

## Ion exchange modules formed from polyhipe foam precursors

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### Abstract

Homogeneous, highly porous, low density, open cellular polyhipe polymer (PHP) has been produced by polymerisation of a high internal phase emulsion. Its surface properties were modified by sulphonation. By incorporating Na<sup>+</sup> ions onto the sulphonated PHP surfaces a modular form of ion exchange resin capable of effective exchange with metal ions in solution was produced. Isotherms were measured for samples of PHP of differing degrees of sulphonation, and compared with data obtained from commercially available ion exchange resins. The capacity of PHP increased with the degree of sulphonation. In single-pass dynamic adsorption tests the PHP showed better column utilization than the commercial resins. © 1998 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

Many materials, both natural and synthetic, exhibit ion exchange properties. The most common of these materials are mineral ion exchangers and ion exchange resins, both of which have a similar basic structure—a framework or skeleton containing surplus negative or positive fixed charges which are compensated by mobile counter ions of the opposite sign. These mobile counter ions can be replaced by exchange with alternative similarly charged ions from an external source. Many different ion exchange resins have been prepared. Not only can the nature and number of fixed ionic groups be varied, but also the composition and degree of crosslinking in the matrix.

Organic based ion exchange resin media are the most utilised. Their main advantages over inorganic materials are high chemical and mechanical stability, high exchange capacity and high exchange rates. Ion exchange resins also have the added benefit that they can be specifically made to suit particular exchange applications. Their structure consists of an irregular, three-dimensional network of crosslinked polymeric chains. Within the matrix are fixed ionic groups such as  $-\text{SO}_3^-$  or  $-\text{COO}^-$  in cation resins, and  $-\text{NH}_3^+$  or  $-\text{NH}_2^+$  in anion resins. Of interest in this work are those resins produced by addition polymerisation processes particularly those

that use styrene and divinyl benzene as the precursor monomers. This group of polymers are widely used in the preparation of many commercially available ion exchange resins, particularly the strong acid cation resins which contain  $-\text{SO}_3^-$  groups.

The fixed charges are balanced by counter ions of opposite charge which are exchangeable for other similarly charged ions. Unlike the fairly regular matrix structure of zeolites the hydrocarbon skeleton of organic based resins are a flexible random network. The amount of crosslinking determines the mesh width between various hydrocarbon chains. In a highly crosslinked polymer the distance between polymer chains is of the order of a few angstrom units (similar to that of many zeolites) but in weakly crosslinked, swollen polymers it can be as much as 100 Å. The degree of crosslinking of the resin determines the swelling ability of the resin and therefore the mobility of the counter ions within the resin structure.

Ion exchange behaviour of polymeric based resins is mainly determined by the fixed ionic groups on the hydrocarbon skeleton. The number of groups determines the overall ion exchange capacity and the nature of the groups affects the ion exchange equilibria and the selectivity of the resin.

Most commercial exchange resins are produced in bead form, usually between 0.5 and 1.5 mm in diameter, and therefore have relatively small fluid/surface contact areas. To increase the surface area, beads of smaller diameter would have to be used which would cause a decrease in permeability

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of the exchange resin bed. The structure of PHP provides larger contact surface areas with the benefit of higher permeability.

## 2. Experimental

The foam modules studied in this work were made by the polymerisation of a high internal phase emulsion (HIPE) comprising a dispersed aqueous phase surrounded by a continuous oil phase. The resulting polymer (which is called polyhipe polymer, PHP) can be elastic or rigid depending on the type and proportion of monomers used in the oil phase.

### 2.1. Preparation of PHP

The preparation of HIPEs and their use in the production of PHP materials has been described by several workers [1–8]; specific details about the methods of preparation of the polyhipe used in this work are available [1]. In this work the continuous oil phase of the HIPE was made from a mixture of styrene crosslinked with divinyl benzene and a water-in-oil emulsifier, Span 80. A typical oil phase composition was styrene 59%, divinyl benzene 26%, and Span 80 15% (by volume). The dispersed aqueous phase comprised a solution of polymerisation initiator, potassium persulphate (0.4% by mass), in double distilled water. Enough aqueous phase was dosed into the stirred oil phase until an aqueous to oil phase ratio of 80:20 (by volume) was achieved. Once polymerised, washed and dried, a PHP of 80% void volume and a degree of crosslinking in the polymer of about 15% was produced. A typical PHP structure is shown in Fig. 1.

