

Preparation and Characterization of a Phosphonylated Polypropylene Ion Exchanger

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ABSTRACT: Because typical ion exchange resins used for treating wastewater contain sulfur binding sites and suffer from application limitations, a new ion exchange system was developed by phosphonylating nonwoven polypropylene fabric (PP). These fabrics were phosphonylated for 0.5, 1, 2, and 4 h; amount of phosphorus on phosphonylated PP increased with an increase in phosphonylation time. After hydrolysis, the appropriate phosphonylated sample was placed in a glass column where a europium (Eu^{3+}), lead (Pb^{2+}), or mercury (Hg^{2+}) salt solution was passed through the fabrics after an equilibration period of 5 min. Filtrate samples were then analyzed by atomic absorption spectroscopy for metal concentration. Results showed that metal binding efficiency for Eu^{3+} increased with an increase in phosphonylation time; Pb^{2+} binding efficiency increased up to 2 h phosphonylation time and then decreased; Hg^{2+} binding efficiency was practically independent of phosphonylation time. PP fabrics were also sulfonated and tested for binding efficiency to determine if phosphorus was a better binding site than sulfur. By comparing the results from phosphonylated PP and sulfonated PP, data showed that phosphonylated PP bound metal ions at a higher efficiency than sulfonated PP. Also, phosphonylated PP had higher binding efficiencies with Eu^{3+} and Pb^{2+} than a commercial exchange resin. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 93–100, 2000

Key words: phosphonylation; polypropylene; metals; ion exchange

INTRODUCTION

Metal contamination in the aquatic environment is a concern because of their toxicity, long persistence, bioaccumulation, and biomagnification in the food chain.¹ Lead waste from mining activities, for example, have decreased or eliminated

directly and indirectly fish and invertebrate populations by increasing mucous production on respiratory surfaces, thereby causing gas exchange to be hindered.^{2,3} Other activities, such as agriculture and industry, have greatly increased mercury concentrations in the environment, thus hindering reproduction, growth, and oxygen exchange of freshwater and marine organisms.⁴ Mercury presence in freshwater food chains is also believed to be a factor in reducing mink (*Mustela vison*) populations in Georgia, North

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Carolina, and South Carolina.⁵ Thus, reduction of metal concentration in effluents is critical for sustainable ecosystems.

Because metal pollution is prevalent throughout the environment, ion exchange may be a way to reduce metal release by anthropogenic activities. Ion exchange is the exchange of ions that occurs on contacting an ionic solid with an electrolyte solution.⁶ The process is accomplished by resins that are synthesized by polycondensation and polymerization; however, polymerization is the preferred technique because of greater chemical and thermal stability of the products.⁷ There are two types of resins: inorganic and organic. Inorganic ion exchange resins were the first commercial resins developed and are resistant to degradation in the presence of high temperatures and ionizing radiation.⁸ However, performance of inorganic resins is hindered by a variety of factors including being stable only within a narrow range of pH and being dissolved by acid solutions.⁹ Organic resins have mainly overshadowed the inorganic resins because of better stability, higher capacity, and better ability to control the products of their synthesis.⁸

The matrix of organic resins contains irregular, three-dimensional networks of macromolecular hydrocarbon chains.⁸ Styrene-divinylbenzene (DVB) is the most common currently used resin. Reacting styrene with DVB produces a heterogeneous degree of cross-linking that varies within the matrix.⁷ This cross-linking affects mechanical properties and the rate of ion exchange. Resins that have low amounts of DVB (approximately 8%) are weaker, affected more easily by oxidation, and have low degrees of cross-linking. Resins that have high degrees of cross-linking from high concentrations of DVB (approximately 20%) are more stable but are brittle.⁷ Because cross-linking decreases polymer porosity, slows bulk transport, and decreases the exchange rate,⁹ various types of ion exchange resins have been developed; however, each has its own limitations.^{7,8}

Although ion exchange is extensively used to purify water, an environmental application of this process that has not been widely utilized is wastewater treatment. The metal finishing and printed circuit board industries are two major electroplating sources of heavy metal effluents that would benefit from this technology. By treating these effluents to remove metals, less toxic substances would be released to the environment.⁸ Current resins are not able to significantly remove metals because of fouling and other problems, so a new

ion exchange material would be helpful in decreasing the amounts of toxic metals found in the environment, thus lowering the concentrations in wildlife and plants. This new type of ion exchanger may provide a solution to the problem of metal release into the environment.

