THE INFLUENCE OF ALUMINUM CONCENTRATION ON MEMBRANE FOULING

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Received: 16.11.2010; Revised: 21.12.2010; Accepted: 11.01.2011

Abstract
Surface waters are the main source of water for industrial and municipal purposes in Poland. Coagulation is one of the classical methods of surface water treatment for drinking purpose. Membrane processes, such as ultrafiltration, are an alternative to water treatment by means of coagulation. Hybrid/integrated processes e.g. coagulation with ultrafiltration are applied in order to increase the effectiveness of removal of organic and inorganic substances. When aluminum is used in the coagulation process, the concentration of the element in the treated water can reach level as high as 0.5 mg/dm^3. The aim of the study was to determine the influence of aluminum on fouling intensity during ultrafiltration of simulated water. Experiments were carried out in the ultrafiltration system MilliporeCDS10 (Millipore&Amicon). The study revealed that the presence of aluminum in waters with low ionic strength decreased the intensity of fouling while in waters with high hardness this effect was insignificant. The intensity of fouling decreased at different aluminum concentrations in waters depending on the nature of organic substances present in water.

Streszczenie
Głównym źródłem zaopatrzenia przemysłu oraz gospodarki komunalnej w wodę w Polsce są wody powierzchniowe. Jedną z klasycznych metod oczyszczania wód powierzchniowych na cele pitne jest koagulacja. Alternatywną metodą do koagulacji są procesy membranowe takie jak ultrafiltracja. W celu zwiększenia efektywności procesu usuwania zanieczyszczeń stosuje się procesy hybrydowe/zintegrowane, takie jak np. koagulacja z ultrafiltracją. Po koagulacji wody z użyciem glinowych koagulantów, stężenie glinu w wodzie może dochodzić do 0.5 mg/l. Celem badań było określenie wpływu glinu na intensywność zjawiska foulingu zachodzącego w trakcie ultrafiltracji wody modelowej. Badania prowadzono w module UF MilliporeCDS10 (Millipore&Amicon). Wykazano, że obecność glinu w wodach o niskiej sile jonowej zmniejsza intensywność foulingu, natomiast w wodach o wysokiej twardości nie odgrywa znaczącej roli. W zależności od rodzaju obecnej w wodzie substancji organicznej, intensywność zjawiska foulingu maleje przy różnej zawartości glinu w wodzie.

Keywords: **Fouling; Ultrafiltration; NOM; Aluminium; pH; SUVA.**

1. INTRODUCTION

Surface waters are the main source of fresh water in Poland. According to Central Statistical Office annual water uptake from surface waters from 2000 to 2009 was equal 9130 hm^3, while from groundwaters 1662 hm^3, out of which 2156 hm^3 was used for exploitation of water-pipe network [1]. Most of surface waters requires treatment. The ecological condition of waters in polish rivers is satisfactory, however, many rivers characterize with unsatisfactory or poor quality waters. The quality of water in rivers (the ecological condition, operational monitoring) is shown in Figure 1.

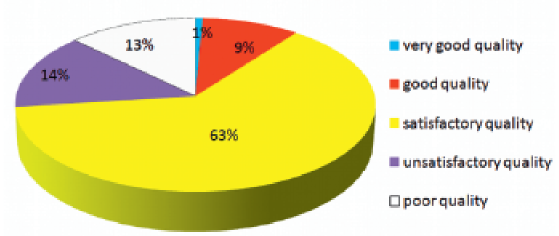

Figure 1.
The condition of rivers in Poland in 2008

In case of lakes, 43.6% of all reservoirs monitored in 2008 were of a very good or a good quality. However, considering the total lakes area and total volume, water with very good and good quality was significantly less, respectively 25.9% and 27.4%. According to number of lakes good quality waters had the greatest share (32.7%), however, considering the total area lakes of poor quality were dominant (32.7%). Taking the total volume into account satisfactory (30.2%) and poor quality waters (29.9%) were majority. The ecological condition of lakes in particular river basins was diversified [3].

