



# Synthesis, characterization, and heavy metal adsorption properties of sulfonated aromatic polyamides

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## Abstract

This work reports on the synthesis of a series of new sulfonated fluorine-containing aromatic polyamides with increasing degree of sulfonation (DS). The chemical structure of the resulting polymers was confirmed by Fourier transform infrared spectroscopy and proton nuclear magnetic resonance (<sup>1</sup>H NMR) which evidenced the presence of amide and sulfonic groups in the proposed concentrations. Afterwards, we carried out a comparative study of heavy metal ion adsorption in membranes based on these aromatic polyamides. The main purpose was to determine the adsorption capacity of the prepared polymer membranes toward Pb<sup>2+</sup> and Hg<sup>2+</sup> in aqueous media at 30°C and pH neutral. The adsorption kinetics was evaluated with the pseudo-first-order and pseudo-second-order models. The adsorption kinetics in all the polyamide membranes followed the pseudo-second-order rate law for both heavy metal ions. It is observed that the adsorption capacities of all the polyamides toward Pb<sup>2+</sup> ions are higher than those of the Hg<sup>2+</sup> ions, and these capacities increase as the DS increases. The equilibrium adsorption amounts,  $q_e$ , were 11.87 mg/g for Pb<sup>2+</sup> and 5.17 mg/g for Hg<sup>2+</sup> ions for the highest sulfonated polymer.

## Keywords

Sulfonated polymer, aromatic polyamide, heavy metal adsorption, lead and mercury, membrane

## Introduction

The presence of heavy metals in the environment resulting from anthropogenic activities has become a serious and growing ecological concern worldwide due to their high toxicity to life forms even in small concentrations.<sup>1,2</sup> Toxic metal ions are released into the natural water resources as well as in the industrial and domestic wastewater in a number of different ways, particularly in developing countries. Metal plating, ceramic, tanneries, mining industry, battery industry, chloroalkali industry, fertilizers, pesticides, paints, pulp, and paper are just some examples.<sup>3–5</sup> The factory processes that generate heavy metals such as lead, mercury, among others, are considered as the most hazardous industries since they are the two important toxic elements commonly found in industrial effluents that cause water and soil pollution besides being extremely harmful to human health. For instance, Pb<sup>2+</sup> is classified as a hazardous material and lead poisoning can cause many diseases such as hypertension, language difficulties, brain damage, dysfunction of the kidneys, the central nervous system,

among others, whereas it is well known that Hg<sup>2+</sup> has a very high tendency to bind to proteins mainly causing damage to the renal system, the central nervous system, delayed physical and mental development of children, the chromosomes, and so forth.<sup>6–9</sup>

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Likewise, as a consequence of the increasing demand on water supply, the use of unconventional water sources such as treated wastewater will be more frequent everytime, especially in historically regions with water shortages. In addition to wastewater purification, interesting processes are those capable of recovering metallic ions efficiently since the price of the noble materials such as heavy metals is constantly increasing. Thus, it is of great interest to recover the valuable materials, water and metals, as well as avoid the environmental detriment. Diverse methods for heavy metal removal from aqueous solution which have been applied successfully include solvent extraction, chemical precipitation, neutralization, dialysis, nanofiltration, reverse osmosis, and adsorption.<sup>10–12</sup> Among these techniques, the latter is by far the most versatile and widely used because of its high efficiency and the availability of different adsorbents. In this sense, polymeric membranes are very promising alternative materials for heavy metal ion adsorption from the aqueous effluents due to their low cost, easy handling, and high affinity toward heavy metal ions.<sup>13,14</sup> Moreover, in comparison with the widely used ion chelating resins, membranes are not compressible and can eliminate the internal diffusion limitations caused by resins used in a flow-by mode.<sup>15,16</sup>

Aromatic polyamides are considered as engineering polymers and suitable heavy metal ion adsorbents due to their high chemical stability as well as excellent thermo-mechanical properties which make them stable in water at different temperatures and environmental conditions. Because of the presence of amide groups, polyaramides tend to retain water and by the introduction of systematic amounts of sulfonic acid groups in the polymer main chain, the material hydrophilicity can be tailored leading to enhanced water absorption and ion exchange properties. Improving the water absorption by tailoring the polymer hydrophilicity also improves the accessibility of adsorption sites and, in turn, heightens the heavy metal adsorption capacity. Hence, sulfonated polyaramides are of great interest in the membrane technology field for their potential application in water and wastewater treatment.

In accordance with the aforementioned, in the present work, we explore the possibility of sulfonating aromatic polyamides to render them novel adsorbents in order to determine whether they could reach acceptable properties for heavy metal adsorption applications. To accomplish this aim, we applied a highly efficient copolymerization approach for the synthesis of a series of new sulfonated polyamides with a degree of sulfonation (DS) around 30 and 60 mol% by direct polycondensation from two different diamines, 5-(trifluoromethyl)-1,3-phenyldiamine combined with specific concentrations of the sulfonated diamine 2,5-diaminobenzenesulfonic acid and isophthaloyl chloride as comonomer. The polymer chemical structures were characterized by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy. If the polymeric membranes were

prepared using solvent evaporation from polymer solutions in *N,N*-dimethylacetamide (DMAc), then the Pb<sup>2+</sup> and Hg<sup>2+</sup> adsorption kinetics from monocationic reagent exchange solutions was assessed. It is expected that the presence of increasing amounts of the sulfonic acid groups will enhance the adsorption of lead and mercury ions onto the polymer membranes leading to novel adsorbents with potential applications in environmental protection.

