# Synthesis and Characterisation of Microporous Polymer Microspheres with Strong Cation-Exchange Character

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Abstract

In this paper the synthesis and characterisation of microporous polymer microspheres with ultra-high specific surface areas (> 1,000 $m^2/g$) and strong cation-exchange character is described. The microspheres were synthesised by the hypercrosslinking of swellable precursor particles which had been produced by precipitation polymerisation, and the strong cation-exchange character, arising from the presence of sulfonic acid groups, was introduced through post-hypercrosslinking chemical modification reactions. Two alkyl sulfate reagents of differing polarity were compared as reagents for the sulfonation reactions, and a synthetic methodology was devised that allowed the sulfonic acid content of the microspheres to be controlled. Following a series of small scale optimisation experiments, optimised conditions were applied on a larger scale to the synthesis of three distinct polymers (HXLPP-SCX) tailored for use as strong cation-exchange (SCX) sorbents in solid-phase extraction (SPE) studies. All three polymers were in the form of polymer microspheres (mean particle diameters 3-5 $\mu$m) with relatively narrow particle size distributions, and had tuneable ion-exchange capacities (IECs) ranging from 1.7 - 2.8 mmol/g and specific surface areas up to 1370 $m^2/g$.

Keywords

Polymer microspheres; hypercrosslinked resin; mixed-mode strong anion-exchanger; solid-phase extraction; sulfonation.

## 1. Introduction

Solid-phase extraction (SPE) is a widely used technique to enrich and isolate analytes from aqueous samples.[1-14] Traditional SPE sorbents are silica-based, and are typically composed of silica particles which can be modified easily to incorporate functional groups on their surfaces to enhance SPE selectivity. While silica-based sorbents are extremely popular, they do suffer from low recoveries in the extraction of polar compounds and can be very unstable at the pH extremes that are all too often demanded by SPE protocols.[15] Carbon-based sorbents, such as graphitised carbon blacks or porous graphitic carbon, are characterised by high thermal and chemical resistance properties and a superior adsorption capacity, however this enhanced sorption capacity can often result in excessive or irreversible binding of analytes.[16] Porous polymeric sorbents overcome the drawbacks of both silica-based and carbon-based materials, to give a product that is extremely stable across the entire pH range, while providing good sorption characteristics coupled with facile elution options. Porous polymeric sorbents have been in use since the 1970s, when Fritz *et al.*[17] highlighted the potential use of the Rohm and Haas macroreticular resins XAD2 and XAD4 for the separation of a wide range of organic impurities from water. These resins required grinding, sizing and purification, which perhaps limited their suitability for everyday use. Since that time, however, synthetic methods for the preparation of beaded polymers with diameters in the micrometer size range have been disclosed; of particular relevance to the current work are those synthetic methods based upon precipitation polymerisation (PP).[18,19]

The most common polymeric sorbent is a copolymer of divinylbenzene (DVB) and styrene, which combines a hydrophobic structure with a specific surface area of between 500-800 $m^2/g$.[20] Incorporation of ion-exchange functionality into a sorbent such as this results in a material with a mixed-mode retention mechanism; organic molecules can bind through reversed-phase interactions with the polymeric backbone, while analytes with ionic functionality complementary to the ionic functionality of the polymer can bind through ionic

interactions. Overall, this results in a more selective and efficient separation of analytes in SPE.

There are different type of commercially available mixed-mode sorbents [ref], examples of them include the Oasis range from Waters [21] and the Strata series commercialised by Phenomenex.[22] Waters have added ion-exchange functionality to their Oasis-HLB sorbent, which is a poly(divinylbenzene-co-vinyl pyrrolidone)–based material with a specific surface area of ~800 $m^2/g$ and mean particle diameter of around 30 $\mu$m. Both sulfonic acid and quaternary ammonium groups have been incorporated into Oasis-HLB to provide strong ion-exchange materials, while carboxylic acids and piperazine moieties have been used to impart weak ion-exchange properties. Similarly, Phenomenex have set in place a series of ion-exchange SPE sorbents by incorporating the same range of functionalities into their Strata-X sorbent, which is a poly(styrene-co-divinylbenzene) resin chemically modified with pyrrolidone groups.

A low particle size combined with a narrow particle size distribution can help to improve the efficiency and packing of these sorbents into SPE cartridges and their performance whilst in use, while higher specific surface areas can enhance their retention properties. Additionally, Davankov-type hypercrosslinked (HXL) resins [23,24], with a microporous structure and specific surface areas in excess of 1,000 $m^2/g$, have been shown to give better retention than the analogous macroporous materials with lower specific surface areas.[25,26] These hypercrosslinked resins can be chemically modified to introduce functionalities that allow for better selectivity in the SPE process, or groups to increase the polarity of the resins, either through a copolymerisation strategy or a post-polymerisation chemical modification approach.

Within our group, a range of polymers in the form of hypercrosslinked polymer microspheres with either strong/weak anion-exchange character or weak cation-exchange character have been synthesised and been shown to compare favourably to the commercially available macroporous sorbents in

the selective extraction of analytes from complex environmental samples.[27-29] In this paper, we report upon the synthesis and characterisation of a new series of hypercrosslinked PP particles with strong cation-exchange (SCX) properties, designed for use as selective sorbents in ion-exchange SPE. We refer to this new class of sorbent by the name HXLPP-SCX.

## 2. Experimental

### 2.1. Materials

Divinylbenzene (DVB) (80 % grade) and *para*-vinylbenzyl chloride (VBC), both supplied by Sigma-Aldrich (Dorset, U.K.) were purified by passing them through a short column of neutral alumina. 2,2'-Azobis(isobutyronitrile) (AIBN), supplied by BDH (Poole, U.K.) was recrystallised from acetone at low temperature. Anhydrous 1,2-dichloroethane (DCE), iron(III) chloride, acetic anhydride, sulfuric acid, lauric acid and tetraethyl ammonium bromide were supplied by Sigma-Aldrich, chlorosulfonic acid was supplied by Acros Organics (Loughborough, U.K.) and sodium chloride was supplied by BDH; all were of high purity as supplied and not purified further prior to use.

