

# Neutralization with Simultaneously Separation of Aluminum Ions from Condensate Water through Cellulose Derivatives-Capillary Polypropylene Composite Membranes

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*Environmental problems that arise from acidic water containing aluminum generated from condensing thermal power plants can be suitably solved using membrane processes. In this paper, simultaneous neutralization with aluminum ion separation, from acidic waters containing aluminum traces, through permeation with polypropylene with inclusions of cellulose derivatives (PP / CellD) capillary composite membranes is approached. Cellulose derivatives considered are: acetylcellulose, carboxymethylcellulose, 2-hydroxyethyl cellulose, methyl 2 hydroxyethyl cellulose. The optimum working parameters for the best performance of composite membrane based on carboxymethylcellulose were determined: operating time and pH of the receiving phase. Simultaneously with the quantitative removal of the aluminum ions, it is obtained an almost neutral pH purified water, compatible with the natural waters in which it can be dispersed.*

*Keywords: composite membranes, cellulosic derivatives, pertraction, aluminum separation*

The unprecedented development of heat generation systems with condensing boilers, both for domestic heating and especially for public buildings (schools, hospitals, administrative spaces, etc) has generated an important environmental problem for the whole European area where there are severe restrictions on the discharge of water into sewage [1-3].

Particularly, in Romania, the majority of condensing boilers are mural thermal plants, where 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 [2].

Although apparently the condensate pH of condensing boilers between 2 and 4 is not too aggressive, however, the range allowed by the European Directive for water spilled directly into the sewerage is limited [4]. Thus, the condensate of the thermal boiler evacuated to the sewerage must be within the required limits, meaning that the pH must be within the range of  $\geq 6.5$ ;  $\leq 8.5$  [5]. A further problem of the condensate is also the content of aluminum [6], or even copper ions [7].

Water treatment by membrane techniques has solved a large part of high effluent problems in small quantities and pH close to the limits allowed for discharge or containing metal ion traces [8-10].

In particular, cellulosic membranes are based on pure regenerated cellulose, native cellulose or derivatives thereof are extensively used [11-13].

Cellulose membranes have been produced for over a hundred years and have been among the first artificial membranes used in potable water production, desalination and food industry [12-15].

The properties of cellulose-based membranes are: biocompatibility, technical and economic accessibility, smoke, water, oxygen, other gases, water permeability, oil and hydrocarbons impermeability, excellent mechanical

strength (flexibility, elasticity, contractility, bend and torsion) the possibility of thermal, chemical and radiation sterilization [16-20].

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 [21-25].

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 [26-28].

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.

## Experimental part

### Materials and methods

#### Materials and apparatus

$\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ , Sodium hydroxide, acetylcellulose, carboxymethylcellulose, 2-hydroxyethyl cellulose, methyl 2 hydroxyethyl cellulose, Sigma Aldrich, standard buffer solutions (pH= 1.68; 4.01; 7.00; 10.01) from EUTECH Instruments.

Ultra pure water was obtained with a Millipore system.

The capillary polypropylene / cellulose derivatives (PP / CD) composite membranes were obtained by impregnating the capillary membrane (PP) with the ionophore [31, 32].

The membrane module (scheme I) has a total area of 1 m<sup>2</sup>, phase shaking (source and receiving) being made with individual peristaltic pumps [33, 34].

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The analyzes were performed with a CAMSPEC UV-VIS spectrometer and an atomic absorption spectrometer Atomic Absorption Spectrometer Perkin Elmer-AAAnalyst 400 [35, 36], respectively.

### 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) was prepared by dissolving aluminum sulfate 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  $1m^2$  [31, 32], 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).

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 spectrometer (AAS PerkinElmer) [36-39].

The pH of the source phase was monitored with a Radelkis pH / mV meter.

### Results and discussions

Environmental issues that arise with the development of the energy industry are multiple [40-42]. Of course, large production units require special attention to both water pollution and air pollution or even soil [43-46]. However, small units producing domestic energy or for public buildings, which are mostly thermal condensing boilers, raise more and more problems. The pH of the condensate (2-4), but also the content of metal cations (aluminum, copper, tin, lead, ...) are aspects that must be taken into consideration for the discharge to the sewerage.

Both aspects presented, acid pH and metal ion content can be suitably solved using membranes and membrane processes [16-18, 31,32].

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.

The ionophore from the composite membrane is a cellulose derivative: acetyl cellulose (AC), carboxymethyl cellulose (CMC), 2-hydroxyethyl cellulose (HEC), methyl 2 hydroxyethyl cellulose (MHEC) (fig. 3).

