NEUTRALIZATION WITH SIMULTANEOUS SEPARATION OF ALUMINUM AND COPPER IONS FROM CONDENSED WATER THROUGH CAPILLARY POLYPROPYLENE AND CELLULOSE DERIVATIVES

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Environmental problems arising from acidic waters containing aluminum and copper from condensing boilers can be adequately addressed using membrane processes. This paper deals with simultaneous neutralization and separation of aluminum and copper ion from acidic waters containing aluminum and copper traces through permeation through capillary composite membranes made of polypropylene with carboxymethyl cellulose (PP /CMC) inclusions. The optimum working parameters for the carboxymethylcellulose composite membrane were determined: operating time and pH of the receiving phase. Simultaneously with the quantitative removal of aluminum and copper ions, an almost neutral pH is obtained, compatible with the natural waters in which it can be dispersed.

Keywords: composite membranes, cellulosice derivatives, pertraction, aluminum separation, cupper separation

1. Introduction

An interesting and unpredictable environmental issue raises condensing plants, with an average output of 20-100 Kw, producing thermal energy in individual homes, associations or small public buildings [1-3].

Particularly, in Europe in the case of mural thermal plants, the condensate in the exhaust pipe goes back to the condensation module, from which it is drained to drain (sewage) by means of the condensate drain siphon [4].

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Although apparently clean water, the condensate pH between 2 and 4 is quite aggressive, because the range allowed by the European Directive for water spilled directly into the sewerage is limited in the range ≥ 6.5; ≤ 8.5 [5]. A further problem of the condensate is also the content of aluminum [6], copper [7] , but sometimes lead, tin or other elements of the pipe alloy composition [8].

Because classical separation techniques: alkaline precipitation, sedimentation, ion exchange, extraction are difficult to apply for obtaining the condensate (houses, public buildings) both because they require chemical treatment as well as complicated separation installations, water treatment by membrane techniques can efficiently solve problems in the case of small quantities effluent having a pH value close to the limits allowed for discharge or containing metal ion traces [9, 10].

Recently cellulose membranes based on pure regenerated cellulose, native cellulose or derivatives thereof are extensively used for treatment of small quantities effluents [11-13].

The uses of cellulose-based membranes are virtually limitless covering: water treatment from the energy industry, chemical and food industry, textiles and leather, agriculture and health, biotechnology and environmental protection [14, 15].

The appearance of composite membranes (inert matrix - cellulose derivative) has helped to increase the selectivity and productivity of membranes by using more and more elaborate cellulose derivatives [16-18].

The concomitant regulation of the thermal power stations condensate pH and the removal of aluminum ions is the subject of this study, which addresses permeation through capillary polypropylene membranes with cellulose derivatives inserts.

2. Experimental part

2.1 Materials and Apparatus

$Al_2(SO_4)_3 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, Sodium hydroxide, carboxy methyl cellulose (CMC), Sigma Aldrich, standard buffer solutions (pH= 1.68; 4.01; 7.00; 10.01) from EUTECH Instruments.

The ultrapure water used to prepare aqueous solutions of aluminum, copper or carboxymethylcellulose was obtained with a Millipore system based on reverse osmosis and ion exchange [19].

The capillary polypropylene / cellulose derivatives (PP/CD) composite membranes were obtained by impregnating the capillary membrane (PP) with the ionophore [19, 20].

The membrane module (Scheme I) has a total area of 1 m2, phase shaking (source and receiving) being made with individual peristaltic pumps [19].

The analyzes were performed with a CAMSPEC UV-VIS spectrometer and an atomic absorption spectrometer Atomic Absorption Sectrometer Perkin Elmer-AAnalyst 400 respectively [19, 21].

2.2. Procedures

Preparation of solutions

Source phase (SP), synthetic aqueous solution, simulating condensate water (pH 2-4, aluminum concentration 10^{-2}-10^{-4} Mol/L of $Al_2(SO_4)_3$ (342.131 g/mol) and copper ions 10^{-6}-10^{-4} Mol/L from $CuSO_4 \cdot 5H_2O$ (249.680 g/Mol), was prepared by dissolving aluminum, respectively copper sulphate in the chosen pH solution.

Receiving phase (RP), the potassium hydroxide solution has a concentration of 10^{-4} to 1 Mol/L and was obtained by contacting the solid substance at 25°C in water.