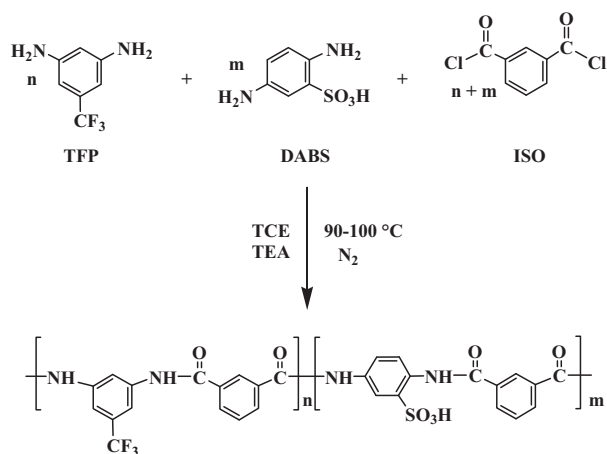
## Experimental part

### Techniques

<sup>1</sup>H NMR spectra were recorded on a Varian spectrometer (Varian inc. nmr spectrometer systems, Palo alto, California, USA) at 300 MHz in deuterated *N,N*-dimethylformamide using tetramethylsilane as internal standard. FTIR spectra were obtained on a Nicolet 510 p spectrometer (Thermo electron corporation, Madison Wisconsin, USA). Glass transition temperatures ( $T_g$ ) were determined in a DSC-7 Perkin Elmer Inc., (Waltham, Massachusetts, USA) at a scanning rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. The samples were encapsulated in standard aluminum differential scanning calorimetry (DSC) pans. Each sample was run twice on the temperature range between 30°C and 300°C. The  $T_g$  values obtained were confirmed by thermo-mechanical analysis (TMA) from the first heating cycle conducted at a rate of 10°C min<sup>-1</sup> under nitrogen atmosphere with a TA Instruments (New Castle, Delaware, USA) Thermomechanical Analyzer TMA 2940. Onset of decomposition temperature ( $T_d$ ) was determined using thermogravimetric analysis, which was performed at a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere with a DuPont 2100 instrument (Ta instruments (formerly DuPont), New Castle, Delaware, USA). Mechanical properties under tension, Young's modulus ( $E$ ) and stress ( $\sigma_u$ ), were measured in a Universal Mechanical Testing Machine Instron 1125-5500 R (Instron, Norwood, Massachusetts, USA) using a 50-kg cell at a crosshead speed of 10 mm min<sup>-1</sup> according to the method ASTM D1708 in film samples of 0.5 mm of thickness at room temperature. Wide-angle X-ray diffraction (WAXD) measurements of polymer films as cast were carried out in a Siemens D-5000 diffractometer (Siemens analytical x-ray instruments inc. Madison Wisconsin, USA) between 4° and 70° 2 $\theta$ , at 35 kV 25 mA, using copper  $K_\alpha$  radiation (1.54 Å). The concentration of metal ions in the solution was measured using a flame atomic absorption spectrophotometer (Thermo Scientific iCE 3000 Series; Thermo fisher scientific, Merckers, Cambridge, UK).

### Reagents

Isophthaloyl chloride (ISO) was recrystallized twice from petroleum ether and dried at room temperature under



**Figure 1.** Synthesis route of sulfonated aromatic polyamides.

vacuum prior to use. 2,5-Diaminobenzenesulfonic acid (DABS) was dried in a vacuum oven at 100°C overnight before use. 5-(Trifluoromethyl)-1,3-phenyldiamine (TFP) was used as received. Triethylamine (TEA) was distilled under atmospheric pressure. Lead(II) chloride ( $\text{PbCl}_2$ ), mercury(II) chloride ( $\text{HgCl}_2$ ), 1,1,2,2-tetrachloroethane (TCE), DMAc, and methanol were used without further purification. All reactants and solvents were purchased from Aldrich Chemical, Co (St. Louis Missouri, USA).

### Polymer synthesis

The polymers were synthesized by direct polycondensation following a procedure previously described.<sup>17</sup> The preparation of the polymer TFP/ISO was performed with equimolar amounts of the diamine TFP and ISO. The preparation of the polymers, TFP/ISO/DABS-30 and TFP/ISO/DABS-60, was carried out with a controlled combination of the sulfonated diamine monomer DABS and the nonsulfonated diamine monomer TFP with ISO in order to obtain polymers with a DS of 30% and 60%, respectively (Figure 1).

**Synthesis of nonsulfonated polyamide TFP/ISO.** In a 50-mL three-neck round-bottomed flask maintained under dry nitrogen atmosphere, 0.3522 g (2 mmol) of TFP and 0.4060 g (2 mmol) of ISO were dissolved in 7.0 mL of TCE. To start the reaction, 1.0 mL (7.1 mmol) of TEA was added slowly and the solution was heated at 90°C for 12 h. Then, the reaction was cooled to room temperature and the solution was poured into an excess of methanol with constant stirring. The precipitate was filtered off and washed thoroughly with methanol and hot water. The polymer obtained was dried in a vacuum oven at 120°C to constant weight.

**Synthesis of sulfonated polyamide TFP/ISO/DABS-30.** In a 50-mL three-neck round-bottomed flask maintained under dry nitrogen atmosphere, 0.2465 g (1.4 mmol) of TFP, 0.1129 g (0.6 mmol) of DABS, and 0.4060 g (2 mmol) of ISO were dissolved in 7.0 mL of TCE. To start the reaction,

1.0 mL (7.1 mmol) of TEA was added slowly and the solution was heated at 90°C for 12 h. Then, the reaction was cooled to room temperature and the solution was poured into an excess of methanol with constant stirring. The precipitate was filtered off and washed thoroughly with methanol and hot water. The polymer obtained was dried in a vacuum oven at 120°C to constant weight.

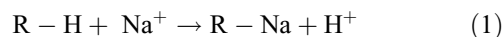
**Synthesis of sulfonated polyamide TFP/ISO/DABS-60.** In a 50-mL three-neck round-bottom flask maintained under dry nitrogen atmosphere, 0.1409 g (0.8 mmol) of TFP, 0.2258 g (1.2 mmol) of DABS, and 0.4060 g (2 mmol) of ISO were dissolved in 7.0 mL of TCE. To start the reaction, 1.0 mL (7.1 mmol) of TEA was added slowly and the solution was heated at 90°C for 12 h. Then, the reaction was cooled to room temperature and the solution was poured into an excess of methanol with constant stirring. The precipitate was filtered off and washed thoroughly with methanol and hot water. The polymer obtained was dried in a vacuum oven at 120°C to constant weight.

### Membranes preparation

Membranes were cast from *N,N*-dimethylacetamide solutions (~8 wt%) of polymer in a Teflon mold at 70°C under slow solvent elimination. The membranes obtained were dried under a vacuum at 160°C for 12 h. Next, the films were immersed firstly in stirring methanol at room temperature for 3 h and secondly in deionized water for 1 h in order to remove the residual solvent. Afterwards, the sulfonated membranes underwent a treatment with 1.0 N hydrochloric acid during 24 h. Then, the films were washed repeatedly with deionized water until the rinse water became neutral. Finally, the membranes were dried under a vacuum at 120°C for 24 h.

### Ion exchange capacity

The ion exchange capacity of the membrane was measured by immersing the weighed dry membrane in a 1.0 N sodium chloride solution for 24 h. The protons exchanged in the reaction



were estimated by titration with a very diluted NaOH solution. The value of ion exchange capacity (IEC) in milliequivalents per gram of dry membrane was obtained as  $\text{IEC} = VC/m_d$ , where  $V$  is the volume in milliliters of the solution of NaOH of concentration  $C$  (meq/mL) used in the titration and  $m_d$  is the mass of the membrane in grams.

