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REMOVAL OF HEAVY METAL IONS
AND HUMIC SUBSTANCES FROM WATER
BY ULTRAFILTRATION MEMBRANES

The results of ultrafiltration removal of humic substances and heavy metal ion admixtures from aqueous solutions have been presented. The membranes applied were made of sulfonated polysulfone. In the experiments, two types of modified polysulfone membranes (of a various percent share of sulfone groups) were applied. Removal of copper and zinc ions as well as co-removal of these ions in the case of solutions containing both metal ions and humic substances were tested.

Ultrafiltration membranes made of sulfonated polysulfone provided efficient separation of heavy metal ions from aqueous solutions, which contained humic substances, by retaining organometallic complexes or co-precipitated metal hydroxides and humic substances. Under conditions favourizing precipitation of metal compounds of low solubility, the slight increase of retention of humic substances was observed, but this effect was concomitant with the decrease of membrane permeability.

1. INTRODUCTION

Humic substances (HA) play an important role in the behaviour and transformation of metal ions in natural environment. They can control metal ion concentrations in soils and natural waters and can affect the mobility of metals in soils and aquifers. The interaction between metal ions and soil particles can also be controlled by humic substances [1], [2]. Humic substances are believed to play a major role in trace metal availability and toxicity to plants and living organisms.

The yield of the reaction, during which metals form complexes with the humic substances in an aquatic environment, is affected by the kind and concentration of the metal, by the kind and concentration of humic susbtances as well as by some other factors (ion concentration, pH, ionic strength of the solution, temperature)[3], [4].

In the past few years, there has been greater and greater interest in the application of pressure-driven membrane processes to the removal of organic and

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inogranic water pollutants [5]–[7]. A number of investigators have concentrated their attention on ultrafiltration and its suitability for removing organic pollutants from water. According to the data reported, removal efficiency (i.e., retention of humic substances) varied from one membrane type to another and in many instances there was a considerable drop in permeability as a result of fouling. LAINÉ and co-workers [8] found that the application of strongly hydrophilic membranes reduced the concentration polarization phenomenon and prolonged the operation.

The experiments on the usability of sulfonated polysulfone membranes for removing HA from an aquatic environment [9] showed that application of porous ion-exchange membranes resulted in both increase of HA retention and decrease of fouling phenomenon.

BHATTACHARYYA et al. [10] reported promising ultrafiltration results with electroplating rinse water containing heavy metal ions. In their experiments, negatively charged, noncellulosic membranes were used. The Donnan exclusion mechanism was primarily responsible for the rejection of ionic solutes by charged membranes, and this process was termed *ultrafiltration* because of relatively low transmembrane pressure in moderately concentrated solutions of low effective osmotic pressures.

The objective of our study was to find out whether heavy metal ions can be removed by sulfonated-polysulfone porous ion-exchange membranes, and how the interaction between metal ions and HA affects the transport properties of the membranes and efficiency of separation processes.

2. EXPERIMENTAL METHODS

2.1. MEMBRANES

The experiments were run with two types of ultrafiltration membranes made of sulfonated polysulfone and cast at the laboratories of the Institute of Organic and Polymer Technology, Technical University of Wrocław, Poland. The membranes were formed from 20% polymer solutions by phase inversion of sulfonated polysulfone (SPS20) or its blend with polysulfone (SPSB/50). The ion-exchange capacities of SPS20 and SPSB/50 amounted to 0.96 mmol/g and 0.52 mmol/g, respectively, at porosities of 85% and 82%, respectively. More details can be found elsewhere [9].

2.2. ULTRAFILTRATION PROCESS

Ultrafiltration was carried out in a laboratory unit shown schematically in figure 1. The system consisted of a 1000 cm^3 vessel and an ultrafiltration membrane with a surface area of 19.6 cm^2. The retentate was recirculated at a flow rate of 30 cm^3/min. Transmembrane pressure of 0.05 MPa was applied, using compressed

nitrogen. The permeate flux was monitored for over 2 hours. For each run, relative permeability (α) and rejection factor (R) were calculated according to the following equations:

$$\alpha = J_{HA}/J_w,\qquad(1)$$

$$R = 1 - \frac{c_p}{c_0} \times 100\%\qquad(2)$$

where J_{HA} and J_w are fluxes of the HA permeate and water, respectively, and c_p and c_0 are concentrations of HA or metal ions in permeate and feed, respectively.
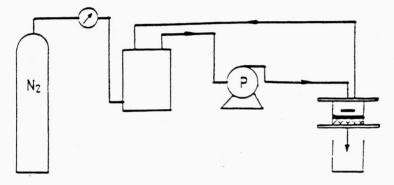

Fig. 1. Schematic setup of ultrafiltration unit

2.3. FEED SOLUTION

In all experiments, the membranes were fed with solutions of Aldrich HA in redistilled water. HA concentrations amounted to 20 and 40 g/m³, whereas these of each metal ion varied, amounting to 1, 5 and 10 g Cu^{2+}/m³ and 1, 5 and 10 g Zn^{2+}/m³. The pH of the solutions was adjusted to the range of 4.4–9.

