

## ALUMINUM UPTAKE FROM NATURAL WATERS BY A RADIATION-GRAFTED MEMBRANE

**Renata Bazante-Yamaguishi, Eduardo Moura, José E. Manzoli, Aurea B.C. Geraldo**

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)

Av. Professor Lineu Prestes 2242

05508-000 São Paulo, SP

[ageraldo@ipen.br](mailto:ageraldo@ipen.br), [ryamaguishi@ipen.br](mailto:ryamaguishi@ipen.br)

**Note:** Polymer Membrane, Polypropylene, Grafting, Aluminum, Natural Water

### ABSTRACT

Styrene grafted, chemically modified polymeric membranes were used to carry off aluminum of drinking water from wells located at Billings dam region. The membranes comprised polymeric substrates of PVC (polyvinylchloride) and PP (polypropylene), which were mutually grafted with gamma radiation. The chemical modification included three basic reaction paths: Friedel-Crafts acylation, 2-methylanisole coupling and a final oxidation; this modification enables aluminum selectivity on the membrane. This chemical process inserts a salicylated derivative bonded onto the aromatic ring of styrene; such molecular arrangement is responsible for complexation of aluminum ions. The aluminum sorption capacity of these membranes was evaluated firstly from an aluminum control solution, where parameters like the ideal pH value for aluminum sorption and the interfering species were studied and correlated to know the best conditions for aluminum uptake. Later, the membranes were used for aluminum remediation of natural waters (real-life samples). The applicability results and limits are then discussed.

### 1. INTRODUCTION

The quality management of surface and groundwater resources applied to drinking water have had important achievements since the 20<sup>th</sup> century; particularly, in the last decades focus has shifted from the detection of heavy metal ions to the detection of aluminum ions. This happened because aluminum clarifying agents (flocculants) are still used for particle removal in water treatment plants, and this practice allows to introduce aluminum ions in low concentration. Other reason is the emergence of studies which associate cerebral sclerosis (Alzheimer's and Parkinson's diseases), osteoporosis and other chronically diseases with high levels of aluminum absorption by human body [1]; additionally, other random disturbances (irritability, seborrhea) seem also to be linked to aluminum concentrations above maximum contaminant level (MCL), which amounts to the maximum of 200 ppb in European and Brazilian regulations and 50~200 ppb for US-EPA regulations.

Aluminum appears in most of both natural and processed human consumption sources; thus, it is mandatory to determine quantitatively its presence in order to take remediation measures. The use of metal ion collectors is mostly used before trace-level response analytic methods [2,3,4]. Modified resins and other adsorbent materials provide physical support to immobilize specific substances, which may contain also specific functional groups that are selective to

specific chemical species. In the case of aluminum, many substances are used for this purpose: Tiron (1,2-dihydroxy-3,5-benzenedisulfonic acid) [5], pyrocatechol violet [6], 8-hydroxyquinoline-5-sulfonic acid – HQS [7,8], Eriochrome Cyanine R, Solochrome Violet, Xylenol orange, Ferron, and Alizarin Red S [9]. Such compounds have at least one set of side hydroxyl groups, hydroxyl-near-ketone groups or oxygen from sulfonic groups near ketone and/or hydroxyl groups, and all of these are classical molecular arrangements for aluminum chelation. Aluminum then binds strongly to groups with high donor tendency, such as negatively charged oxygen, and thus complexes are formed.

Aluminum complexes with salicylic acid are an alternative to the above substances, since its derivatives also have high equilibrium constants [10] and under low to medium pH, their sorption capacity is high compared to calcon, HQS and tiron [11] which also have high aluminum sorption capacities. Salicylic acid and its derivatives have a simpler molecular arrangement and their synthesis in solid supports is not complex [12,13]; in such cases, poly(styrene-co-divinylbenzene) resins like Amberlite XAD-2 and XAD-4 have been known to support salicylate synthesis from classical organic reactions.

Salicylated membranes are synthesized from a first step of styrene grafting by gamma irradiation on a polymer support, such as polypropylene (PP). Several organic reactions were then carried out to achieve the final product. The aluminum sorption capacity of these salicylated membranes was evaluated firstly from an aluminum control solution, where parameters like the ideal pH value for aluminum sorption and the interfering species were studied and correlated to know the best conditions for aluminum uptake. Later, the membranes were used for aluminum remediation of natural waters (real-life samples).

