ADVANCES IN BAROMETRIC TREATMENT OF WASTEWATER

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Abstract: *An effect of adding thiosemicarbazyde to the compositions for the metal surface chemical treatment on effectiveness of the wastewater baromembrane cleaning has been investigated. Concentration of Fe^{3+} u Cu^{2+} ions in the source solutions was ensured by the standard preliminary wastewater treatment procedure (70 mg/dm^3). The most optimal complexation agent content was found as 10 mg/dm^3.*

Key words: *baromembrane cleaning, ultrafiltration, nanofiltration, complexation, membrane, filtration coefficient, specific productivity.*

Introduction

Contamination of the industrial wastewater with various heavy metals compounds often becomes a serious ecological problem [1-3]. The contamination with copper and iron compounds is mostly caused by the discharges from the stages of surface chemical treatment of various steel and copper alloys ware. These compounds (mostly water- and liposoluble) are highly toxic and can cumulate in the environment causing pathological changes in the central nervous, immune and reproduction human systems [4-7].

Deep and effective water cleaning and wastewater treatment is one of the most topical social and technological question and various membrane technologies has recently become one of the key solutions for extraction of the soluble metals compounds. Effectiveness of the membrane extraction can be advanced if the metal compounds have been transformed into a complex form. Complex compounds are less mobile and can be strongly fixed on the surface of membranes or adsorbers, which ensures both reduction of the metal compounds discharge and also significant reduction of their migration in the environment [8-12].

Previous investigations [13, 14] proved that thiosemicarbazyde derivatives can form complex compounds with the heavy metals ions and they were selected as complex-formation agent in the present investigation.

Experimental

An influence of the thiosemicarbazyde derivatives on effectiveness of the baromembrane cleaning of wastewaters produced from the stages of surface treatment of the steel St-10 and copper alloys has been investigated in this work. The wastewaters were collected after intense surface treatment of the metal ware at Chernivtsi machinery plant, which caused relatively high content of the heavy metals ions (70 mg/dm^3 of Fe^{3+} and Cu^{2+}). The complexing agent content was 10 mg/dm^3. This concentration ensures the most effective cleaning of the wastewater. Lower concentration of the agent causes less effective cleaning and higher concentration would not provide better results.

All the experiments were carried out in the static non-flow baromembrane cell at forced filtration of the source solutions through the membrane. Following membranes “Vladipor” (made by “Polymersynthesis", Russia) were involved in the experiments:

1. Composite ultrafiltration membrane UPM-4 based on the aromatic polysulfonamide "Sulfon-4T).
2. Composite nanofiltration membrane based on the polyamide substrate OPMN-P.

All the membranes were preliminary moulded under the pressure of 2.5 MPa in order to reach stable specific membrane productivity by the distilled water. A membrane impede factor *R* and membrane specific productivity I_V were used to determine the membrane's effectiveness. It is known [7, 8] that these parameters are mainly controlled by the working pressure, nature and concentration of the solution to be separated.

The *R* factor was calculated according to: $R = \frac{C_{sr} - C_{perm}}{C_{sr}} \cdot 100\%$, where C_{sr} and C_{perm} are concentrations of source solution (before filtration) and permeate (after filtration) respectively.

Specific productivity was calculated using the formula $J_v = \frac{V}{S \cdot \tau}$, where *V* – volume of the permeate; *S* – working surface area of the membrane and *t* – filtration time.

The impede factor for the copper and iron ions was found rising at increasing of the ultrafiltration working pressure from 0.1 to 0.25 MPa (see Fig. 1). This effect is caused by closer packing of the metal complexes on a membrane surface. Further increase of the pressure resulted in slow rising of *R*, which achieved 99 % and more under the pressure 0.75 MPa. As the working pressure increases from 0.1 to 1.0 MPa, the specific productivity of UPM-20 membrane linearly raises for 10 times and more for both Fe^{3+} and Cu^{2+} ions. Further increase of the pressure results in insignificant rising of the specific productivity due to the sediment formed on the membrane surface.

It was found that the maximal impede factor for the solutions containing thiosemicarbazide complexes of copper and iron can be reached for the ultrafiltration under working pressure 0.75 MPa.

