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## APPLICATION OF IN-LINE COAGULATION/ULTRAFILTRATION PROCESS IN WATER TREATMENT

An in-line coagulation (without sedimentation step)/ultrafiltration process was investigated. An attempt to establish the influence of aluminium-type coagulant and its dose as well as the membrane type and water pH on permeate flux and final water quality was undertaken. Three aluminium-based coagulants, i.e., alum, polyaluminium chloride and sodium aluminate, were tested on 30 kDa ultrafiltration membranes made of regenerated cellulose and polyethersulfone. In the process investigated, alum or polyaluminium chloride used as coagulants proved to be more efficient in the removal of NOM (natural organic matter) from treated water and in reduction of membrane fouling, compared to ultrafiltration. When coagulation was carried out in the conditions of charge neutralisation (low pH) the membrane susceptibility to fouling was lower than that in conditions of sweep flocculation. In alkaline solution, both membranes tested were strongly blocked by NOM particles and anionic products of coagulant hydrolysis.

### 1. INTRODUCTION

In membrane water-treatment processes, we deal with two major problems, i.e., the quality of the produced water, which is related to the rejection of target solutes, and the membrane fouling leading to permeate flux decline and consequent reduction in the efficiency of the filtration process. Nowadays we observe an extensive use of ultrafiltration for treatment of water. However, the economic use of membrane filtration systems is often limited by fouling, which increases drops in the applied pressure and cleaning frequencies, and the associated decrease in the removal efficiency is observed. Currently, the most common method of preventing the fouling is pretreating the influent necessary for membrane process in conventional unit processes. A variety of pretreatment processes for UF have been investigated including coagulation, activated carbon adsorption, adsorption on iron oxides or other pre-formed settleable solid phases, or ozonation.

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Coagulation, as a pretreatment process, can substantially reduce the concentration of natural organic substances found in raw water; thus, it can decrease the membrane potential for fouling and enhance membrane rejection. Ordinary coagulation, one of the common modes of this process, consists in coagulation and sedimentation being carried out in separate tanks ahead of the membrane. However for small membrane systems such complex water treatment train is not advisable and many works is going on simplification of membrane-based waterworks. One of the solutions is application of in-line coagulation. "In-line coagulation" means coagulation before membrane filtration, without a sedimentation or pre-filtration step [1], [2].

GUIGUI et al. [2] have reported that when coagulation is performed in well established conditions, larger flocks are formed and this reduces fouling during membrane filtration. Large flocks are not adsorbed in the membrane pores and form more porous cake on the membrane surface. However the structure of the cake formed by the flocks of coagulant depends on the coagulation conditions. LEE et al. [3] stated that the cake produced under sweep coagulation conditions (pH 6.5–8) was more compressible than that formed under conditions of charge neutralisation (pH < 5.5). It is also supposed [4] that flocks of coagulant should reach certain size prior to their membrane filtration, in order to avoid pore clogging. LAHOUSINE-TURCAUD et al. [5] found that coagulated humic substances (> 80  $\mu\text{m}$ ) did not deposit on microfiltration membrane surface.

The objective of the study was to investigate the influence of pre-coagulation with 3 types of aluminium-based coagulants carried out as an in-line process with ultrafiltration on the effectiveness of NOM (natural organic matter) elimination and membrane fouling. The influence of coagulant type, its dose and membrane type as well as the water pH on membrane fouling and NOM elimination was analyzed.

## 2. MATERIALS AND METHODS

Experiments were carried out on a model solution prepared from natural water flowing out from The Great Batorow Peatbag (southwest Poland) and dechlorinated tap water. Properties of the feed water are presented in the table.

Table 1

The feed water properties	
Parameter	Value
Colour, $\text{g}/\text{m}^3$	$68 \pm 6$
Absorbance of 254 nm, $\text{cm}^{-1}$	$0.425 \pm 0.007$
TOC, $\text{g C}/\text{m}^3$	$9.43 \pm 0.41$
pH*	$7.7 \pm 0.1$

\* pH of the solution tested ranged from 5 to 10 and was adjusted by addition of 0.1 M NaOH or HCl.