#### Receiving phase the 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  $Al_2(SO_4)_3$ .

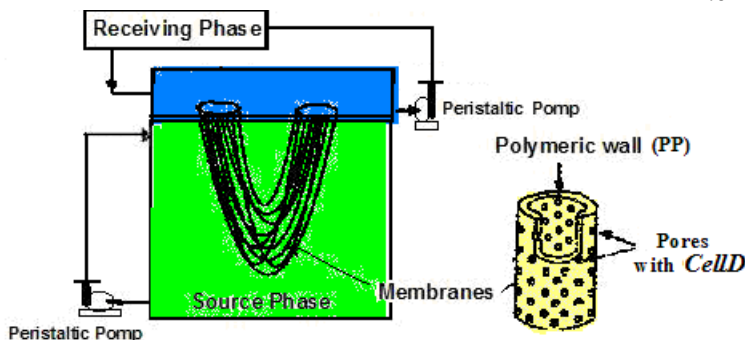


Fig. 1. The scheme of permeation installation

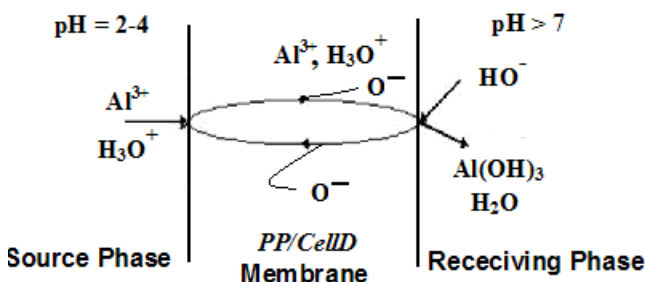


Fig. 2. Separation by pertraction with pH gradient: (a)  $H_3O^+$  + chemical species of interest;  $Al^{3+}$ - competitive chemical species;  $HO^-$ -specific chemical reagent for the chemical species  $Al^{3+}$ ,  $O^-$  membrane ionophore,  $Al(OH)_3$  - insoluble compound

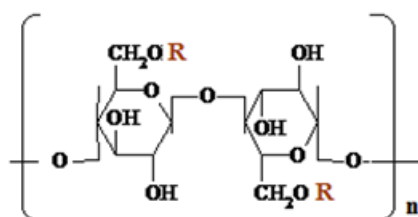


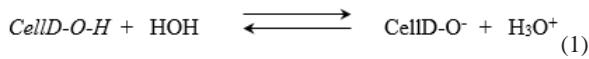
Fig. 3. Cellulose derivatives used as ionophores in the composite membrane PP/CellD: a) acetylcellulose (AC), b) carboxymethylcellulose (CMC), c) 2 hydroxyethyl cellulose (HEC), d) methyl 2 hydroxyethyl cellulose (MHEC)

R = a) acetyl; b) carboxy-methyl; c) hydroxy-ethyl; d) methyl-hydroxy-ethyl

The receiving phase flow ( $Q_{RP}$ ) is varied between 5 and 25 L/s at pH 14 in the receiving phase. The operating time is kept constant, 4 h, 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 a-d)

The differences for the four types of membranes studied are both in the evolution of the source phase pH increase and in the limit pH reached at the maximum operating rate of the receiving phase. Thus, the efficiency of cellulose-derived ionophore polypropylene membranes decreases in the order of: CMC > AC > MHEC > HEC.

These differences are correlated with the decrease in acid constants,  $K_a$ , of the groups: carboxymethyl > acetyl > methylhydroxyethyl > hydroxyethyl.



$$K_a = \frac{[\text{CellD-O}^-][\text{H}_3\text{O}^+]}{[\text{CellD-O-H}]} \quad (2)$$

#### 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 ( $\text{Al}^{3+} 10^{-3} \text{ M}$ ;  $\text{pH} = 2$ ) 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.

Figure 5 shows significant differences in the evolution of aluminum ion concentration and pH in the source phase at 4 h operating time at the four pH values of the receiving phase.

In order to avoid solubilization of the cellulose derivative in the receiving phase, it is preferable to choose the pH = 12, which is a good compromise between the need for neutralization and removal of the metal ion and the presumptive losses of the cellulose derivative if it would operate with the receiving phase in open system.

The operating time used in the previous experiments, 4 h, was chosen so that the condensation water treatment was done twice, with fresh receiving phases, within 8 h working time for the workers.

In order to see if this working time is close to the optimum time of a treatment cycle without changing the receiving phase, has varied in the given experimental conditions: polypropylene membrane installation with carboxymethylcellulose inserts (PP / CMC), source phase ( $\text{Al}^{3+} 10^{-3} \text{ M}$ ,  $\text{pH} = 2$ ) 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 (fig. 6).