### 2.2. Synthesis

#### 2.2.1. Synthesis of Swellable Precursor Particles by PP.

In a typical synthesis, VBC (6.925 mL, 7.500 g, 0.058 mol), DVB-80 (2.735 mL, 2.500 g, 0.018 mol) (2 %w/v total monomer in feed relative to solvent) and AIBN (0.278 g, 1.695 mmol, 2 mol % relative to the total number of polymerisable double bonds) were charged to a 1 L Nalgene® bottle together with 500 mL of acetonitrile (ACN). The bottle was placed into an ultrasonic bath for 10 minutes and was then purged with $N_2$, whilst on an ice bath, for 10 minutes before being sealed under $N_2$. The bottle was placed onto a low profile roller, which was housed in a temperature-controlled incubator, and rolled slowly about its long axis. The temperature was ramped from room temperature to 60 °C over a period of around 2 hours and then held at 60 °C for a further 46 hours. The product was filtered under vacuum on a 0.2 *μ*m nylon filter membrane and then washed in sequence with 50 mL volumes of ACN, toluene, methanol and acetone. The product, in the form of a white powder, was dried overnight at 40 °C *in vacuo* (1.721 g, 17 %). Elemental microanalysis: Expected 76.0 % C, 6.5 % H, 0.5 % N, 17.0 % Cl; Found 76.4 % C, 6.4 % H, 0.5 % N, 16.8 % Cl. FT-IR: $\tilde{\nu}$/cm$^{-1}$ (KBr), 3022, 2922, 2850,

1605, 1586, 1510, 1445, 1266 (C-H wag of $CH_2$-Cl), 990, 901, 831, 796, 709 (C-Cl str.). Langmuir specific surface area: < 5 $m^2$/g.

2.2.2. Synthesis of Hypercrosslinked Polymer Microspheres (HXLPP).

In a typical hypercrosslinking reaction, swellable precursor particles (PP; 1.200 g, 5.663 mmol of VBC residues) were charged to a dry, three-necked, round-bottomed flask equipped with a reflux condenser and an overhead mechanical stirrer. Anhydrous DCE (30 mL) was added and the precursor particles were left to swell fully under $N_2$ at room temperature for 1 hour. $FeCl_3$ (in a 1:1 mole ratio with respect to the $CH_2Cl$ content of the particles) in DCE (30 mL) was added and the mixture heated to 80 $^oC$ for 18 hours. The product was recovered from the reaction medium by filtration on a 0.2 *μ*m nylon filter membrane and washed in sequence with 50 mL volumes of methanol, aqueous $HNO_3$ (pH 1) (2 washes), methanol and acetone. The orange-coloured product was then extracted with acetone overnight in a Soxhlet apparatus and washed with MeOH and diethyl ether before drying *in vacuo* overnight at 40 $^oC$ (1.082 g, 73 %). Elemental microanalysis: Expected 91.7 % C, 7.7 % H, 0.6 % N, 0 % Cl; Found 82.8 % C, 7.0 % H, 1.0 % N, 4.5 % Cl. FT-IR: $\tilde{\nu}$/$cm^{-1}$ (KBr), 3021, 2927, 2857, 1604, 1560, 1510, 1448, 1297, 1267 (C-H wag of $CH_2$-Cl), 894, 826, 710 (C-Cl str.). Langmuir specific surface area: 1210 $m^2$ $g^{-1}$

2.2.3. Sulfonation using Acetyl Sulfate.

Acetyl sulfate solution was prepared freshly prior to each experiment as follows. Acetic anhydride (0.150 mL, 0.163 g, 1.597 mmol) and anhydrous DCM (1 mL) were charged to a round-bottomed flask under an $N_2$ atmosphere. The flask was placed on an ice bath to cool the reaction mixture and conc. sulfuric acid (0.066 mL, 0.120 g, 1.293 mmol) added. The flask was removed from the ice bath and allowed to equilibrate to room temperature.

Hypercrosslinked polymer microspheres (HXLPP; 1.010 g, ~8.620 mmol of aromatic residues) were charged to a three-necked, round-bottomed flask

fitted with an overhead mechanical stirrer and a reflux condenser, under an $N_2$ atmosphere. Anhydrous DCM (30 mL) was added and the reaction mixture was left for 1 hour to wet the beads. The acetyl sulfate solution was added to the HXL beads *via* syringe. The reaction was then heated to 40 °C, with stirring, for 2 hours. After 2 hours, propan-2-ol (1 mL) was added. After 30 minutes, the reaction mixture was cooled to room temperature and the product was filtered on a 0.2 *μ*m nylon filter membrane and washed with water to hydrolyse any remaining acetyl sulfate. The product was extracted with water in a Soxhlet apparatus overnight. The product, in the form of an orange powder, was then dried at 40 °C *in vacuo* for 48 hours (0.891 g, 80 %). Elemental microanalysis: Expected 81.7 % C, 6.2 % H, 0.3 % N, 3.2 % Cl, 3.3 % S, 4.9 % O; Found 83.9 % C, 6.7 % H, 0.4 % N, 2.9 % Cl, 0.5 % S. FT-IR: $\tilde{\nu}$/cm$^{-1}$ (KBr), 3020, 2927, 2857, 1606, 1511, 1450, 1360 ($SO_2$-O str.), 1265 (C-H wag of $CH_2$-Cl), 1213 ($SO_2$-O), 892, 818, 710 (C-Cl str.).