Membranes permeation

The installation used for the permeation study provides a usable membrane surface area of 1m2 [21, 22], the source phase solution volume is 3 L, and the receiving phase is 300 mL. The two phases are recirculated outside of the membranes (SP) and, respectively, through membranes (RP), by means of individual peristaltic pumps which can provide flow variations between 2 and 200 mL/s (Fig. 1).

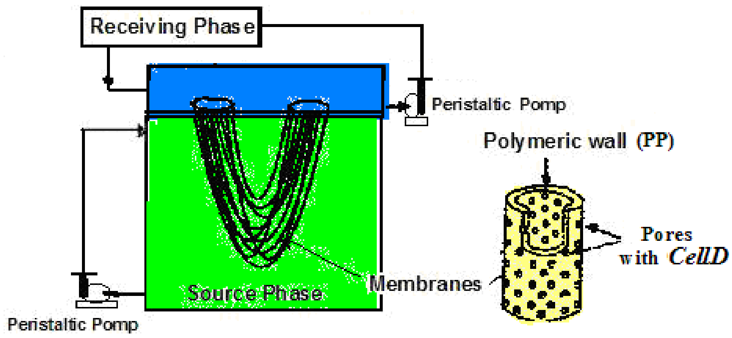


Fig. 1. The scheme of permeation installation

Samples for analysis are taken at pre-established times using 1 mL syringes and analyzed on the UV-VIS CAMSPEC spectrometer (for the receiving phase) and for validation of results at atomic absorption spetometer (AAS PerkinElmer) [23-25]. The pH of the source phase was monitored with a Radelkis pH/mV meter.

3. Results and discussion

The environmental problems that arise with the development of thermal energy systems (condensing plants) are becoming increasingly important, and therefore it is important to consider the discharge of condensate into the sewage system, because the condensate water has an acid pH and content of metal cations (aluminum, copper, tin, lead). These aspects (acid pH and metal ion content) can be suitably solved using membranes and membrane processes [22-28].

Practically, using the condensation water (pH = 2-4, containing Al^{3+}) as the source phase, the H_3O^+ ions and the aluminum ions are removed by the membranes if the receiving phase has a basic pH (Fig. 2). The interaction of the hydrous and aluminum ions with the cellulose derivative is complex involving both the functional and free hydroxyl groups of the cellulose [20, 27,27].

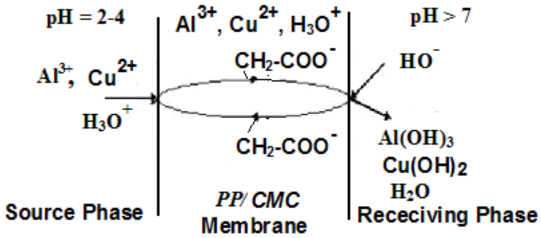


Fig. 2. Separation by pertraction with pH gradient: (a) H_3O^+ - chemical species of interest; Al^{3+} and /or Cu^{2+} competitive chemical species; HO^- - specific chemical reagent for the chemical species ; Al^{3+}, - CH_2-COO- membrane ionophore, Al $(OH)_3$, $Cu(OH)_2$ - insoluble compounds

The ionophore from the composite membrane, a cellulose derivative: carboxymethyl cellulose (CMC), (Fig. 3) is one of the most performing ingredients [20].

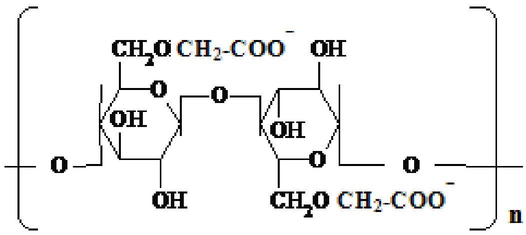


Fig. 3. Cellulose derivatives used as ionophores in the composite membrane: PP/CMC: carboxymethylcellulose (CMC)

Receiving phase optimal flow rate determination

In order to determine the optimal flow rate of the receiving phase, the source solution, with a volume of 10 times higher than the receiving phase, was recirculated at a constant rate of 100 mL/s at standard pH of 1.68 and 4.01 and a concentration of 10^{-4} Mol/L of $Al_2(SO_4)_3$ and $CuSO_4 \cdot 5H_2O$.

The receiving phase flow (Q_{RP}) is varied between 5 and 25 mL/s at pH 14 in the receiving phase. The operating time is kept constant, 4 hours, for each working flow. The experimental study shows that the source phase neutralization occurs totally in the working time at receiving phases flows above 15 mL/s (Fig. 4).