As HIPE flows quite readily, it is easily polymerised in moulds of any shape. Modules of PHP were generally produced as circular rods with diameters of 30 or 50 mm and lengths of 50 to 200 mm.

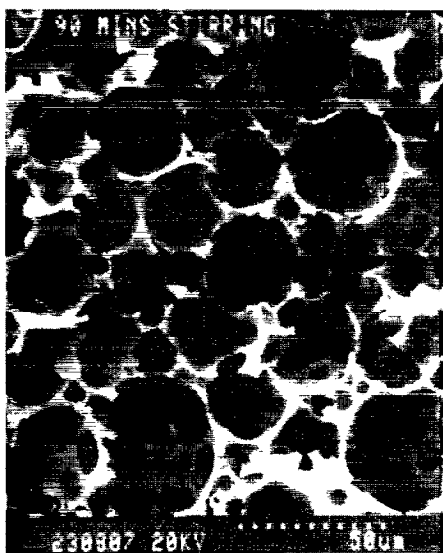
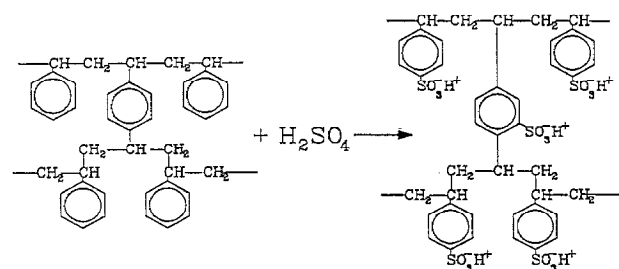


Fig. 1. SEM micrograph of the typical PHP cellular structure formed, showing the main cells interconnected by the smaller windows.

### 2.2. Sulphonation of PHP modules for ion exchange

Sulphonation of styrene–divinyl benzene based PHPs renders them capable of adsorbing quantities of aqueous solutions containing soluble salts [6], and alters their surface from hydrophobic to hydrophilic.

After sulphonation the PHP becomes acidic due to the  $-\text{SO}_3^- \text{H}^+$  groups attached to the benzene rings of the crosslinked polystyrene chain. Under normal conditions monosulphonation occurs so that only one  $-\text{SO}_3\text{H}$  group is present on each of the benzene rings. By expressing the degree of sulphonation as the percentage of available benzene rings in the polymer structure that attain  $-\text{SO}_3^- \text{H}^+$  groups, a quantitative assessment of the degree of sulphonation can be made using a titrimetric analysis. The chemical structure of sulphonated crosslinked polystyrene PHP is



assuming that all the available benzene rings become sulphonated (100% sulphonation); 100% sulphonation cannot be attained in PHP modules due to internal stresses caused by swelling of the polymer.

Commercially produced strong acid cation resins are manufactured by contacting polymeric beads with sulphuric acid at a temperature of about 100°C in a stirred vessel [9,10]. The mixing time depends on the amount of crosslinking in the polymer and on the bead size. As acid is absorbed into the polymer structure considerable swelling occurs, causing the beads to fracture. The relatively simple sulphonation process used for polymer beads becomes more complex when dealing with PHP due to the larger size of the starting material. Acid has to be drawn into the interior of the porous structure to contact all surfaces of the PHP. As the PHP modules are relatively thick (30 mm diameter) with a small pore size (between 2 and 10  $\mu\text{m}$ ) and the concentrated acid quite viscous, allowing the modules to soak in the acid was not an effective technique to achieve uniform wetting. To overcome these problems, a vacuum was applied to the PHP which was immersed in acid, drawing out most of the trapped air from the module so that acid would enter the submerged module on release of the vacuum. By applying and releasing the vacuum several times acid was drawn into the module.