2.2.4. Sulfonation using Lauroyl Sulfate.

Lauroyl sulfate solution was prepared freshly prior to each experiment as follows. Lauric acid (0.067 g, 0.323 mmol) was dissolved in cyclohexane (3 mL) under an $N_2$ atmosphere. Chlorosulfonic acid (0.022 mL, 0.038 g, 0.323 mmol) was added and the mixture was stirred at room temperature for 1 hour under $N_2$.

Hypercrosslinked polymer microspheres (HXLPP; 0.252 g, ~2.155 mmol of aromatic residues) were charged to a three-necked, round-bottomed flask fitted with an overhead mechanical stirrer and a reflux condenser, under an $N_2$ atmosphere. Anhydrous DCE (30 mL) was added. This was left for 1 hour to wet the beads. The lauroyl sulfate solution was added to the HXL beads *via* syringe and the reaction was heated to 50 °C, with stirring, for 24 hours. After 24 hours, the product was recovered by filtration on a 0.2 *μ*m nylon filter membrane and washed with petroleum ether (b.p. 60-80 °C). The product was extracted in a Soxhlet apparatus overnight with petroleum ether (b.p. 60-80 °C). The product, in the form of a brown powder, was then washed with petroleum ether (b.p. 30-40 °C) and oven-dried *in vacuo* at 40 °C for 24 hours

(0.256 g, 92 %). Elemental microanalysis: Expected 81.7 % C, 6.2 % H, 0.3 % N, 3.2 % Cl, 3.3 % S, 4.9 % O; Found 72.3 % C, 6.7 % H, 0.4 % N, 3.2 % Cl, 2.5 % S. FT-IR: $\tilde{\nu}$/cm$^{-1}$ (KBr), 3019, 2923, 2852, 1606, 1510, 1449, 1222 ($SO_2$-O str.), 889, 821, 710 (C-Cl str.)

2.2.5. Determination of Ion-Exchange Capacity.

0.050 g of sulfonated polymer was placed into a beaker with 10 mL of a 2 M solution of NaCl (or 0.05 M tetraethyl ammonium bromide solution) and allowed to stir for 30 minutes. The pH was recorded and the solution was then titrated with 0.0098 M NaOH. The volumes of NaOH added and corresponding pH values were recorded, and a pH curve then plotted to allow the ion-exchange capacity, expressed in mmol/g, to be calculated.

2.3. Physico-Chemical Characterisation

Precipitation polymerisations were carried out using a Stuart Scientific S160 incubator (Surrey, UK) and a Stovall low-profile roller system (NC, USA). All of the polymerisations were carried out in Nalgene® plastic bottles.

C, H and N elemental microanalyses were carried out simultaneously using a Perkin Elmer 2400 Series II analyser. Halogen and sulfur contents were determined by standard titration methods.

SEM was carried out using a Cambridge Instruments Stereoscan 90. Samples were coated in gold prior to SEM imaging.

Fourier Transform Infrared (FT-IR) spectroscopic analysis was performed using a Perkin-Elmer Spectrum One FT-IR spectrometer. The sample was prepared as a disc with spectroscopic grade KBr in a RIIC press at 10 tons. The sample was scanned over the range 4000-400 cm$^{-1}$ in transmission mode.

The surface area measurements were performed using a Micromeritics ASAP 2000 nitrogen sorption porosimeter. Samples were degassed overnight under vacuum at 100 ºC prior to analysis. Analysis was *via* nitrogen sorption, carried out at 77 K.

# 3. Results and Discussion

## 3.1. Preparation of Hypercrosslinked Polymers

The hypercrosslinked resins were prepared by a method previously developed within our group [30]. Precursor beads were first synthesised *via* precipitation copolymerisation of divinylbenzene (DVB) and vinybenzyl chloride (VBC) in a ratio 25:75 (w/w). These precursor beads thus contained a high level of pendent chloromethyl groups that could be further reacted in the hypercrosslinking reaction, thus generating material with ultra-high specific surface area. This material was then modified by subsequent reaction, to introduce the functionality required to allow use as a strong cation-exchange resin; sulfonic acid groups. The high abundance of aromatic residues present in the hypercrosslinked resin should allow a sulfonation reaction to be carried out in a facile manner.

### 3.1.1. Precipitation Polymerisation

Precipitation polymerisation (PP) can be used to prepare monodisperse microspheres incorporating a range of vinyl monomers in the presence of a multivinyl crosslinker. The higher the level of crosslinker that is included in the precipitation, the higher the yield and the more mechanically robust are the microspheres. The microspheres prepared were derived from a 25/75 (w/w) DVB/VBC feed ratio. Although the level of DVB was low, this monomer ratio was chosen to ensure that the resultant products would contain a high Cl content and could thus be further reacted in the HXL reactions. As a consequence of the lower level of DVB, it was expected that the microspheres would not have smooth surfaces and the particle size distribution of the products would not be as narrow as materials prepared with higher DVB loadings.

Elemental microanalysis was used to analyse the products, with the results being compared to the expected values to ensure incorporation of both monomers in the products. As the yields of products from such

polymerisations involving low crosslinker levels are often ~20 %, it is feasible that the products are composed solely of DVB. However, evidence of Cl present in the products confirmed the inclusion of VBC (Table 1).

### 3.1.2. Hypercrosslinking

Microporosity can be introduced into microspheres containing high levels of pendent chloromethyl groups using a Friedel-Crafts reagent, such as $FeCl_3$. The Friedel-Crafts catalyst can form a complex with the chlorine atom of the alkyl chloride groups, present through incorporation of VBC, causing charge separation. This leaves behind a positively charged methylene group, which can react with an electron rich aromatic residue elsewhere in the polymer to form a methylene bridge.