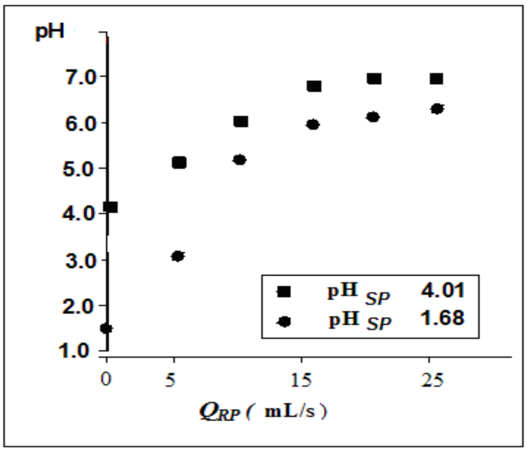


Fig. 4. Variation of performance parameters for neutralization depending on the recirculation flow of the receiving phase with membrane based on CMC

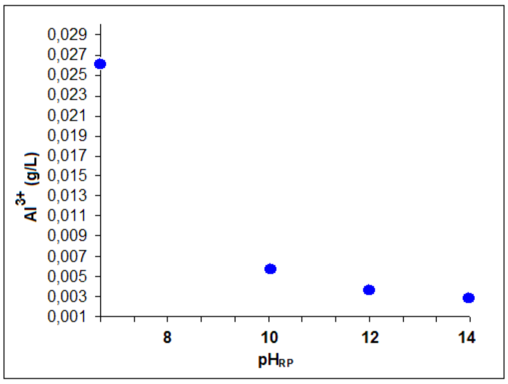
It can be appreciated that a flow rate of 20 mL/s of the receiving phase could be an optimal operating parameter in both technical and economical terms.

Determination of pH and optimal working time

In order to determine the pH and optimum working time, the polypropylene membrane installation with carboxymethylcellulose (PP/CMC) inserts was used, the source phase (Al^{3+} and Cu^{2+} 10^{-3} M; pH = 2) with a flow rate of 200 mL/s is contacted one at a time with receiving phases at a flow rate of 20 mL/s and pH = 7.00; 10.01; 12 and 14.

In Fig. 5 are observed significant differences in the evolution of aluminum, copper ion concentration and pH in the source phase at 4 hour operating time at the four pH values of the receiving phase (Fig. 5 a-c).

Although the increase in the pH of the receiving phase is favorable both for the neutralization of the condensate and the removal of the two ions, it is recommended to limit it to the value of 12, in which the losses of carboxymethylcellulose in the receiving phase are avoided. However, it is possible to operate above this pH value if the receiving phase is recirculated in a closed system, with systematic pH correction at the chosen value, when a solubilization of the carboxylic derivative no longer affects the balance of materials.



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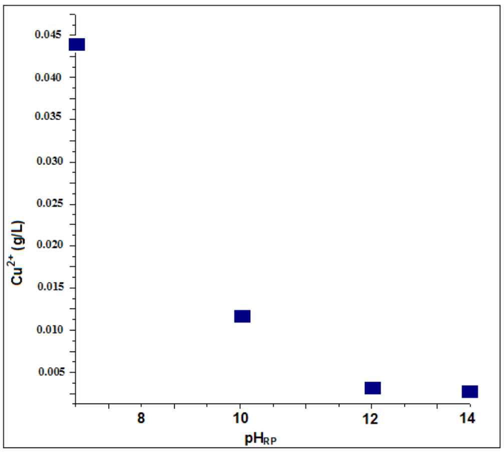

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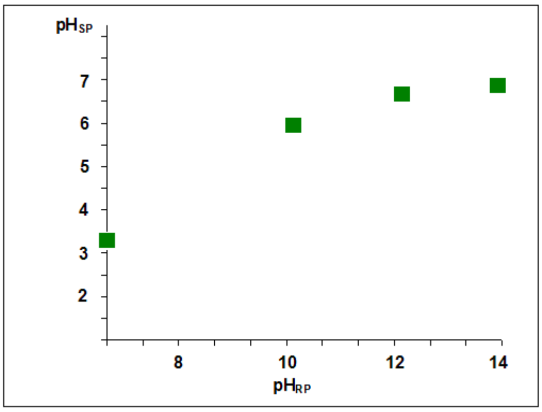
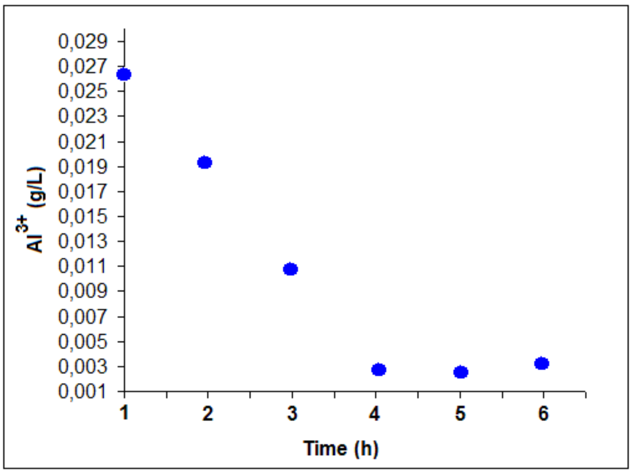