### Water uptake

Weighed dry membranes were immersed and kept in deionized distilled water overnight. The membranes were removed from water, gently blotted with filter paper to

remove surface water and weighed. This process was repeated three times. From the weight of the dry membrane and the membrane equilibrated with water, the water uptake ( $W_u$ ) is obtained as follows:

$$W_u = \frac{\text{weight wet membrane} - \text{weight dry membrane}}{\text{weight dry membrane}} \times 100 \quad (2)$$

### Heavy metal adsorption using batch method

Monocationic reagent exchange solutions were prepared from  $\text{PbCl}_2$  and  $\text{HgCl}_2$  dissolved in deionized water. The  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  adsorption kinetics were evaluated by separately adding 0.2 g of each adsorbent to 10 mL of 0.1 N solutions of each adsorbate, reacting for 24 h, taking aliquots after 0.5, 1, 2, 3, 4, 5, 6, 10, 12, and 24 h of contact. The aliquots required centrifugation to separate any suspended material. Afterwards, the residual concentrations of heavy metal ions in the centrifuged liquids were determined by atomic absorption spectrometry. The amount of metal adsorbate adsorbed by the polymer membrane  $q_e$  ( $\text{mg g}^{-1}$ ) was calculated using the following equation:

$$q_e M = V(C_0 - C_e) \quad (3)$$

where  $C_0$  and  $C_e$  are the initial and final heavy metal ion concentrations in solution ( $\text{mg L}^{-1}$ ), respectively;  $M$  is the amount of adsorbent used (g); and  $V$  is the volume of the solution (L).

### Adsorption kinetics

In order to analyze the adsorption rate of heavy metal ions onto the sulfonated polyamide membranes, pseudo-first-order and pseudo-second-order rate equations were employed to interpret the experimental data. Lagergren's first-order rate equation is represented by:<sup>18</sup>

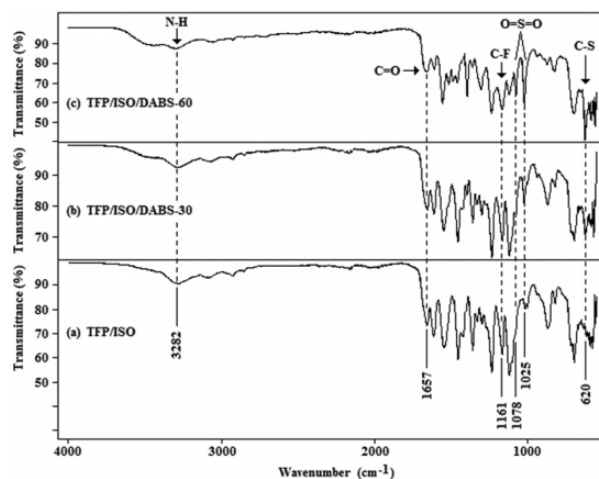
$$\ln(q_1 - q_t) = \ln q_1 - k_1 t \quad (4)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of heavy metal ion adsorbed onto the membrane at time  $t$ ,  $k_1$  is the pseudo-first-order rate constant ( $\text{h}^{-1}$ ), and  $q_1$  ( $\text{mg g}^{-1}$ ) is the final equilibrium adsorption amount.  $k_1$  can be determined by the linear plot of  $\ln(q_1 - q_t)$  versus  $t$ .

The adsorption kinetics was also calculated as a second-order reaction by the following equation:<sup>18</sup>

$$\frac{dq_t}{dt} = k_2(q_2 - q_t) \quad (5)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{h}^{-1}$ ) is the second-order rate constant of adsorption,  $q_2$  ( $\text{mg g}^{-1}$ ) is the amount of adsorbate ( $\text{Pb}^{2+}$  or  $\text{Hg}^{2+}$ ) adsorbed at equilibrium, and  $q_t$  ( $\text{mg g}^{-1}$ ) is the adsorbate contacting the adsorbent at any time  $t$ . At boundary conditions,  $t$  varies between 0 and  $t$  and  $q_t$  between 0



**Figure 2.** FTIR spectra of (a) nonsulfonated polyamide TFP/ISO, (b) sulfonated polyamide TFP/ISO/DABS-30, and (c) sulfonated polyamide TFP/ISO/DABS-60. TFP: 5-(trifluoromethyl)-1,3-phenyldiamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid; FTIR: Fourier transform infrared.

and  $q_i$ ; hence, the integrated equation takes the form of equation 6 where  $k_2 q_2^2$  is the initial adsorption rate:

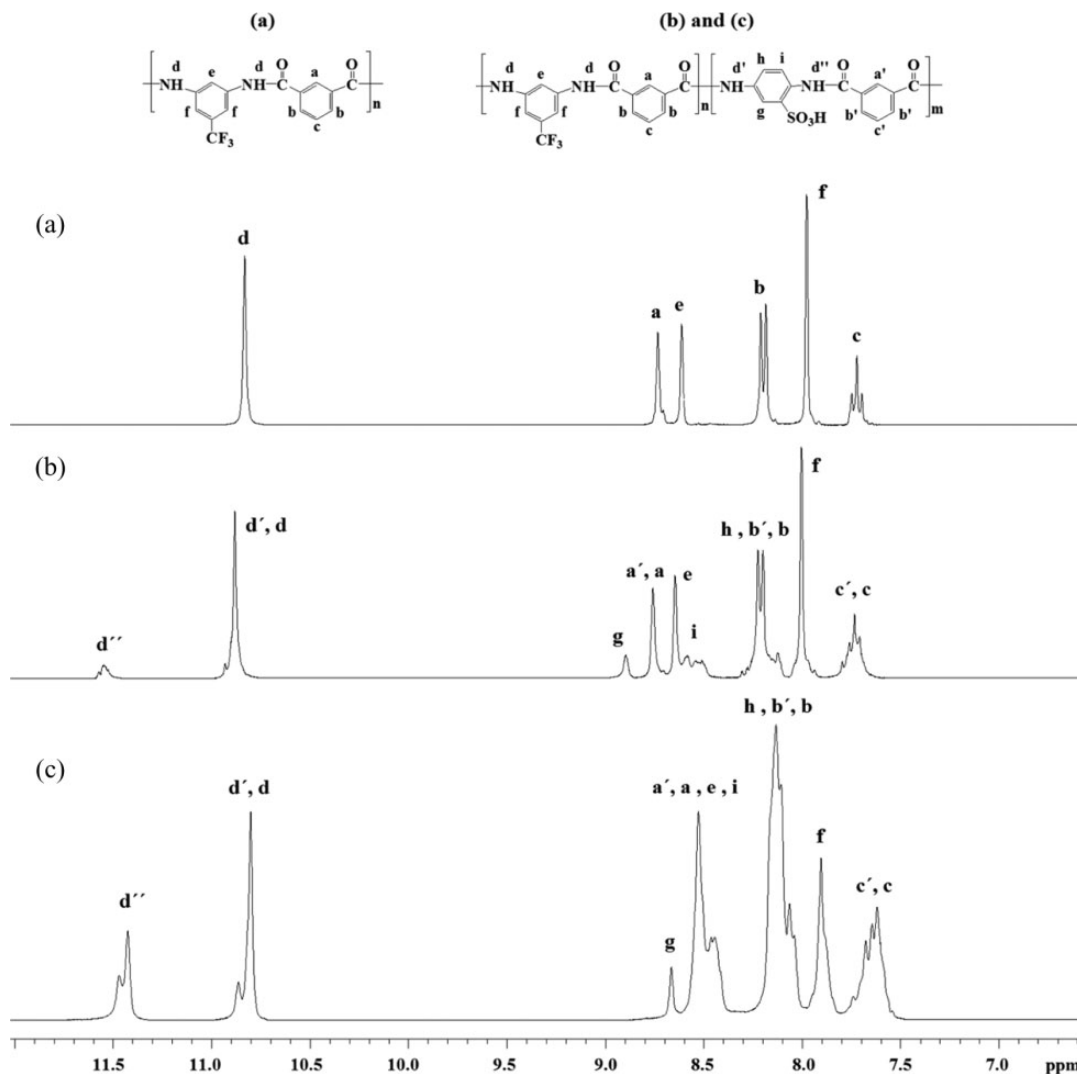
$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \left(\frac{1}{q_2}\right)t \quad (6)$$