Because there are limitations to the ion exchange resins currently being used, a new exchanger that was not cross-linked may lead to materials with improved binding efficiency and without the problems such as variations in mechanical strength and swelling. By chemically fixing phosphorus onto nonwoven, high-density polypropylene (PP) fabric, a new type of exchanger that is not cross-linked and has a large surface area could be developed that would remove metals from solution. The advantages of this system are that diffusion of ions would not be hindered by cross-linking in the resin, and an improvement in exchange rates would result because of a large surface area. Because this exchanger uses a thermoplastic polymer as a backbone, it would have a lower water content, no swelling, high surface area, better mechanical strength, a smaller particle diameter as compared with the other exchangers, and could be reused as plastic after extraction of the metals. Not only could this new exchanger be utilized in treating wastewater, the chemical industry could benefit by using it to recover rare metals.

EXPERIMENTAL

Materials

PP fabric was obtained from AMOCO, Corporation (Chicago, IL, USA) and had an approximate density of 0.08 g/cm³. The fabric was white and nonwoven. Phosphorus trichloride (PCl₃), 98%, fuming sulfuric acid (H₂SO₄) containing 30% free SO₃, 37% hydrochloric acid (HCl), europium nitrate (Eu(NO₃)₃), lead nitrate (Pb(NO₃)₂), mercuric chloride (HgCl₂), and atomic absorption standards for europium, lead, and mercury were obtained from Aldrich Chemical Company (Milwaukee, WI, USA). Amberjet 1500H ion exchange resin was donated by Rohm and Haas (Philadelphia, PA, USA).

Preparation of Phosphonylated Substrates

The gas phase phosphonylation (GPP) was carried out as described by McCaig^{10,11} was used

after recently introduced modifications.¹² Conversion of its PCl functionality was conducted as described by Shalaby.¹²

Preparation of Sulfonated Substrates

All glassware was dried at approximately 160°C and assembled while hot. A 250-mL three-necked flask was secured to a ring stand with a clamp. A 90° connecting tube was placed in the flask along with a pennyhead stopper. A funnel, which contained a coarse, porosity B (70–100 μm) disc, was connected to the flask and then secured by a beaker clamp to the ring stand, and a cap adapter and o-ring joint were secured to the funnel body with a pinch clamp. The 90° connecting tube was attached to a firestone valve, which was connected to a vacuum source and argon. All ground glass areas were coated with stopcock grease. After closing the cap adapter, the apparatus was flame dried at 25 mm Hg and cooled while still under vacuum. The apparatus was then purged with argon. The flask was partly submerged in a 30°C oil bath. The cap adapter was connected to an oil bubbler containing Duoseal vacuum oil that was connected to a water bubbler. Argon was then introduced through a flow meter, which was attached to the 90° connecting tube.

Under a continuous argon flow of 40 mL/min, 5 mL fuming H₂SO₄ was added with a glass pipette. The temperature of the oil bath was then increased to 45°C. After reaching and maintaining this temperature, approximately 0.5 g of PP was placed in the funnel on the coarse disc laterally. One experimental set-up remained viable for up to 2 h, so more than one sample was prepared during this time. Sulfonation reaction times of 15, 20, and 30 min were tested.