## **2. EXPERIMENTAL**

The PP substrate undertook two kinds of processes: irradiation (styrene grafting) and chemical (production of a salicylic acid derivative).

### **2.1. Styrene Grafting on PP by Gamma Irradiation**

Goodfellow's PP foils with thickness of 0.10 mm were used to obtain square samples of 30 mm; these samples were washed in analytic grade ethanol and dried at room temperature. The chosen monomer was commercial grade styrene, pre-treated by inhibitor removal with molecular sieves. The grafting media was an 1:1 and 1:3 styrene/solvent mixture, where analytic grade n-butanol and n-octanol were applied [14].

The mutual irradiation grafting was performed by  $^{60}\text{Co}$  source from Gamma Cell M-220, where irradiation process was performed at 50 kGy of absorbed dose and 1.50 Gy/h of dose rate.

All samples were homo-polymer extracted by toluene immersion (2 days), followed by several cycles of ethanol washing; finally, the samples were vacuum dried at 30 °C. The styrene grafted samples were analyzed by gravimetric analysis to determinate the grafting yield; the final values have been averaged from a series of three measurements.

## 2.2. Production of salicylic acid derivative on styrene grafted membranes by organic chemical synthesis

This process comprised three basic sets of chemical reactions: Friedel-Crafts acylation, 2-methylanisole coupling plus final oxidation and O-demethylation, this last step providing the aluminum selectivity.

### 2.2.1. First set of reactions

**Friedel-Crafts acylation of polymer samples:** following the method described by Sarvari and Sharghi [15] the reaction was carried out with acetylchloride (reagent and solvent simultaneously) and a 3-5 mmol ZnO solution at room temperature for 5 minutes. The reaction stopped when polymer samples were washed with 1:1 hydrochloric acid aqueous solution, followed by several immersions in water and in methanol.

**Samples oxidation:** the acylated samples were then oxidized by KMnO<sub>4</sub> (15 mmol) and NaOH (0.14 mmol) aqueous solutions at room temperature during 8 hours and after this time, the samples were washed again several times with distilled water.

**Samples chlorination:** the oxidized samples were air dried and flushed with thionyl chloride at 60 °C for 1-10 minutes with intermittent stirring. These final oxidation and chlorination reactions were based on the method described by Boudenne et al. [13].

### 2.2.2. Second set of reactions

**Friedel-Crafts acylation of polymer samples:** chlorinated polymer samples reacted with 2-methylanisole (reagent and solvent simultaneously) in the presence of 3-5 mmol ZnO at room temperature for 60 minutes with intermittent stirring. The samples were washed several times with distilled water and methanol.

**Polymer samples oxidation:** the second step (samples oxidation) of the first set of reactions was repeated. After reaction, the polymer samples were submitted to several washes with distilled water; the MnO<sub>2</sub> residue formed by this reaction was then removed from the samples

by immersing them in 1:1 HCl aqueous solution and with a final washing cycle with distilled water and methanol.

### 2.2.3. **Third set: O-demethylation**

It was based upon the method described by Kende et al. [16], where dried samples were immersed in toluene and 2 mmol anhydrous aluminum chloride mixture at room temperature overnight with stirring. After this reaction, the samples were immersed in 1:1 HCl aqueous solution and washed several times with distilled water and methanol; the dried final product is the aluminum selective membrane and it had a light brown color.

## 2.3. **Salicylated membrane characterization**

The reaction molar yield in each step was determined by gravimetric analysis. The reaction steps were monitored qualitatively by Mid-ATR-FTIR performed by a Perkin-Elmer FTIR spectrophotometer model spectrum 100. The morphology of membrane was obtained by SEM (Scanning Electronic Microscopy) by a Tabletop Hitachi SEM model TM-3000.

## 2.4. **Aluminum uptake tests**

For all aluminum uptake tests the salicylated polymer membrane samples were immersed in aluminum solution with several concentrations prepared from aluminum standard solution for AAS (Aldrich) and from analytic grade  $KAl(SO_4)_2$  dissolution in distilled water.

The quantitative analysis was performed by UV-Vis spectrophotometry by a Thermo Scientific UV-Vis spectrophotometer model Genesys 10S, with a 1.6 ml flux cell (1 mm path length) fitted to a multi-roller peristaltic pump.