The concentration of HA was determined spectrophotometrically at 254 nm (Carl Zeiss Jena, M-40 Specord).

3. RESULTS AND DISCUSSION

3.1. REMOVAL OF HUMIC SUBSTANCES BY ULTRAFILTRATION

In order to examine the potentiality for HA removal from water by ultrafiltration involving sulfonated polysulfone membranes, the model solution of HA (20 g/m³) was filtered through SPS20 and SPSB/50 membranes. The pH of model solution varied from 4 to 11.
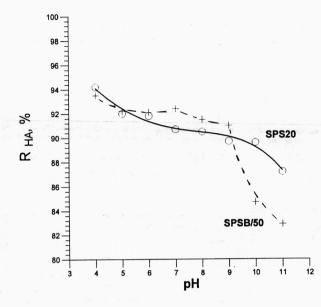
Fig. 2. Effect of pH on HA rejection factor for SPS20 and SPSB/50 membranes
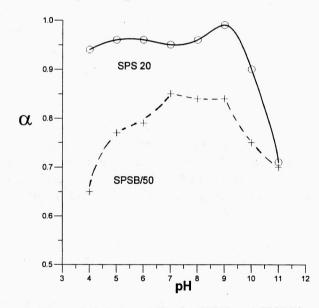$(HA = 20 \ g/m^3, \ \Delta p = 0.05 \ MPa)$

Fig. 3. Effect of pH on relative permeability for SPS20 and SPSB/50 membranes
$(HA = 20 \ g/m^3, \ \Delta p = 0.05 \ MPa)$

For both types of membranes the retention factor of HA was found to decrease
with the increasing pH value (figure 2). WILSON [11] states that aggregation of HA
molecules decreases with increase in pH due to greater ionic repulsion forces between

HA molecules. At pH > 10, which corresponds to maximum HA polydispersity, a drastic decrease in HA retention factor for both membranes is stated.

SPSB/50 membranes, which have a more compact skin than the SPS20 membranes, provide a better retention of low-molecular (weigth) particles, but at pH $\geq$ 10 the SPS20 membrane of a larger share of charged groups shows higher value of R_{HA}.

The importance of electrostatic repulsion was also substantiated by the value of relative permeability (α) (figure 3). At low pH, α-values were also low (particularly for SPSB/50 membranes) due to the cumulation of poorly dissociated organic particles on the membrane surface. The increase of pH restricts the fouling phenomenon because of the dissociation of the –COOH and –OH groups. The pH-dependence of the fouling phenomenon was particularly distinct in the case of membranes of SPSB/50 type. When the share of sulfone groups in the SPSB/50 membranes was smaller they were more vulnerable to fouling than SPS20 membranes.

3.2. REMOVAL OF METAL IONS BY ULTRAFILTRATION

Copper ion removal. The potentiality for copper ion removal was investigated by ultrafiltration of $Cu(NO_3)_2$ at varying Cu^{2+} concentrations (1, 5 and 10 g/m^3) through sulfonated polysulfone membranes. The results are presented in table 1.

Table 1

Separation and transport properties of SPS20 and SPSB/50 membranes with respect to aqueous solutions containing copper ions (pH = 7)

C_{Cu} (g/m^3)	SPS20		SPSB/50	
	R_{Cu} (%)	α	R_{Cu} (%)	α
1	38.9	1.00	41.2	0.98
5	26.4	1.00	34.1	0.96
10	19.2	0.98	25.7	0.92

From these data it can be seen that the efficiency of retention of metal ion by both membrane types as well as the value of relative permeability (α) decreased with the increasing initial concentration of copper ions in the solution. Such a decrease results from the formation of slightly soluble copper compounds ($Cu(OH)_2$ or $CuCO_3 \cdot Cu(OH)_2$) which precipitated at the membrane surface, thus clogging the skin pores and, consequently, reducing the permeability of the membrane. SPSB/50 membranes had a more compact skin allowing retention of the aforementioned species in larger amounts and, at the same time, producing a more distinct drop in permeability. This

finding was corroborated by the experiments run on copper ion solutions at pH = 5. The efficiency of Cu^{2+} retention by both SPS20 ans SPSB/50 membranes did not exceed 9%, and the hydraulic efficiency of the process remained unchanged.