The linear variation of  $t/q_t$  versus  $t$  allows the calculation of  $q_2$  and  $k_2$ . The validity of the assumed order of reaction and calculated equation was tested by comparison between calculated and experimental  $q_e$ .

## Results and discussion

As shown in Figure 1, sulfonated aromatic polyamides with controlled degrees of sulfonation were successfully synthesized by polycondensation reaction from a mixture of an aromatic fluorinated diamine (TFP), a diamine bearing a sulfonic acid group (DABS), and ISO. The DS was tailored by adjusting the ratio of diamine TFP to diamine DABS. The polymers obtained were white fibers whose size was smaller as the sulfonated diamine concentration in the polymer was increased. Membranes prepared by casting from polyamide solutions in DMAc were translucent with a yellowish coloration that intensified as the DS increased. Furthermore, the rigidity of the membranes also increased with increasing the DS being quite flexible when fully hydrated and becoming somewhat brittle as they dried out.

The hydrolytic stability of the sulfonated membranes was also investigated by aging the membrane samples (100–150 mg) in 500 mL of deionized water at 90°C up to 72 h. Under these conditions, the ionomer membranes did not dissolve and exhibited fairly good toughness level as they only broke when the films were hardly bent. The latter indicated the quite good hydrolytic stability of the membranes.



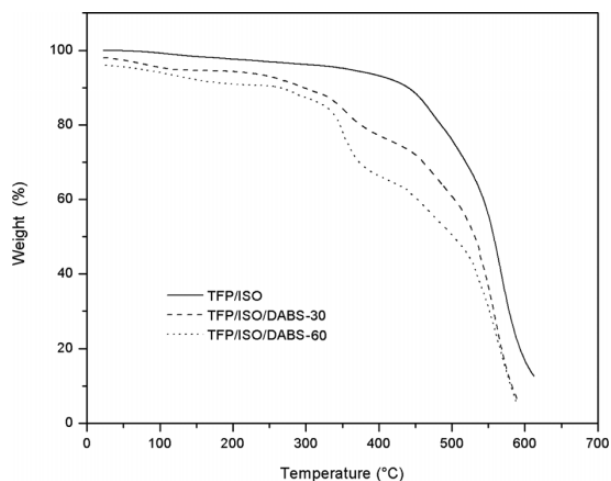
**Figure 3.**  $^1\text{H}$  NMR spectra of (a) nonsulfonated polyamide TFP/ISO, (b) sulfonated polyamide TFP/ISO/DABS-30, and (c) sulfonated polyamide TFP/ISO/DABS-60. TFP: 5-(trifluoromethyl)-1,3-phenyldiamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid;  $^1\text{H}$  NMR: proton nuclear magnetic resonance.

FTIR spectroscopy was used to confirm the chemical structure of the polyamides. The comparative FTIR spectra of the nonsulfonated polyamide TFP/ISO and the polyamides TFP/ISO/DABS with different DS are shown in Figure 2. The characteristic absorption band for the amide group is observed around  $3282\text{ cm}^{-1}$  (N–H), the representative band of the amide carbonyl groups (–CO–NH–) is shown at  $1657\text{ cm}^{-1}$ , the absorption band of aromatic C=C stretching is exhibited at  $1550\text{ cm}^{-1}$ , and the absorption band due to the C–F stretching is observed at  $1161\text{ cm}^{-1}$  in all of the synthesized polymers.

It is worth noting that there are several characteristic bands that appeared only in the sulfonated polyamides and clearly indicate that the –SO<sub>3</sub>H groups were successfully introduced in the polymer chains. For instance, the bands displayed at  $1078$  and  $1025\text{ cm}^{-1}$  are attributed to the symmetric and asymmetric O=S=O stretching vibrations of

the sulfonic acid group, respectively, whereas that observed at  $620\text{ cm}^{-1}$  is assigned to the C–S stretching vibration. These three characteristic bands increase gradually as the concentration of the sulfonated diamine in the macromolecule is also increased.

The chemical structures as well as the compositions of the nonsulfonated polyamide TFP/ISO and the polyamides TFP/ISO/DABS with different DS, respectively, were confirmed by  $^1\text{H}$  NMR. The comparative  $^1\text{H}$  NMR spectra of the corresponding polymers is presented in Figure 3 and indicate that the integration area ratio of each proton agrees with the expected structure of all of the polyamides. For the TFP/ISO polyamide, the characteristic H<sub>d</sub> signal appears at 10.83 ppm and corresponds to the protons found in the –NH– moiety. H<sub>a</sub>, H<sub>b</sub>, and H<sub>c</sub> at 8.73, 8.21, and 7.72 ppm, respectively, correspond to the aromatic protons of ISO, whereas the H<sub>e</sub> and H<sub>f</sub> signals at 8.61 and 7.97 ppm



**Figure 4.** Thermal decomposition under the nitrogen atmosphere of nonsulfonated polyamide TFP/ISO (solid line), sulfonated polyamide TFP/ISO/DABS-30 (dashed line), and sulfonated polyamide TFP/ISO/DABS-60 (dotted line). TFP: 5-(trifluoromethyl)-1,3-phenylenediamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid.

correspond to the aromatic protons of TFP. It is observed that new proton interaction signals arise due to the introduction of the sulfonic acid groups in the macromolecular architecture and correspond mainly to the protons near the sulfonic acid group  $H_g$ ,  $H_h$ ,  $H_i$ ,  $H_{d'}$ , and  $H_{d''}$ . For instance, the peak at 8.66 ppm only appears in the spectra of sulfonated polymers and it is attributed to the *ortho* proton  $H_g$  with respect to the sulfonic acid group which appears at downfield due to the electron-withdrawing effect of the ionic group. The aromatic hydrogen atoms  $H_i$  and  $H_h$  near the  $-SO_3H$  group were detected at 8.46 and 8.06 ppm, respectively, while the signals of those protons attached to the amine moiety of the sulfonated monomer,  $H_{d'}$  and  $H_{d''}$ , appeared at 11.42 and 10.21 ppm.