After the reaction time had elapsed, the sample was removed with forceps and placed in 300-mL distilled water and sonicated for 3 min by a Branson Ultrasonic Cleaner Model 1210 with settings of 143 W and 47 kHz. The sample was finally placed on a drying rack and allowed to dry at room temperature. All samples were stored in a vacuum dessicator at 15 mmHg. The samples were analyzed by Quantitative Technologies, Incorporated (QTI) (Whitehouse, NJ, USA) for percent sulfur content. The sample was combusted in oxygen over peroxide so the sulfate dissolved in the solution and was then titrated with barium perchlorate to a colorimetric end point using dimethylsulfonic acid as the indicator. The end point was a color change from purple to blue to

aqua. The sulfonation reaction was carried out as described by Shalaby.¹²

Characterization and Testing of Activated Substrates Breaking Strength Test

Unphosphonylated and phosphonylated PP fabric samples were cut approximately 1 cm in width and approximately 4 cm in length. The thickness of each sample averaged 0.6 mm. A Satec T1000 Materials Testing System was used to test samples to failure in tension. The following were the testing parameters: 20 mm test specimen length and 500 mm/min head rate. The samples were placed in grips and pulled apart until they broke. Calculations were done to determine the amount of stress each sample could withstand.

Determination of Binding Efficiency

The binding efficiency tests were each conducted on untreated PP fabric, along with 15-, 20-, and 30-min sulfonated PP and 0.5-, 1-, 2-, and 4-h phosphonylated PP, and Amberjet 1500H ion exchange resin. All samples were tested in triplicate.

Metal solutions were prepared from metal salts diluted with distilled water in volumetric flasks. The following solutions were used: 1.7×10^{-4} M europium (III) (Eu³⁺), 5×10^{-4} M lead (II) (Pb²⁺), and 0.05 M mercury (II) (Hg²⁺).

Approximately 0.3 g of the appropriate sample was placed in a flex-column glass tube to form a plug about 8.5 cm from the top of the tube. For Amberjet 1500H, a small amount of steel wool was used to hold the resin beads in place and prevent them from flowing through the glass tube. Ten milliliters of 1.7×10^{-4} M Eu³⁺ aqueous solution was added and allowed to equilibrate with the fabric for 5 min. The solution was then forced through the fabric with air and collected. Ten milliliters of distilled water were added to the tube and immediately forced through with air to remove any metal mechanically bound to the fabric. This filtrate was collected and added to the Eu³⁺ filtrate. This procedure was repeated in triplicate for each metal. Samples were then analyzed by graphite furnace atomic absorption spectroscopy for Eu³⁺ concentration.

The above equilibration procedure was followed for a 5×10^{-4} M Pb²⁺ solution. Samples were analyzed by graphite furnace atomic absorption spectroscopy for Pb²⁺ concentration.

The same equilibration procedure was followed for a 0.05 M Hg²⁺ solution. Samples were ana-

lyzed by cold vapor atomic absorption spectroscopy for Hg^{2+} concentration.

Analytical Methods

A graphite furnace atomic absorption spectrophotometer (AAS) was used to analyze Eu^{3+} and Pb^{2+} , whereas cold vapor generation (VGA) was used to analyze Hg^{2+} . Operating conditions for the AAS were the following: for Eu^{3+} , 283.3 nm wavelength, 0.5 nm slit width, and a calibration range of 120–1000 ng/mL; for Pb^{2+} , 459.4 nm wavelength, 0.5 nm slit width, and a calibration range of 15–50 ng/mL; for Hg^{2+} , 254.1 nm wavelength, 0.5 nm slit width, and a calibration range of 1–50 ng/mL. All samples were diluted with MilliQ water.