As seen in Fig. 2, the membrane's productivity remains practically unchanged (~ 0.2 $m^3/(m^2$ hour) for the iron-containing solutions and ~ 0.17 for the copper-containing systems) if the concentration of Fe^{3+} and Cu^{2+} in the source solution ranges from 5 to 70 mg/dm^3. Extraction ratio exceeds 99.9 % for both ions and for all examples (Table 1).

The maximum permissible concentration of Fe^{3+} ions in the wastewater to be collected in the municipal sewage system is limited by 2.0 mg/dm^3 (and 0.3 mg/dm^3 for Cu^{2+}) [15]. Concentration of iron and copper in the wastewater after ultrafiltration meets this requirement (see Table 1) and this water can be collected in the municipal sewage system.

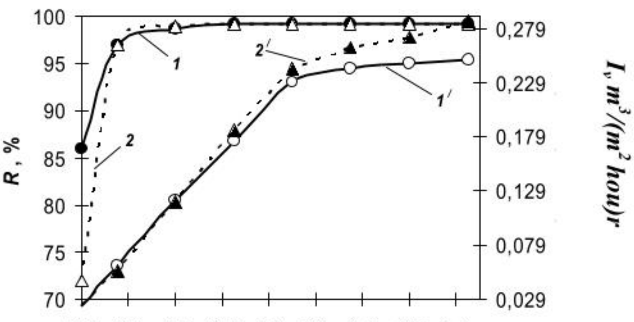

Figure 1. Dependence of the extraction ratio for iron (1) and copper (2) ions at the membrane UPM-20 and the membrane's specific productivity (1`, 2`) on the working pressure.

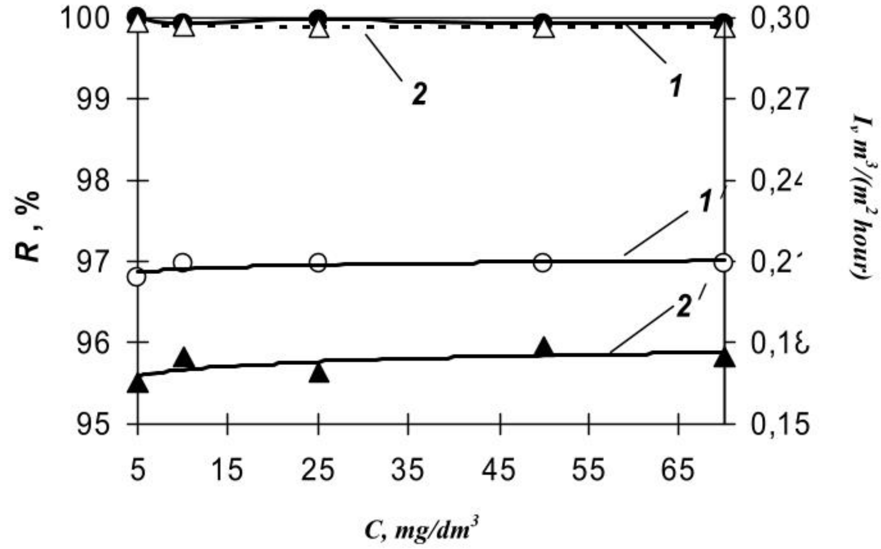

Figure 2. Dependence of the extraction coefficients for iron (1) and copper (2) and the membrane UPM-20 productivity (1` and 2`) on the ions concentration. Working pressure 0.75 MPa.

Table 1: Dependence of the concentration of Fe^{3+} и Cu^{2+} in the ultrafiltration permeate on the ions concentration in the source solution.

Initial concentration, mg/dm^3	Concentration in the permeate, mg/dm^3	
	Fe^{3+}	Cu^{2+}
5	0.000	0.030
10	0.070	0.010
25	0.075	0.0325
50	0.040	0.055
70	0.049	0.091

Changes of the ions concentration before and after the cleaning of membrane, as a function of the treated solution amount, is an important characteristic of the membrane productivity and effectiveness of the wastewater cleaning process. Sampling degree is another characteristic of the process. This value is calculated as a ratio of the total permeates flux (Q_p) to incoming flux of untreated wastewater (Q_i) and it is equal to 100 % in the end of filtration.

As seen in Fig. 3, the extraction coefficients of Fe^{3+} and Cu^{2+} do not depend on the sampling degree and remain close to 100 % even for $Q_p/Q_i = 96$ %.

