

Iono-molecular Separation with Composite Membranes

VIII. Recuperative aluminium ions separation on capillary Polypropylene S-EPDM composite membranes

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Environmental problems occurring in isolated or hardly accessible inhabited areas can be adequately addressed using membranes and membrane processes. In the present paper, the recuperative separation of aluminum ion from the aluminum sulfate-treated water through permeation using capillary composite membranes, from polypropylene with ethylene propylene diene terpolymer sulfonic acid (PP / S-EPDM) inclusions is followed by the reaction of complexation with 8-hydroxy quinoline. The installation used for studying the permeation process provides a usable surface area of 1 m², the source phase solution volume is 3 L, and the receiving phase is 300 mL. The two phases are recirculated through the outside of the membranes (SP) and respectively through membranes (RP), by means of individual peristaltic pump that can provide flow variations between 2 and 200 mL / min by varying the intensity of the power supply. The optimal operating parameters were determined: operating time, pH and receiving phase flow, thus achieving an ionic flux (IR) above 10⁻¹¹ mol / cm² . s and a recovery factor (RF) over 90%.

Keywords: composite membranes, EPDM, pertraction, aluminum separation, 8-hydroxy quinoline

Membranes and membrane processes have stepped in the industrial application field for almost half a century: desalination, potable water treatment and purification, hydrometallurgy, biotechnology, food industry and agriculture, fully demonstrating their selectivity, productivity, robustness and simplicity in operation, reduced investment and competitive costs [1-3].

In the last decade, research in this area is called to solve some complex environmental issues from isolated or hardly accessible areas such as depressions [4-6], but also to increase the membrane and membrane processes selectivity, while improving the ratio between useful surface and membrane module volume [7,8].

Whether we are talking about the removal of microparticles or harmful compounds from air or water, or we are addressing the recovery of some organic (dyes, polymers, proteins) or inorganic (oxides, heavy metal ions) substances determining for success of the chosen process the are the type and performance of the membranes [9,10].

Using composite membranes complex processes were performed: colloidal ultrafiltration [11], pervaporation [12], pertraction [13], electrodialysis [14], and liquid membranes [15], which were evaluated in terms of process performance using as target substances nitrophenols [16].

The results obtained for the removal and separation of nitrophenols are promising because the composite membranes have demonstrated high selectivity and outstanding fluxes [17,18].

The process that focused attention through directed selectivity brought to the separation is pertraction (fig. 1), which combines the different mediated permeation velocity of the chemical species in the receiving phase through the membrane, with selective extraction by means a chemical reaction in the receiving phase (acceptor).

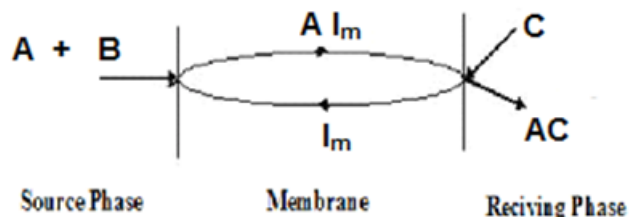


Fig. 1. Separation conducted by pertraction: A-chemical species of interest, B- competitive chemical species, C- specific reagent for the chemical species A, I_m - Membrane ionophore, AC-useful compound

The pertraction is a membrane process of great interest both because selectivity can be imposed through the membrane ionophore (I_m) or chemical species C, and because this substance (C), if properly chosen, can result in a practical utility AC compound, so the separation becomes recovering [19,20].

In the previous study, it was shown, for the case of nitrophenols that by suitable coupling, esterification or etherification reactions can be obtained by percolation: dyes, medicaments, antidepressants [21].

In the present paper, the recuperative separation of aluminum ion from the aluminum sulfate-treated water through permeation using composite membranes, followed by the reaction of complexation with 8-hydroxy quinoline is approached.

Experimental part

Materials and methods

Materials and apparatus

$Al_2(SO_4)_3 \cdot H_2O$, $MgSO_4$, $CaSO_4$, and 8-hydroxyquinoline, Sigma Aldrich, standard buffer solutions (pH = 1.68; 4.01; 7.00; 10.01) from EUTECH Instruments.

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Capillary polypropylene / ethylene propylene diene terpolymer sulfonic acid (PP / S-EPDM) composite membranes were obtained by capillary membrane (PP) impregnation with ionophore (S-EPDM) [21, 22].

The membrane module has a total area of 1m² [10, 21], phase recirculation (source and receiving) being made with peristaltic pumps.

