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Impact of water state in membranes on the purification of copper-containing aqueous solutions by complexation–ultrafiltration

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ABSTRACT

This paper deals with the investigation of ultrafiltration membranes of different chemical natures: polysulfone, polysulfoneamide, and polyamide ones produced by Vladipor (Russia) and Osmonics (USA). Coefficients of Cu(II) retention by membranes under investigation and transmembrane fluxes were determined in the process of ultrafiltration treatment of water containing Cu(II) and polyethyleneimine. The water state and quantity in membranes were also determined by the method of differential scanning calorimetry. The relationship of the transmembrane Cu(II) transfer and membrane total moisture content, amount of free and bound water in the membranes under investigation was established. Based on the data obtained by the DSC method and membrane total moisture content values, an assumption was made on the possibility of forming on the surface of the membranes a layer of Cu(II)–PEI complexes and partial overlapping by them at the mouths of membrane pores or penetration of these complexes into the pores of the membranes.

Keywords: Complexation; Differential scanning calorimetry; Ultrafiltration process; Water state

1. Introduction

The problem of water decontamination from heavy metals remains urgent since pollution of natural waters takes place as a result of the vital activity of man and the development of industry. Different methods are used to decontaminate such waters: sorption on natural [1] and synthetic [2] sorbents, coagulation and flocculation [3,4], the membrane methods — electro- and baromembrane [5–7]. With this in mind, combinations of methods of sorption and baromembrane treatment [8–10], micelle formation and complexation with subsequent membrane separation [11–25] are often used.

In this connection it was interesting to investigate regularities of Cu(II) ion retention in the presence of polyethyleneimine (PEI) by membranes of different chemical natures in the process of purification of a copper-containing solution by the method of complexation–ultrafiltration and to determine the effect of changes of the membrane total moisture content and water state in the membranes on this process.

2. Experimental

In order to investigate the process of Cu(II) ion retention by ultrafiltration (UF) membranes in the presence of PEI, this study used the method of complexation–ultrafiltration. To this end we applied different UF membranes: polysulfone — PW, ER, EW — (Osmonics, USA); polysulfoneamide — UPM-10, UPM-20, and UPM-50; and the UFM-30 polyamide membrane (Vladipor, Russia). The molecular-weight cut-off of these membranes is 10–100 kDa. Specifications of the membranes under investigation are presented in Table 1.

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Table 1
Characteristics of the investigated membranes

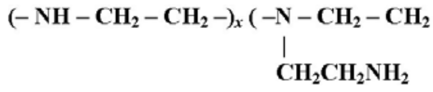
Membrane	Manufacturer	Material	MWCO, kDa	Max. *P*, MPa	pH	Transmembrane flux at *P* = 0.1 MPa, l/m^2·h	Max. temp., ºC
UPM-10	Vladipor, Russia	Polysulfoneamide	12.7	0.6	2–12	15	100
UPM-20	Vladipor, Russia	Polysulfoneamide	17.0	0.6	2–12	60	100
UPM-50	Vladipor, Russia	Polysulfoneamide	64.5–67.0	0.6	2–12	72	100
UFM-30	Vladipor, Russia	Polyamide	24.0	0.6	2–12	150	100
PW	Osmonics, USA	Polysulfone	10.0–12.0	0.2	2–11	25	90
ER	Osmonics, USA	Polysulfone	15.0–30.0	0.35	2–11	42	90
EW	Osmonics, USA	Polysulfone	50.0–100.0	0.17	2–11	75	90

Using the above-mentioned membranes we treated solutions having 3 mg/l Cu(II) and 9 mg/l PEI, i.e., at the concentration ratio Cu(II):PEI of 1:3. The most complete binding of copper into complexes takes place at this ratio. Reduction of Cu(II) retention coefficients at C_{PEI}:$C_{\mathrm{Cu(II)}}$ concentration ratios below the optimum is explained by the fact that the amount of PEI used is insufficient for binding the whole metal into stable complexes. At C_{PEI}:$C_{\mathrm{Cu(II)}}$ concentration ratios above the optimum, the metal retention coefficients are reduced owing to a possible formation of aggregates from PEI molecules at high concentrations of the polymer, resulting in reduced accessibility of PEI active centers due to the emergence of steric obstacles [26].

Working solutions were prepared at 20°C. Cu(II)-containing solutions were prepared from $\mathrm{CuCl_2 \times 2H_2O}$ salt of chempure grade (Aldrich, USA). Solutions under investigation had pH values in the range 7.8–7.9.