The procedure for quantitative analysis is based in eriochrome cyanine R method [17]. In this assay, an aliquot of sample containing aluminum is transferred to a graduated flask and a five volume hydrogen peroxide solution is added; this mixture has the pH adjusted to 6.0 (using either 0.2 M NaOH or 0.2 M HCl); a volume of 0.1 % eriochrome cyanine R solution is added and after the mixture is diluted in a 1.3 M acetate buffer solution pH 6 with a volume corresponding to a half of graduate flask volume. The total volume is completed with distilled water. The 535 nm wavelength absorbance measurements are then obtained after 10 minutes of solution mixture.

### **2.4.1. Capacity Determination**

The aluminum uptake capacity is determined in batch method from a specific mass of dry membrane that is immersed in a standard aluminum solution with a specific concentration and volume [18]. The membrane is kept immersed overnight in a sealed flask; in the following day, the aluminum concentration is determined by UV-Vis spectrophotometry from an aliquot. The membrane is removed from solution for determining the water content (weighting the humid and the dry material after 30 °C vacuum oven).

The aluminum weight capacity ( $Q_{Al}$ ) is determined from the final concentration determined by UV-Vis spectrophotometry, related to unitary weight in grams of membrane.

### **2.4.2. Aluminum Sorption Ideal pH value and Interfering Agents**

The pH of mixture is adjusted to 2.5, 5, 6, 7 and 8 by using buffer solutions  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  0.1 M and  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$  0.1 M. The sorption kinetic curve was plotted for times of 5, 10, 15, 20, 25, 30 and 60 minutes.

For interfering agents evaluation, Zn and Cd are added to the mixture in concentration value close to that for aluminum (70 ppm). Thus, the membrane sorption kinetic curve was plotted in the same time values for pH test described above.

### **2.4.3. Aluminum Removal from Natural Waters**

Natural water samples were obtained from drinking water wells at Billings dam region in São Paulo city, where historical analytic results indicate aluminum levels above MCL [19]. The samples were obtained in dry season (may-august/2011 and 2012). Details on the collection of the samples are described in ref. [20].

Two water sources were verified: samples of a spring water (source) and of a well (P9) close to the dam margins (5 m to 10 m). The quality of these water samples is shown in Table 1.

Modified membranes were in contact with a distinct volume of sample in batch process under turbulent agitation by overnight. The aluminum was removed from membranes with chloride acid solution 1 M. The solution containing aluminum was putted in a volumetric flask and the aluminum determination was performed as described in item 2.4.

**Table 1: Water quality of water sources [21]**

Parameters	Sample type	
	Source (may/2012)	P9 (august/2011)
Metals (by ICP-OES)		
Al (ppm)	< 0,05	1.389
Cu (ppm)	< 0,05	< 0,05
Fe (ppm)	< 0,05	< 0,05
Hg (ppm)	< 0,05	< 0,05
Mn (ppm)	< 0,05	< 0,05
Pb (ppm)	< 0,05	< 0,05
Zn (ppm)	< 0,05	< 0,05
Ba (ppm)	< 0,05	< 0,05
Cr (ppm)	< 0,05	< 0,05
Cd (ppm)	< 0,05	< 0,05
TDS (ppm)	20	145
Turbidity (UNT)	1,10	2,29
pH	4,40	5,01
DO (mg/l)	5.8	1.6

### 3. RESULTS AND DISCUSSION

#### 3.1. Membrane Synthesis

Table 2 shows the degree of grafting of used samples. The results are dependent of type of polymer and grafting media composition. Gamma irradiation promote high values of degree of grafting due the very low dose rate of used source. Besides the quantitative characterization of these samples, an important remark is their visual aspect: low degree of grafting result in flat and smooth samples; the increase of this parameter promote a creased and wrinkled appearance in the final product.