The HXL products produced in this manner were extremely hygroscopic, as they were highly strained when dried, and thus readily uptake any solvent that they come into contact with, meaning that they take up water on contact with air. This made it difficult to analyse accurately these products by techniques such as elemental microanalysis, as there are always interfering compounds present (*i.e.*, oxygen due to water taken up from the air or residual solvent, *etc.*). Nevertheless, elemental microanalysis was carried out and, despite the discrepancy, it was clear that the Cl content had dropped relative to the poly(DVB-co-VBC) precursor. Evidence that the HXL reaction has occurred was manifest as a decrease in the Cl content of the HXL material relative to its precursor (Table 1).

Nitrogen sorption porosimetry is another useful technique for analysing these products, with the specific surface area being calculated using the Brunauer-Emmett-Teller (BET) isotherm. Upon HXL, the surface area should increase from a few $m^2/g$ to somewhere in excess of > 1000 $m^2/g$. Table 1 shows the nitrogen sorption porosimetry data obtained for both a precursor polymer and its corresponding HXL material (PP-1 and HXL-1, respectively).

The data obtained from nitrogen sorption analysis shows that upon HXL, many changes occur to the internal structure of the microspheres. The total pore volume is greatly increased, while the average pore diameter is decreased from macroporous levels, towards microporous territory. This is quite intuitive as the HXL reaction forms many crosslinks in the microspheres, thus creating new pores from existing ones. The BET c value, calculated as the gradient of the BET plot, shows a very significant change. In the precursor, PP-1, the c value is high and positive. This indicates that the BET plot has taken the correct form and thus the nitrogen sorption onto the surface of the pores will be in several layers. After HXL, however, the c value becomes negative, indicating that the data no longer fits the BET isotherm, and thus the nitrogen does not sorb onto the surface in several distinct layers. Instead, the Langmuir isotherm must be used in order to manipulate the data correctly and calculate the specific surface area. The Langmuir isotherm instead deals with sorption of the nitrogen onto the surface in a single layer. This change in sorption mode, and thus calculation of specific surface area, can be rationalised from the average pore diameters of the two materials. As the pore size has been greatly reduced, it follows that the amount of nitrogen that can access each pore has been reduced and therefore can only form a single layer in the space provided.

Previously within our group [31] it has been shown that for the HXL of suspension polymerisation-derived precursors, the fall in chlorine content was most dramatic within the first 15 minutes of the reaction. Further reaction, for up to 18 hours, resulted in a much reduced rate of chlorine loss compared to the first 15 minutes. As the particles described here were prepared by precipitation polymerisation and showed different pore characteristics after HXL, a small time study was carried out; HXL reactions were carried out on PP-derived DVB/VBC precursors for 5, 10 and 15 minutes as well as the standard 18 hours, in order to establish how the Cl content and specific surface area vary with time. The results from each of these experiments can be seen in figure 1.

From the elemental microanalysis results it can be seen that when the HXL reaction was carried out for just 5 minutes, the chlorine content has fallen dramatically. From 10 minutes to 18 hours, the loss of chlorine is minor, indicating that the majority of the reaction occurs within the first 5 minutes.

Simultaneously, after only 5 minutes, a considerable increase in surface area, from ~0 to 1200 $m^2/g$ is observed. After 10 minutes of reaction a further increase to 1500 $m^2/g$ is observed, however this remains unchanged after 15 minutes of reaction. Reaction for 18 hours results in a small increase in surface area to 1700 $m^2/g$, again showing that the majority of the surface area is introduced in the initial 5 minutes of reaction. These results support the previous findings in our group that the HXL reaction proceeds very rapidly indeed, resulting in ultra-high specific surface area materials in a very short space of time.

3.2. Acetyl Sulfate *vs*. Lauroyl Sulfate

While harsh conditions, such as concentrated sulfuric acid have been shown to be successful for sulfonation of polystyrene [32], much milder conditions involving the use of acetyl [33] or lauroyl sulfate [34] have also been used effectively for this reaction. The first reaction was carried out in such a way as to introduce the acetyl sulfate at a level of 15 mol% relative to the number of aromatic residues present in the HXL polymer, as this was shown previously by Martins *et al.* [35] to be the maximum level of sulfonation to give $SO_3H$ groups exclusively. Sulfonation above this level is believed to lead to the formation of sulfone bridges, which may effectively help to increase the degree of HXL in the system but this will occur at the expense of the cation exchange capacity of the material, as the sulfone bridges do not have an acidic H. A second reaction was carried out using the acetyl sulfate reagent at a level of 30 mol% with respect to the aromatic residues present. The purpose of this reaction was to test the theory of the sulfone bridge formation in the HXL materials, as the original methodology used branched polymers whereas the materials used here were highly porous resins which had had their internal structure locked *via* the HXL reaction. The branched polymers

would be more flexible and therefore more likely to adopt different conformations during the sulfonation reaction, which would allow the sulfonic acid residues to come into close contact with each other and therefore react to give sulfone bridges. With the HXL resin, however, the structure was much more rigid and there was a possibility that the sulfonic acid groups would not come into contact with each other and therefore would not be able to react.

The second sulfonation method employed used lauroyl sulfate instead of acetyl sulfate (both methods outlined in Figure 2). This method was used previously by Cameron *et al.* [36] for sulfonation of poly(styrene-co-DVB) polyHIPE® materials which are similar in nature to the HXL resins used here (i.e., hydrophobic and highly porous styrenic materials) and gave a higher level of sulfonation than the acetyl sulfate method (2.2 mmol/g vs. 4.0 mmol/g for acetyl and lauroyl sulfate, respectively). In this method the higher hydrophobicity of the lauroyl group compared to the acetyl group should, in theory, be more compatible with the HXL material. This should then, in turn, permit a higher degree of sulfonation as the lauroyl sulfate reagent could better penetrate the HXL particles and react with a higher percentage of aromatic groups. Table 2 shows the microanalytical data obtained for the products from both methods of sulfonation.