The studies were conducted in a laboratory cross-flow installation presented in Fig. 1. The working area of the membrane in the cell was 1.21 dm^2, solution flow rate over the membrane under study was 0.4 m/s, volume of the solution under study was 8.0 l, and working pressure was 0.2 MPa. Permeate samples of 100 ml each were taken at 0.5 h intervals. The duration of experiments was 2–3 h. The degree of permeate collection ranged from 0.063 to 0.65. Concentration of Cu(II) was determined using the photometric method [27].

As noted above, PEI (Aldrich, USA) with a branched structure having a molecular mass of 60 kDa was used as a complexing agent; its repeated structural element has the form



$$(-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-)_x\,(-\underset{\substack{|\\ \mathrm{CH_2CH_2NH_2}}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-)_y$$

Experiments on selection of PEI were carried out earlier [14]. PEI is characterized by its ability to form complex compounds with Cu(II) and other heavy metal ions. Stability of complexes of PEI and ions of heavy metals estimated by the Bjerrum method that implies the titration of PEI with acid in the presence of variable amounts of complexing ions makes it possible to arrange the latter in the order of growing stability of corresponding coordinating compounds with PEI in the following series [28]:

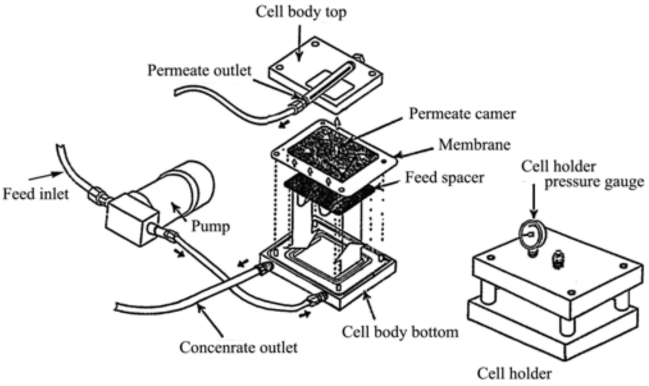
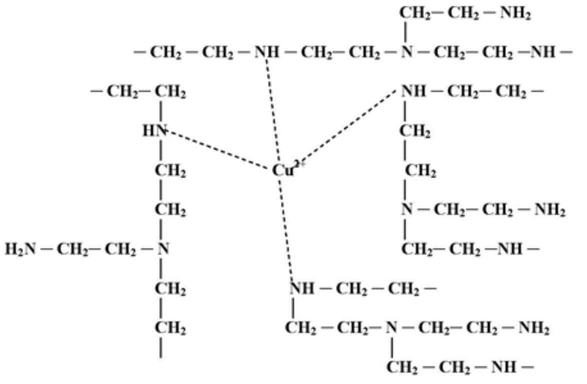


Fig. 1. Laboratory installation for cross-flow ultrafiltration.

$\mathrm{Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Pb^{2+} > Mn^{2+}}$.

As can be seen, copper forms stable complexes with PEI. The stability constant of complex of copper and PEI is $10^{16.6}$ [28].

The feasible structure of chelate complexes of PEI and Cu(II) corresponds to the following scheme:



However, the complexes of PEI and metal obtained at the stage of disposal of the resultant concentrate subsequently can be easily destroyed, for example, by acidation or electrolysis [12,28]. The PEI properties listed allow its repeated use in the combined complexation-ultrafiltration process designed for the treatment of polluted waters.

Copper retention coefficients for each of the membranes under investigation and transmembrane fluxes under the given conditions were calculated by the established procedure [29]. The membranes used, both the initial and taken after the separation process of solution containing copper and PEI, were investigated using differential scanning calorimetry (DSC). This method is commonly used for determining the amounts of free and bound water in various objects [30–32].

From the endotherms obtained, the water state in membranes (free and bound) was determined and its amount was calculated. Endotherms were recorded using a microcalorimeter DSM-2M at the scanning rate of 4 deg/min [33,34]. A sample of a membrane under study having a mass of 0.0047–0.0067 g was pressed into a container and subjected to cooling with liquid nitrogen during 1–2 min up to a temperature of $-50\,^{\circ}$C. Next, the system was kept for several minutes at $-50\,^{\circ}$C until equilibrium was achieved. Endotherms of the initial membranes (membranes kept in distilled water for ~24 h) and the membranes after the water treatment process for Cu(II) removal with the layer from PEI and complexes Cu(II)–PEI onto the membranes surface were recorded at temperature intervals of $-50\,^{\circ}$C – +20 °C. Calculation of the amount of free water was conducted on the basis of endotherms of ice melting. The amount of bound water was determined by the difference between the total moisture content and the amount of free water [35]. Moisture content of the membranes under investigation was determined by drying samples to constant mass at temperatures of 30–35 °C [36]. The accuracy of determination of the bound and free water quantity in membranes was ±0.01 $g_{\text{water}}/g_{\text{dry membrane}}$.

