in adequate water resources and an emphasis on water reuse. Additionally, due to advances in membrane technology, costs of membrane systems decreased, promoting their use as an alternative to conventional treatment methods.

Microfiltration (MF) and ultrafiltration (UF), due to relatively big pores, have been employed primarily for removal of microorganisms and particles from waters. MF is effective in turbidity and particulate organic matter removal as well as bacteria, protozoans and algae. UF can also be used for removing viruses and some of the organic matter particles. Efficiency of NOM separation by UF membranes is influenced by many factors, i.e.: NOM character, molecular weight distribution, water pH and ionic strength, membrane cut-off. Generally UF is effective in high-molecular weight fraction of NOM. 60% of the operating UF plants treat water with low total organic carbon (TOC), since TOC rejection is usually below 20% [15].

The processes of nanofiltration (NF) and reverse osmosis (RO) are capable of separating almost all NOM particles from water. As it was demonstrated by many authors, e.g., [16], [17], [18], removal of TOC and trihalomethane (THM) as well as haloacetic acid (HAA) precursors varies from 60 to more than 99%. The variation in removal of disinfection by-products precursors is dependent (especially in NF) upon a number of factors, including the type of membrane, the raw water quality and the conditions of membrane system operation.

CHELLAM et al. [17] compared the effectiveness of separation of THM precursors in different processes and found that MF removed less than 25% of DBP precursors, conventional treatment – 63%, while NF > 95% (figure 4).

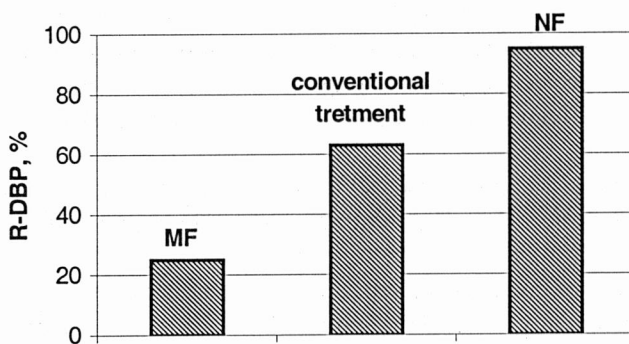


Fig. 4. Effectiveness of disinfection by-products removal by microfiltration, conventional treatment and nanofiltration [17]

Membrane filtration processes are prone to fouling, with a progressive decline in membrane flux with time because of the accumulation of material retained at the membrane surface. NOM is believed to play a major role in the fouling process. Permeate flux occurs, firstly, due to a gel formation when the solubility limit is exceeded in the concentration polarisation layer, or, secondly, because of adsorption.

Among many methods applied to decrease membrane fouling, combination of membrane system with other techniques seems to be very promising. Integration of NF and RO with conventional treatment processes or with MF/UF will result in maintaining the permeate flux at a constant level and in fouling retardation. As neither MF nor UF can ensure high quality of treated water for high-organic content in surface source waters, MF or UF could be combined with other processes. Integration of MF or UF with conventional process will allow us to apply those low-pressure processes in effective separation of NOM and to decrease membrane fouling.

3. HYBRID MEMBRANE PROCESSES

Integration of membrane separation with other physicochemical technique sets in motion hybrid membrane process. Based on LIPNIZKI's at al. definition [19] *hybrid process* is a process package consisting of generally different unit operations, which are interlinked and optimised to achieve a predefined task. Hybrid processes are more than just integrated processes. A true hybrid process makes it possible to circumvent the technical limitations (generally thermodynamic) that are imposed on at least one of the component unit operations. A weaker definition includes economic considerations as well as technical ones.

Two general types of hybrid processes can be distinguished:

- S (separation) type – hybrid process consisting of processes which are “essentially performing the same function”. The component parts of this type of hybrid process serve a common purpose (e.g. division of feed components into A and B). Furthermore, the common purpose could not be achieved by either component alone.

Within the frame of the type S two solutions can be taken into consideration:

1. An interlinked interdependent combination achieving a binary split, which is referred to as S1 hybrid process.

2. A combination of consecutive separation processes achieving a split that neither could achieve (technically or economically) alone. This is referred to as S2 hybrid process. Hybrid processes of the type S are presented in figure 5.