The microanalysis results show that sulfur was incorporated successfully into the HXL material through use of acetyl sulfate. However, the values obtained were much lower than the levels expected. For the 15 mol% and 30 mol% sulfonation reactions, it was expected that the level of sulfur present in the resultant material would be 3.3 % and 6.1 %, respectively. As both reactions yielded products with only ~0.5 % sulphur, it was clear that the method had not worked as efficiently as intended. When lauroyl sulfate was used as the sulfonating agent at a level 15 mol%, relative to the aromatic rings in the HXL polymer, the expected level of sulfur from the elemental microanalysis (assuming 100 % reaction) was also 3.3 %. The product in this instance contained sulfur at a level of 2.5 %, which was far closer to the expected level than was obtained with the acetyl sulfate reagent. Information about any sulfone bridge formation cannot be ascertained from this data alone.

It has therefore been shown, in practice, that the more hydrophobic reagent does indeed afford a much higher level of sulfur in the final product. This may be due to the better compatibility of the reagent with the HXL polymer, however there was a large difference in the reaction time between the two different methods (1 hour vs. 24 hours for the acetyl and lauroyl sulfate reagents, respectively), which may also have contributed to the higher degree of sulfonation when using the lauroyl sulfate reagent.

Previous experience within our group has shown that HXL particles are tricky to analyse accurately by techniques such as elemental microanalysis due to their extremely hygroscopic nature. With this in mind, titration is perhaps a more accurate method for ascertaining the degree of sulfonation, i.e., the number of moles of sulfonic acid groups introduced through reaction, of these HXL polymers. The material was first subjected to a cationic-exchange reaction, which replaced the acidic protons of the sulfonic acid groups with cations of differing size. The two cation-exchange reagents used were aqueous solutions of sodium chloride (NaCl) and tetraethyl ammonium bromide (TEABr). In order for exchange to occur, the cation had to be able to penetrate the polymer material and reach the sulfonic acid groups, thus as the cations in these reagents ($Na^+$ and $TEA^+$) were of different sizes, a similar result for both titrations would indicate that all of the sulfonic acid groups are accessible to large and small cations. A higher degree of sulfonation indicated by titration with NaCl than with TEABr would suggest that some of the sulfonic acid groups are inaccessible to large cations and that size-exclusion effects are playing a role.

This was more accurate in showing the number of $SO_3H$ groups as any sulfone bridges (which would appear as sulfur content in the microanalysis results) would have no acidic character and would therefore not undergo exchange. When coupled with the elemental microanalysis results, this may be able to give an indication of sulfone bridge formation. The data in table 3 shows that for the materials prepared by reaction with acetyl sulfate, there is a very good correlation between the microanalytical and titration-derived ion-

exchange capacities. However, in the case of the materials prepared via reaction with lauroyl sulfate, the sulfur content calculated using the microanalysis data was lower than that calculated by titration. This confirms that the microanalysis results are not totally indicative of the true levels of each element present for the HXL materials. In the case of the ion-exchange materials, the titration data is more important as the method used to calculate IEC is very close in nature to the conditions that will be employed in the SPE or ion-chromatography applications.

3.3. Optimisation of Reaction Conditions.

As lauroyl sulfate was shown to be the most effective reagent for the sulfonation of the hypercrosslinked particles, a series of experiments was carried out to optimise the reaction conditions. The three main considerations in the method were reaction time, reaction temperature and the number of moles of sulfate reagent added. Each of these parameters was altered twice in order to discover how the method was affected by such changes to the reaction conditions. Table 4 shows the characterisation data for the products obtained under the different conditions.

As the original sulfonation method had a long reaction time (24 hours), the optimisation experiments used reduced reaction times. The times chosen were 5 hours and 2 hours. In the original method, the IEC was 1.2 mmol/g. When the time was reduced to 5 and 2 hours, the IEC values increased slightly to ~1.3 mmol/g (with the exception of the $TEA^+$ cation experiment at 5 hours). This increase was very small and relatively insignificant, therefore it would seem that the reaction time is not an important factor of the reaction and that the reaction is complete in 2 hours or less. This is significant, as a 2 hour reaction time is much more favourable than a 24 hour reaction period. A 2 hour reaction time is also comparable to the conditions employed with the acetyl sulfate reagent, and this therefore shows that the lauroyl sulfate was indeed a better reagent for the sulfonation of the HXL material.

The reaction temperature used in the original sulfonation method was 50 °C. The new temperatures used were room temperature and 80 °C. Again, there was an increase in the IEC, this time to ~1.5 mmol/g, however the increase was, again, relatively small and showed that temperature is not a very important variable in this reaction. Reaction at 80 °C did cause more of an increase in the IEC than reaction at room temperature, however this was also not by a significant amount. The fact that the reaction proceeds efficiently at room temperature is very favourable.

The last parameter changed was the number of moles of lauroyl sulfate reagent used in the reaction. The lauroyl sulfate was added in at levels of 20 mol% and 50 mol%, relative to the number of aromatic rings present in the non-functionalised polymer, in order to further test the theory of sulfone bridge formation and allow access to polymers with higher still ion-exchange capacities. The IEC values obtained were 2.7 and > 3 mmol/g for 20 and 50 mol% of lauroyl sulfate, respectively, which is greatly increased relative to the materials prepared using 15 mol% of the sulfate reagent.

For all of the experiments carried out, there is a very good correlation between the IEC values measured using the two cation-exchangers. This shows that the polymers are equally accessible to both small and large cations, which makes them very amenable to ion-exchange chromatography or SPE of water samples which can potentially contain a complex mixture of large and small cationic species.