3. Results and discussion

Fig. 2 presents the relationships characterizing a variation of the retention coefficients and values of the transmembrane fluxes of membranes under investigation in the process of UF treatment of solutions containing Cu(II) ions and PEI. From the results obtained (Fig. 2a), it follows that the copper retention coefficients for the UPM-10, UPM-20, and PW membranes are sufficiently close: 0.96, 0.95, and 0.90 respectively. However, the comparison of their transmembrane fluxes (Fig. 2b) indicates that the highest flux of 56.6 l/m^{2}h is obtained for the UPM-20 membrane. This indicator for UPM-10 and PW membranes has the values 10.6 and 18.0 l/m^{2}h respectively.

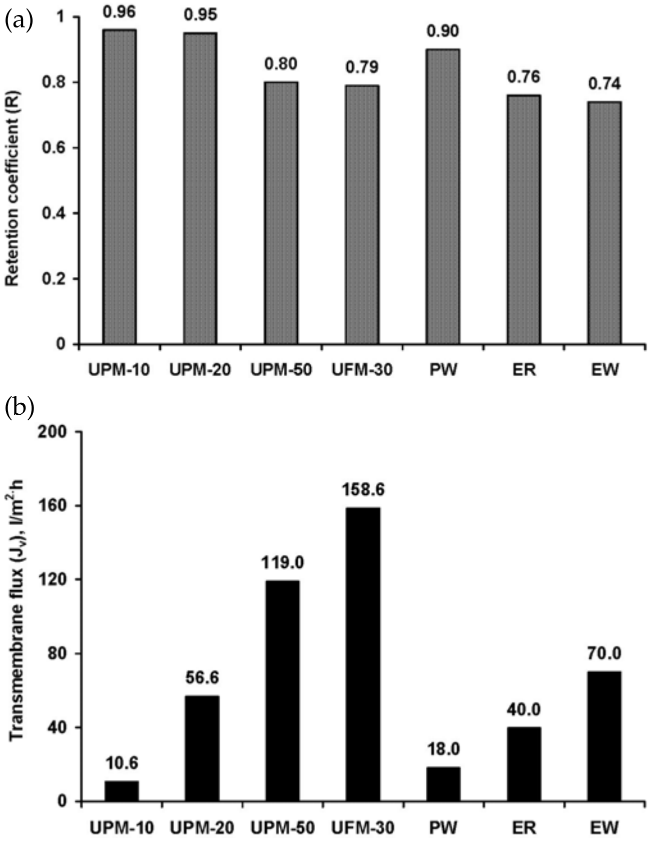


Fig. 2. Retention coefficients of Cu(II) by membranes (a) and transmembrane fluxes (b) at $P = 0.2$ MPa.

The membrane total moisture content, water state and amount of free and bound water in the membranes under study allowed us to explain the variation of transmembrane transfer of copper through these membranes.

Fig. 3a displays endotherms of initial membranes. In practice, all endotherms have one peak in the temperature interval of -1.4–$-4.7\,^{\circ}$C. Depending on the size of pores in a membrane the position of the endothermic peak is shifted one or the other direction within the temperature range. On endotherms of the EW, ER and UFM-30 membranes in the initial state, one can observe, in addition to the main peak, shoulders at lower temperatures, indicating the presence of pores of different sizes in given membranes. It is well known that reduction of pore size results in the reduction of water freezing temperature in the membrane [35]. Analyzing the endotherms obtained, one can suggest that the membranes having lower water freezing temperatures possess maximum retention capacity. Besides the size of pores in a membrane, their number, i.e., total porosity of membrane, is an important factor. The total porosity can be characterized by total moisture content of the membrane. Also it was of interest to calculate the amount of free and bound water in the membranes under investigation (Tables 2, 3).