Polyhipe foam modules were sulphonated for different periods and at different temperatures. Generally 98% (by mass) concentrated acid was used with reaction temperatures of between 20° and 100°C for periods of between 2 and 24 h. If the reaction temperature was raised the duration of the reac-

Table 1  
Effect of temperature and reaction time on the degree of sulphonation of samples of PHP

Sulphonation procedure	Degree of sulphonation (%)
40°C for 2 h	13
40°C for 4 h	16
60°C for 2 h	22
80°C for 2 h	24
80°C for 6 h	44



Fig. 2. SEM micrograph of sulphonated PHP.

tion was reduced. Whatever combination of processes used, the highest degree of sulphonation attained without fracture of the polyhipe modules was about 45%. After being washed and dried their degrees of sulphonation were measured using a titrimetric analysis. Table 1 shows the results of these tests. Beads of strong acid cation exchange resin (in the hydrogen form) were also tested using a similar procedure showing that they had degrees of sulphonation between 98% to 100%.

Fig. 2 shows an SEM of the structure of a sulphonated polyhipe showing that during sulphonation part of the polyhipe structure was etched by the acid, which had the effect of enlarging existing pores and producing new smaller pores within the cell walls.

### 2.3. Equilibrium isotherms

Equilibrium adsorption tests were carried out using a challenge solution of lead ions ( $\text{Pb}^{2+}$ ) in double distilled water. An apparatus made entirely from plastic components was used to house tubular polyhipe modules of known dry mass. The modules were closed at one end so the solution passed radially through into a central drainage channel. The challenge solution was circulated between the module and a stirred container via a peristaltic pump. The apparatus is shown schematically in Fig. 3. Several tests were completed using polyhipe modules which had been sulphonated for dif-

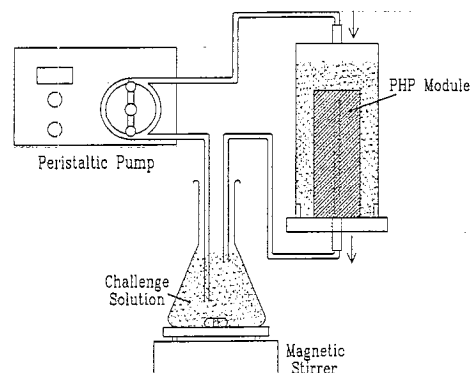


Fig. 3. A schematic diagram of the apparatus used for the ion adsorption tests.

fering lengths of time and so had different degrees of sulphonation.

The concentration of lead ions in the circulating solution was allowed to reach equilibrium, determined by periodic sampling of the solution. The concentration of lead ions was measured using a Perkin-Elmer 3030 atomic absorption spectrophotometer. After steady state had been reached, the solution concentration was increased by adding a small concentrated sample of lead solution. The mass of lead on the resin was calculated and isotherms showing the amount of lead per gram of resin against the equilibrium concentration in the solution were plotted. Similar tests were done using commercially available resins; these were Amberlite IR-120, a strong acid cation resin, and HP-333, a weak acid cation resin (both supplied by Rohm and Haas). As these resins were in the form of beads, a known dry mass of beads was added straight into the stirred challenge solution. Equilibrium was attained more rapidly than with the polyhipe modules; typically a 30-min sampling time was used.

### 2.4. Dynamic tests

In many applications, the process stream makes a single pass through the adsorbent. To establish whether the polyhipe modules could be effectively utilised under these conditions, once through tests were conducted. In these tests a challenge solution of known and constant concentration of  $\text{Ca}^{2+}$  ions was passed through a polyhipe module or bed of resin and the concentration of the effluent was measured. The polyhipe modules were 50 mm in diameter and were sealed against the side of the housing so that the challenge solution passed longitudinally through them.