Coagulation is one of the classical methods used in treatment of surface water for drinking purposes. During coagulation fine suspended matter like particles of clay and silts, bacteria and algae, and, what is the most important, negatively charged colloidal humic substances are removed. These negatively charged colloids repulse each other what results in sol formation in natural waters. In order to precipitate colloids from water, positively charged substances (electrolytes, other colloids) are added. The most popular coagulants are hydrated aluminum or iron sulphates, sodium aluminate, iron (III) chloride. The coagulation of colloids is favored by the increase of electrolyte concentration or by the addition of oppositely charged colloid [4]. Aluminum posses amphoteric properties. According to Dojlido [5] under pH<4 aluminum appears in the form of $[Al(H_2O)_6]^{3+}$ ions, under pH>7 in the form of $[Al(OH)_4(H_2O)_2]^-$ ions, while under pH in the range 4-7 it is present as intermediate forms like: $[Al(OH)(H_2O)_5]^{2+}$, $[Al(OH)(H_2O)_4]^+$, $[Al(OH)_3]^0_{aq}$ in equilibrium with $Al(OH)_{3,s}$. According to Szafraniak [6] under pH=6-8 aluminum forms hardly soluble compounds ($Al(OH)_3$), while under pH<6 it forms positively charged hydroxides which are able to polymerize. Aluminum characterizes with a low solubility in water. Usually it appears in concentration range from decimal parts to 1 mg/dm^3, hardly ever exceeds 0.5 mg/dm^3 (after the treatment by means of coagulation $[Al^{3+}] \leq 0.5$ mg/dm^3) [6]. The regulation of The Minister of Health on quality required of drinking water [7] defines the permissible aluminum concentration at the level of 0.2 mg/dm^3.

Membrane processes such as ultrafiltration are an alternative to coagulation water treatment method. Ultrafiltration is a process during which colloids and suspended particles as well as high molecular weight compounds are removed. The removal is depending on molecular weight cut off (MWCO) of a membrane. The main limitation of the method is the decrease of membrane permeability during treatment process caused by accumulation of organic and inorganic substances on the membrane surface and inside membrane pores (so called fouling). In order to increase the effectiveness of removal of organic and inorganic substances hybrid/integrated processes are applied e.g. coagulation with ultrafiltration. Hybrid systems not only improve the quality of treated water but also decrease membrane fouling [8].

The aim of the study was to determine the influence of aluminum on fouling intensity and on the degree of removal of organic substances during ultrafiltration of simulated water.

2. THE METHODOLOGY OF THE STUDY

Simulated waters containing dextranes and sodium salts of humic acids were introduced to ultrafiltration system. The composition of the feed water was changed by pH correction and calcium ions content as well as by variation of mass ratio of humic substances and dextranes. The composition of feed waters is shown in Table 1.

Experiments were carried out in the ultrafiltration system MilliporeCDS10 (Millipore&Amicon) with the use of the flat sheet membranes and dead end mode (the feed was introduced perpendicularly to the membrane surface). Scheme of ultrafiltration system was presented in [9].

UF process was carried out under constant pressure equal to 0.1 MPa. Every filtration cycle required the use of a new membrane, which was conditioned according to the producer recommendation. Polyacrylonitrile (PAN) membranes of cut off 20 kDa and average distilled water flux (20°C) equal to 82.8±17.7 [dm^3/m^{2}h] were used. Analyses of total organic carbon (TOC) and dissolved organic carbon (DOC) content as well as UVA_{254} absorbance were made for all feeds and obtained permeates.

Table 1.
The composition of filtrated waters

Experiment no	Constant parameters	Varying parameters
1	$[Ca^{2+}]$=0 mg/dm^3, $X_{H/D}$=0.5	pH=5-9, $[Al^{3+}]$=0-0.5 mg/dm^3
2	$X_{H/D}$=0.5, pH=5	$[Ca^{2+}]$=0-200mg/dm^3 $[Al^{3+}]$=0-0.5 mg/dm^3
3	$[Ca^{2+}]$=0 mg/dm^3, pH=7	$X_{H/D}$=0.1-0.9, $[Al^{3+}]$=0-0.5 mg/dm^3
4	$X_{H/D}$=0.9, pH=7	$[Ca^{2+}]$=0-200 mg/dm^3 $[Al^{3+}]$=0-0.5 mg/dm^3

The intensity of fouling was determined using Unified Modified Fouling Indexes (UMFI) established for cake formation assumed as the main fouling mechanism. The method of indexes determination was discussed in [10].

3. RESULTS AND DISCUSSION

3.1. Influence of aluminum dose and pH on fouling intensity

The first part of the study focused on the investigations of the influence of aluminum presence on membrane fouling under various pH during ultrafiltration. The waters of low ionic strength and constant mass ratio of humic substances to dextrans were filtered. Two doses of aluminum ions were applied – 0.25 mg/dm^3 and 0.5 mg/dm^3. Results of the experiments are shown in Figure 2.