We also observed that the more content of sulfonated diamine in the polyamides the higher the intensities of the signals of these protons. All the other peaks,  $H_a$ ,  $H_b$ , and  $H_c$ , correspond to other aromatic hydrogen atoms of the chemical structure of the sulfonated polyamides that are also present in the nonsulfonated polyamide TFP/ISO. In order to determine the DS, from Figure 3(b) and (c), the relationship between the areas of protons, which does not change in the polyamide TFP/ISO and the series of polyamides TFP/ISO/DABS,  $H_f$ , and the proton *ortho* to the  $-SO_3H$  group in the sulfonated polyamides,  $H_g$ , was calculated. The DS values calculated from the  $^1H$  NMR spectra for the polyamides TFP/ISO/DABS-30 and TFP/ISO/DABS-60 were 28.9% and 58.2%, respectively. These results are in agreement with the DS values expected from the monomer feed molar ratios (30% and 60%, respectively). The latter evidenced that the concentration of the sulfonated moieties proposed for the chemical structures of the polyamides was successfully controlled by changing the molar ratio of nonsulfonated to sulfonated diamines.

Figure 4 shows the thermal decomposition thermograms of sulfonated and nonsulfonated polyamide membranes. The thermograms have been shifted by 2% from each other starting from the one corresponding to TFP/ISO in order to better appreciate the differences in the decomposition of all the aromatic polymers. All the polyamides synthesized have similar decomposition profiles that show an initial weight loss up to 100°C commonly associated with the release of absorbed water.<sup>19</sup> This moisture retention increases as the concentration of the hydrophilic  $-SO_3H$  groups also increases in the polymer backbone, hence nonsulfonated polyamide TFP/ISO exhibits a mass loss around 2 wt% at 100°C, whereas the polyamide bearing 60 mol.% sulfonic acid groups, TFP/ISO/DABS-60, shows the highest mass loss at 100°C (6 wt%). The polyamide TFP/ISO exhibits the highest thermal stability as compared with the sulfonated polyamides since its onset of decomposition temperature,  $T_d$ , is observed at around 455°C which is attributed to the initial degradation of the aromatic polymer backbone. The thermograms for the sulfonated polyamides TFP/ISO/DABS-30 and TFP/ISO/DABS-60 show similar profiles with two stages in the thermal decomposition. The first weight loss observed around 320°C is mainly associated with the cleavage of C–S bonds, namely the elimination of the sulfonic acid moieties which increases as the  $-SO_3H$  group content in the polymer is also increased.<sup>20</sup> The second weight loss about 455°C is ascribed to the aromatic main chain thermal degradation of the ionic polymers.

Table 1 shows the glass transition temperature,  $T_g$ , values of the nonsulfonated polyamide TFP/ISO as well as the polyamide series TFP/ISO/DABS with different DS. From Table 1, it is seen that all the sulfonated polymers have higher  $T_g$  values in comparison with that of the nonsulfonated polymer. In addition, the more the content of the sulfonic acid group in the polyamide, the higher the  $T_g$  value observed. The latter suggests that the introduction of  $-SO_3H$  groups in the polymer backbone may have two effects on the  $T_g$  of the aromatic polyamides. Firstly, the ionic character of the sulfonic acid group causes a significant increase in interaction between polymer chains and strongly reduces their conformational mobility. Secondly, due to their molecular bulkiness, the  $-SO_3H$  groups increase the energy barrier for intersegmental bond rotations hindering the torsional movement within the polymer backbone. Both effects inhibit the ability of the polymer chains to attain the relaxation process, thus increasing the chain stiffness and in turn the polymer  $T_g$ . These effects have also been observed for other sulfonated polymers.<sup>21</sup>

Stress–strain measurements in tension for the films of the polymers synthesized were carried out and the results are also listed in Table 1. The values of tensile strength of the films were in the range of 85–101 MPa, whereas the elastic modulus values were in the range of 1693–2073 MPa. The experiments were stopped at the maximum stress

**Table 1.** Physical properties of aromatic polyamides.

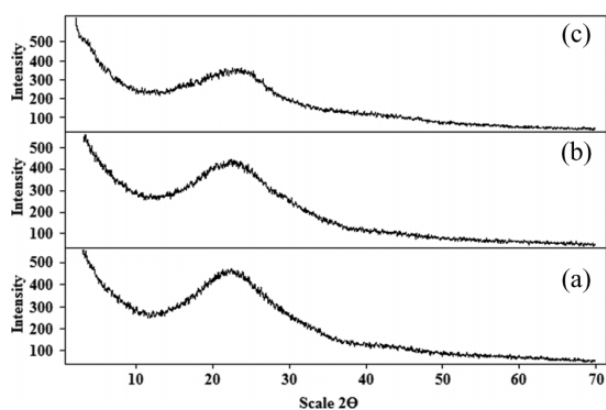
Polymer	DS <sup>a</sup> (%)	T <sub>g</sub> (°C)	T <sub>d</sub> (°C)	s (MPa)	E (MPa)	d <sub>spacing</sub> (Å)
TFP/ISO	0	185	455	85	1693	4.01
TFP/ISO/ DABS-30	28.9	210	320 <sup>b</sup> 455 <sup>c</sup>	90	1896	3.99
TFP/ISO/ DABS-60	58.2	228	320 <sup>b</sup> 455 <sup>c</sup>	101	2073	3.90

TFP: 5-(trifluoromethyl)-1,3-phenyldiamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid; <sup>1</sup>H NMR: proton nuclear magnetic resonance.

<sup>a</sup>Determined by <sup>1</sup>H NMR.

<sup>b</sup>Thermal decomposition assigned to the losses of the sulfonic acid groups.

<sup>c</sup>Thermal decomposition assigned to the aromatic main polymer chain.