### 3.4. Synthesis of SPE Sorbent Materials with Strong Cation-Exchange Character.

With a suitable method developed for the production of sulfonated HXL particles, the next step was to repeat the synthesis on a larger scale, in order to produce sufficient material to be taken forward for use in mixed-mode ion-exchange SPE. As before, the sulfonation reaction was carried out using 15, 20 and 50 mol% of the lauroyl sulfate reagent relative to aromatic residues in

the material. All reactions were carried out at 80 °C for 5 hours in order to achieve the maximum possible level of sulfonation

Elemental microanalysis was yet again carried out on the products, as well as titration with both of the cation-exchangers used previously to assess the ion-exchange capacity of the polymers. The results of all analyses are shown in table 5. The microanalysis results show a decreased level of sulfonate groups at 50 mol% of sulfate reagent. As the formation of sulfone bridges results in a loss of sulfur and therefore reduced sulfur levels, the microanalysis results alone would have suggested that sulfone bridges had formed within the material. However, the IEC calculated by titration using an ion-exchange methodology disputes this. As the titration-derived sulfur levels were much more reliable in showing the behaviour of the materials for the intended application, these results help to support the assumption that the microanalysis of the HXL materials is inaccurate.

The titration-derived IEC values show that as the level of sulfate reagent used in the reactions was increased, the ion-exchange capacity of the materials also increased. This shows that the lauroyl sulfate method gives good control over the ion-exchange capacity and thus that it is possible, using this method, to tune the properties of the sulfonated polymers to the specific needs of an application.

The Langmuir specific surface areas of the sulfonated materials were measured, with higher specific surface areas indicating better suitability for the intended SPE or chromatography applications. These specific surface areas are presented in table 5. As the surface areas observed are all in excess of 1000 $m^2/g$ these materials are expected to be well-suited to the intended SPE application.

SEM was also used in order to show that the sulfonation reaction did not alter the size and shape of the particles, as this would potentially hinder the packing of these polymers into columns in the desired applications. Monodisperse, spherical particles are ideal for packing into SPE cartridges

and chromatography columns, therefore the sulfonation reaction should ideally not have any detrimental effect on the size or shape of the particles. The SEM images obtained for the sulfonated particles at each level of sulfonation, are shown in figure 3. The SEM micrographs show particles with diameters of 4-6 $\mu$m, with the size distribution being not quite monodisperse, but still relatively narrow. The particles seemed to have aggregated to some extent, possibly during sample preparation prior to SEM analysis. They also became charged during the SEM analysis making the images, particularly of the material sulfonated with 50 mol% of lauroyl sulfate, slightly blurry. Despite this, the product is in the form of spherical particles and the particle size distribution is relatively narrow, which should allow for the material to pack well in an SPE cartridge or chromatography column. The high level of lauroyl sulfate and high temperature used in the production of the sulfonated particles did not cause any apparent damage to the particles. FT-IR was also used to analyse the sulfonated materials; an increase in broadness of the peak at ~1220 $cm^{-1}$, ascribed to an $SO_2$-O stretch, was observed with increasing IEC. This was accompanied by a change in the shape of the peak. This can be seen in figure 4.

## 4. Conclusions

In conclusion, the efficiency of sulfonation of HXL polymers using two alkyl sulfate reagents was studied and it was shown that the more hydrophobic lauroyl sulfate reagent generates polymers with higher sulfonic acid group content than the less hydrophobic acetyl sulfate reagent. A series of strong cation-exchange polymer particles have thus been synthesised and characterised fully, using lauroyl sulfate to impart sulfonic acid groups onto the HXL materials. These particles, with diameters of 3-6 $\mu$m, have been prepared with varying degrees of sulfonation and have sufficiently high specific surface areas (in excess of 1000 $m^2\ g^{-1}$) which implies that they will be well-suited for use as SPE sorbents for the extraction of cationic species from real water samples. The ease with which the sulfonic acid contents could be varied gave rise to materials with ion-exchange capacities of between 1.2 and 2.8 mmol/g, and demonstrates how this method can be used to prepare materials with finely tuned ion-exchange capacities, in line with the requirements of a specific application. The materials prepared are ready to be evaluated for use as strong cation-exchange sorbents for the solid-phase extract selectively basic compounds, such as pharmaceuticals, from environmental water samples. The data generated from this study will be reported elsewhere.

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Figure Captions

Figure 1. Changes in chlorine content and Langmuir specific surface area, with time, during HXL.

Figure 2. Schematic representation of the synthetic procedure used in the synthesis of the sulfonated HXL resins.

Figure 3. SEM images of the sulfonated HXL sorbents: (a) HXL resin sulfonated with 15 mol% lauroyl sulfate, (b) HXL resin sulfonated with 20 mol% lauroyl sulfate, (c) HXL resin sulfonated with 50 mol% lauroyl sulfate. The applied acceleration voltage of the incident electron beam was ? kV.

Figure 4. FT-IR spectra obtained for each of the sulfonated HXL sorbents: (a) HXL resin sulfonated with 15 mol% lauroyl sulfate, (b) HXL resin sulfonated with 20 mol% lauroyl sulfate, (c) HXL resin sulfonated with 50 mol% lauroyl sulfate.