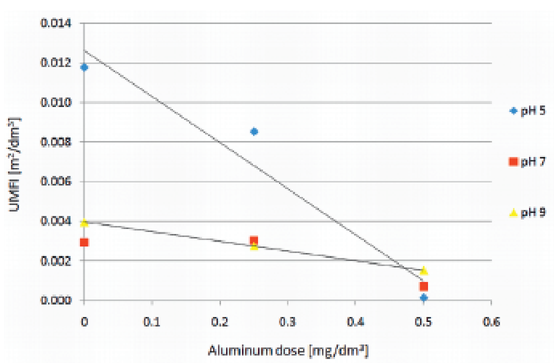

Figure 2.
The influence of aluminum dose on fouling depending on pH of feed water

The significant influence of aluminum dose on UMFI value was observed for feed water pH equal to 5. The increase of aluminum dose resulted in the decrease of fouling intensity. In acidic environment aluminum forms positively charged hydroxides which are able to neutralize negatively charged colloidal organic substances. As a result of neutralization, sediment (flocks) can be formed what protects membrane pores from blocking. The linear dependence of UMFI and Al dose was also observed for the feed water pH equal to 9. However, it was noticed that fouling intensity was much lower (almost 3 times) than under pH = 5 for water without Al ions. In case of waters of pH = 7, the decrease fouling intensity was observed only after aluminum dose amounted 0.5 mg/dm^3. It can be explained by the form of aluminum in water of neutral reaction. The decrease of fouling intensity caused by the presence of aluminum was also observed by *Carroll et al.* [12] and *Jung et al*. [13]. Polypropylene microfiltration membrane and natural water of pH = 6 were used by Carroll [12], while regenerated cellulose and polysulfone ultrafiltration membranes and natural water of pH = 7.8 were used in Jung [13] investigations. The decrease of values of organic impurities removal (TOC, DOC, UVA) with the increase of aluminum dose was observed in the investigated pH range. The increase of value of TOC removal for aluminum dose 0.5 mg/dm^3 only in case of feed water pH = 9 was noticed. The change of values of impurities removal is shown in Figure 3. In Figure 4 photos of membranes after ultrafiltration of waters differ in pH and aluminum dose are shown.

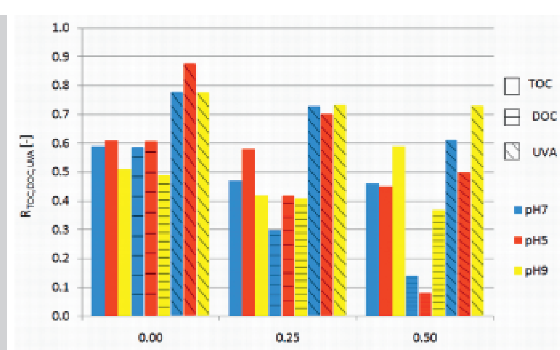

Figure 3.
The influence of aluminum dose on retention coefficients of organic impurities depending on water pH

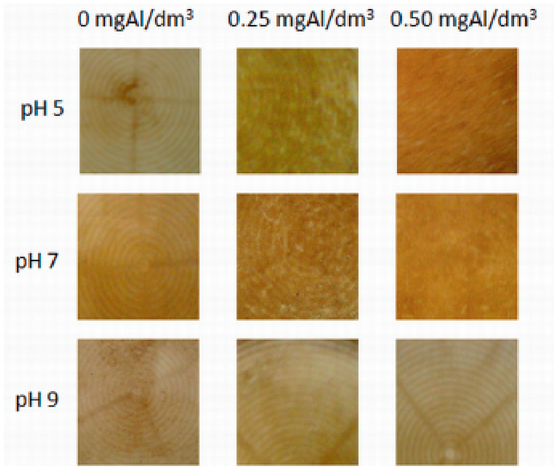

Figure 4.
Photos of membranes after filtration of waters of different aluminum content and pH

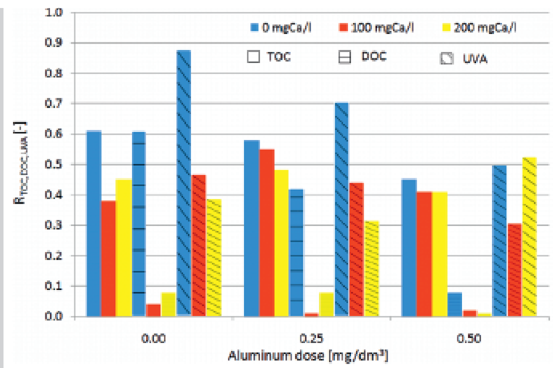

Figure 6.
The influence of aluminum dose on retention coefficients of organic impurities for waters differ in calcium ions content (pH 5, xH/D=0.5)

It can be explained by shifting of the compounds with high molecular weight into smaller molecules under low pH and high ionic strength conditions [11].