Both extraction coefficients show similar dependence on Q_p/Q_i but dependencies of specific productivities on Q_p/Q_i for the copper- and iron-containing systems are different (see Fig. 3). The membrane productivity remains practically unchanged and equal to ~ 0.18 m^3/(m^2 hour) for the copper-containing solutions at any Q_p and shows strong dependence on Q_p/Q_i for the iron-containing systems. Initial membrane productivity in this case was close to the previous value (~ 0.18 m^3/(m^2 hour)). Baromembrane processes are usually kept at Q_p/Q_i = 60-70 % and the membrane productivity lowered to 0.027-0.019 m^3/(m^2 hour) for this value. This lowering can be assessed as 84-88 % from the initial membrane productivity. A membrane requires cleaning service if its productivity drops for 10-15 % [16] therefore, in this case the membrane cleaning would be required just in few minutes, which makes this process practically inapplicable to the iron-containing wastewater.

We suppose that filtration of the copper-containing solutions either forms easily permeable deposit on the membrane surface or the deposited particles can be easily moved during the filtration. Decreasing of the membrane productivity during processing the iron-containing solutions indicates formation of the dynamic membrane [17].

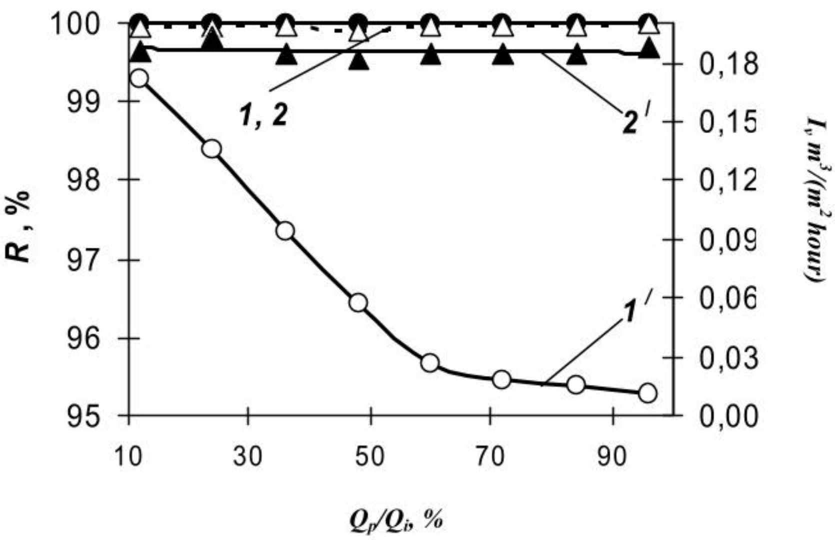

Figure 3. Dependence of the extraction coefficients for the iron (1) and copper (2) ions and specific productivity of UPM-20 membrane (1` and 2`) on the permeate output. Working pressure P = 0,75 MPa.

A mechanism of the ultrafiltration can be understood as a function of the media pH. pH of the source iron-containing solution is 2.95 and 3.40 for the copper-containing system. Iron hydrates start to form at pH = 2.3 and copper compounds – at 5.5 [17]. Therefore, the pH value for the iron-containing solution ensured covering the membrane surface with the dense deposit of insoluble hydroxocompounds, which caused deceleration of the filtration rate.

The filtration mechanism was determined through calculation of the convective filtration equation coefficients [18]. The process of filtration can run through four possible mechanisms according to [18]:

1. Monofiltration when each single particle blocks each single pore. This process of filtration can be described using an equation

$$I_v = I_0 - k_1 q,$$

where I_0 and I_v denote the initial and current permeate flux respectively; q – amount of the filtrated liquid passed through the membrane during the time τ and k_1 is a constant. This is rather unusual case.

2. Filtration with gradual blocking of the pores with several particles. This process can be described using an equation

$$\tau/q = 1/I_0 + k_2\tau/2,$$

where k_2 is a constant.

3. Combined filtration, which engages both above cases. This case can be described as

$$1/I_v = 1/I_0 + k_3 q/2,$$

where k_3 is a constant.

4. Filtration with deposition on the membrane surface. This process can be described as

$$\tau/q = 1/I_0 + k_4 q/2,$$

where k_4 is a constant.

Kinetic parameters of all the above process stay linear in their appropriate coordinates. Our calculations proved that the second mechanism prevails during the first hour of the filtration process (see Fig. 4, line 1).