Instrument calibration for europium analysis used 5 calibration points, whereas 4 calibration points were used for lead and mercury analysis. Every fifth sample was a MilliQ water blank, and the calibration standards were analyzed at the end of an analytical batch to assure that the calibration curve was maintained. Reagents used for the mercury analysis included 25% stannous chloride (SnCl_2) and 5 M HCl. The flow rate of the sample into the VGA was measured to be 6–8 mL, whereas each reagent flow rate was found to be 0.8–1.2 mL.¹³ Calculations were completed to determine the amount of metal bound to the fabric per weight of the phosphonylated PP fabric by comparing the original concentration of each metal solution to the concentration found in the filtrate samples.

Statistical Analysis

One-way analysis of variance (ANOVA) was used to compare the results of the metal binding efficiency for both sulfonated and phosphonylated PP fabric. Tukey's Studentized Range Test was used

Table I Percentage of Phosphorus at Various Reaction Times^a

Phosphonylation Time (h)	Average Percent Phosphorus
0.5	0.86 ± 0.13^b
1	0.98 ± 0.29
2	1.2 ± 0.23
4	1.4 ± 0.42

^a $n = 3$.

^b mean \pm standard deviation.

Table II Breaking Strength of Phosphonylated Polypropylene Fabric

Phosphonylation Time (h)	Stress (kPa)	Percent of Strength Lost
0 (control)	2318	
0.5	3758	0
1	979	57.7
2	834	64.0
4	403	82.6

to determine which samples were significantly different from the control. Statistical Analysis System (SAS) (SAS Institute Cary, NC)¹⁶ program was used to conduct the above analyses. The level of significance was 0.05.

RESULTS AND DISCUSSION

Phosphonylation

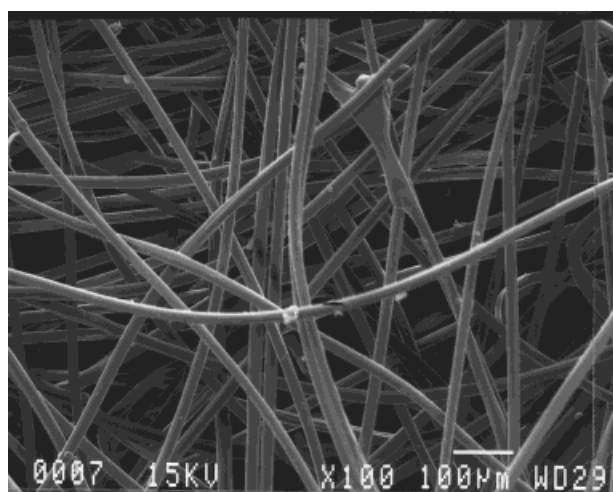
The reaction for phosphonylating PP was in question because there is no accurate data to show on which carbon the predominate substitution takes place.¹⁴ So, based on phosphonylation surface treatment studies using polyethylene (PE) conducted by McCaig¹⁰ and Ramaswamy and Krishnaswamy,¹⁵ the methyl group probably contains the phosphorous group. However, further characterization, such as nuclear magnetic resonance (NMR) analysis, is needed to support this idea.

Phosphonyl groups were introduced chemically onto PP, but an increase in the reaction time did not influence concentration of these groups (Table I). The reaction time, however, did affect the strength of the fabric. When the reaction was allowed to proceed 4 h, 82.61% of tensile strength was lost whereas fabric reacted for 1 h lost 57.7% (Table II). Scanning electron microscopy (SEM) showed that the longer the fabrics were phosphonylated, the more extensive the fractures became (Figs. 1 and 2). These fractures may provide more surface area to the fabric, thereby increasing the amount of phosphorus that could be bound to the surface. Although the microfractures may have aided in binding phosphorus, they may have also compromised the strength of the fabric, which caused the decrease in breaking strength with an increase in reaction time.

