Functionalized PU Foam for Water Filtration

Nidal H. Abu-Zahra, Subhashini Gunashekar

Abstract—Polyurethane foam is functionalized with Sulfonic acid groups to remove lead ions (Pb^{2+}) from drinking water through a cation exchange process. The synthesis is based on addition polymerization of the -NCO groups of an isocyanate with the –OH groups of a polyol to form the urethane. Toluene-diisocyanateis reacted with Polypropylene glycol to form a linear pre-polymer, which is further polymerized using a chain extender, N, N-bis(2-hydorxyethyl)-2-aminoethane-sulfonic acid (BES). BES acts as a functional group site to exchange Pb^{2+} ions. A set of experiments was designed to study the effect of various processing parameters on the performance of the synthesized foam. The maximum Pb^{2+} ion exchange capacity of the foam was found to be 47ppb/g from a 100ppb Pb^{2+} solution over a period of 60 minutes. A multistage batch filtration process increased the lead removal to 50-54ppb/3g of foam over a period of 90 minutes.

Keywords—Adsorption, Functionalized, Ion exchange, Polyurethane, Sulfonic.

I. INTRODUCTION

POLYURETHANE foam is considered to be one of the most versatile polymeric materials. It has good thermal insulating properties, low moisture-vapor permeability, high resistance to water absorption, and a relatively high specific strength. The major components are an isocyanate and a polyol (or a mixture of polyols). A blowing agent and a catalyst are used to accelerate the foam formation. The foams can be synthesized as open-cell foams or as closed-cell foams based on the initial raw materials concentration.

Open cell polyurethane foams are known to exhibit a reasonable amount of ion exchange capacity and are being considered as suitable ion exchange media for heavy metal ions removal [1]. Farag et al. [2] showed that open-pore polyurethane microspheres exhibit low cation exchange capacity. Their research on foams prepared by chemical bonding of specific functional groups (-SH) was used to adsorb mercury ions from mercury (II) chloride and methyl mercury (II) chloride in the range of 0.4 to 400 ppb. This led researchers to consider the functionalization of polyurethane foams as an effective medium to eliminate heavy metal ions either by adsorption or pre-concentration mechanisms. Functional groups like hydroxyl, ketone, and carboxylic acids have been found to adjust the surface energy and improve the hydrogen binding in polymers [3]. This property is the basis

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for functionalization of polyurethane foams either by surface or structural modification. Moon et al. [4] developed a CEDI (continuous electro deionization) medium to deionize aqueous media to a high level, without the need for chemical regeneration, by synthesizing functionalized polyurethane foam. A chain extender was used during synthesis to functionalize the pre-polymer. This led to the bulk functionalization of polyurethane foam with an increase in ion exchange capacity as the number of sulfonic acid groups increased. Functionalization of polyurethane foams by surface modification has led to systems capable of adsorbing heavy metal and trace metal ions [5]-[9].

Research on graft and composite foam systems have established their efficiency to treat heavy metal ions [10]-[12]. Polyurethane foams modified by grafting acrylo nitrile and acrylic acid by gamma irradiation method reported by Meligi [10] have shown that the adsorption of heavy metal ions like Zn(II), Fe(II), Ca(II), Ni(II), Cu(II) and Pb(II) were affected by pH, atomic weight and initial contaminant concentration. In a study by Jang et al. [11], hydroxyapatite (HAP) - polyurethane foams were synthesized for Pb^{2+} ion adsorption. A maximum adsorption capacity was determined to be 150mg/g for the composite with 50 wt% HAP. The study also concluded that higher HAP concentration exhibited higher Pb^{2+} ion adsorption capacity. Less uniform dispersion of HAP in the foam led to slower adsorption and adsorption was dominant at higher pH levels. Another type of polyurethane composite foam containing alginate was synthesized by Sone et al. [12], which had a structure similar to a weak cation exchanger. Results from this study showed that Pb^{2+} adsorption was sensitive to lower pH and competing cations and the Pb^{2+} ion adsorption using this foam ranged from 20 ppb to ~ 100ppb in 2 hrs.