**Table 2: Styrene grafting process onto PP samples**

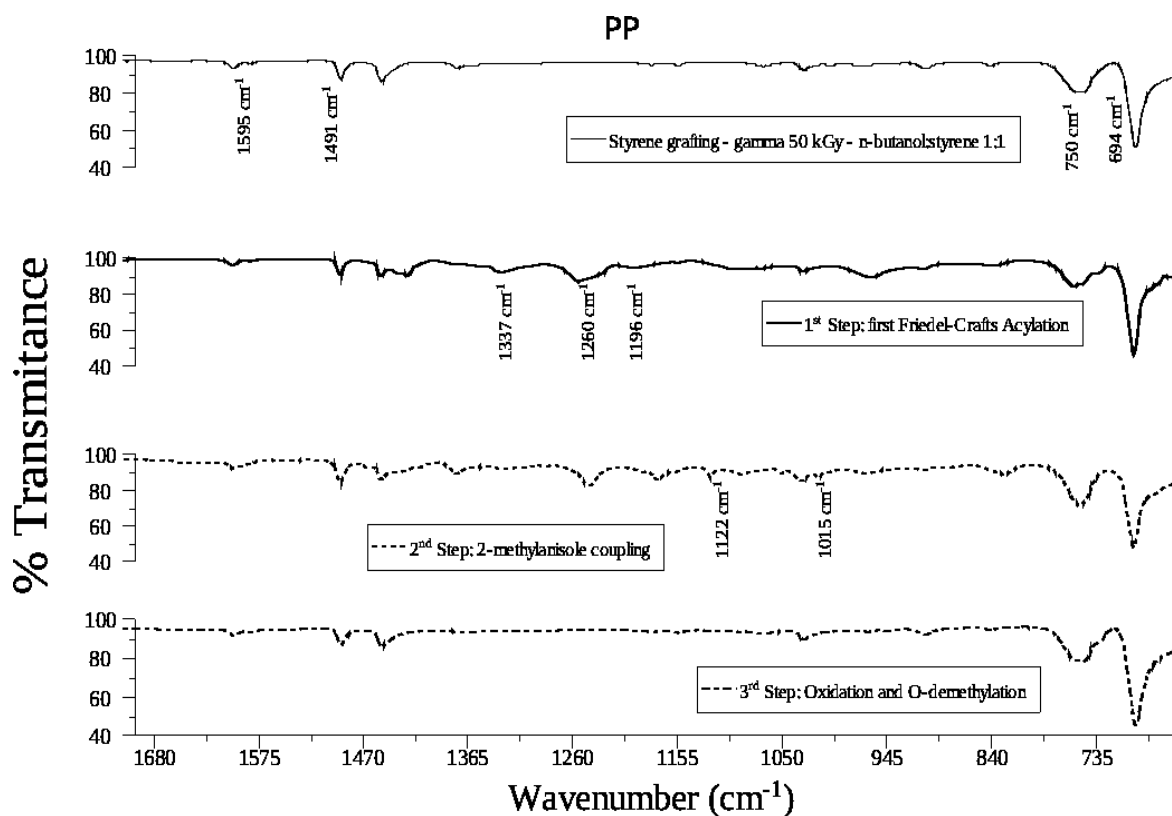
Sample	Grafting media	Degree of grafting (%)
PP-1	Styrene:n-butanol 1:1	91.5 (0.6)
PP-2	Styrene:n-octanol 1:1	77.3 (4.3)
PP-3	Styrene:n-octanol 1:3	27.1 (5.5)

These different kind of samples when submitted to the first step of chemical modification present different values of reaction yield. This step is the most important in the chemical modification set for it will determine the qualitative and the quantitative quality of selective membrane as final product. A good performance of this step depends on the catalyst contents and acylation reagent access to the samples. When the reaction is performed with ZnO concentration below 2 mmol (related to molar concentration of styrene in grafted polymer substrate) the reaction yield is low (about 9% for grafted PP). Values between 3 and 5 mmol of this catalyst yield more than 20 % for grafted PP.

Since PP does not swell in acetylchloride, grafted PP samples underwent two different pre-treatments to increase their reaction yield; these pre-treatments consisted of swelling the samples on toluene and chloroform for one hour. The acylation reaction applied in the samples immersed in toluene resulted in yields around 60%; for PP samples immersed in chloroform, the reaction yields increased to 84%.

Once a good performance is obtained in the first step of chemical modification, the following reaction sets achieve high reaction yields, above 65 %.