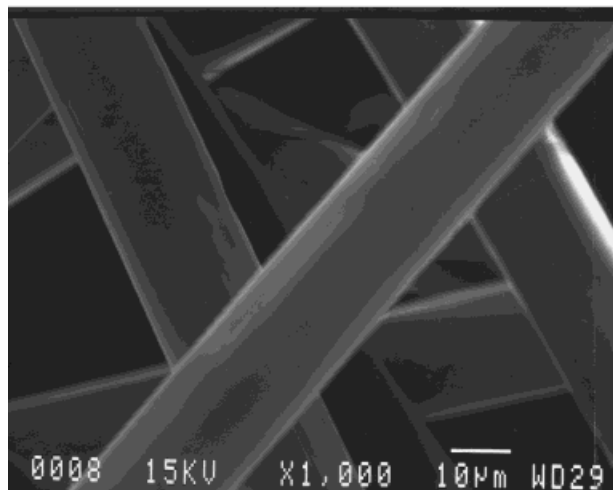
PP phosphonylated at all four times bound Eu^{3+} at higher efficiencies than the control. There was also a correlation of an increase in metal ion

binding with an increase in reaction time, even though, there was only a small difference in the binding efficiency between fabric phosphonylated for 2 and 4 h, which averaged to be 1.608 mg/g and 1.610 mg/g, respectively (Table III). The binding efficiency of all the phosphonylation times except 0.5 h were significantly different from the control ($p = 0.0019$).¹⁶

The phosphonylated fabric bound Pb^{2+} , and the highest binding was achieved by 2-h treatments. When 0.5-h treatments were compared with the control, there was only a 1.6×10^{-3} mg/g increase in binding efficiency. Binding continued to increase to a maximum average of 1.044 mg/g

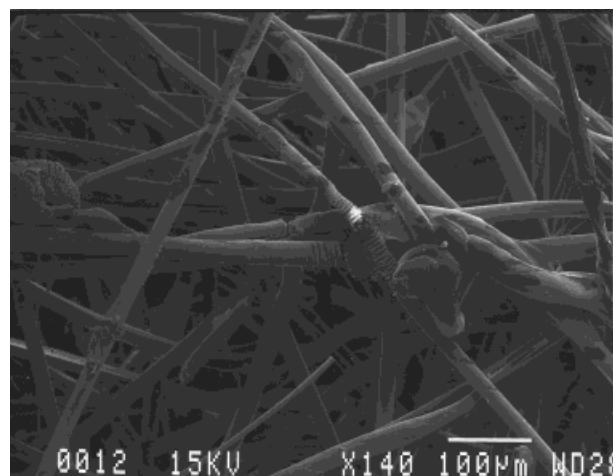


(a)

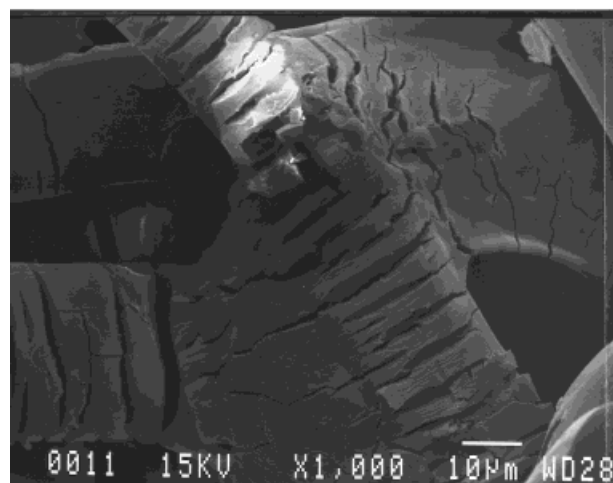


(b)

Figure 1 SEM micrographs of polypropylene fabrics prior to phosphonylation at (a) 100 × and (b) 1000 × magnification. (Reproduced at 70% of original size).