Ultra pure water was obtained with a Millipore system.

The analyses were performed with a UV-VIS CAMSPEC spectrometer and respectively an atomic flame emission spectrometer PHLAFO 4. Atomic Adsorption Spectrometer Apparatus PerkinElmer AAnalyst 400 for the analysis validation.

Procedures

Solution preparation

The source phase (SP), represented by synthetic aqueous solution that simulates a water that has been treated with aluminium sulphate, was achieved by dissolving equimolar amounts of Al₂(SO₄)₃ (342.131 g / mol), MgSO₄ (120.361 g / mol) and CaSO₄ (136.134 g / mol) in the pure water so that the concentration of each is at the solubility limit of the heaviest soluble sulphate, calcium sulphate, cca. 0.3%. The stock solution is 10⁻³ mol / L (M) for each of the three cations studied.

Receiving phase (RP), 8-hydroxyquinoline (HQx) (145.161 g / mol, pK_{a1} = 5.017; pK_{a2} = 9.812) solution was obtained by contacting the solid substance at 25°C in ultrapure water or standard buffer solutions, a saturated solution (less than 1 mg / mL) being obtained.

Permeation through membrane

The installation used for studying the permeation process provides a usable surface area of 1 m² [21], the source phase solution volume is 3 L, and the receiving phase is 300 mL.

The two phases are recirculated through the outer membranes (SP) and membranes (RP), respectively, by means of individual peristaltic pumps that can provide flow variations between 2 and 200 mL / min by varying the intensity of the power supply.

Samples for analysis are taken at pre-established time intervals using 1 mL syringes and analyzed using UV-Vis CAMSPEC spectrometer (for the receiving phase) and for result validation at atomic absorption spectrometer (AAS PerkinElmer).

The results of permeation analyzes are used in terms of ionic fluxes (IF) and recovery factor (RF), according to relations (1) and (2):

$$IF = \frac{M}{S \cdot t} \quad (\text{mol/cm}^2\text{xs}) \quad (1)$$

where: M= moles of permeate (l)

S = the effective surface area of the membrane (cm²)

t = time (s)

$$RF = (c_o - c_f) / c_o \quad (2)$$

where: c_f - is the final concentration of the ion,

c_o - initial concentration of the ion

$$R = (A_o - A_{\text{sample}}) / A_o \quad (2')$$

where: A_o - initial sample solutions absorbance

A_{sample} - current samples absorbance

Results and discussions

Environmental problems occurring in isolated or hard-to-reach inhabited areas [23-26] can be adequately solved using membranes and membrane processes [27-29].

Whether its air particle removal or water treatment and purification, membrane processes can prove their usefulness because they can be applied with remarkable results for small communities [8, 10].

A particular case is the need to remove the aluminum ions from the waters resulting during treatment with aluminum sulfate as a flocculant.

Both the low aluminum concentration and the significant water volumes that should be purified suggest that a membrane process can solve this problem technically and economically.

Starting from the previous results obtained using a standard pertraction module [8, 21] and desiring to separate aluminum in the form of a useful complex compound namely, 8-hydroxyquinoline [30], this study aimed to establish the optimal operational and performance parameters: operating time, receiving phase flow through the membrane system, working pH, and ion flow and recovery factor.

The study was performed on a standard aqueous solution, simulating the ionic charge of aluminum sulfate treated with Ca²⁺, Mg²⁺ and Al³⁺, which constituted the source phase. Membrane system receiving phase was achieved by saturation of pure water with 8-