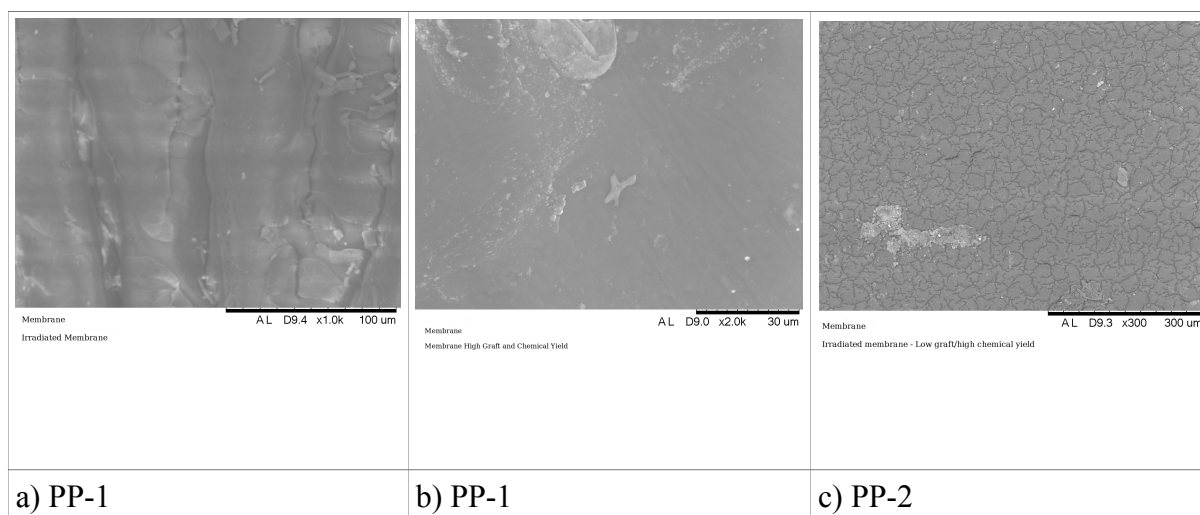
Fig. 1 show the ATR-FTIR spectra of PP styrene grafted samples for all steps of modification. The first spectrum shows the spectrum of initial substrate after gamma irradiation process; characteristic absorption bands of grafted styrene occur at  $690\text{ cm}^{-1}$  (out-of-plane C-H bond vibrations of the aromatic ring), at  $750\text{ cm}^{-1}$  (out-of-plane bending H atoms bonds in the aromatic ring), at  $1491\text{ cm}^{-1}$  and  $1595\text{ cm}^{-1}$  (plane deformation of C=C bonds of styrene backbone). The next spectrum the product resulting of first Friedel-Crafts, where absorption bands at  $1196\text{ cm}^{-1}$  and at  $1260\text{ cm}^{-1}$  (arylketones) and at  $1337\text{ cm}^{-1}$  (deformation vibration of CO-CH<sub>3</sub> bond) are present. The third spectrum shows the vibrational behavior of product from 2-methylanisole coupling reaction on polymeric substrate, with absorption bands at  $1122\text{ cm}^{-1}$  (vibration of C-O bond at ethoxy group) and at  $1015\text{ cm}^{-1}$  (deformation band of tri-substituted phenyl). The last spectrum shows the last step of chemical modification of polymer membrane samples, where the deprotection of the methoxy group caused the disappearing of the absorption band at  $1122\text{ cm}^{-1}$ .



**Figure 1: ATR-FTR spectra of PP styrene grafted samples submitted to the chemical modification.**

The chemical modification applied at polymer membrane samples is less aggressive than the modification made by Boudenne et al. [16]. The majority of reactions described here were carried out at room temperatures and the utilization of organic solvents was minimized, since the polymer substrates were not reinforced mechanically nor previously submitted to the cross-linking process. The final product based on PP matrix kept its membrane shape. Fig. 2a shows a micrograph of PP-1 sample before the chemical modification; fig. 2b and 2c show micrographs of PP-1 and PP-2 after the chemical modification, respectively with high and low degrees of grafting. In the case of fig. 2b, high yields are obtained in the chemical process, and a smooth surface for the membrane is seen before and after the chemical modification process. However, fissures and crackings appear in membranes with low degree of grafting and it suggests chemical process is more aggressive to these samples.





**Figure 2: Micrographs of styrene grafted membranes with high degree of grafting without chemical modification (PP-1)(a); the same substrate PP-1 chemically modified (high yield)(b) and with low degree of grafting and chemically modified – high yield (PP-2)(c).**

### 3.2. Aluminum uptake tests

#### 3.2.1. Aluminum Capacity Membrane

Table 3 shows the results of Al uptake capacities of modified membrane samples obtained with distinct salicylation yields. PP-1 is the sample with high degree of grafting. The membrane with high degree of salicylation has high aluminum uptake capacity.