Single-pass tests were conducted on an apparatus that enabled a constant flow rate of challenge solution through a bed of exchange media. The apparatus was similar to that shown in Fig. 3, but instead of the effluent being returned to the feed solution container it flowed to drain. A challenge solution was made using double distilled water containing a known amount of calcium chloride to provide  $\text{Ca}^{2+}$  ions; concentrations of 50 to 250 ppm were chosen (which represents concentrations typically found in domestic water supplies).

The concentration of the effluent was monitored with time, until it was the same as the feed concentration (i.e., the resin had become exhausted). Graphs of outlet concentration against throughput volume were then plotted. The mass of resin in each bed was taken into account so that comparative graphs between differing resins could be made. The exchange resin bed volumes and geometry were kept the same for all the tests.

Single-pass effluent profiles were obtained from both sodium and hydrogen forms of sulphonated PHP. These were compared with effluent profiles obtained from commercially available strong and weak acid cation exchange resins, using both the hydrogen and sodium forms of each resin. Some styrene crosslinked with divinyl benzene beads supplied by Puro-lite (IP 5300), sulphonated in a similar manner to the PHP, were also tested to provide a strong acid cation resin with a comparable degree of sulphonation to that of PHP.

### 3. Results and discussion

#### 3.1. Degree of sulphonation and exchange capacity

Results showed that by increasing the degree of sulphonation of the polyhipe an increase in the adsorption capacity of the resin could be achieved. As the degree of sulphonation is a measure of the number of  $-\text{SO}_3^-$  groups attached to the polymer structure, this result was expected as more ionic groups provide more positions for the adsorption (or exchange) of ions from solution. Fig. 4 shows a comparison between adsorption isotherms of different polyhipe modules and a weak acid cation exchange resin and Fig. 5 compares the polyhipe modules with a strong acid cation exchange resin. The polyhipe resins compare well with a commercially available weak acid cation resin, having over double the adsorption capacity for lead ions. But when compared with a commercially available strong acid cation resin they have only about a tenth of its capacity.

All resins produced isotherms that were similar in shape to the Type I adsorption isotherm [11], which can be described by the Langmuir equation:

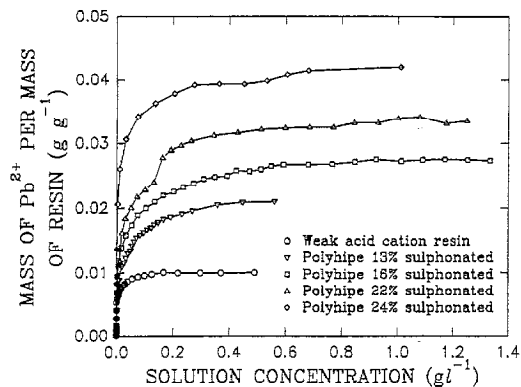


Fig. 4. PHP equilibrium isotherms for lead ions.

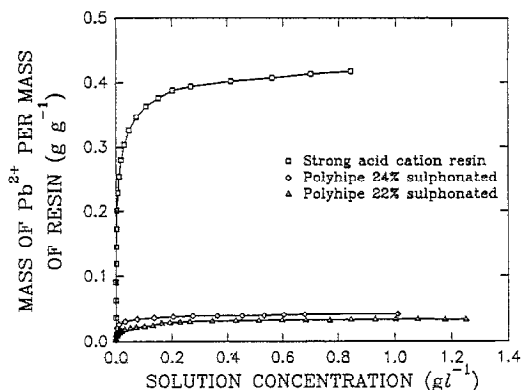


Fig. 5. PHP and strong acid cation exchange resin equilibrium adsorption isotherms for lead ions.