3.2. Influence of aluminum dose and calcium ion concentration on fouling intensity (experiment no 2)

In the second part of the study, waters of pH = 5 containing equal mass ratios of humic substances and dextranes (the greatest intensity of fouling in the first part of the study) were used. The influence of aluminum dose on fouling intensity under various calcium ion concentration was investigated. Results of the experiment are shown in Figure 5. Waters containing calcium ions in the amount of 100 and 200 mg/dm^3 caused negligible fouling of similar intensity regardless of the aluminum presence in the feed in comparison with waters of low ionic strength. Also the waters examined by Carroll and Jung [12, 13] had a low ionic strength (4-20 mg Ca^{2+}/dm^3). However, degrees of removal of organic impurities (TOC, DOC, UVA) were higher for waters of low ionic strength (Fig. 6).

3.3. Influence of aluminum dose and humic substances concentration on fouling intensity

In the third part of the study the influence of aluminum dose on the intensity of membrane fouling during filtration of waters of various content of humic substances, low ionic strength and pH = 7 was investigated. Similarly as in the first part of the study two doses of aluminum ions were applied. Results of the experiment are shown in Figure 7. The greatest fouling was observed for waters containing humic substances with high concentration. In case of the mixture of humic acids and polysaccharides, the aluminum dose equal to 0.5 mg/dm^3 caused the decrease of the fouling intensity. For waters containing insignificant amount of humic substances, the intensity of fouling decreased with the dose 0.25 mg/dm^3.

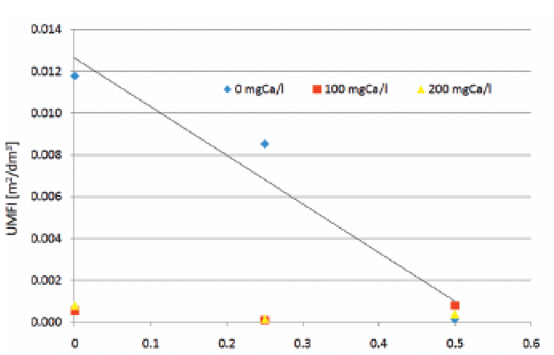

Figure 5.
The influence of aluminum dose on fouling for waters differ in calcium ions content (pH 5, xH/D=0.5)

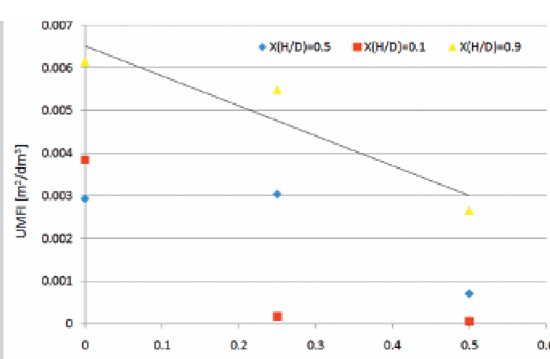

Figure 7.
The influence of aluminum dose on fouling for waters of different content of humic substances

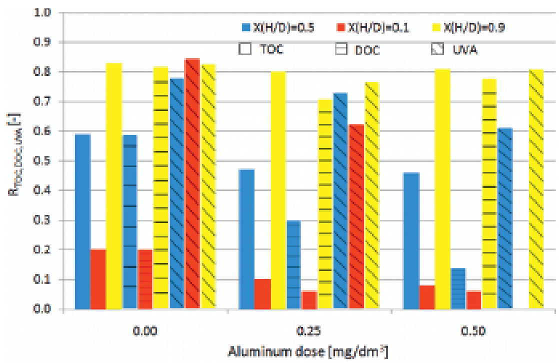

Figure 8.
The influence of aluminum dose on retention coefficients of organic impurities for waters of different content of humic substances

The decrease of values of retention coefficient of organic impurities with the increase of aluminum dose in waters of small or medium humic substances content was observed (Fig. 8). In case of waters containing mainly humic substances, degrees of retention of organic impurities were constant regardless of the aluminum dose in the feed. In Figure 9 photos of membranes after ultrafiltration of waters differ in aluminum dose and mass ratios of humic substances and dextranes.