**Figure 5.** X-ray diffraction pattern of (a) nonsulfonated polyamide TFP/ISO, (b) sulfonated polyamide TFP/ISO/DABS-30, and (c) sulfonated polyamide TFP/ISO/DABS-60. TFP: 5-(trifluoromethyl)-1,3-phenyldiamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid.

and it was found that the nonsulfonated polyamide TFP/ISO presented the lesser elastic modulus as well as stress in tension of all of the polyamides obtained. The foregoing could be attributed to the highest conformational mobility of the aromatic polymer chains. It was also observed that these mechanical properties were enhanced due to the presence of increasing amounts of sulfonic acid groups in the polyamides that in turn raised the interchain interaction and thus the rigidity of the polymer chains. For instance, the values for the polymer bearing the highest concentration of  $-\text{SO}_3\text{H}$  groups, TFP/ISO/DABS-60, are higher in comparison with those determined for the sulfonated polymer with the lower DS. This fact suggests that the presence of the bulky sulfonic acid moieties pending on the phenyl ring of the polyamides TFP/ISO/DABS-30 and TFP/ISO/DABS-60 strongly restricts the ability of the polymer chains to adopt different conformations which is reflected in a higher elastic modulus and tensile strength as compared with their nonsulfonated analogue TFP/ISO. These results showing a general trend with increasing the DS are similar to those reported for other sulfonated aromatic polymer structures.<sup>21</sup>

WAXD measurements of the as cast sulfonated and non-sulfonated polymer films show in Figure 5 typical polyamide patterns with one broad diffraction peak with a maximum around  $22^\circ 2\theta$ .<sup>22</sup> The latter evidences that all these polymers as cast are amorphous since no crystallinity was detected either by WAXD or in the thermal measurements described previously. Further, a measure of their mean intersegmental distance or chain packing density could be obtained from the  $d$ -spacing value at the angle of maximum reflective intensity in the amorphous trace using Bragg's equation,  $n\lambda = 2d\sin\theta$ .<sup>23</sup> A comparison on the average  $d$ -spacing, also reported in Table 1, indicates that this parameter decreases gradually as the concentration of the sulfonated moiety in the macromolecular architecture is also increased. This is likely due to the increased polymer interchain interaction induced by the ionic character of the sulfonic acid groups.

The kinetic parameters for the adsorption of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions by the sulfonated polymer membranes at  $30^\circ\text{C}$  are given in Table 2. Based on the coefficients obtained, it is observed that the experimental data related to the adsorption process of the two heavy metal ions onto the polyamide membranes fit to second-order kinetics ( $R^2$  0.990–0.998) as defined by equation 6.

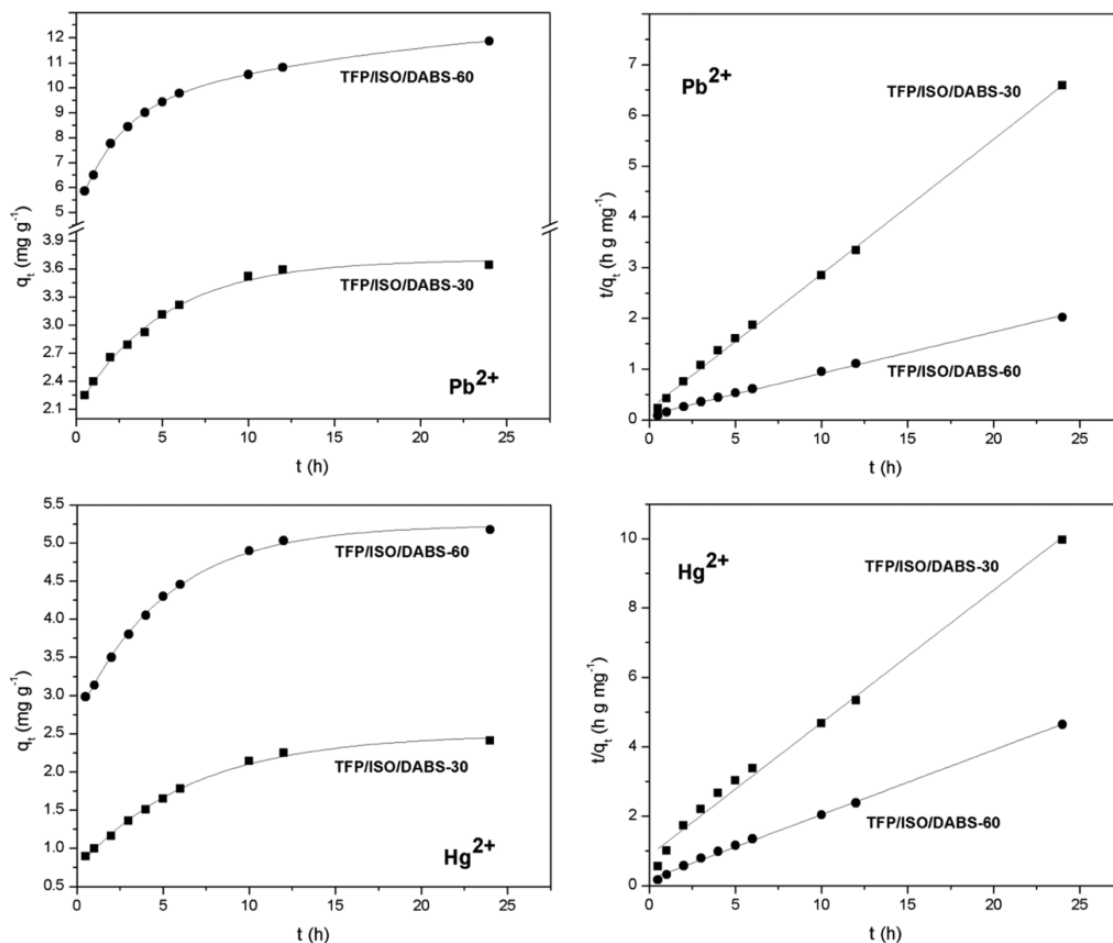
As it is shown in Figure 6, for all the adsorption experiments, the amount of heavy metal ion adsorbed onto the sulfonated polymer membrane increased quickly with time and then slowly reached equilibrium. The rate of metal ion adsorption is higher in the beginning on account of a larger surface of the adsorbent being available for the adsorption of heavy metal ions. The single, smooth, and continuous adsorption curves leading to saturation in Figure 6 also indicate that  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  adsorption kinetics from monocationic solutions were completed and equilibrated after 12 h of contact, suggesting the possible formation of a single layer of metal ions on the surface of the adsorbent. The amounts of heavy metal ion adsorbed onto the polymer membrane TFP/ISO/DABS-30 at equilibrium ( $q_e$ ) at  $30^\circ\text{C}$  are  $3.64 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$  ion and  $2.40 \text{ mg g}^{-1}$  for  $\text{Hg}^{2+}$  ion, whereas those found for the polymer membrane TFP/ISO/DABS-60 are  $11.87 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$  ion and  $5.17 \text{ mg g}^{-1}$  for  $\text{Hg}^{2+}$  ion. According to the latter, the adsorption amounts at equilibrium ( $q_e$ ) of the polyamides bearing sulfonic acid groups increase along with the increase of DS for the two heavy metal ions. Furthermore, the maximum adsorption amount of the nonsulfonated polyamide TFP/ISO is  $0.62 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$  ion and  $0.29 \text{ mg/g}$  for  $\text{Hg}^{2+}$  ion, which confirmed that the adsorption capacities of the sulfonated polyamides are mainly attributed to the complex of the sulfonated moieties with heavy metal ions.