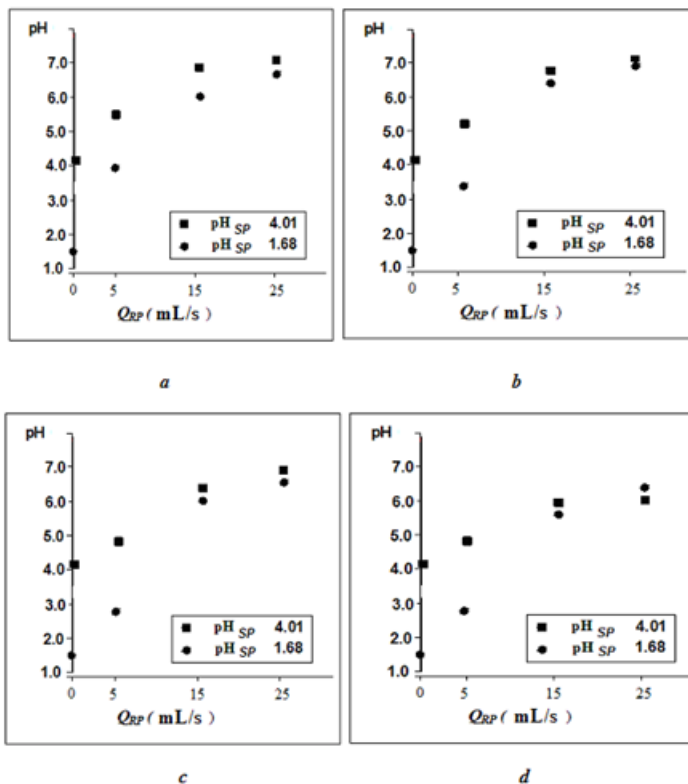


Fig. 4. Variation of performance parameters for neutralization and pretraction of aluminum according to the recirculation flow of the receiving phase with membrane based on: a- CMC; b- AC; c- MHEC; d-HEC

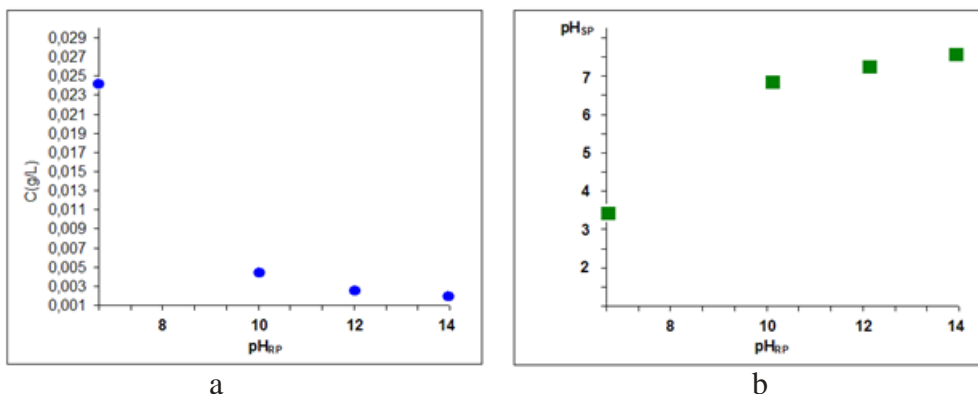


Fig. 5. Parameters performance variation for aluminum pretraction (a) and neutralization (b) depending on receiving phase pH

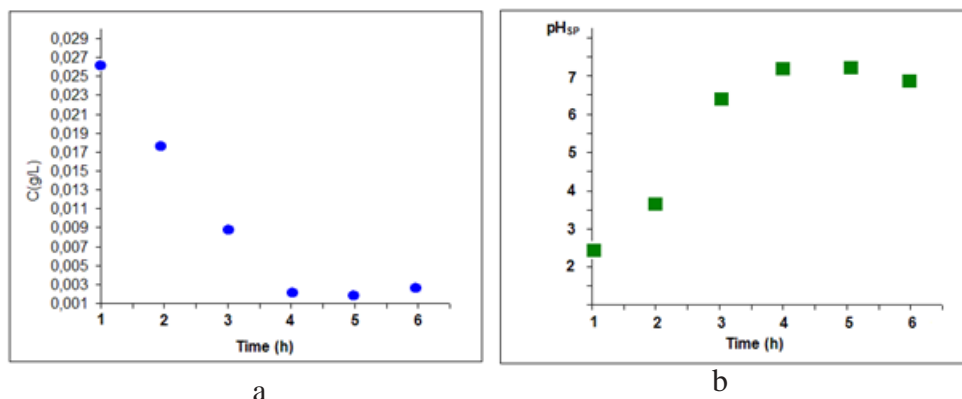


Fig. 6. Aluminium petraction variation (a) and neutralization (b), depending on the operating time

From the results shown in figures 6a and 6b, the previously chosen working time, of 4 h, is approaching to the optimum value of 4-5 h, both in terms of aluminum ions elimination, especially neutralization.

It is noted that exceeding the 4 h interval results in a performance regression, especially in the case of neutralization, which suggests an inverse process controlled by dialysis due to lowering of the pH gradient.

Simultaneously with the quantitative removal of the aluminum ions, it is obtained an almost neutral pH purified water, compatible with the natural waters in which it can be discharged.

## Conclusions

Environmental problems that arise from acidic water containing aluminum from condensing boilers can be adequately addressed using membrane processes.

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.

The cellulose derivative considered: acetyl cellulose (AC), carboxymethyl cellulose (CMC), 2-hydroxyethyl cellulose (HEC), methyl 2 hydroxyethyl cellulose (MHEC).

The efficiency of cellulose-derived ionophore polypropylene membranes decreases in the order: CMC > AC > MHEC > HEC.

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