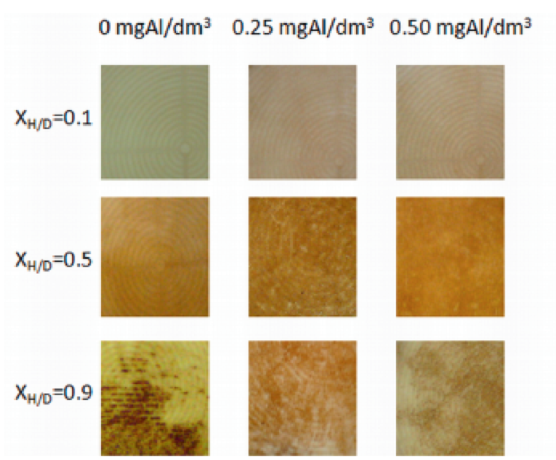

Figure 9.
Photos of membranes after ultrafiltration of waters of different aluminum and humic substances content

3.4. Influence of aluminum dose and calcium ion concentration on fouling intensity (experiment no 4)

In the fourth part of the study waters of pH = 7 containing mainly humic substances (the highest fouling intensity in the third part of the study) were used. Similarly as in the second part of the study the influence of aluminum dose on fouling under various calcium ions concentration was investigated. Results of the experiment are shown in Figure 10. Waters of low ionic strength caused negligible fouling of similar intensity regardless of the aluminum dose in comparison with waters of calcium ions content 100 and 200 mg/dm^3. This phenomenon was also observed in the second part of the study.

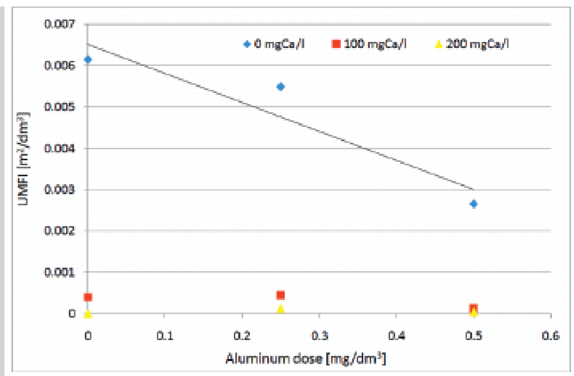

Figure 10.
The influence of aluminum dose on fouling for waters differ in calcium ions content (pH = 7, mainly humic substances)

For the low ionic strength feed insignificant differences in retention coefficients of organic impurities under various aluminum doses were observed (R_{TOC} = 80-83%). In the presence of calcium ions the increase of the removal of TOC with the increase of aluminum dose for feeds of medium ionic strength was noticed (from 74% to 83%). However, for feeds of high ionic strength the decrease of the organic impurities retention with the increase of aluminum dose was observed (from 82% to 71%). Calcium cations decrease the solubility of humic substances and increase their aggregation [14]. On the other hand they cause the decrease of the apparent molecular weight of organic substances. It can be supposed that the ionic strength caused by calcium ions has greater influence on retention coefficients than the aluminum dose.

4. CONCLUSIONS

The concentration of calcium ions influences the intensity of fouling of ultrafiltration PAN membrane as well as the degree of organic impurities removal in waters of acidic character. The increase of concentration of aluminum ions causes the decrease of both, the fouling intensity and the retention coefficients of organic substances. Such dependences are not observed in case of waters which characterize with high ionic strength, in which the influence of aluminum is insignificant.

The influence of aluminum on fouling intensity and on the degree of organic impurities removal depends on the type of organic substances present in water. The most intensive fouling is observed for waters containing mainly humic substances. The increase of aluminum dose in waters of high humic substances content decreases the fouling intensity. For waters of more heterogenic composition (the mixture of humic substances and polysaccharides) the decrease of fouling is observed only if the aluminum dose reaches 0.5 mg/dm^3. In case when negligible amounts of humic substances are present in waters the high concentration of aluminum is not necessary to decrease the fouling intensity.

To sum up, the presence of aluminum in waters of low ionic strength positively influences fouling intensity – while in waters of significant hardness it is insignificant. The intensity of fouling decreases with different aluminum concentration in waters depending on the type of organic substances.

ACKNOWLEDGEMENTS

This work was performed by the financial support from The Polish Ministry of Education and Science under grant no. N N523 421637.

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