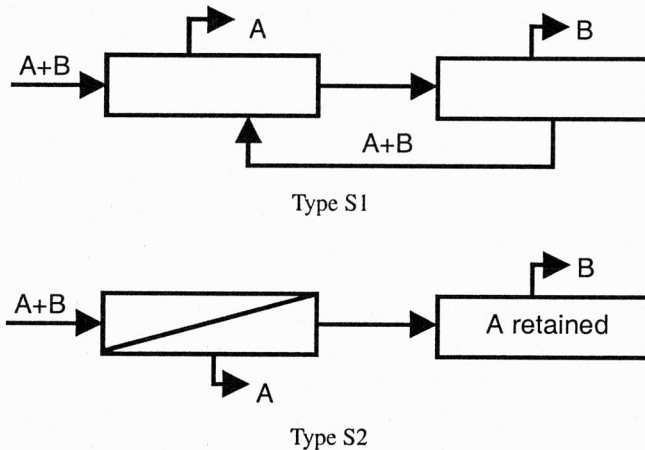


Fig. 5. Hybrid processes of the type S [19], [20]

- R (reactor) type – hybrid process which is an offspring of two different processes. This type of processes includes the combination of reactor and separation proc-

esses. In such hybrid processes, a membrane process removes either the product of a reaction from the reactor/bioreactor (R1 type) or by-product (R2 type). Hybrid processes of the type R are presented in figure 6.

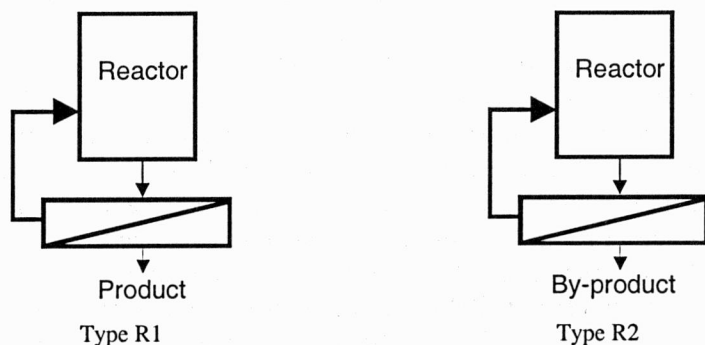


Fig. 6. Hybrid processes of type R [19], [20]

In the system of type R, generally two process designs can be adopted – the first one with external membrane unit, and the second one with the membrane unit directly integrated with reactor (figure 7).

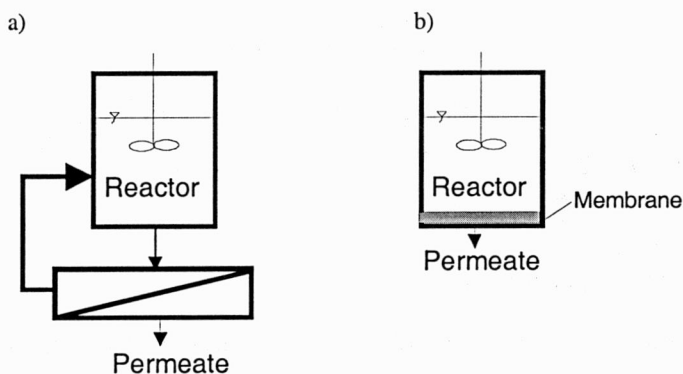


Fig. 7. Basic layouts of the hybrid processes of type R:
a) with external membrane unit, b) with internal membrane unit [19]

4. HYBRID PROCESSES BASED ON PRESSURE-DRIVEN MEMBRANE TECHNIQUES IN WATER TREATMENT

Advances in membrane technology and tough water quality regulations are making membranes more desirable treatment option. Especially due to the fact that they easily fit source water quality, site limitation and operator's skill level.

As was mentioned earlier, the main problem in exploitation of the membrane systems for water treatment is the decrease of permeate flux observed with time. The limitation of this disadvantageous phenomenon requires incorporation of foulant removal into water treatment train. The water treatment train that can be applied includes:

- conventional treatment followed by NF or RO,
- MF or UF followed by NF or RO.