**Table 3: Aluminum uptake capacity of modified membrane samples**

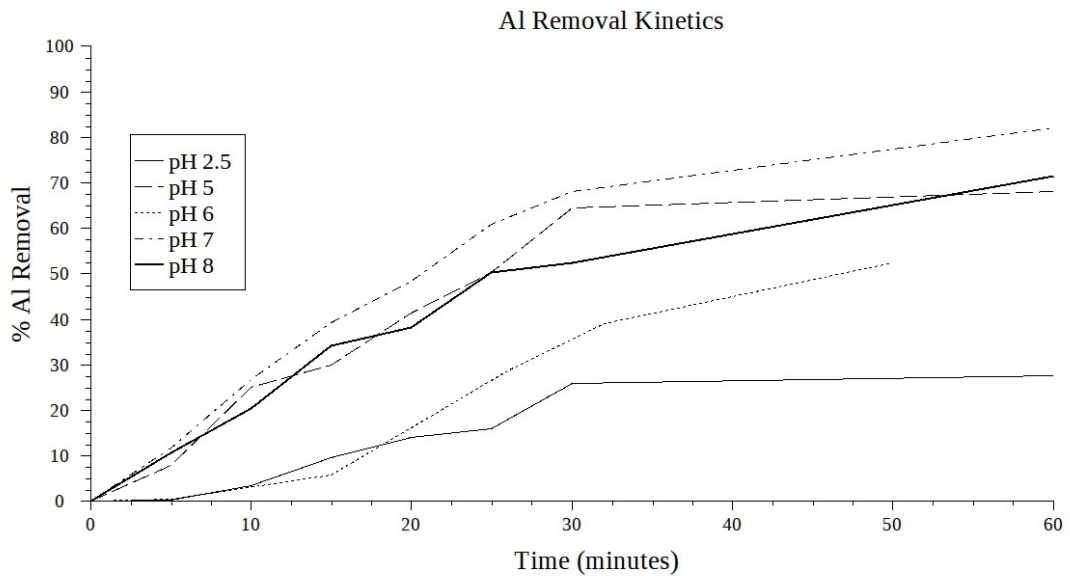
Modified Membrane Samples	Salicylation Yield (%)	Al uptake capacity (mg Al/g membrane's)
PP-1-a	66.8	7.0
PP-1-b	7.60	0.8

#### 3.2.2. Aluminum Uptake Kinetics

The aluminum sorption kinetic behavior is classical in this case: initially the aluminum sorption is high, but the sorption intensity is lower after a distinct sorption time value; in this step, the membrane is leaning towards saturation.

Fig. 3 shows this behavior for a specific pH values. These results shows pH 7 is the optimum value for aluminum sorption from liquid solution.

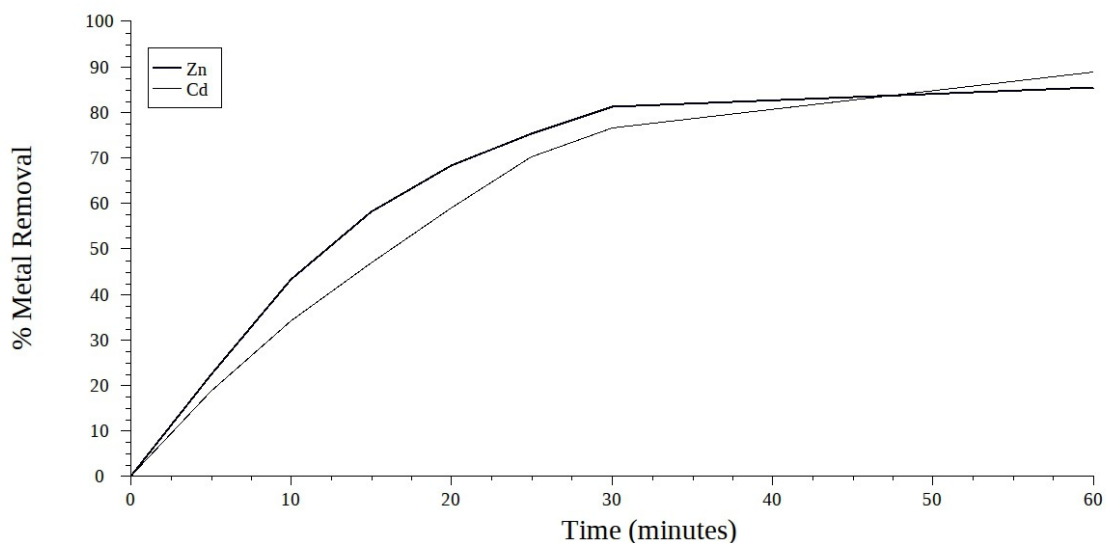
**Figure 3: Aluminum removal from liquid solutions in distinct pH values in function of sorption time.**