Then the process runs under the mixed mechanism for about 80 min (Fig. 4, line 2). Finally the process turns to the fourth mechanism (Fig. 4, line 3).

As the abovementioned changes occur, general hydrodynamic resistance of a membrane raises but the rate of this rise slows down as the mechanism turns from the second to the fourt.

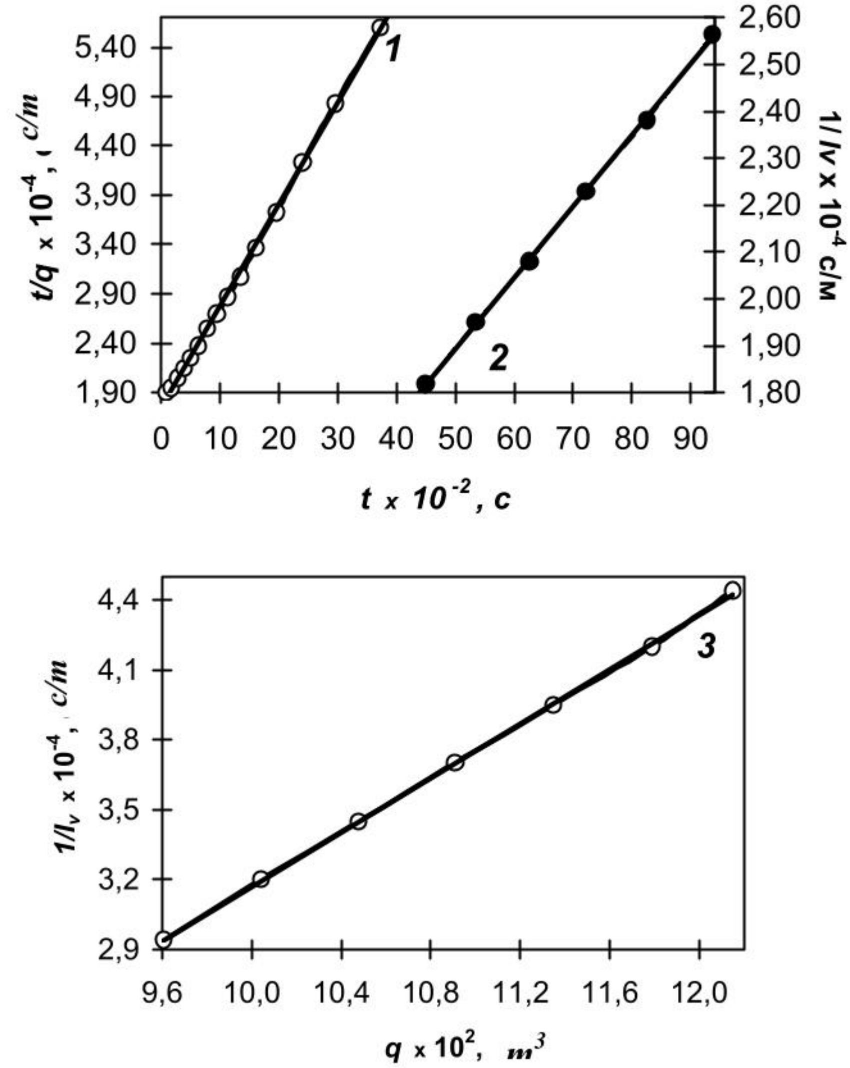

Figure 4. Kinetic parameters of the ultrafiltration of an iron-containing solution in the convective filtration theory coordinates. Membrane UPM-20, P = 0.75 MPa.

The mechanism 4 is the most effective and the mechanism 1 is the worst effective way of filtration [18]. Ultrafiltration of the iron-containing solution involves the mechanism 1, which makes this filtration technology ineffective for such solutions. However, baromembrane method or nanofiltration can be employed in this case.

Nanofiltration is a transitional cleaning method between ultrafiltration and reverse osmosis.

This is one of the baromembrane cleaning methods where a membrane can filter out the particles of 2 nm or more [19]. Therefore, bigger particles of hydroxocompounds would not be filtrated out and can pass through the membrane pores. Our experimental investigations have been carried out using a membrane OPMN-N and under the working pressure of 1.5 MPa [20].

Extraction coefficients for iron and copper were found equal almost to 100 % and independent on the permeate collection rate. Iron content in the solution after treatment was 0.007 mg/dm^3 and copper content was from 0.007 to 0.07 mg/dm^3. These values meet requirements [15] for collection the treated water in the regular municipal sewage.