Three aluminium-based coagulants, i.e., alum ( $\text{Al}_2(\text{SO}_4)_3$ ),  $\text{NaAlO}_2$  and polyaluminium chloride (PAC 10WA), provided by Złotniki Chemical Co. have been applied. The coagulation was carried out at the aluminium doses equal to 1.79, 2.87 and 3.59  $\text{g Al/m}^3$ , which corresponded to 25, 40 and 50  $\text{g alum/m}^3$ . The samples were stirred rapidly for 3 min, followed by 20 min flocculation. Then the solution (with flocs of hydrolyzed coagulants) underwent an ultrafiltration process. In this study, Millipore ultrafiltration membranes of 30 kDa cut-off made of polyethersulfone (PES) and regenerated cellulose (C) were used. The operating pressure was 0.1 MPa. The coagulation/ultrafiltration set-up is given in figure 1.

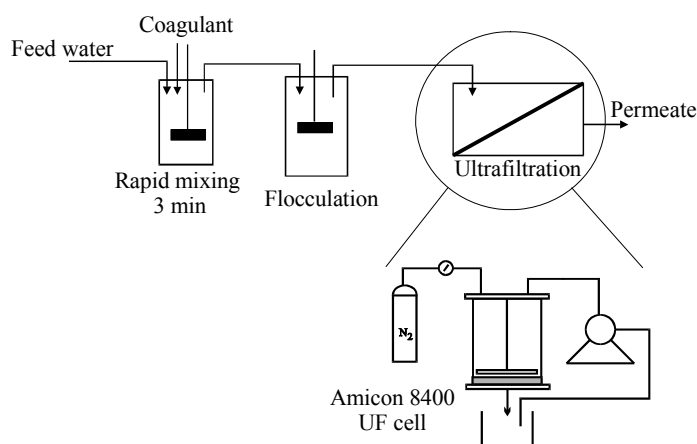


Fig. 1. Schematic diagram of the in-line coagulation/ultrafiltration process

### 3. RESULTS AND DISCUSSION

#### 3.1. NOM REMOVAL

Figure 2 shows the effects of coagulant type and its dose on the removal of TOC, colour, and  $\text{UV}_{254}$ . As can be inferred from the results presented, the application of alum or polyaluminium chloride in the pretreatment step resulted in more efficient removal of organic matter, while the use of sodium aluminate did not affect the separation of organic substances. Similar results were obtained when water was pretreated by standard method, i.e., samples after flocculation, prior to ultrafiltration, underwent sedimentation [10]. It can be easily seen that even the lowest doses of coagulants increased the effectiveness of NOM removal. In the case of both membranes tested and

all doses of alum and polyaluminium chloride, the retention coefficients of  $UV_{254}$  were much higher and colour intensities much greater than the degree of TOC removal. As reported in the literature [7], [8], during coagulation higher molecular weight and more hydrophobic fractions of NOM are preferentially removed. These fractions have generally higher  $UV_{254}$  absorbance and colour intensities.