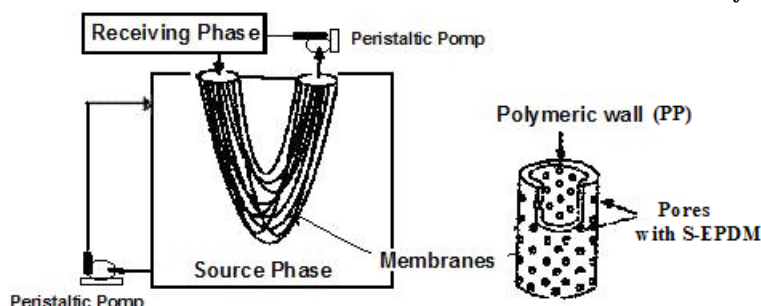


Fig. 2. The permeation installation

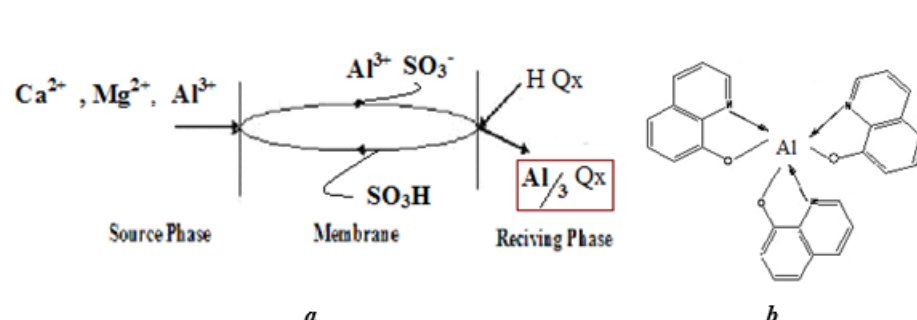


Fig. 3. Separation by directed pertraction: (a) Al³⁺- chemical species of interest; Ca²⁺, Mg²⁺ - competing chemical species; HQx- specific reagent for the chemical species Al³⁺, -SO₃H - membrane ionophore, Al₃Qx - useful compound; (b) useful compound structure

hydroxyquinoline, in order to obtain a useful compound by separating the aluminum through the PP / S-EPDM membrane (fig. 3).

Determining the optimal flow rate of the receiving phase

In order to determine the optimal flow rate for the receiving phase, source solution having a 10 times higher volume, was recirculated at a constant flow rate of 100 mL / m²min and maintained at pH 4.

The receiving phase (Q_{RP}) is varied between 5 and 25 L / m²min at pH = 4 and 7 in the receiving phase. Operating time is kept constant, 5 h, for each working flow rate.

The aluminum ion flow (IF) through the membrane increases with the increase of the receiving phase flow over the entire operating range (fig. 4a), while the recovery factor (RF) rises in the range 5-15 L / m²min, after which a stagnation is observed (fig. 4b).

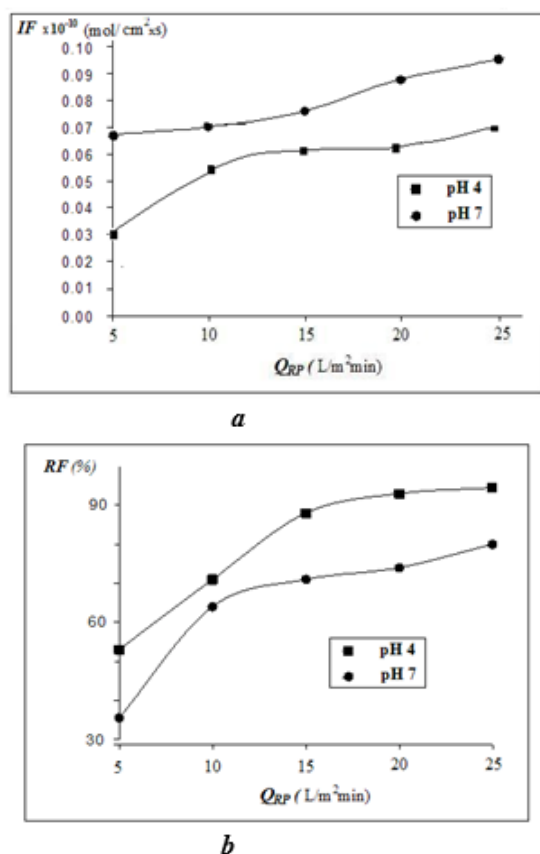


Fig. 4. Variation of aluminum pertraction performance parameters depending on recirculation flow of receiving phase: a- ion flow (IF) and b- recovery factor (RF)

The flow rate of the receiving phase is chosen at minimum 20 L / m²min for all subsequent experiments to ensure a relatively high ion flow, but also for the recovery factor to enter the corresponding field (fig. 4b).

However, increasing the flow rate of the receiving phase over 25 L / m²min is not recommended because of the secondary foaming phenomena appearance, and also due to the increase in energy consumption.

Determination of pH and optimal working time

In order to determine the pH and optimum working time, the source phase (Al^{3+} 10⁻³ M; Mg^{2+} 10⁻² M; Ca^{2+} 10⁻³ M) with pH = 4 (where all ions are free in solution), is contacted one at a time with receiving phase having pH = 4.01; 7.00 and 10.01, saturated in 8 hydroxyquinoline.

Figure 5 shows the significant differences in the concentration of aluminum and magnesium ions in the source phase during operation at the three pH values of the receiving phase (fig. 5).