This research is focused on the development of a bulk functionalized polyurethane foam system using a chain extender. Chain extenders are low-molecular multifunctional species. They can be used to balance the backbone structure of polymers [13]. This makes them suitable for selective elimination of heavy metal ions. In this paper we discuss the modified synthesis process formulated by Moon et al. [4] using N, N-bis (2-hydorxyethyl)-2-aminoethane-sulfonic acid (BES) chain extender to eliminate lead ions from aqueous media. In addition, we will present a broad range of characterization of the functionalized foam in order to better understand the capabilities and limitations of the foam to remove lead ions.

II. EXPERIMENTAL WORK

Polypropylene glycol 1200 (PPG; Sigma Aldrich Co. LLC) was dried in a vacuum oven at 70°C for 24 hours before use.

Toluene diisocyanate (TDI; 2,4-80%, 2,6-20%, Alfa Aesar), Dimethyl Sulfoxide (DMSO; Alfa Aesar, 99.9%pure), N,N-bis(2-hydroxyethyl)-2-aminoethane-sulfonic acid (BES; Alfa Aesar, 99% pure), Dibutyltindilaurate (DBTL, Sigma Aldrich Co. LLC, 95% pure) were used as received. The experimental set up consists of a 3-neck round bottom reaction flask placed in an oil bath fitted with a mechanical stirrer and a condenser at the center neck, nitrogen gas inlet and outlet at the right neck and a drop funnel at the left neck. The reaction is carried out at 65-70°C in an inert atmosphere. The 3-neck flask was initially charged with TDI and allowed to stabilize at 70°C in saturated nitrogen atmosphere. A drop funnel is filled with a pre-weighted amount of PPG and was added drop wise and allowed to react with TDI for 3-4 hours until an initial isocyanate content of 11-12% was reached as determined by ASTM D 5155, di-n-butylamine method. A pre-weighted amount of BES dissolved in DMSO at 70°C was added drop wise into the reaction flask. The reaction was allowed to proceed until an isocyanate content of 7-8% is reached. The tin catalyst is added at the end and the prepolymer is decanted into a glass mold. Based on the amount of PPG used, a pre-weighted amount of distilled water is added along with the surfactant. The mixture is stirred at 2500-3000rpm for 10-15 seconds. This initiates the reaction of water with the remaining isocyanate groups forming an intermediate compound and eventually releasing CO_2 gas to form the cellular structure [14].

In order to determine the optimum chain extender (BES) content, molar ratio of PPG and TDI, and the chain extender reaction time (CERT) a set of experiments was designed to explore the effect of these parameters on the physical and ion exchange capacity of the foam. Table I shows a detailed list of the compositions used to prepare the foam samples. Samples A1-A4 has a variable BES/DMSO content with all other variables maintained at fixed levels. Samples B5-B7 are prepared with varying PPG/TDI ratios; whereas samples C8-C10 have different chain extender reaction times (CERT). Samples A3, B6, and C8 represent the same composition used in the study of the three design variables.

TABLE I
DESIGN OF EXPERIMENTS

EXP	PPG (g)	TDI (g)	BES (g)	DMSO (g)	DBTL (g)	SURF (g)	H₂O (g)	CERT (min)
A1	50	18.3	0	0	2	0.25	6	40
A2	50	18.3	3.4	7.8	2	0.25	6	40
A3	50	18.3	6.7	15.7	2	0.25	6	40
A4	50	18.3	10	23.5	2	0.25	6	40
B5	50	9.1	6.7	15.7	2	0.25	6	40
B6	50	18.3	6.7	15.7	2	0.25	6	40
B7	50	27.4	6.7	15.7	2	0.25	6	40
C9	50	18.3	6.7	15.7	2	0.25	6	60
C8	50	18.3	6.7	15.7	2	0.25	6	40
C10	50	18.3	6.7	15.7	2	0.25	6	90

The demolded functionalized foam was cut into small cubes (1 gram each) maintaining a constant volume. The cubes were washed in distilled water and conditioned in 2N NaCl solution

for 4hrs. Polyurethane foams require homogeneous rearrangement of its polymeric bonds for effective ion exchange, as the foam does not experience stress-free conditions after synthesis. This was confirmed during our study since conditioned foams exhibited better Pb^{2+} ion removal efficiency compared to their unconditioned counterparts. Standard Pb^{2+} solutions of 100ppb were prepared from a stock solution of 1ppm. The conditioned foams were then soaked in 25ml of Pb^{2+} solution in a beaker with a magnet. The beaker was then covered to avoid contamination and placed on a stirrer. Foams were exposed to the Pb^{2+} solution for various time periods. 10ml of each sample was filtered into 15ml centrifuge tubes and some nitric acid was added to make it a 2% nitric acid solution to stabilize the Pb^{2+} for ICP-MS analysis.