Thus, when ultrafiltration of Cu^{2+} containing solutions is carried out under conditions similar to those in natural water (pH ≈ 7), it can be expected that the hydraulic efficiency of the membranes will not decrease dramatically due to the deposition of slightly soluble copper compounds.

Zinc ion removal. The usability of sulfonated polysulfone membranes in removing zinc compounds from aqueous solutions was tested via ultrafiltration of model $ZnCl_2$ solutions with varying concentrations of zinc ions (1, 5, 10 g Zn^{2+}/m^3) and pH = 7. The results are gathered in table 2.

Table 2

Separation and transport properties of SPS20 and
SPSB/50 membranes with respect to aqueous
solutions containing zinc ions (pH = 7)

C_{Zn} (g/m^3)	SPS20		SPSB/50	
	R_{Zn} (%)	α	R_{Zn} (%)	α
1	25.0	1.00	30.2	1.00
5	8.3	1.00	15.9	0.99
10	7.1	0.98	7.9	0.97

As shown by these data, the maximum retention factor of zinc ions (R_{Zn}) amounted to 30%. This efficiency should be attributed primarily to the retention of slightly soluble zinc compounds ($Zn(OH)_2$ and $ZnCO_3$ which form at pH = 7), and partly to the exchange of Zn^{2+} ions for H^+ ion of the sulfone groups of the polymer matrix. Again, the more compact structure of the SPSB/50 membranes allowed more efficient retention of zinc compounds, but this was concomitant with a considerable drop in permeability.

3.3. CO-REMOVAL OF HA AND METAL IONS BY ULTRAFILTRATION

Co-removal of copper and HA. Figure 4 relates the efficiency of ultrafiltration in removing copper ions and HA from aqueous solutions to a number of parameters. pH of the solution was the most influential, contributing markedly to the bonding of copper ions by organic ligands. At pH between 5 and 7, the efficiency of copper

removal increased up to 94% (at initial Cu^{2+} concentration of 1 g/m^3). Raising the pH level to 9.0 made the copper retention factor (R_{Cu}) fall below 80%, irrespective of the initial copper concentration. Such a behaviour can be explained by the following mechanism: at pH $\approx$ 7, organometallic complexes are very stable [12], and free copper ions are precipitated in the form of slightly soluble inorganic compounds. The rise in pH accounts for the bonding of copper ions by inorganic ligands.
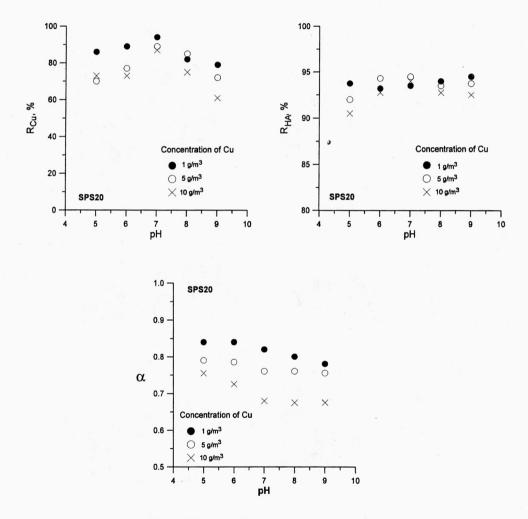

Fig. 4. Effect of pH and copper concentration
on HA rejection factor R_{HA}, copper rejection factor R_{Cu}
and relative permeability α for SPS20 membrane ($\Delta p = 0.05$ MPa)