(a)



(b)

Figure 2 Polypropylene fabrics phosphonylated for 4 h at (a) 140 × and (b) 1000 × magnification. (Reproduced at 70% of original size).

at 2-h treatment and then decreased to an average of 0.7608 mg/g for 4-h treatment (Table III). Binding by PP phosphonylated for 1, 2, and 4 h were found to be significantly different from the control ($p = 0.0001$).¹⁶ The lowest binding of Hg^{2+} occurred by 1-h phosphonylated PP (20.06 mg/g), and the highest binding was 69.05 mg/g by 4-h treatment (see Table III). There was no definite pattern between the amount bound and the phosphonylation time; however, there was only a 7.41% increase in mercury binding from 2- to 4-h treatments. All phosphonylation times were not significant ($p = 0.1815$) with respect to binding efficiency.¹⁶

Table III Binding Efficiency of Selected Metal Ions by Phosphonylated High-Density Polypropylene Fabric^a

Phosphonylation Time (h)	Average Binding (mg/g)		
	Eu ³⁺	Pb ²⁺	Hg ²⁺
0	0.88 ± 0.11 ^b	0.043 ± 0.075	0.0 ± 0
0.5	1.2 ± 0.14	0.045 ± 0.078	42 ± 7
1	1.6 ± 0.29 ^c	0.70 ± 0.18 ^c	20 ± 21
2	1.6 ± 0.15 ^c	1.0 ± 0.083 ^c	64 ± 50
4	1.6 ± 0.16 ^c	0.76 ± 0.20 ^c	69 ± 61

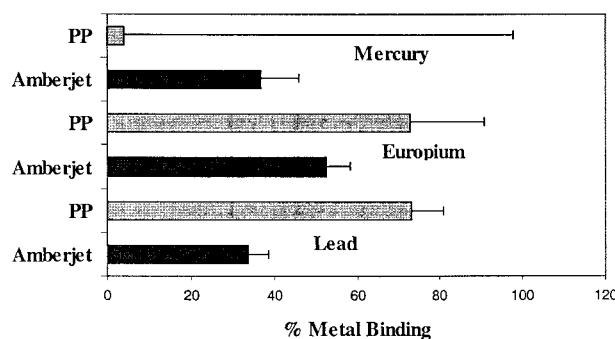
^a $n = 3$.^b Mean ± standard deviation.^c Significantly different from the control ($\alpha = 0.05$).

The general trend of the metal binding efficiency of 2-h treated fabrics having a close or a better binding efficiency than 4-h phosphonylated PP may be explained by saturation of the binding sites by the metal ions. The unevenness of the phosphonylation process may have increased this random pattern of binding because certain sections of the fabric that were exposed to the solution contained less phosphorus and microfractures than other sections. Because GPP weakened the samples the longer the reaction was allowed to proceed, the 4-h phosphonylated fabric lost some of its surface area, which prevented more phosphorus binding at the fabric surface. Although surface area was not measured, sections of the fabric were visibly thinner. Another possible explanation was a portion of phosphorus formed a water-soluble fraction due to over-phosphonylation; therefore, this phosphorus may have been lost in the postphosphonylation procedure.

Based on SEM/energy-dispersive X-ray (/EDX) results, over-phosphonylation resulted in the loss

of almost all P-C bonds during the postphosphonylation treatment when the polymer polyetheretherketone (PEEK) was treated by GPP.¹⁰ Although the structures and reaction conditions of PP and PEEK are different, some of the P-C bonds may have been lost by sonication. Along with causing the most tensile strength to be lost, the 4-h treatments made the PP fabric more fragile; due to this increase in fragility, the sonication process may have caused fibers to become separated from the sample, which decreased available binding area.