III. RESULTS AND DISCUSSION

The foam samples prepared according to Table I showed that the physical characteristics of the foam; such as its color, odor, pore size and structure depend primarily on the DMSO content. Foam samples A1, A2, and A3 had a similar color and were odorless due to the low amounts of DMSO used and lower chain extender reaction times (CERT). Foams with a higher DMSO content or higher CERT exhibited a brownish color. The flexibility of the foam, color and odor seemed to increase with increasing DMSO content and CERT as shown in samples A3, A4, C9 and C10. The rigidity of the foam increased with increasing TDI content in sample B7. Lower amounts of TDI in sample B5 did not favor foaming. The samples with this composition were not suitable for testing.
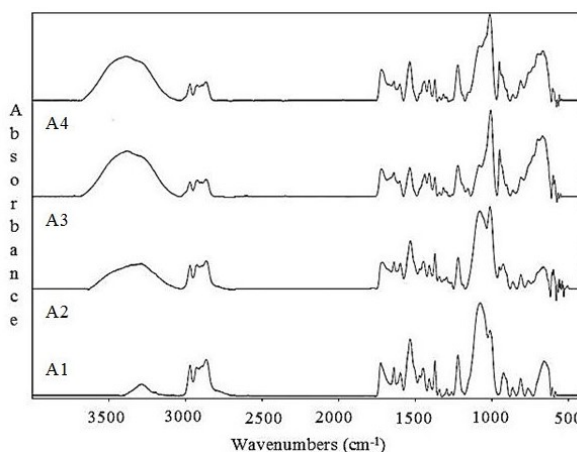

Fig. 1 FTIR spectrum of samples A1-A4

FTIR analysis of the functionalized polyurethane foam shows the presence of O-S-O peak at ~1060cm⁻¹. Sample A1, Fig. 1, shows a clear C-O-C peak at 1100cm⁻¹ as it does not contain any chain extender with the sulfonic groups. The O-S-O peaks start to appear in other samples and this peak partially overlaps with the C-O-C band. The asymmetrically stretched S=O peak appears at 1350cm⁻¹. The urethane carbonyl peaks appear at 1700cm⁻¹. The NH band and H-NH band appear at

3000cm^{-1}. These indicate that the sulfonic functional groups were successfully integrated into the backbone of the polyurethane. Similarly, the FTIR spectrum for samples B7 to C10, which have higher TDI and CERT, are shown in Fig. 2.

Sung and Schneider [15] reported that urea microdomains in PU foams are known to possess bidentate hydrogen bonding which is associated with a 1640cm^{-1} absorbance observed via FTIR. The presence of hydrogen bonding also leads to the hard segments packing in an organized manner. In another study, Aneja et al. [16], compared the isomers of TDI and determined that the 1640cm^{-1} absorbance was found to decrease as the 2,4 TDI isomer content increased and suggested that the symmetry of the isocyanate moiety had a considerable impact on the packing behavior of the urea hard segments. From Fig. 2 it is clearly evident that samples A3 and B7 do not show any significant peaks at 1640cm^{-1}.
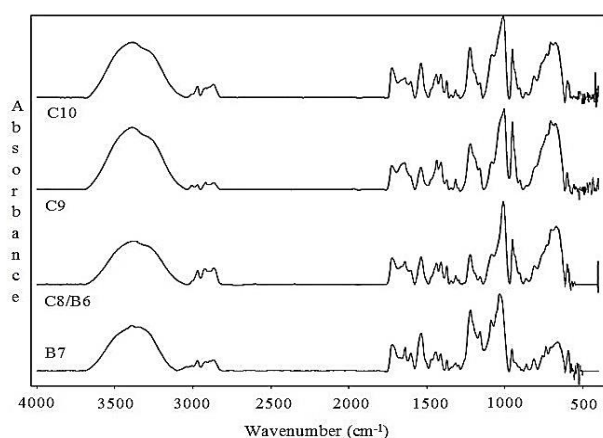