The pH level was also found to affect the permeability of the membranes. Thus, when pH rose from 5 to 7, the decrease of the α-value averaged 3%. Further rise in pH (to 9.0) was without any significant effect, which should be attributed to the deposition of organometallic and inorganometallic complexes on the membrane surface. At increasing pH, the dissociation of the OH-groups in organic ligands as well as greater repelling forces between organic colloids and membrane material compensated the drop in permeability which was due to the precipitation of slightly soluble copper compounds.
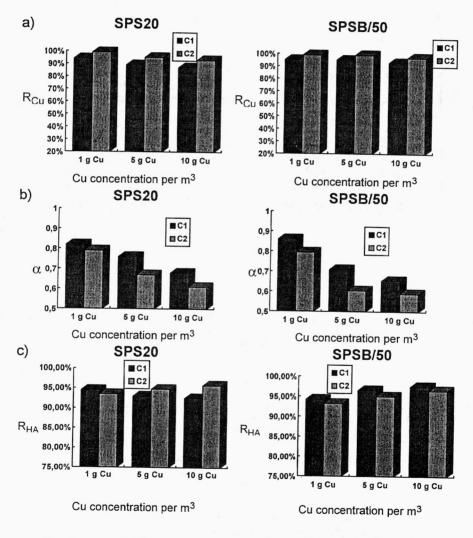

Fig. 5. Effect of HA and copper concentration on HA rejection factor R_{HA}, copper rejection factor R_{Cu} and relative permeability α for SPS20 and SPSB/50 membranes ($C1 = 20$ g HA/m^3, $C2 = 40$ g HA/m^3, $\Delta p = 0.05$ MPa, pH = 7)

On analyzing the relationship between pH and R_{HA} we arrived at the following findings: the plots in figure 4 were similar to those obtained for the solutions where copper compounds were absent, and there was no crucial relationship between pH and R_{HA} when pH fell in the range from 5 to 9. The slight increase of the R_{HA} value at 10 g Cu^{2+}/m^3 and pH $\approx$ 7 might be attributed to the co-precipitation of organic ligands and slight solubility of copper compounds.

Initial concentrations of HA or Cu^{2+} as well as the type of the membrane applied had small effect on the co-removal of Cu^{2+} and HA, if at all. SPS20 and SPSB/50 yielded similar R_{Cu} and R_{HA} values (figure 5).

The increase of HA concentration from 20 to 40 g/m^3 made the R_{Cu} value rise by 5.5% on average. At the same time the increase in the initial concentrations of HA and Cu^{2+} brought about a considerable decrease of the α-value. SPSB/50 membranes (which had a more compact skin and showed a poorer hydrophilic affinity as compared to SPS20 membranes) provided slightly higher values of R_{HA} and R_{Cu}, but this effect was concomitant with a greater loss of hydraulic permeability when Cu^{2+} concentration increased. The cake that had formed on the membrane surface by deposition of organic and inorganic species produced and additional filtering layer, thus increasing hydraulic resistance.

The membranes under study provided a comparatively low efficiency (41% or below) of copper ion removal, which was considerably improved (to 86–99%) in the presence of HA approaching the range from 93 to 98%. The transport and separation properties of SPS20 and SPSB/50 membranes were found to be almost identical.

Co-removal of zinc and HA. The contribution of pH to the efficiency of the ultrafiltration process involving solutions which contained zinc ions and HA was investigated and the results are plotted in figure 6. In the parameter range examined, no distinct relation was found to occur between initial zinc concentration and HA retention, only at pH = 9 and initial Zn^{2+} concentration of 10 g/m^3 the R_{HA} value was increased (compared to the solutions with lower initial Zn^{2+} content). This increase was associated with the co-precipitation of humic colloids and $Zn(OH)_2$, but there was a concomitant decrease of relative permeability (α), which is of importance at the higher initial Zn^{2+} concentrations. Thus, at the initial concentration of 1 g Zn^{2+}/m^3 the α-value dropped from 0.88 at pH = 7 to 0.83 at pH = 9. At the concentration of 10 g Zn^{2+} per 1 m^3 of feed solution, the α-value decreased from 0.84 to 0.73 at pH = 7 and pH = 9, respectively. At the pH range from 5 to 7, the α-values did not markedly differ from each other and were found to be only slightly affected by the initial concentration of zinc ions.

The co-existence of zinc ions and HA had a favourable influence on the efficiency of Zn^{2+} ion removal. At a pH $\approx$ 7, the value of R_{Zn} amounted to 84.8%, 65.3% and 45.8% for the initial Zn^{2+} concentrations of 1 g/m^3, 5 g/m^3 and 10 g/m^3, respectively. Compared to the efficiency of Cu^{2+} removal, the R_{Zn} value was lower