At pH = 4 of the receiving phase, the aluminum concentration in the source phase decreases steeply in the first 180 min of operation, while the magnesium ion concentration decreases slowly, insignificantly (fig. 5a).

After an operating time of about 240 min the ion concentration remains quasi- constant. Increasing the pH of the receiving phase at 7 leads to a continuous downward variation of source phase concentration for about 180 minutes for both ions, but with a steeper slope for the aluminum ions (fig. 5b).

Interestingly is that at pH = 10, the two studied ions have a similar decrease in concentration in the source phase (fig. 5c) over the entire time interval studied.

The results obtained impose for an adequate phase separation of aluminum ion at pH = 4 for the receiving phase and an operating time of maximum 240 min.

At higher pH values in the receiving phase (7 and 10) is noted a competition between the two ions, which are transferred simultaneously through the membrane.

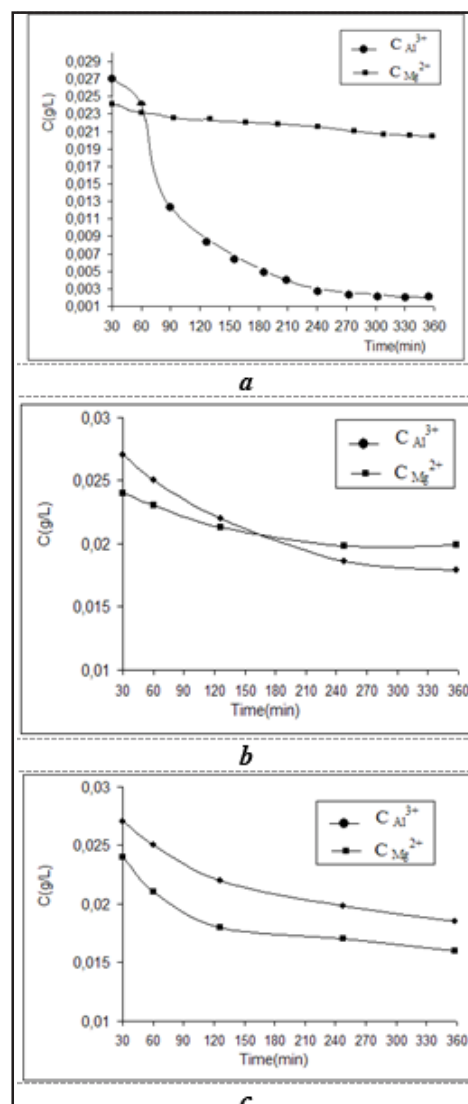
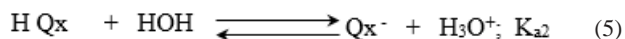
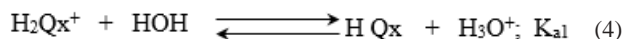


Fig. 5. Variation of aluminum and magnesium ion concentration in the source phase depending on the operating time and pH of the receiving phase: a) pH=4; b) pH=7; c) pH=10

Experimental observations are in agreement with the mode in which the two ions form complexes with 8-hydroxyquinoline: aluminum ion at pH = 4, and magnesium ion at pH greater than 9 [31].

In this pH range, the solubility of oxine in pure water is imposed by the ionization through the reaction with water molecules, relations (4) and (5) [31,32]:



Each ionization equilibrium is characterized by the corresponding acidity constants, the relationships (6) and (7) [32, 33]:

$$K_{a1} = \frac{[\text{H Qx}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Qx}^+]} \quad (6)$$

$$K_{a2} = \frac{[\text{Qx}^-][\text{H}_3\text{O}^+]}{[\text{H Qx}]} \quad (7)$$

Formulas (4-7) allow the calculation of 8-hydroxyquinoline concentration in acid and conjugated base form at equilibrium depending on the solution pH, the relationship (8-11).

$$C_0 = [\text{H}_2\text{Qx}^+] + [\text{H Qx}] + [\text{Qx}^-] \quad (8)$$

Taking into account the total concentration of dissolved acid and the K_{a1} and K_{a2} acid constants of H Qx , the equilibrium concentrations of the H_2Qx^+ , H Qx and Qx^- species can be deduced, depending on the concentration of hydrogen ions, respectively, depending on pH, equations (9-11).