Schemes and Figures

Figure 1

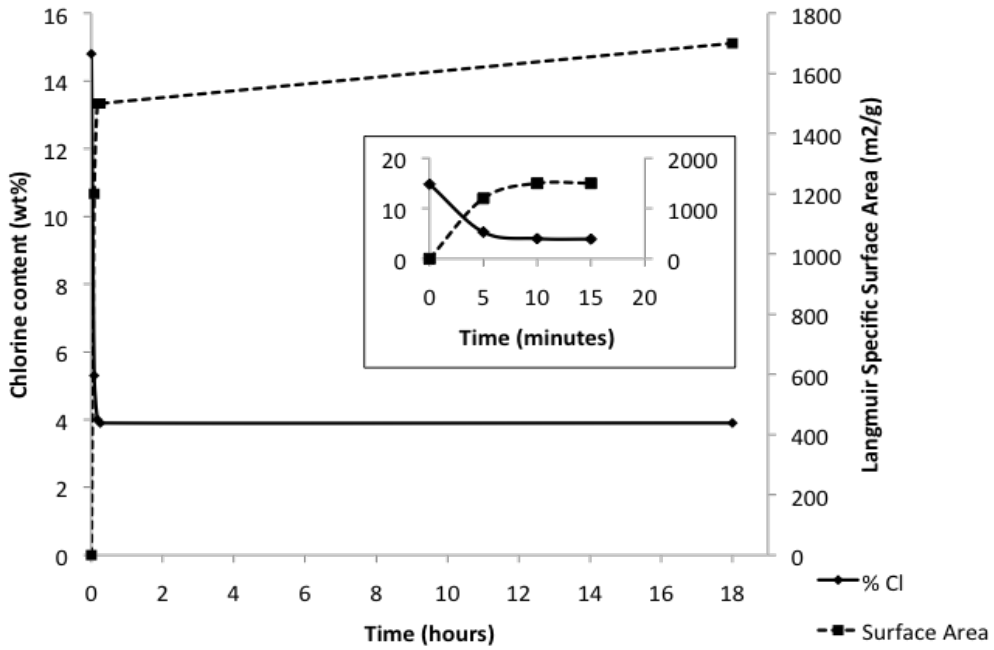
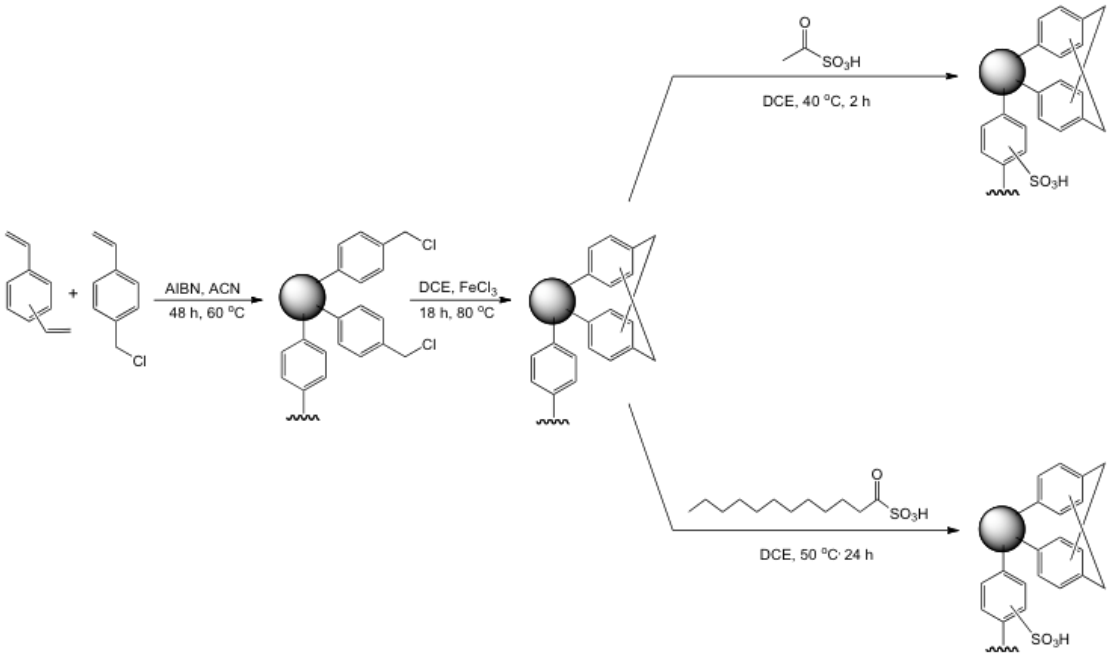


Figure 2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48 h, 60 °C
DCE, FeCl3
18 h, 80 °C
Cl
Cl
Cl
O
SO3H
DCE, 40 °C, 2 h
SO3H
O
SO3H
DCE, 50 °C· 24 h
SO3H