The performance of 2-h phosphonylated PP was also compared with the commercial ion exchange resin Amberjet 1500H. Results showed that phosphonylated PP bound 72% Eu³⁺ whereas Amberjet 1500H bound 52%. The phosphonylated PP also bound 73% Pb²⁺ whereas Amberjet 1500H bound 34%. However, Hg²⁺ binding efficiency of the phosphonylated PP did not improve compared with the commercial resin (3.9% and 37%, respectively) (Fig. 3). The increase in binding efficiency of Eu³⁺ and Pb²⁺ by phosphonylated PP may be due to the fiber not containing crosslinkages that would hinder the diffusion of the ions. Amberjet 1500H contains sulfonic acid

**Figure 3** Comparison of metal binding between phosphonylated polypropylene fabrics and the commercial resin Amberjet 1500H.**Table IV Percentage of Sulfur at Various Reaction Times^a**

Sulfonation Time (min)	Average % Sulfur
15	0.42 ± 0.053 ^b
20	0.60 ± 0.25
30	0.22 ± 0.093

^a $n = 3$.^b mean ± standard deviation.

Table V Binding Efficiency of Selected Metal Ions by Sulfonated High-Density Polypropylene Fabric^a

Sulfonation Time (min)	Average Binding (mg/g)	
	Pb ²⁺	Hg ²⁺
0	0.043 ± 0.075 ^b	0.0 ± 0
15	1.1 ± 0.93	53 ± 43
20	0.07 ± 0.12	103 ± 35 ^c
30	0.12 ± 0.13	37 ± 19

^a $n = 3$.^b Mean ± standard deviation^c Significantly different from the control ($\alpha = 0.05$).

as functional groups, so it was less effective than phosphorus for binding two of the three metals tested. One possible explanation of why the commercial resin bound Hg²⁺ better is that sulfuric acid is more electronegative than phosphoric acid because it has a higher pK_a (2.1 and -3, respectively). Whereas the pK_f for MeHg-SO₃ is 8.11, the pK_f for MeHg-OPO₃ is 5.03; therefore, sulfonates have a higher affinity for Hg.

Sulfonation

As in the case of low-density polyethylene,¹⁷ the sulfonation process caused the PP fabrics to discolor, and the color intensified with the increase in sulfonation time. This discoloration varied between samples sulfonated for 15 and 30 min.

Sulfonic acid groups were chemically introduced into PP. However, uniform sulfonation was not consistently accomplished (Table IV). There were no significant differences in sulfur percentage between the sulfonation times ($p = 0.0708$). A possible reason for the nonuniformity is that the fabric may have been over sulfonated. This would degrade the polymer and some of the sulfonated regions may have been dissolved in the postsulfonation rinsing of the fabrics.

The binding efficiency of sulfonated PP to Eu⁺³ was negligible. However, the results contradict the general behavior of ion exchange resins because the higher the valence charge of an ion, the greater will be the preference of the exchanger for it in dilute solutions.¹⁸ Meanwhile, lead ion binding was increased by sulfonation; however, there was not a pattern of binding with this metal. The highest binding of 1.07 mg/g occurred by PP treated for 15 min, and the lowest binding of 0.0704 mg/g was seen in fabric treated for 20 min

(Table V). These results may be explained by uneven sulfonation of the fabric; however, further characterization is needed to support this idea. No significant difference ($p = 0.804$) in binding was found among the treatment groups.¹⁶ Sulfonation generally improved PP binding efficiency of mercury. Fabric treated for 20 min had the highest binding of 103 mg/g, whereas the lowest binding was done by fabric treated for 30 min (Table V). The variability may also be due to uneven treatment of the samples. Only the binding efficiency of PP sulfonated for 20 min was found to be significantly different from the control ($p = 0.0166$).¹⁶

CONCLUSION

Nonwoven PP fabric can be surface-modified to form linear, nonswellable cation exchangers through chemically affixed sulfonic or phosphonic groups. When sulfonated and phosphonylated PP ion exchangers are compared, phosphonylated PP overall had a higher binding efficiency than sulfonated PP. The new cation exchanger, and particularly those carrying the phosphonate groups, are more effective in binding Pb⁺² and Eu⁺³ ions than a commercial sulfonic acid cross-linked ion exchanger; however, more research with various types of commercial ion exchangers needs to be conducted.

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