Similarly to the ultrafiltration, the membrane specific productivity remains stable for filtration of the copper-containing solution and equal to 0.0608-0.0610 m^3/(m^2 hour). In case of the iron-containing solution this value slowly decreases with raise of the permeate collection ratio. The membrane should be cleaned [16] after its productivity drops for 15 %, which occurs at Q_p/Q_i = 72 %.

Small size of the nanofiltrating membrane pores causes difference in dependence of the specific productivity on the permeate collection rate for the iron- and copper-containing systems. A particle of the iron hydroxocompound is big enough and can not pass through the pore. This assumption is also proved by calculation of the kinetic parameters of the filtration process according to the equations of the convective filtration [18] (see Fig. 6).

Our results prove that the filtration runs according to the mechanism 4 (sediment formation of the membrane surface). The sedimentation passes through two stages: the faster and slower. This two-stage mechanism can be caused either by gradual filling of the first sediment layer with the iron hydroxocompounds particles and switching to filling of the second layer or by concurrent sedimentation of hydroxo- and thiosemicarbazyde complex compounds of iron.

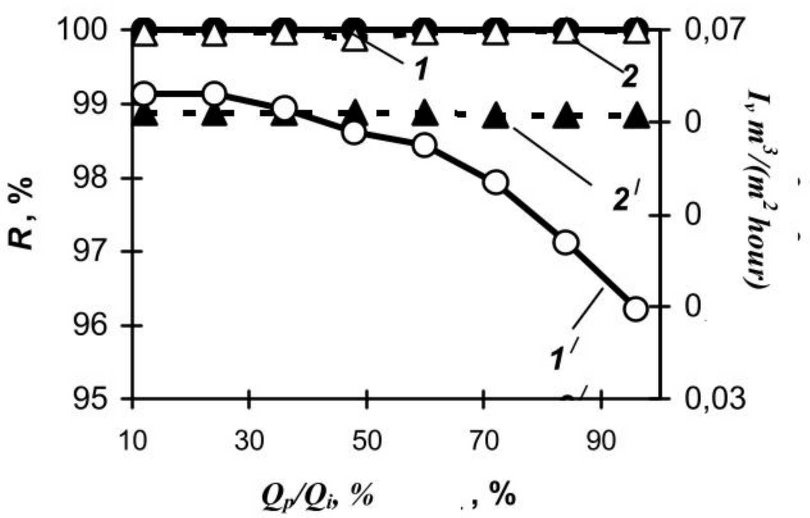

Figure 5. Dependence of the extraction coefficients for the iron ions (1) and copper (2) and specific productivity of OPMN-P (*1*′, *2*′) on the permeate collection ratio.

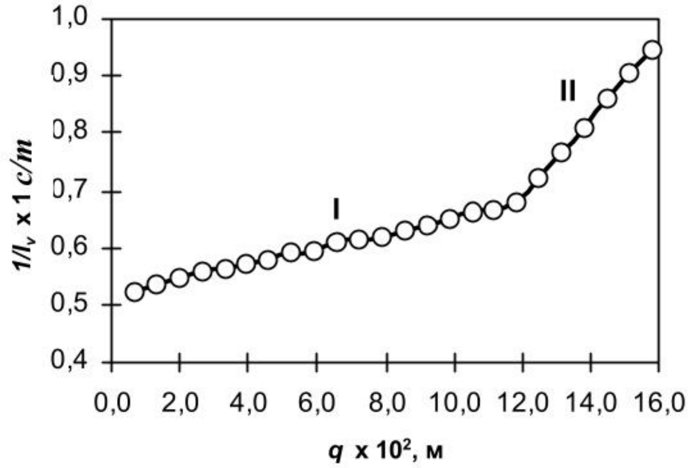

Figure 6. Kinetic parameters for filtration of the iron-containing solution in the convective filtration theory coordinates. Membrane – OPMN-P.

Conclusion

Baromembrane methods can be effective for cleaning the copper- and iron-containing wastewater. Cleaning effectiveness can be improved through preliminary fixing the metal ions into the complex compounds. Cleaned solutions can be discharged to the municipal sewage system or recycled within inner industrial water lines. Ultrafiltration ensures better cleaning for the copper-containing solutions and nanofiltration is more effective for the iron-containing systems.

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