c

Fig. 5. Parameters performance variation for aluminum (a), copper (b) pertraction and neutralization (c) depending on receiving phase pH

The required 4 hour operating time is justified by the need of using fresh receiving phases or with the pH to the required value twice for the 8 hour working period. Verification of this working range was done by varying the actual operating time without the intake of the receiving phase.

In the given experimental conditions: polypropylene membrane installation with carboxymethylcellulose inserts (PP/CMC), source phase (10^{-3} Mol/L of $Al_2(SO_4)_3$ and CuSO4 with pH = 2) with a flow rate of 200 mL/s and a receiving phase with a flow rate of 20 mL/s and a pH of 12, operating time has been varied (Fig. 6).



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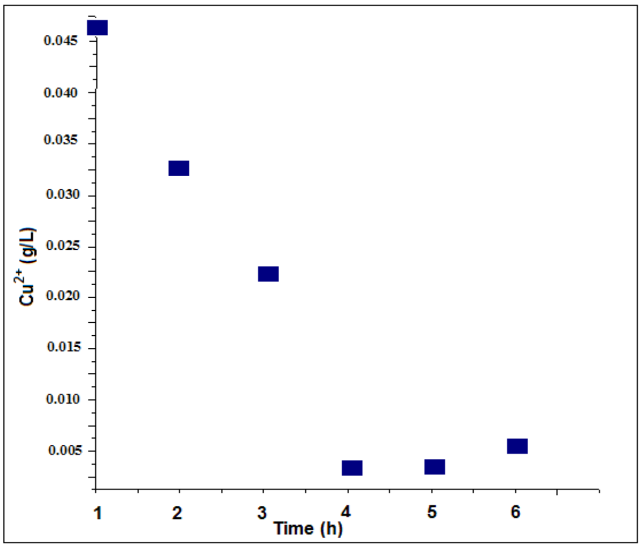

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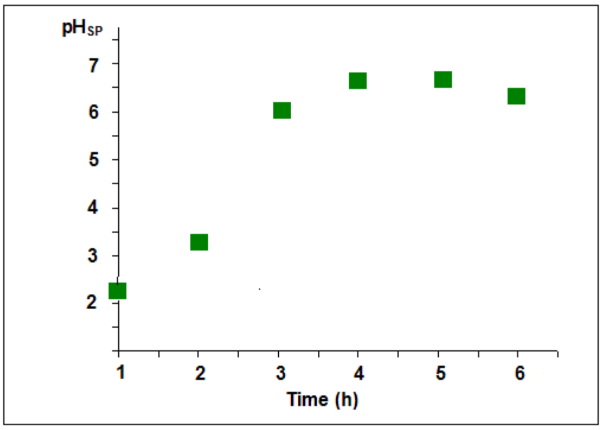

c

Fig. 6. Petraction variation for aluminium (a) and copper (b) and neutralization (c), depending on the operating time

From the results shown in Figs. 6 a, b and c, the self-imposed working time of 4 hours corresponds largely to the optimum value of 4-5 hours, both in the removal of aluminum or copper ions, especially in terms of neutralization. It is interesting to note that after 4 hours the performance of the process, especially the neutralization, decreases suggesting an osmotic or retro-dialysis process, generated by lowering the pH gradient.

4. Conclusions

Membrane processes can help to avoid environmental problems that are generated by acidic waters with aluminum and copper traces generated by boilers producing thermal energy in condensation. The concomitant reduction of the condensation pH of the thermal plants and aluminum and copper ions removal is the subject of the present study, which addresses permeation through polypropylene capillary membranes with carboxymethylcellulose inserts. The optimal operating parameters were determined: the flow rate, pH of the receiving phase and working time. It is interesting to note that after 4 hours of operation, process performance, especially neutralization, decreases suggesting an osmotic or retro-dialytic process, caused by a decrease in pH gradient.

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