Fig. 2 FTIR spectrum of samples B7-C10

The polyurethane foam samples were analyzed using a Varian ProStar HPLC system using a PLgel 5mm mixed C column. HPLC grade dimethyl formamide (DMF) was used as the eluent with a flow rate of 1ml/min. The UV detector was set to detect at 569nm. Foam samples were dissolved in DMF to get a 0.5% w/v concentration and 25ml of the sample was injected into the column [17]. The main purpose of this analysis was to determine the effect of DMSO on the foam structure during synthesis. BES is a chain extender that links the isocyanate groups in the linear polymer chains through its hydroxyl groups thereby increasing the molecular weight of polyurethane. DMSO is a strong organic solvent that dissolves polyurethane. Since BES is insoluble in other organic solvents, the use of DMSO cannot be eliminated from the foam synthesis process. Hence both BES and DMSO have an opposing effect on the polyurethane foam.

Gel Permeation Chromatography (GPC) shows that the retention time, to elute higher molecular weight or larger molecules, decreases as the DMSO content and CERT increase during synthesis. This can be seen in Fig. 3 for samples A1-A4. Sample A1 has no DMSO and it elutes at 11.4 minutes. As the amount of DMSO increases in samples A2-A4, we can see larger molecules eluting earlier than 11.4

minutes followed by smaller molecules after 11.4 minutes. This can be attributed to the breakup of the polyurethane chains with higher DMSO content.
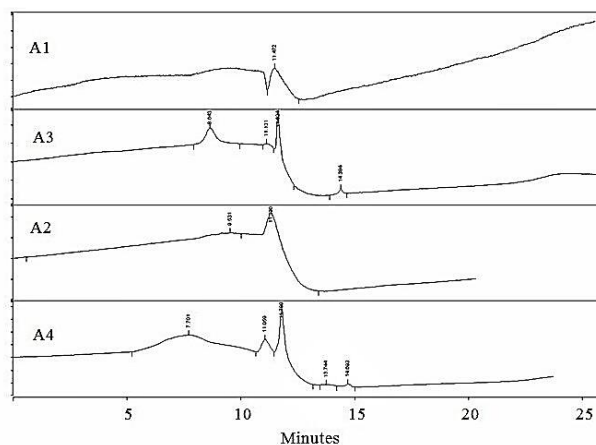

Fig. 3 High and low molecular weight compounds of functionalized polyurethane foam samples based on BES/DMSO content

Samples A2 and B7 seem to show a similar elution trend. A2 has lower amounts of DMSO and B7 has a higher TDI content in its composition. This provides additional isocyanate groups for functionalization; therefore, lowering the ability of DMSO to break up the polymer chains during synthesis. Hence increasing the TDI content in the foam composition without affecting the structural integrity of the foam may be a way to reduce the cleaving effect of DMSO.

Similarly, Fig. 4 shows GPC analysis for samples B7, C9, and C10. It is evident that increasing CERT has the same effect on samples C9 and C10. Even at reasonable amounts of DMSO, higher CERT seems to cleave polymer chains resulting in a large molecular weight distribution in the foam sample. These factors influence the distribution of the functional group in the foam and affect the Pb^{2+} ion removal capacity of the foam.
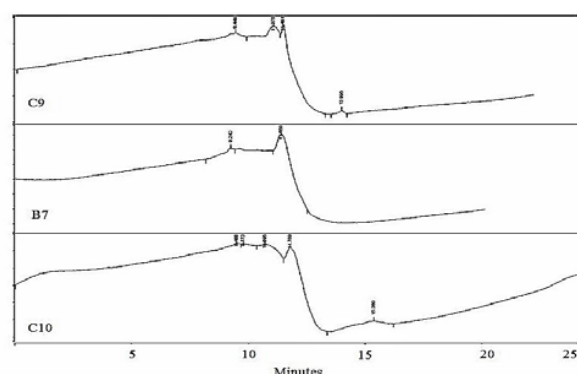

Fig. 4 High and low molecular weight compounds of functionalized polyurethane foam samples based on CERT

The peak retention times for all the samples are summarized in Table II.