### 3.2.3. Aluminum Selectivity Tests

Aluminum selectivity of modified membranes was verified and the results are in Fig. 4. All results show the same kinetic behavior when the membrane is in contact with solutions containing the same concentrations of Al and Zn or Al and Cd at pH 7.

These results suggest aluminum sorption kinetic is the same in each studied case. The aluminum sorption is higher than 80 % in about 1 hour of process.



**Figure 4: Aluminum removal from liquid solutions with Zn and Cd as interfering agents.**

### 3.2.4. Aluminum Removal from Natural Waters

Table 4 shows the results of aluminum uptake by modified membranes with distinct aluminum uptake capacities (the same samples of Table 3) in contact of natural water samples (see Table 1). For each kind of water sample the aluminum levels are distinct and very close to that presented in Table 1 (item 2.4.3). These results suggest salicylated membranes obtained from irradiation step process are effective in water aluminum removal.

**Table 4: Aluminum Uptake from Natural Water Samples**

Water Sample Type	Modified Membrane used	Al uptake (mg Al/liter)
Source	PP-1-a	0.0118
P9	PP-1-b	1.9214

## 4. CONCLUSIONS

Styrene grafted PP membranes by ionizing radiation process were chemically modified and this process comprised three basic steps: a) Friedel-Crafts acylation, b) 2-methylanisole coupling and c) Final oxidation and O-demethylation (aluminum selective characteristic). All tested PP samples achieved the chemical modification and conserved their shape and

morphology. Finally, alternative and less aggressive reactions were applied to obtain the final product.

The modified membranes thus obtained are effective for aluminum removal from water, with the best results with pH 7 for the control solution. Moreover, these modified membranes presented good aluminum selectivity even in the presence of interfering species Zn and Cd. Aluminum removal by salicylated membranes was also an effective process for natural water samples; however, more tests should be done.

## ACKNOWLEDGMENTS

The authors are grateful to financial support of FAPESP (São Paulo State Research Support Foundation – Brazil) process 2011/23426-8. We also thank to Mr. Hiroshi Oikawa for Mid-ATR-FTIR spectroscopy, to work group of Accelerator facility at Radiation Technology Center (CTR) at IPEN-CNEN/SP: Ms. Elisabeth S.R. Somessari, Mr. Carlos G. Silveira, Mr. Hélio A. Paes, and Mr. Carlos A. Souza.