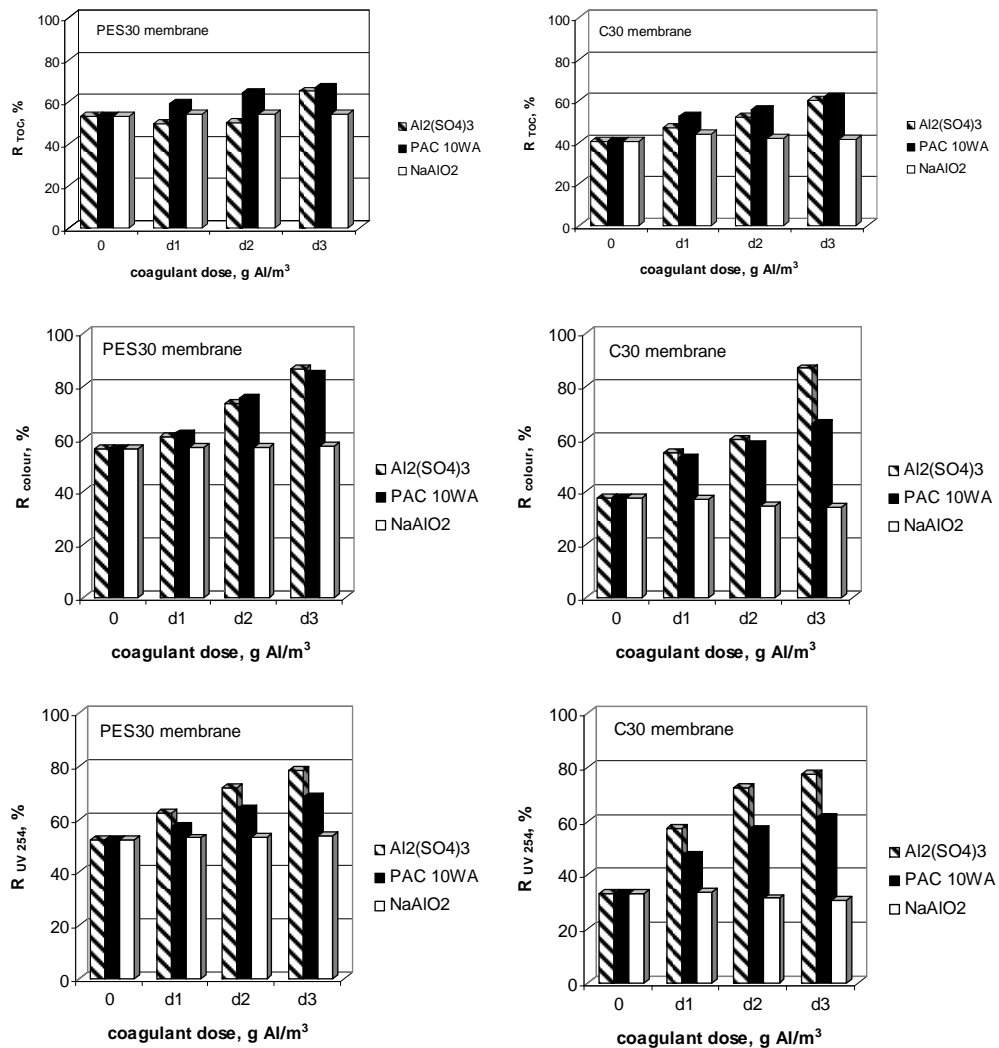


Fig. 2. Effect of coagulant type and dose on the efficiency of NOM removal in the in-line coagulation/ultrafiltration process with PES and C membranes ( $d_1 = 1.79 \text{ g Al/m}^3$ ,  $d_2 = 2.87 \text{ g Al/m}^3$ ,  $d_3 = 3.59 \text{ g Al/m}^3$ )

Analyzing the influence of the solution pH on the efficiency of NOM removal (figure 3) it can be easily seen that an increase in pH is responsible for an increase in the retention of organic substances in independent ultrafiltration process. At pH values lower than the value of ionization constant of molecules of humic substances, the latter take a compact coiled conformation owing to the suppression of the dissociation of carboxylic and phenolic groups. This diminution in the size of organic molecules in acidic medium reduces their retention by membranes. At a higher pH the ionization of functional groups of NOM molecules takes place, resulting in expansion of organic substances particles due to electrostatic repulsion between segments of macromolecules. Electrostatic repulsion between NOM particles and membrane polymer increases also the effectiveness of water treatment. Polyethersulfone membranes show a significant negative zeta potential at  $\text{pH} > 2.4$ ; this potential increases along with an increase in pH [12]. As reported by TAKAGI et al. [13] cellulose membrane itself has no fixed charge. An effective membrane charge is due to adsorption of anions. Anions are more readily dehydrated and adsorbed on a membrane surface in an aqueous solution irrespective of whether the surface is uncharged or positively charged. For both the membranes investigated an increase of water pH resulted in an increase of their negative charge, thus promoting an electrostatic repulsion of charged organic macromolecules.

In an in-line coagulation/ultrafiltration, an increase of pH resulted in a decrease of process effectiveness. In acidic medium, where NOM coagulation due to charge neutralization dominates, big flocks of hydrolyzed coagulants with adsorbed NOM molecules are formed. They are very effectively retained by UF membranes. An increase of pH, especially above 8, allowed the anionic products of the hydrolysis of coagulants to be formed, thus the coagulation of NOM particles was impossible. At pH 10, the observed effect of NOM separation due to ultrafiltration and due to integrated process was almost the same.

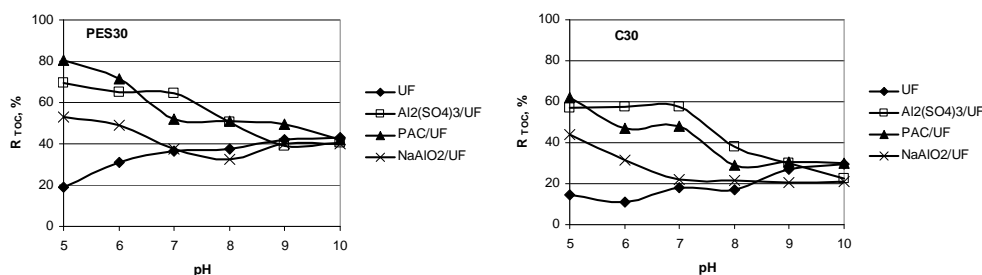


Fig. 3. The influence of pH on the changes in TOC retention coefficient in the in-line coagulation/ultrafiltration process with PES and C membranes (coagulant dose:  $3.59 \text{ g Al/m}^3$ )