Figure 3

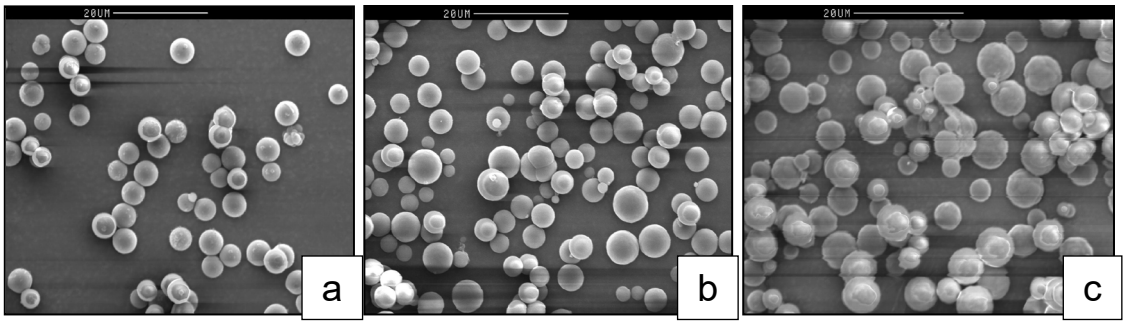
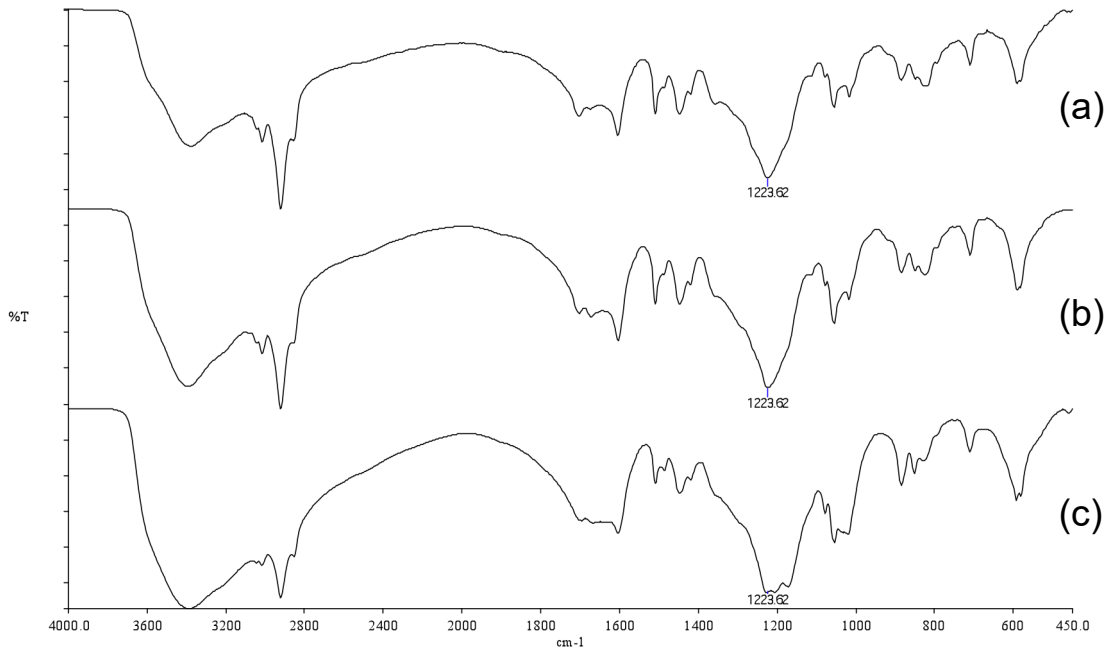


Figure 4


(a)
(b)
(c)
1223.62
1223.62
1223.62
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1

Tables

| Polymer ref. | Microanalysis (%) | | | | Langmuir specific surface area ($m^2/g$) | Ave. pore diameter (nm) |
|---|---|---|---|---|---|---|
| | C | H | N | Cl | | |
| PP-1 | 76.4 | 6.4 | 0.5 | 16.8 | < 5 | 5.5 |
| HXL-1 | 82.8 | 7.2 | 1.0 | 3.9 | 1700 | 2.3 |

Table 1 – Microanalysis and nitrogen sorption data for precusor and HXL polymers.

| Polymer code | Sulfate reagent used | Mol% sulfate reagent | Microanalysis (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | Cl | S |
| HXL | n/a | n/a | 82.9 | 6.3 | 0.3 | 3.9 | 0.0 |
| HXL-S1 | Acetyl Sulfate | 15 | 83.9 | 6.7 | 0.4 | 2.9 | 0.5 |
| HXL-S2 | Acetyl Sulfate | 30 | 77.7 | 6.5 | 0.4 | 2.9 | 0.6 |
| HXL-S3 | Lauroyl Sulfate | 15 | 72.3 | 6.7 | 0.4 | 3.2 | 2.5 |

Table 2 – Elemental microanalysis results for the sulfonation of HXL polymers using both acetyl and lauroyl sulfate reagents.

| Polymer code | Sulfate reagent used | Mol% sulfate reagent | S content from microanalysis (mmol/g) | IEC (mmol/g) | |
|---|---|---|---|---|---|
| | | | | NaCl | TEABr |
| HXL-S1 | Acetyl sulfate | 15 | 0.2 | 0.3 | 0.3 |
| HXL-S2 | Acetyl sulfate | 30 | 0.2 | 0.2 | 0.2 |
| HXL-S3 | Lauroyl sulfate | 15 | 0.8 | 1.2 | 1.2 |

Table 3 – Comparison of ion-exchange capacities calculated by microanalysis and titration.

| Polymer code | Time (h) | Temp. (°C) | Mol% lauroyl sulfate | S content from microanalysis (mmol/g) | IEC (mmol/g) | |
|---|---|---|---|---|---|---|
| | | | | | NaCl | TEABr |
| HXL-S3 | 24 | 50 | 15 | 0.8 | 1.2 | 1.2 |
| HXL-S4 | 2 | 50 | 15 | 0.6 | 1.3 | 1.3 |
| HXL-S5 | 5 | 50 | 15 | 0.3 | 1.3 | 1.0 |
| HXL-S6 | 24 | r.t. | 15 | 0.7 | 1.4 | 1.5 |
| HXL-S7 | 24 | 80 | 15 | 0.7 | 1.5 | 1.5 |
| HXL-S8 | 24 | 50 | 20 | 1.4 | 2.7 | 2.7 |
| HXL-S9 | 24 | 50 | 50 | 1.6 | 3.3 | 3.1 |

Table 4 – Ion-exchange capacities calculated for products obtained under different sulfonation conditions.

| Polymer code | Mol% sulfate used | S content from Microanalysis (mmol/g) | IEC (mmol/g) | | Langmuir specific surface area ($m^2/g$) |
|---|---|---|---|---|---|
| | | | NaCl | TEABr | |
| HXL-SCX1 | 15 | 1.0 | 1.7 | 1.8 | 1070 |
| HXL-SCX2 | 20 | 2.0 | 2.0 | 1.9 | 1160 |
| HXL-SCX3 | 50 | 0.9 | 2.8 | 2.6 | 1370 |

Table 5 – Characterisation data for the SPE sorbent materials.