## REFERENCES

1. L. Tomijevic, "Aluminum and Alzheimer's Disease: After a Century of Controversy, Is there a Plausible Link?", *J. Alzheimers Disease*, **23(4)**, pp.567-598 (2011).
2. S. Motelier and H. Pitsch, "Determination of Aluminium and its Fluoro Complexes in Natural Waters by Ion Chromatography", *J. Chrom. A*, **660**, pp.211-217 (1994).
3. G. Tangen, T. Wickstrøm, S. Lierhagen, R. Vogt, W. Lund, "Fractionation and Determination of Auminum and Iron in Soil Water Samples Using SPE Cartridges and ICP-AES", *Environ. Sci. Technol.*, **36**, pp.5421-5425 (2002).
4. S. Khan, T.G. Kazi, J.A. Baig, N.F. Kolachi, H.I. Afridi, A.Q. Shah, G.A. Kandhro, S. Kumar, "Separation and Preconcentration of Trace Amounts of Aluminum Ions in Surface Water Samples Using Different Analytical Techniques", *Talanta*, **80**, pp.158-162 (2009).
5. M. Luo and S. Bi, "Solid phase extraction–spectrophotometric determination of dissolved aluminum in soil extracts and ground waters", *J. Inorg. Biochem.*, **97**, pp.173–178 (2003).
6. J. Tria, P.R. Haddad, P.N. Nesterenko, "Determination of Aluminium Using High Performance Chelation Ion Chromatography", *J. Sep. Sci.*, **31**, pp. 2231 – 2238 (2008).
7. J. Carnevale and P.E. Jackson, "Analysis of Aluminium in Pharmaceutical Products by Post-Column Derivatization Ion Chromatography", *J. Chrom. A*, **671**, pp.115-120 (1994).
8. M. Luo, S. Bi, C. Wang, J. Huang, "Determination of Aluminum in Soil Extracted with a Modified Anion-Exchange Resin as a Solid-Phase Adsorbent by ICP-AES", *Anal. Sci.*, **20**, pp.95-99 (2004).
9. M-B Luo, H. Wu, J. Zhang, D. Shen, S-P Bi, "Determination of Aluminum Fractionation in Soil Extracts by Using Eriochrome Cyanine R Modified Anion-Exchange Resin as Solid Phase Extraction Cartridge Coupled with ICP-AES", *J. Sep. Sci. Technol.*, **43**, pp. 2225-2241 (2008).
10. A.E. Martell, R.J. Motekaitis, R.M. Smith, "Aluminium Complexes of Hydroxyaliphatic And Hydroxyaromatic Ligands in Aqueous Systems - Some Problems and Solutions", *Polyhedron*, **9(2-3)**, pp.171-187 (1990).
11. T. Kiss, K. Atkari, M. Jezowskaboiczuk, P. Decock, "Complexes of Al(III) with Hydroxyaromatic Ligands", *J. Coord. Chem.*, **29(1-2)**, pp.81-86 (1993).

12. P.K.Tewari and A.K. Singh, "Thiosalicylic Acid-immobilized Amberlite XAD-2: Metalsorption Behaviour and Applications in Estimation of Metal Ions by Flame Atomic Absorption Spectrometry", *Analyst*, **125**, pp.2450-2355 (2000).
13. J-L Bodenne, S. Boussetta, C. Brach-Papa, C. Branger, A. Margailan, F. Theraulaz, "Modification of Poly(styrene-co-divinylbenzene) Resin by Grafting on an Aluminium Selective Ligand", *Polym. Int.*, **51**, pp.1050-1057 (2002).
14. E. Moura, J. E. Manzoli, A.B.C. Geraldo, 2012 "Effects of solvent polarity on mutual styrene grafting onto polypropylene by electron beam irradiation", *Rad. Phys. Chem.*, **81(9)**, pp.1309-1313 (2012).
15. M.H. Sarvari and H. Sharghi, "Reactions on a Solid Surface. A Simple, Economical and Efficient Friedel-Crafts Acylation Reaction over Zinc Oxide (ZnO) as a New Catalyst", *J. Org. Chem.*, **69(20)**, pp.6953-6956 (2004) .
16. A.S. Kende, Y-G Tsay, J.E. Mills, "Total Synthesis of (f)-Daunomycinone and (f)-Carminomycinone", *J. Am. Chem. Soc.*, **98(7)**, pp.1967-1969 (1976) .
17. A.I. Vogel, Vogel's Textbook of Quantitative Chemical Analysis, 5th ed., Longman Scientific & Technical, Essex, England (1989).
18. F. Helfferish, Ion Exchange, McGraw-Hill Book Co. Inc., NY, USA (1962).
19. "Águas Superficiais Publicações/Relatórios - 2000-2012" <http://www.cetesb.sp.gov.br/agua/aguas-superficiais/35-publicacoes/-/relatorios> (2012).
20. R. Bazante-Yamaguishi, A.B.C. Geraldo, A.C. D. Guedes, M.R. Souza, S. Milani, "Estudo do Nitrato em Água Potável de uma Comunidade Pesqueira da Represa Billings", *XI Reunião Científica do Instituto de Pesca – RECIP*, 8-10 abril 2013, pp.182-184, São Paulo, SP.
21. Projeto "Estudo da Contaminação de Metais e Microbiológico da Água Subterrânea (Poços) na Comunidade Pesqueira do Bororé: Sustentabilidade e Educação voltada ao Saneamento ambiental no Reservatório Billings. <http://ilhadobororesaudavel.blogspot.com.br/2011/11/estudo-da-contaminacao-por-metais-e.html>