## 3.2. MEMBRANE FOULING

The experimental results obtained during in-line-coagulation of water containing NOM or its ultrafiltration through C and PES membranes (figure 4) showed that membrane fouling was considerably reduced compared to untreated water. Under most experimental conditions, the normalized permeate flux through C membranes was slightly higher than that through PES membranes.

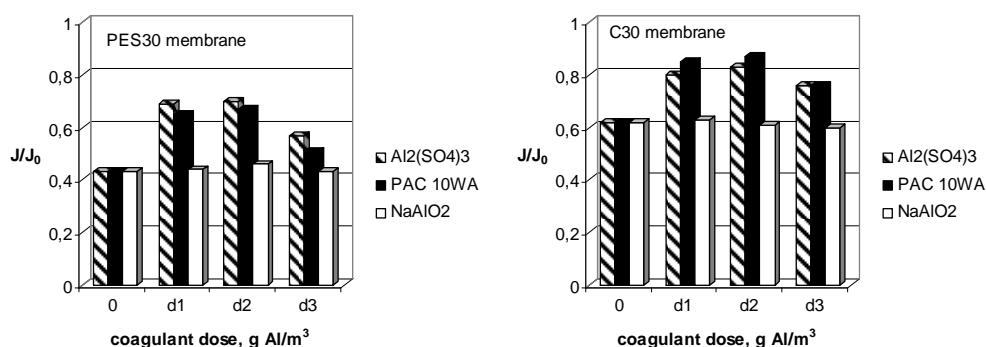


Fig. 4. The influence of coagulant type and its dose on flux decline in the in-line coagulation/ultrafiltration process with PES and C membranes ( $d_1 = 1.79 \text{ g Al/m}^3$ ,  $d_2 = 2.87 \text{ g Al/m}^3$ ,  $d_3 = 3.59 \text{ g Al/m}^3$ , natural pH)

Material hydrophobicity is a significant factor in the membrane fouling. The contact angles of 40 and 60 degrees are typically reported for regenerated cellulose membranes and polyethersulfone membranes, respectively [6]. As PES membranes are more hydrophobic than C ones, their tendency towards fouling is stronger.

The effect of water pH as well as coagulant and membrane types on an in-line coagulation/ultrafiltration process performance was investigated by analyzing the changes in relative permeate flow. As can be inferred from data presented in figure 5, an increase of water pH is responsible for the decrease of membrane permeability. The best results, i.e., the lowest membrane fouling, were obtained at pH 5, where the contribution of charge neutralization to NOM coagulation was the greatest. With an increase of water pH, a decrease of membrane flux was observed. At pH approaching 7 the mechanism of a sweep coagulation is dominant and a sharp decrease of membrane permeability is observed. LEE et al. [3] found that aluminium flocks formed by sweep coagulation are more compressible than the flocks formed by charge neutralization, thus the resistance of the cake formed on membrane surface is stronger. This may explain the results obtained. At pH above 8, due to formation of negatively charged products of coagulant hydrolysis, anionic NOM particles are not coagulated, thus aluminium derivatives may penetrate membrane pores and block them. These results are consistent with those obtained by CHOI and DEMPSEY [1] as well as SOFFER et al.

[11], who have reported that the resistance of membrane to filtration was lower in charge neutralisation coagulation conditions than in the sweep floc conditions.

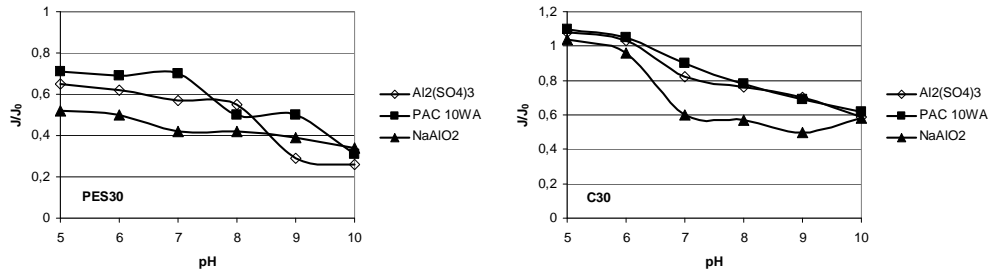


Fig. 5. The influence of water pH on relative membrane flux in an in-line coagulation/ultrafiltration process (coagulant dose of  $3.59 \text{ g Al/m}^3$ )