MF or UF can be employed as stand-alone processes in surface water treatment; however they allow a limited removal of NOM. To obtain a substantial NOM removal, pretreatment is indispensable. Water pretreatment can be done either by:

1. Direct addition of chemicals before the membrane treatment.
2. Additional of chemicals into the water in a membrane unit.
3. Additional unit process of NOM removal prior to the membrane process.

In the last scenario, MF or UF might be implemented in existing water treatment plants, improving final water quality.

Of different processes the best result of NOM removal will be obtained after integration of membrane processes with coagulation or PAC adsorption (figure 8).

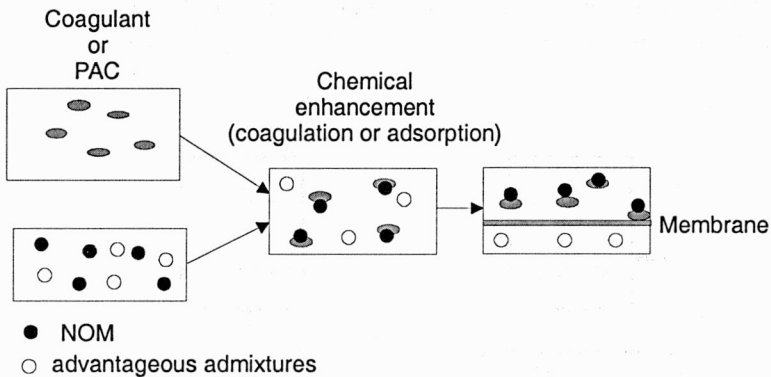


Fig. 8. Combination of coagulation or PAC sorption with membrane separation in water treatment

Application of hybrid process composed of coagulation and MF or UF results in higher NOM removal and lower coagulant doses [21]–[23]. Those effects are obtained because conditions of coagulation and coagulant selection could be optimized for the purpose of NOM removal as particle removal is assured. Integration of coagulation with membrane separation allows us to achieve two main goals, very important in membrane technology: optimisation of process hydrodynamics and modification of the components of the feed stream.

Combination of PAC adsorption with MF or UF is also very effective in NOM removal [15], [24], [25]. It was proved that such a hybrid system is very effective in separation of low-molecular weight NOM fraction, which cannot be removed by MF

or UF alone. PAC cake, formed on the membrane, prevented the membrane surface from NOM adsorption/deposition and the pores from plugging, thus stabilised permeate flux.

5. CONCLUSIONS

Natural organic substances are the common component of natural waters. They may strongly affect the water quality, therefore have to be separated from water intended for consumption. As either conventional or membrane-based processes have many disadvantages, in the case of NOM removal, combination of those processes must be applied to reach the main goal, i.e. potable water of the highest quality. It was demonstrated that hybrid processes based on coagulation or activated carbon adsorption and microfiltration or ultrafiltration are very effective in NOM removal during water treatment.

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ZASTOSOWANIE HYBRYDOWYCH PROCESÓW MEMBRANOWYCH DO USUWANIA NATURALNYCH SUBSTANCJI ORGANICZNYCH Z WODY

Naturalne substancje organiczne występujące powszechnie w wodach powierzchniowych i podziemnych stanowią mieszaninę wielu związków organicznych. Nie stanowią one bezpośredniego zagrożenia, ale ponieważ mogą wpływać na przebieg procesów uzdatniania wody oraz na jej końcową jakość, więc muszą być z niej usuwane. Zarówno konwencjonalne procesy uzdatniania wody, jak i techniki membranowe mają wiele wad, dlatego integracja tych metod, czyli zastosowanie procesów hybrydowych, umożliwia osiągnięcie zakładanego celu, tzn. uzyskanie wody o najwyższej jakości. Procesy hybrydowe, będące połączeniem koagulacji lub adsorpcji na węglu aktywnym oraz mikrofiltracji lub ultrafiltracji, pozwalają efektywnie usuwać naturalne substancje organiczne z wody.