TABLE II
RETENTION TIME USING GPC ANALYSIS

Sample	Peak Retention time (mins)				
A1	11.4				
A2	9.5	11.3			
A3	8.6	11.1	11.6		
A4	7.7	11	11.7	13.7	14.6
B7	9.2	11.4			
C9	9.4	11	11.4	13.9	
C10	9.4	9.7	10.6	11.7	15.3

In addition, foam samples were analyzed using a Topcon SM-300 SEM/EDX instrument. The samples were coated using a sputter coater before analysis. Elemental analysis by EDX performed on the foam sample after soaking in 100 ppb standard Pb^{2+} solution for 2 hrs shows the presence of Pb^{2+} in the bulk of the foam sample along with sulfur and various other elements, as shown in Fig. 5. This confirms the Pb^{2+} ion exchange with sulfonic acid groups in the functionalized polyurethane foam.
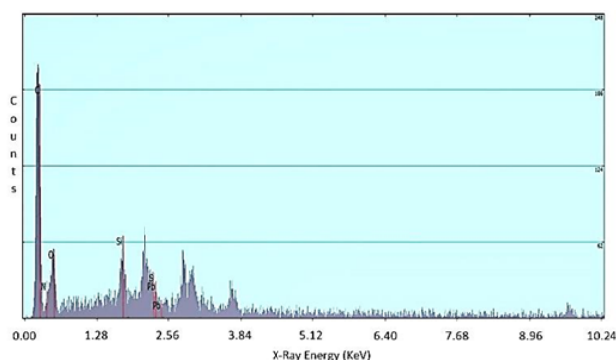

Fig. 5 EDX Elemental Analysis for sample A3

Lead ion exchange capacity of the foam was measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is a powerful analytical technique that allows detection of trace elements at parts per billion (ppb) and parts per trillion (ppt) levels. Foam samples A1 to C10 were analyzed at 1, 2 and 12hr time intervals and the results are shown in Figs. 6 to 8; respectively. A1 foam samples (0 BES) showed some Pb^{2+} removal in the absence of sulfonic functional groups, this indicates that the mechanism of Pb^{2+} ion removal is not solely by ion exchange [18]. Polyurethane foams are well known for their adherence properties and it may have contributed to the Pb^{2+} removal without BES content. It can also be observed that this behavior changes with exposure time, where the initial exposure of 1 hr resulted in 36 ppb/g removal rate compared to 24 ppb/g after 12hrs. This can be attributed to the leaching of Pb^{2+} ions back into the solution from the foam surface.
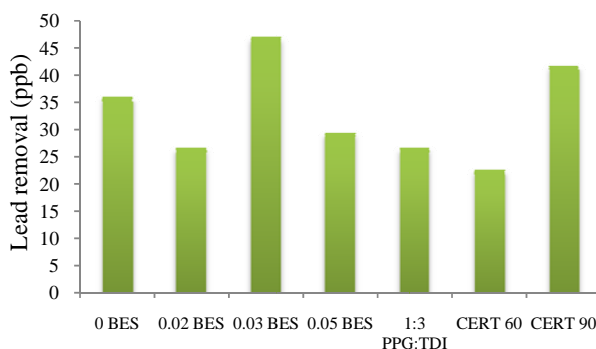

Fig. 6 Lead ions removed by foam samples after 1 hr exposure

Foam samples A2 (0.02 BES) showed a steady increase in Pb^{2+} ion removal from 26 to 30 ppb/g over a period of 1-12 hrs. This can be attributed to the lower amounts of BES used during synthesis. The availability of fewer functional groups for ion exchange along with surface adsorption may be the main reason for this behavior. However, A3 foam samples (0.03 BES) seemed to exchange higher amounts of Pb^{2+} ions (47 ppb/g) at lower time intervals and the lead ion removal capacity seemed to reach a saturation limit between 2 and 12 hrs. Further exposure to the lead solution did not show any significant increase in Pb^{2+} removal capacity.
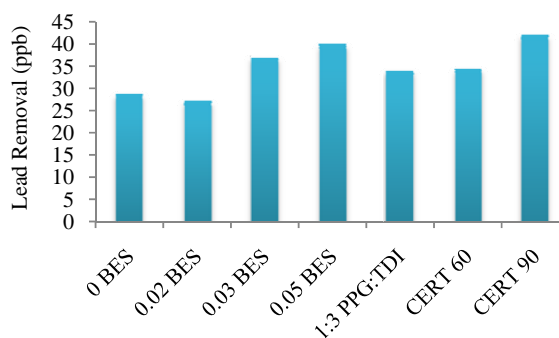