due to the poorer ability of Zn^{2+} ions to form complexes with HA (Iving–Williams series). And that is why the efficiency of Zn^{2+} ion removal by ultrafiltration decreased noticeably with the increasing initial concentration of this species.
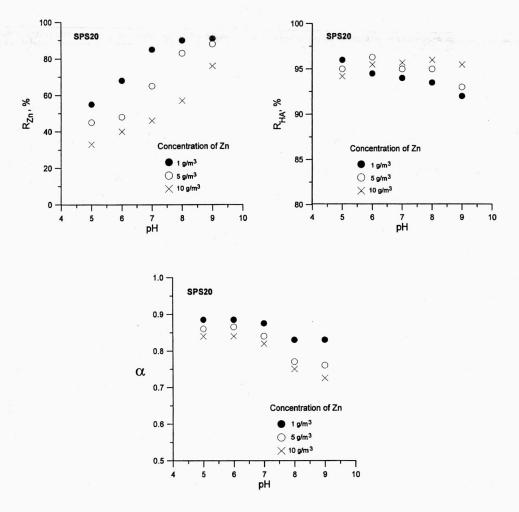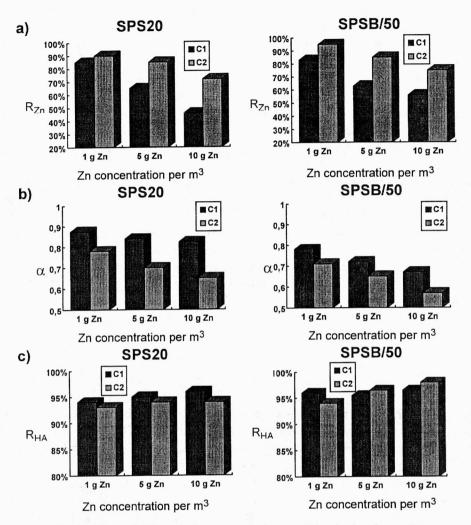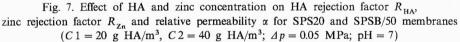

Fig. 6. Effect of pH and zinc concentration on HA rejection factor R_{HA}, zinc rejection factor R_{Zn} and relative permeability α for SPS20 and SPSB/50 membranes (20 g HA/m³, $\Delta p = 0.05$ MPa)

Figure 7 presents the removal efficiency provided by two types of membranes and the following parameters: HA concentration, 20 and 40 g/m³; Zn^{2+} concentration, 1, 5 and 10 g/m³; pH = 7. As shown by these plots, the concentrations of Zn^{2+} ions

a)

b)

c)

Fig. 7. Effect of HA and zinc concentration on HA rejection factor R_{HA}, zinc rejection factor R_{Zn} and relative permeability α for SPS20 and SPSB/50 membranes ($C1 = 20$ g HA/m^3, $C2 = 40$ g HA/m^3; $\Delta p = 0.05$ MPa; pH = 7)

had small effect on the R_{HA} values (the contribution of copper ions to the efficiency of HA removal was similar). They approached those achieved by ultrafiltration of aqueous solutions where zinc ions were absent ($\approx 95\%$). And, again, SPSB/50 membranes retained HA more efficiently than SPS20 did. If HA and Zn^{2+} concentrations in the feed solution were 40 and 10 g/m^3, respectively, the value of R_{HA} was higher (98.6%) than when the initial HA concentration amounted to 20 g/m^3 (96.4%). This was due to the compact structure of the SPSB/50 membrane

which had been noticeably stronger clogged by the precipitating zinc compounds. This finding was corroborated by the α-values which were lower than those for the SPS20 membrane. Furthermore, the permeability of SPSB/50 membranes was by more than 20% lower when the initial zinc concentration rose from 1 to 10 g/m^3 (at an initial HA concentration of 40 g/m^3). The application of SPS20 membranes reduced this disadvantageous phenomenon only by about 16%.

When the concentration of zinc ions in the feed solution was low (1 g/m^3), their removal effciency in the permeate approached 90%. When the solution was filtered through the SPS20 membrane at an initial HA concentration of 20 g/m^3, zinc ion concentration in the permeate amounted to 0.15 g/m^3, but became twice as high with the increase of initial HA concentration from 20 to 40 g/m^3. The increase of zinc ion concentration in the feed solution to 10 g/m^3 at a concomitant increase of HA content from 20 to 40 g/m^3 produced permeate concentrations of 5.4 and 2.9 g Zn^{2+}/m^3, respectively. At initial zinc concentration of 10 g/m^3 and HA concentration of 20 g/m^3, the permeate concentration of zinc ions totalled 4.4 g/m^3 and decreased to 2.6 g Zn^{2+}/m^3 when HA content in the feed solution rose to 40 g/m^3.