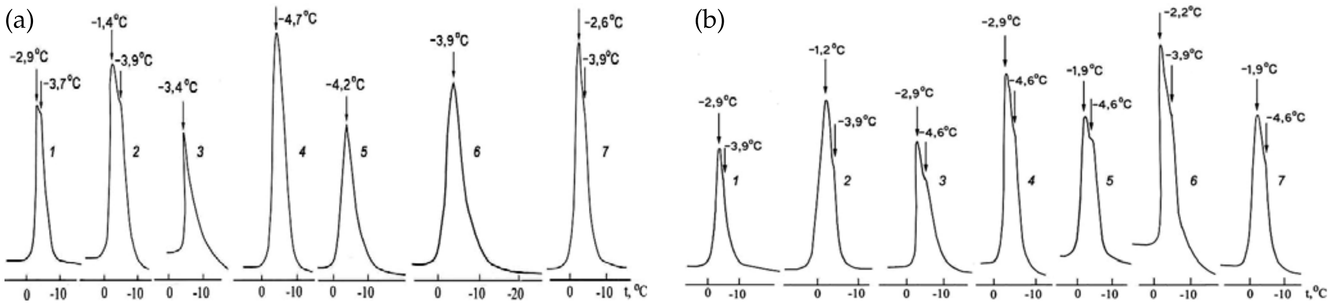


Fig. 3. Endotherms of ice melting in the initial UF membranes after immersing them into distilled water (a) and in the UF membranes after pressurizing Cu(II)-containing solution through the membrane cell in the presence of PEI (b): 1, EW; 2, ER; 3, PW; 4, UPM-10; 5, UPM-20; 6, UPM-50; 7, UFM-30.

Table 2
Water state in the initial UF membranes after them immersing into distilled water

Water state	EW	ER	PW	UPM-10	UPM-20	UPM-50	UFM-30
Moisture content, %	24	45	24	43	50	48	51
Free water, g/g$_{\text{dry membrane}}$	0.3	0.77	0.22	0.62	0.68	0.72	0.82
Bound water, g/g$_{\text{dry membrane}}$	0.01	0.05	0.09	0.12	0.34	0.21	0.22
Transmembrane flux at P = 0.2 MPa, l/m$^2\cdot$h	134	82	52	25	121	158	465

Table 3
Water state in the UF membranes after pressurizing Cu(II)-containing solution through the membrane cell in the presence of PEI

Water state	EW	ER	PW	UPM-10	UPM-20	UPM-50	UFM-30
Moisture content, %	28	46	36	45	46	51	56
Free water, g/g$_{\text{dry membrane}}$	0.34	0.72	0.42	0.61	0.73	0.73	0.9
Bound water, g/g$_{\text{dry membrane}}$	0.05	0.12	0.16	0.08	0.13	0.3	0.36
Transmembrane flux at P = 0.2 MPa, l/m$^2\cdot$h	70	40	18	10.6	56.6	119	158.6

It should be noted that during the water treatment process for removal of Cu(II) ions in the presence of PEI the dynamic layer may be formed onto the membrane surface and block the membrane pores. That is why the results obtained on the state of water in initial membranes (Table 2) can serve as reference marks for determination of changes in the investigated membrane structure after water purification from Cu(II) ions. Fig. 3b presents endotherms of UF membranes analyzed after water treatment from Cu(II) in the presence of PEI. Ice melting endotherms of the UF membranes investigated after the water treatment from Cu(II) have a somewhat different shape as compared with the waveform of endotherms of initial membranes (Figs. 3a and 3b). Main peaks with shoulders at lower temperatures can be identified at all the endotherms (Fig. 3b), unlike the endotherms of initial membranes PW, UPM-10, UPM-20, and UPM-50 where more than one peak without shoulders can be identified (Fig. 3a).

Analysis of the endotherms obtained (Figs. 3a and 3b) indicates that endotherms of the EW and ER membranes analyzed after the process of treatment of polluted water are slightly distinguishable from the initial ones. On the endotherm of the UFM-30 membrane (after the treatment), the position of the main peak shifts to the low-temperature region, while the position of the shoulder is in the high-temperature region. Endotherms of PW, UPM-10, UPM-20, and UPM-50 membranes having one peak in the initial condition are modified. The peaks on endotherms of the initial UPM-10 and UPM-50 membranes transform into shoulders on endotherms of the same membranes analyzed after the treatment of polluted water against the background of new main peaks emerging at high temperatures (Fig. 3b). On endotherms of the PW and UPM-20 membranes analyzed after treatment, we can observe the emergence of a main peak in the high-temperature region as compared with the shoulder that is shifted to the low-temperature region as compared with positions of peaks on the endotherms of initial membranes (Figs. 3a and 3b).