$$[\text{H}_2\text{Qx}^+] = C_0 \left(1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}_3\text{O}^+]^2} \right)^{-1} \quad (9)$$

$$[\text{H Qx}] = C_0 \left(1 + \frac{[\text{H}_3\text{O}^+]}{K_{a1}} + \frac{K_{a2}}{[\text{H}_3\text{O}^+]} \right)^{-1} \quad (10)$$

$$[\text{Qx}^-] = C_0 \left(1 + \frac{[\text{H}_3\text{O}^+]}{K_{a1}} + \frac{[\text{H}_3\text{O}^+]}{K_{a1}K_{a2}} \right)^{-1} \quad (11)$$

Correlating concentrations suggested by the relationships (4-11) with the constants for studied ions complexes formation with 8-hydroxyquinoline [31, 34] it

can be illustrated which ions will be separated depending on the pH of the receiving phase (fig. 6).

The results of ion transport (fig. 5) correlate with the theoretical information suggested in the diagram from figure 6, justifying the variation in the concentration of the aluminium and magnesium ions depending on the pH of the receiving phase.

It must be emphasized that at high pH values a competition exists between the formation of 8-hydroxyquinoline complexes and the corresponding hydroxyls due to the increase in the hydroxyl ions concentration. It was found (fig. 7) that at pH 10 in the receiving phase there is a slight variation in the concentration of calcium ion in the source phase which can be justified by immobilizing this ion as calcium hydroxide in the receiving phase.

Ion permeation was studied at the pH of the membrane system phases (fig. 3) greater than 2, so that the S-EPDM sulfonic groups are ionized.

The following optimal parameters have been established for the separation of aluminum ions from an aqueous solution containing equimolar amounts of magnesium and calcium ions:

- membrane module with a usable area of 1 m²;
- capillary composite membranes with sulphonic ionizing groups (S-EPDM/PP);
- source phase pH, 4;
- receiving phase pH, 4;
- the constant flow of the source phase (through the capillary membrane fascicle), 100 L / m²min
- receiving phase flow (through the capillary membrane), over 20 L/m²min;
- receiving solution saturated in 8-hydroxyquinoline at pH= 4;
- operation time: over 180 min.

In the presented conditions, an ionic flux (IR) above 10⁻¹¹ mol / cm² s and a recovery factor of over 90% is obtained. Aluminum is recovered under the form of a complex with 8-hydroxyquinoline.

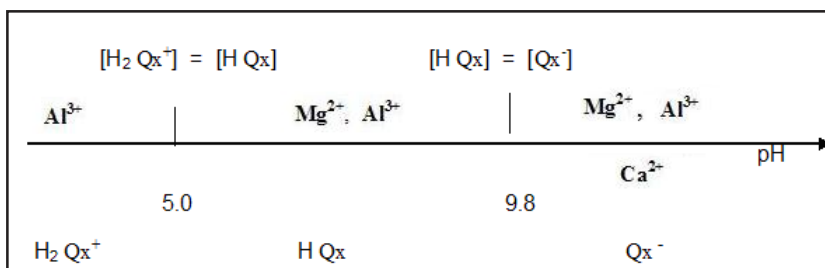


Fig. 6. Diagram of the 8-hydroxyquinoline speciation, based on pH, correlated with the ions that are separated according to the receiving pH phase

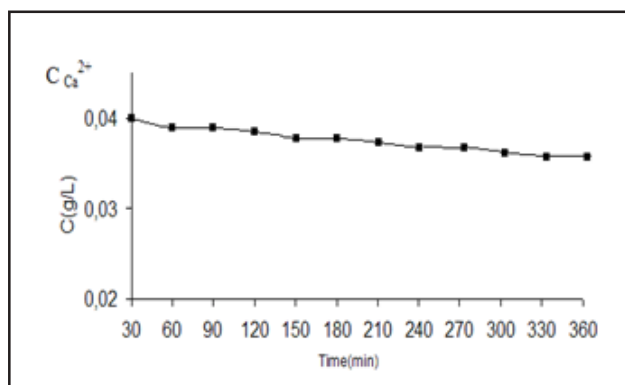


Fig. 7. Variation of calcium ion concentration in the source phase at pH = 10 in the receiving phase

Conclusions

Approaching the recovery of aluminum ion from aluminum sulfate-treated water through permeation using polypropylene capillary composite membranes with ethylene propylene diene terpolymer sulfonic acid (PP/S-EPDM) inclusions, followed by a complexation reaction with 8-hydroxyquinoline allowed us to operate at an ionic flux (IR) of over 10^{-11} mol/cm²·s and a recovery factor (RF) of over 90%.

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