Summing up, there were only slight differences between the SPS20 and SPSB/50 membranes in the efficiencies of zinc ion removal, or co-removal of Zn^{2+} and HA. These removal or co-removal efficiencies were found to be similar to those obtained for the aqueous solutions containing copper ions.

4. CONCLUSIONS

Ultrafiltration membranes made of sulfonated polysulfone provided efficient separation of copper ions from aqueous solutions, which contained humic substances, by retaining organometallic complexes or co-precipitated metal hydroxides and humic substances. The efficiency of zinc ion removal was slightly poorer.

The presence of metal ions had little influence on the efficiency of humic substances removal. Only under conditions favourizing precipitation of slightly soluble metal compounds the retention of humic substances was slightly better, but this effect was concomitant with the decrease of membrane permeability.

REFERENCES

[1] EVANS L.J., Env. Sci. Technol., 1989, 23, 1047.
[2] McCARTHY J.F., ZACHARA J.M., Env. Sci. Technol., 1989, 23, 496.
[3] CABANISS S.E., Env. Sci. Technol., 1990, 24, 583.
[4] BENEDETTI M.F. et al., Env. Sci. Technol., 1995, 29, 446.

[5] AWWA Membrane Technology Committee: Committee Report. JAWWA, 1992, 84, 59.
[6] Fu P. et al., JAWWA, 1995, 86, 55.
[7] Jacangelo J.G. et al., JAWWA, 1995, 87, 64.
[8] Lainé J.-M. et al., JAWWA, 1989, 81, 61.
[9] Kabsch-Korbutowicz M. et al., Sep. Sci. Technol., 1994, 29, 2345.
[10] Bhattacharyya D. et al., JWPCF, 1979, 51, 176.
[11] Wilson D., Geochim. Cosmochim. Acta, 1980, 44, 1311.
[12] Świderska-Bróż M., *Interakcja związków humusowych z wybranymi metalami ciężkimi oraz jej wpływ na usuwanie badanych metali z wody*, Prace Naukowe Inst. Inż. Ochr. Środowiska PWr., nr 54, 1985.

USUWANIE JONÓW METALI CIĘŻKICH I SUBSTANCJI HUMUSOWYCH Z WODY PRZY UŻYCIU MEMBRAN ULTRAFILTRACYJNYCH

Przedstawiono wyniki badań nad ultrafiltracyjnym oczyszczaniem roztworów wodnych zawierających substancje humusowe oraz domieszki jonów metali ciężkich. W badaniach zastosowano dwa typy membran wykonanych z sulfonowanego polisulfonu (membrany o różnej zawartości grup sulfonowych). Zbadano efektywność usuwania jonów miedzi i cynku oraz współusuwania tych jonów z roztworów zawierających jony metali oraz substancje humusowe.

Membrany ultrafiltracyjne wykonane z sulfonowanego polisulfonu umożliwiają skuteczną separację jonów metali ciężkich z wodnych roztworów kwasów humusowych, gdyż zatrzymują kompleksy metaloorganiczne lub powodują współstrącanie wodorotlenków metali i substancji humusowych. W warunkach sprzyjających wytrącaniu słabo rozpuszczalnych związków metali obserwowano nieznaczny wzrost skuteczności zatrzymywania substancji humusowych, lecz efekt ten połączony był ze spadkiem przepuszczalności membran.

УДАЛЕНИЕ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ И ГУМИННЫХ ВЕЩЕСТВ ИЗ ВОДЫ С УПОТРЕБЛЕНИЕМ УЛЬТРАФИЛЬТРАЦИОННЫХ МЕМБРАН

Представлены результаты исследований ультрафильтрационной очистки водных растворов, содержащих гуминные вещества, а также примеси ионов тяжелых металлов. В исследованиях были применены два типа мембран, выполненных из сульфированного полисульфона (мембраны разного содержания сульфонных групп). Исследована эффективность удаления ионов меди и цинка, а также соудаления этих ионов из растворов, содержащих ионы металлов, а также гуминные вещества.

Ультрафильтрационные мембраны, выполненные из сульфированного полисульфона дают возможность эффективного разделения ионов тяжелых металлов из водных растворов гуминных кислот, так как они задерживают металлоорганические комплексы или вызывают соудаление гидроокисей металлов и гуминных веществ. В условиях, благоприятствующих осаждению слабо растворимых соединений металлов наблюдался незначительный рост эффективности задерживания гуминных веществ, но этот эффект был связан с понижением проницаемости мембран.