It should be noted that shoulders on endotherms of all membranes after the treatment are identified at temperatures of −3.9°C (Fig. 3b, curves 1, 2, and 5) or at −4.6°C (Fig. 3b, curves 3, 4, 6, and 7). This can be explained by the varying porosity of the UF membranes under study that is corroborated by quantitative data of free and bound water in the initial membranes and those after the treatment, and also by total moisture content (Tables 2 and 3). The analysis of the obtained results shown in Tables 2 and 3 demonstrated that the amount of free and bound water in the membranes following the treatment by them of copper-containing solutions undergoes changes.

The presence of a great amount of free water in the membranes investigated after the treatment (Table 3) may result from the formation on the surface of the membranes of a layer of the Cu (II)–PEI complexes. In addition, it is possible that the Cu(II)–PEI complexes partially overlap the mouths of membrane pores or these complexes penetrate the pores. As a result, the pores either become narrower or the number of pores involved in the treatment process decreases. Accordingly, this results in an increase or a decrease of the amount of bound water in the membranes.

Total moisture content of the membranes also undergoes changes in the treatment process. The EW membrane has the minimal moisture content both in the initial state and after treatment of copper-containing solutions (24% and 28% respectively). This can be explained by the presence in the given membrane of a great number of micropores (Table 1) whose moisture content is not properly recorded by the DSC method. The retention coefficient for copper by this membrane is minimal and equals 0.74. In this case the transmembrane flux is 70.0 l/m^2 h. It should be also noted that the ER membrane having an average value of moisture content (46%) possesses pores of large dimensions, which is indicated by higher melting points of ice in the membrane indicated by the endotherms (Figs. 3a and 3b, curves 2) compared with the endotherms of the UPM-10 and UPM-20 membranes having the same moisture content. The retention coefficient of the ER membrane is rather low too (0.76), which is proof of the presence in it of large pores.

The formation of a layer of the Cu(II)–PEI complexes on the surface of the membranes leads to an increase of total moisture content of the membranes investigated after treatment (Table 3). As can be seen from the results given in Table 3, the UPM-20 membrane is an exception. It is possible this is related to the presence in the PEI solution of its low-molecular fraction [37]. With such a PEI copper forms the complexes also. These complexes, getting into the membrane pores, can either be retained in them or pass into the permeate. Large-pore membranes (EW, ER, UPM-50, UFM-30) do not retain these complexes well despite a different chemical nature of the polymer framework. As a result, the copper retention coefficient of these membranes is low (0.74–0.80) although the transmembrane fluxes are sufficiently high (40.0–158.6 l/m^{2}h). When using small-pore membranes (PW, UPM-10), the Cu(II)–PEI low-molecular complexes along with high-molecular ones are involved in the formation of a layer on the surface of the membranes without penetrating their pores. The retention coefficients of the PW and UPM-10 are 0.90 and 0.96 respectively, while the transmembrane fluxes in this case are small (18.0 and 10.6 l/m^{2}h).

When using the UPM-20 membranes for copper treatment, the Cu(II)–PEI low-molecular complexes may penetrate the membrane pores, partially clogging them, which also results in a decrease of the amount of bound water and the total moisture content of the membrane. This reduces the transmembrane flux in the process of treating copper-containing solutions, while the retention coefficient for copper in the UPM-20 membrane is high (0.95).

4. Conclusions

This paper provided the following results:

- Main characteristics of the membrane process were determined: retention coefficients and transmembrane fluxes for UF membranes of different chemical natures during the process of treatment of copper-containing solutions by the complexation–ultrafiltration method.
- The amount of free and bound water in membranes, both initial and investigated after treatment of solutions containing the complexes of Cu(II)–PEI, was found by the method of DSC. Based on the data obtained and membrane total moisture content values, an assumption was made about the possibility of forming a layer on the surface of the membranes from the Cu(II)–PEI complexes and the partial overlapping by them at the mouths of membrane pores or penetration of these complexes into the pores of the membranes. This is what affects the separation characteristics of the membranes rather than the chemical nature of their polymer framework.
- It was shown that among the membranes investigated, the UPM-20 membrane features optimal separation characteristics for the given baromembrane process: high retention coefficient with simultaneous maintenance of sufficiently high transmembrane flux.

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