In order to analyze whether the time of flocculation influences the membrane performance in an in-line coagulation/ultrafiltration process, water sample after rapid mixing with coagulant followed by the flocculation carried out for different times underwent ultrafiltration. As  $NaAlO_2$  was not an effective coagulant in treating water solution, these experiments were done only for alum and polyaluminium chloride. The results presented in figure 6 confirm the theory put forward by other researchers that too small flocs formed during rapid mixing may cause pore blocking. The main reason for flocculation is production of big, agglomerated flocs of destabilised NOM particles and products of coagulant hydrolysis. As the time of flocculation is not long enough, very small suspended particles are formed. They may penetrate the membrane pores, or form dense cake on membrane surface resulting in membrane flux decline. This effect was not observed by HOVE and CLARK [9], who found that ultrafiltration membranes were not prone to fouling by not fully formed flocs. They observed this phenomenon for microfiltration membranes only.

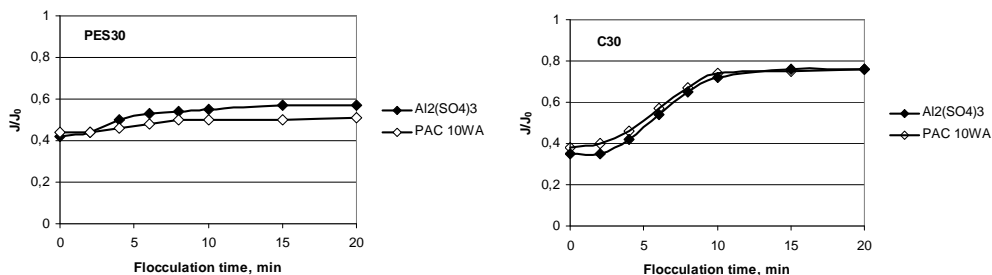


Fig. 6. The influence of flocculation time on membrane relative permeability in an in-line coagulation/ultrafiltration process (coagulant dose of  $3.59 \text{ g Al/m}^3$ , natural pH)

#### 4. CONCLUSIONS

In the phase of water treatment, an in-line coagulation/ultrafiltration process with the use of alum or polyaluminium chloride allowed an improved removal of NOM from treated water and reduced membrane fouling. When coagulation was carried out in the conditions of charge neutralisation, membrane susceptibility to fouling was lower than that in sweep flocculation. In alkaline solution, both membranes tested were strongly blocked by NOM particles and anionic products of coagulant hydrolysis. It seems that the process investigated might be beneficial and effective in solving the problem encountered in small membrane-based water treatment plants.

#### ACKNOWLEDGEMENTS

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#### ZASTOSOWANIE PROCESU KOAGULACJI/ULTRAFILTRACJI W UKŁADZIE *IN-LINE* DO OCZYSZCZANIA WODY

Badano zintegrowany proces koagulacji/ultrafiltracji w układzie *in-line*, tj. bez wydzielonego etapu sedymentacji. Określono wpływ typu koagulantu glinowego, jego dawki oraz typu membrany i odczynu wody na właściwości transportowe membran oraz końcową jakość uzdatnionej wody. Jako koagulantów do badań użyto: siarczanu glinu, polichlorku glinu oraz glinianu sodu. Membrany ultrafiltracyjne były wykonane z regenerowanej celulozy oraz polietersulfonu, a ich *cut-off* wynosiło 30 kDa.

Zastosowanie w analizowanym procesie siarczanu glinu lub polichlorku glinu pozwoliło zwiększyć skuteczność usuwania naturalnych substancji organicznych oraz zmniejszyć intensywność blokowania membran w porównaniu z efektami uzyskiwanymi podczas ultrafiltracyjnego oczyszczania wody. Gdy dominującym mechanizmem separacji makrocząstek była neutralizacja ich ładunku (niskie pH), wtedy podatność membran na blokowanie była mniejsza niż obserwowana w warunkach koagulacji wymiatającej. W środowisku alkalicznym w przypadku obydwu membran stwierdzono intensywne ich blokowanie przez makrocząsteczki organiczne i anionowe produkty hydrolizy koagulantów.