Polymeric adsorbents used in heavy metal ions removal have granulometric nature in most of the cases and several materials with a wide range of adsorption capacities for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  have been reported. Table 3 shows a comparison of the adsorption capacity results of various types

**Table 2.** The kinetic parameters for the adsorption of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions by the sulfonated polyamide membranes.

Polymer	Heavy metal ion	Pseudo-first-order model			Pseudo-second-order model		
		$k_1$ ( $\text{h}^{-1}$ )	$q_1$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{h}^{-1}$ )	$q_2$ ( $\text{mg g}^{-1}$ )	$R^2$
TFP/ISO/DABS-30	$\text{Pb}^{2+}$	0.2784	3.642	0.976	0.3278	3.763	0.998
	$\text{Hg}^{2+}$	0.1944	2.409	0.988	0.1676	2.615	0.990
TFP/ISO/DABS-60	$\text{Pb}^{2+}$	0.1478	11.87	0.971	0.0659	12.25	0.996
	$\text{Hg}^{2+}$	0.2341	5.174	0.992	0.1884	5.369	0.998

TFP: 5-(trifluoromethyl)-1,3-phenylenediamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid.

**Figure 6.** Heavy metal ion adsorption kinetics from monocationic solutions by the sulfonated polymer membranes (lines are only representative).

of adsorbents with those found in this study. For instance, the application of Nafion 117, a commercial ionomer membrane, for the removal of different heavy metal ions from solutions has been explored and the maximum value of metal adsorption in this sulfonated fluoropolymer membrane was found to be  $58.0 \text{ mg g}^{-1}$  for  $\text{Pb}^{2+}$ .<sup>24</sup> The  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  adsorptions on polyacrylamide/attapulgit were investigated in batch systems and the results showed a maximum adsorption capacity for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  of  $30.4$  and  $130.7 \text{ mg g}^{-1}$ , respectively.<sup>25</sup> Moreover, cross-linked nanochelating resins based on poly(methylmethacrylate-

co-maleic anhydride) have also been prepared and the maximum chelation capacity of one of the prepared resin beads for  $\text{Hg}^{2+}$  was found to be  $85.8 \text{ mg g}^{-1}$ .<sup>26</sup> Another resin based on a cross-linked graft copolymer of acrylic acid onto poly(vinyl alcohol) has also been prepared and its mercury ion retention capacity was determined at different concentration of sorbate, the maximum  $\text{Hg}^{2+}$  uptake capacity was found to range from  $31.2 \text{ mg g}^{-1}$  at moderate level of sorbate until  $116.4 \text{ mg g}^{-1}$  at relatively higher dose of sorbate.<sup>27</sup> Other batch sorption studies carried out on chitosan have also revealed an adsorption capacity for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  of



**Table 3.** Heavy metal ion adsorption capacity for different materials in the literature.

Adsorbent	Pb <sup>2+</sup> adsorption capacity (mg g <sup>-1</sup> )	Hg <sup>2+</sup> adsorption capacity (mg g <sup>-1</sup> )	Physical form	pH	Reference author
Nafion 117	58.0	—	Membrane	5.9	24
Polyacrylamide/attapulgit	30.4	130.7	Particles	4	25
Co-g-AP <sub>3</sub> <sup>a</sup>	—	85.8	Beads	6	26
X-AA-g-PVA <sup>b</sup>	—	31.2	Particles	5	27
Chitosan	26.0	24.0	Particles	7	28
Thiacalix[4]arene-loaded resin	25.9	—	Particles	6	18
Poly(VP-PEGMA-EGDMA) <sup>c</sup>	18.2	—	Beads	6	29
Poly(PET-g-AAm) <sup>d</sup>	14.0	—	Fibers	5.5	30
Rice husk ash	9.8	3.0	Particles	5.8	31
Poly(ethylene terephthalate)	1.3	—	Fibers	5.5	30
MBT-clay <sup>e</sup>	0.7	2.7	Particles	3.5	32
Pozzolana	—	1.0	Particles	6.5–7.3	33
TFP/ISO/DABS-60	11.8	5.1	Membrane	7	This study
TFP/ISO/DABS-30	3.6	2.4	Membrane	7	This study

TFP: 5-(trifluoromethyl)-1,3-phenyldiamine; ISO: isophthaloyl chloride; DABS: 2,5-diaminobenzenesulfonic acid.

<sup>a</sup>Cross-linked and grafted resin based on poly(methylmethacrylate-co-maleic anhydride).

<sup>b</sup>Cross-linked graft copolymer of acrylic acid onto poly(vinyl alcohol).

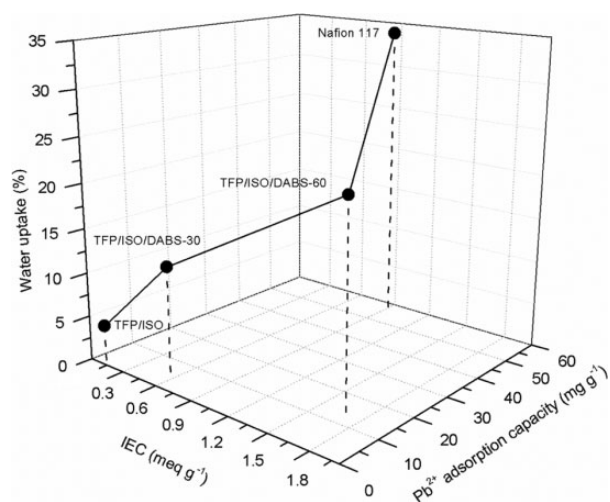
<sup>c</sup>Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate).

<sup>d</sup>Grafted acrylamide (AAm) monomer onto poly(ethylene terephthalate).

<sup>e</sup>2-Mercaptobenzothiazole loaded on previously treated clay.