Fig. 7 Lead ions removed by foam samples after 2hrs exposure

Foam samples of A4 (0.05 BES) showed a rather unique trend in comparison to A2 and A3. With higher BES content, one would assume the foam to yield a higher and faster Pb^{2+} removal capacity due to the increase in sites for ion exchange. On the contrary, ICP results showed a steady increase in Pb^{2+} ion removal at lower time intervals (29ppb/g after 1hr and 40ppb/g after 2hrs) and a tapered down and saturated level at prolonged exposures. This behavior may be attributed to the composition of A4 samples which lacks additional isocyanate groups necessary to bond with the additional sulfonic groups from BES. In addition, the presence of excess DMSO used to dissolve BES may have led to structural disintegration at the molecular level limiting the uniform availability of functional groups for ion exchange in the foam.
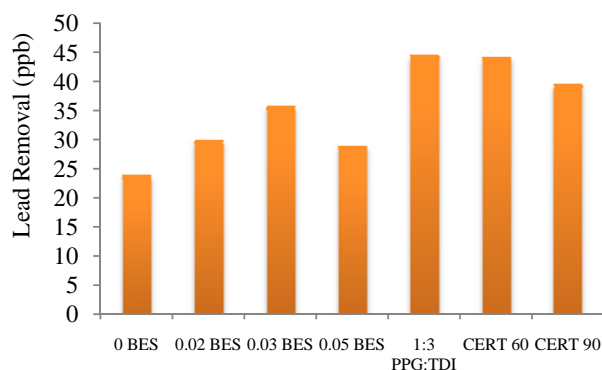
Fig. 8 Lead ions removed by foam samples after 12 hrs exposure

Fig. 9 Lead removal capacity from multi stage filtration process

The composition of B5 was unsuitable to synthesize the foam and hence there are no results on lead removal capacity from these samples. Composition of B6 and C8 are similar to that of A3 and the lead removal capacity results are the same as was discussed earlier. The foam sample of B7 was quite rigid compared to its counterparts due to the higher amounts of TDI in the composition. Pb^{2+} ion removal increased steadily with time in this foam composition from 26 to 45ppb/g. This can be attributed to the availability of excess isocyanate groups for the chain extender (BES) to react with and form additional sites for ion exchange.

For samples C9 and C10, the content of PPG/TDI and BES/DMSO was maintained the same as in A3 and the CERT was increased from the initial 40 minutes to 60 and 90 minutes; respectively. The Pb^{2+} ions removal capacity of C9 increased steadily from 22 to 44ppb/g. This may be due to the additional bonding of the –OH groups from BES to the –NCO groups in TDI leading to a higher degree of functionalization of the polymer back bone with longer CERT. C10 foam samples with the highest CERT of 90 minutes performed similar to A3. However the higher CERT affected the foam structure, color, and odor and made it less appealing. This may be due to the effect of DMSO which tends to disintegrate the foam structure similar to A4 and C9.