26.0 and 24.0 mg/g, respectively.<sup>28</sup> The adsorption capacity of a thiocalix[4]arene-loaded resin toward Pb<sup>2+</sup> ion was investigated by batch adsorption experiments and the amount of heavy metal ion adsorbed onto the sulfonated resin at equilibrium at 30°C was found to be 25.9 mg g<sup>-1</sup>.<sup>18</sup> Likewise, poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads have been prepared and it was found that the chelation capacity of these beads was 18.2 mg g<sup>-1</sup> for Pb<sup>2+</sup>.<sup>29</sup> Other studies have shown that the adsorption equilibrium amount of Pb(II) ion onto pure poly(ethylene terephthalate) (PET) fibers was 1.3 mg g<sup>-1</sup> and that this value was increased up to 14.0 mg g<sup>-1</sup> by grafting acrylamide onto PET fibers.<sup>30</sup> Finally, the use of a wide variety of natural and industrial low-cost adsorbent materials for heavy metal removal from aqueous solutions has also been reported. Some of these low-cost adsorbents include rice husk ash, MBT-clay, pozzolana, among others. These materials have shown an adsorption capacity for Pb<sup>2+</sup> and Hg<sup>2+</sup> up to 9.8 and 3.0 mg g<sup>-1</sup>, respectively.<sup>31–33</sup> It can be seen from Table 3 that the sulfonated aromatic polyamides prepared in this study show comparable adsorption capacities with respect to other adsorbents, revealing that these novel sulfonated materials are suitable for the removal of Pb<sup>2+</sup> and Hg<sup>2+</sup> from aqueous solutions.

Figure 7 shows the relationship between the IEC,  $W_u$ , and Pb<sup>2+</sup> adsorption capacity of all the new polymers studied here. For comparative purposes, the Nafion 117 membrane is also presented.<sup>24</sup> The IEC provide information on the density of ionizable functional groups in the membrane which are to a great extent responsible for the heavy metal



**Figure 7.** Water uptake and Pb<sup>2+</sup> adsorption capacity of aromatic polyamide membranes as IEC increases. IEC: ion exchange capacity.

adsorption capacity of the material; thus, the experimental IEC of the aromatic polyamide membranes TFP/ISO, TFP/ISO/DABS-30, and TFP/ISO/DABS-60 was determined at 30°C and found to be 0.12, 0.60 and 1.73 meq/g, respectively. Further, the ion adsorption process requires a significant amount of water to coordinate with heavy metal ion as it interacts with the membrane. Therefore, selecting polymer membranes able to absorb enough water are appropriate for this purpose. In this regard, the  $W_u$  of these aromatic polyamide membranes was also determined and, as

expected, the  $W_u$  increased along with the increase of IEC since the sulfonic acid groups are hydrophilic and hence the membranes with higher IEC can absorb more water because of the increase of the hydrophilicity. In this sense, the polymer bearing the highest concentration of  $-\text{SO}_3\text{H}$  groups, TFP/ISO/DABS-60, showed the highest water absorption (22.8%), followed by the polymer with the lower DS TFP/ISO/DABS-30 (12.5%) and the nonsulfonated polyamide TFP/ISO (4.3%). Similarly, it was also found that the more the IEC in the aromatic polyamide membrane, the higher the adsorption capacity for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$ .

It is worth noting that compared to Nafion 117 (IEC = 0.89 meq/g and  $W_u = 34.0\%$ ),<sup>24</sup> the TFP/ISO/DABS-60 membrane exhibits a higher IEC but a lower  $W_u$  (Figure 7). This decrease in water absorption could be attributed not only to the higher rigidity of the aromatic chain of TFP/ISO/DABS-60 compared to that of Nafion 117 which results in the restriction of free volume, but also to the lower acidity of the sulfonic acid groups attached to the aromatic moieties. In this regard, the different distribution of ion domains seems to play a crucial role in the heavy metal adsorption capacity of the membrane. The TFP/ISO/DABS-60 membrane is likely to develop less ion-rich domains which cause the ions to migrate with less ease than in Nafion 117. In addition, the arylsulfonic functions were only strong acids in the sulfonated polyamide, while the high electronegativity of the fluorine atoms makes  $-\text{SO}_3\text{H}$  a superacid in Nafion 117. Therefore, the TFP/ISO/DABS-60 membrane dissociates less  $\text{H}^+$  than Nafion 117, diminishing the sites available for  $\text{Pb}^{2+}$  adsorption in the structure.

As mentioned previously, the sulfonated fluorine-containing polyamide membranes used in this study prefer the metal with the higher atomic number and increasing ionic radii. This behavior can be attributed to the fact that metal affinity for the sulfonated polymer membranes is mainly due to the electrostatic interaction between the hydrophilic negatively charged sulfonic acid groups and the counter metal ions in the solution. The higher the atomic number of the counterion, the larger the electrostatic attraction, thus the sulfonated polymer membranes prefer  $\text{Pb}^{2+}$  over  $\text{Hg}^{2+}$ . Moreover, larger counterions most likely produce ionic clusters of lower water content.<sup>34</sup> Since the water content of ionic clusters in the membranes decreases as the size of the counterions increases, the presence of the competing hydronium ions ( $\text{H}_3\text{O}^+$ ) also decreases; thus, the competitive adsorption of  $\text{H}_3\text{O}^+$  and metal ions for the same active adsorption sites favors the larger counterion ( $\text{Pb}^{2+}$ ) compared to the smaller counterion ( $\text{Hg}^{2+}$ ) because the electrostatic attraction between the metal ion and the functional groups in the membrane surface is also likely to be increased. In order to clarify this issue, further research concerning the adsorption properties of this kind of ionomers in different medium, pH value, temperature, and initial concentration of several heavy metal ions is actually being carried out by our group and it will be the subject of a forthcoming paper.

## Conclusions

Novel sulfonated aromatic polyamides with controlled DS were successfully synthesized by direct polycondensation from a mixture of an aromatic fluorine-containing diamine and an aromatic diamine bearing a sulfonic acid group and isophthaloyl chloride. The DS was tailored effectively by adjusting the ratio of the fluorinated diamine to the sulfonated diamine. The equilibrium adsorptions of the sulfonated polymer membranes toward  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions were successfully investigated by batch adsorption experiments. The adsorption kinetics in the sulfonated polyamide membranes followed the pseudo-second-order rate law for both heavy metal ions and the adsorption amounts at equilibrium ( $q_e$ ) increase along with the increase of DS for the two heavy metal ions. The sulfonated polymer membranes show a greater affinity for the adsorption of lead ions than for mercury ions as revealed the fact that  $q_e$  for  $\text{Pb}^{2+}$  is more than twice that of the  $\text{Hg}^{2+}$  ion in the polyamide membrane with the highest DS. These results suggest that sulfonated aromatic polyamides can be effectively used as heavy metal adsorbents and have potential applications in environmental protection, particularly for the removal of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions from water and waste water. The new sulfonated adsorbents have higher adsorption properties than other adsorbents used in previous works in the literature.

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