From the above results, the foam samples of A3 showed the highest Pb^{2+} ion removal capacity of 47ppb/g of the foam for an exposure period of 1hr and C10 had removed 42ppb/g in 2hrs. For the exposure time of 12hrs, B7 had the best lead removal capacity of 45ppb/g followed by C9 at 44ppb/g. In order to improve the lead removal capacity of the foam, a three stage batch filtration method was set up where multiple pieces (three) of virgin foam were soaked in 50ml of standard Pb^{2+} solution for a period of 30 minutes; consecutively as opposed to a single piece of foam soaked in a 25ml for a period of 1, 2 and 12 hrs time intervals. Foam samples with compositions A3 and C10 were selected for this study. This set up improved the lead removal efficiency of the A3 foam to 50ppb and the C10 foam to 54ppb over a period of 1.5hrs. The results are shown in Fig. 9.
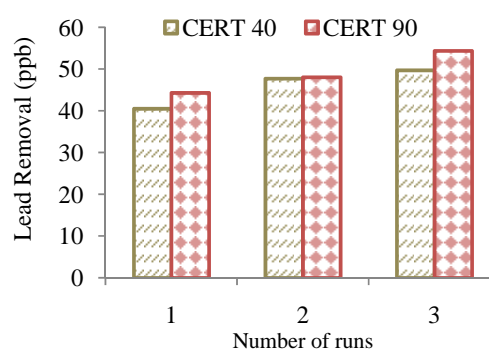
One would expect this process to be more efficient and render the solution lead free after multiple runs; however the lead removal efficiency of the foams seems to slow down as the Pb^{2+} concentration decreases in the solution. This may make it difficult for the few lead ions to efficiently seek ion exchange sites or merely adsorb on the foam surface. Additional experiments, results of which are not included in this study, have shown that the lead removal capacity of the foam is lower and much slower in solutions containing less than 50ppb Pb^{2+} ions.

Based on the above results, A3 foam samples were analyzed at 6.5 and 8.5 pH levels over a period of 2 days, the results of which are shown in Fig. 10. Since the foam is considered for drinking water applications, it was not tested at other pH levels. The lead removal capacity of the foam seemed to be unaltered at pH of 6.5. The maximum lead removal capacity was measured to be 51 ppb/g after soaking the foam for a period of 2 hrs in lead solution.
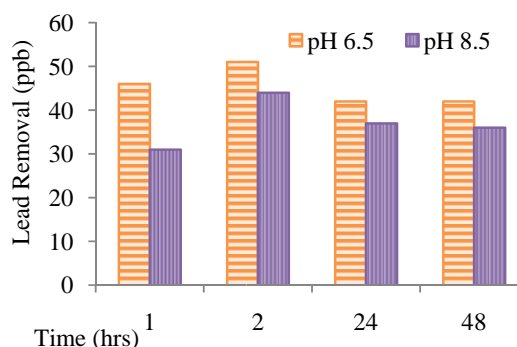

Fig. 10 pH analysis of functionalized polyurethane foam

The lead removal capacity of the foam seemed to taper down and saturate after 2hrs. Lead removal capacity of the foam also seemed to decrease as the pH of the solution increases to 8.5. This may be due to the neutralization of sulfonic acid groups at higher pH levels which in turn diminishes the availability of functional groups for ion exchange. The foam seems to have a better lead removal capacity at lower pH values for the same reason.

IV. CONCLUSION

Polyurethane foams containing PPG and TDI with sulfonic acid functional groups were synthesized using BES chain extender dissolved in DMSO for Pb^{2+} ion removal from aqueous solutions. The effect of various parameters; such as PPG/TDI ratio, BES/DMSO content, and chain extension reaction time (CERT) on the Pb^{2+} ion removal capacity of the foam, were studied. The maximum measured Pb^{2+} removal efficiency from the above method was between 42–47ppb/g of the foam. The lead removal mechanism seemed to be a combination of adsorption and ion exchange mechanisms in the functionalized foam. This was later confirmed during elemental analysis by EDX.

The foam with the molar composition of 1 mole of PPG, 2 moles of TDI, 0.6 moles of BES and 4 moles of DMSO with a CERT of 40 minutes seemed to be the most stable structurally and had the highest lead removal efficiency of 47ppb/g for 1 hr exposure in lead solution. It was observed that higher amounts of BES did not improve the lead removal capacity of the foam due to the absence of additional isocyanate groups needed to bond with the chain extender to provide sites for ion exchange. The presence of excess DMSO also seemed to affect the Pb^{2+} ion removal capacity of the foam as it seemed to disintegrate the foam structure and prevent uniform distribution of functional groups in the bulk of the foam. Higher CERT also showed a similar effect due to the excess time available for DMSO to break up the polyurethane chains. GPC characterization confirmed polymer chain disintegration due to higher DMSO content and increased CERT in these experiments.

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