$$\frac{\phi}{\phi_m} = \frac{\alpha c}{1 + \alpha c} \quad (1)$$

where  $\phi$  is the amount of adsorbed species on 1 g of adsorbent when it is in equilibrium with a solution containing adsorptive species of concentration  $c$ . The maximum amount of adsorbed species on 1 g of adsorbent is given by  $\phi_m$  and  $\alpha$  is an empirical constant related to the energy of adsorption. To compare the Langmuir isotherm against experimental data Eq. (1) can be rewritten as:

$$\frac{c}{\phi} = \frac{c}{\phi_m} + \frac{1}{\alpha \phi_m} \quad (2)$$

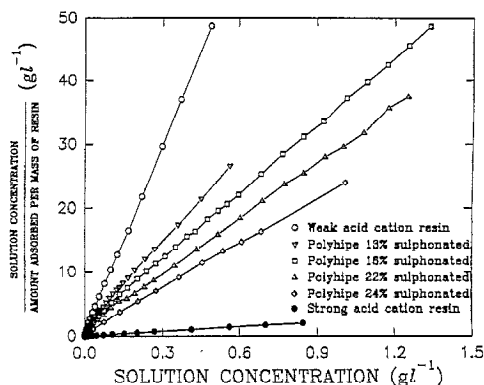


Fig. 6. The fit of experimental data to the Langmuir isotherm equation.

Table 2

Langmuir coefficients and maximum adsorption capacities for PHP compared with a commercial resin

Resin type	Degree of sulphonation (%)	Maximum exchange capacity, $\phi_m$ (g $\text{Pb}^{2+}$ / g resin)	Langmuir coefficient, $\alpha$
Strong acid resin (Amberlite IR-120)	~98	0.417	103
PHP (2 h, 80°C)	24	0.042	72
PHP (2 h, 60°C)	22	0.034	31
PHP (4 h, 40°C)	16	0.028	29
PHP (2 h, 40°C)	13	0.021	40

By replotting the adsorption isotherms in Figs. 4 and 5 on modified axes, shown in Fig. 6, values of the Langmuir coefficient and maximum adsorption capacity for the various resins were obtained. These are given in Table 2. To improve the capacity of polyhipe better sulphonation techniques need to be developed, but the potential of polyhipe does not lie in its overall capacity but in its extended surface area and relatively high permeability. Due to the structure of polyhipe only 20% to 30% of the bulk volume of material is solid, therefore less polymer is available to provide ion exchange sites. In comparison, in a bed of ion exchange resin beads 60% to 70% of the bulk volume is occupied by solid material, providing more sites for ion exchange. However, the extended surface area of polyhipe gives a greater contact area between the resin and the flowing solution, enabling more effective adsorption from the solution and better utilisation of the solid part of the bulk volume.

### 3.2. Dynamic tests

The capacity of an ion exchanger can be expressed in a number of ways. Titrimetric analysis determines the number of ionic groups for a given amount of resin; when in the hydrogen form this can be interpreted as the total or 'scientific' capacity. Under some operating conditions not all the available counter ions may take part in the exchange process, giving rise to the capacity under specific operating conditions; this is the so-called apparent or effective capacity. The

'degree of column utilisation' is defined as the fraction of resin in a column that has been effective in the exchange reaction and is given by the ratio of the breakthrough to total capacities of the resin.

Both acid and salt forms of the  $-\text{SO}_3^-$  groups are strong electrolytes, remaining highly ionised under most conditions. Therefore the difference in exchange characteristics between the sodium and hydrogen forms of these resins are less pronounced. However, all the tests showed that the sodium forms of the sulphonic resins were able to remove more  $\text{Ca}^{2+}$  ions for a given throughput of challenge solution than the hydrogen forms of the same resins. This is shown in Fig. 7a to c and the parameters are summarised in Table 3.

The reason for better exchange (with calcium ions) of resins in the sodium form compared to those in the hydrogen form may be partially explained through consideration of a number of factors:

(1) If it can be assumed that the binding forces between a counter ion and a fixed ionic site on the resin are essentially electrostatic, then according to the Coulomb law as a counter ion approaches an ionic site the more strongly it will be attracted. The hydration radius of a hydrogen ion is larger than that of a sodium ion [12], and the approach of a calcium ion to an ionic site would be hindered by the larger hydrated ion.

(2) For resins in the sodium form, exchange with calcium ions would yield sodium ions which become part of the aqueous phase without any overall change in pH. However, with

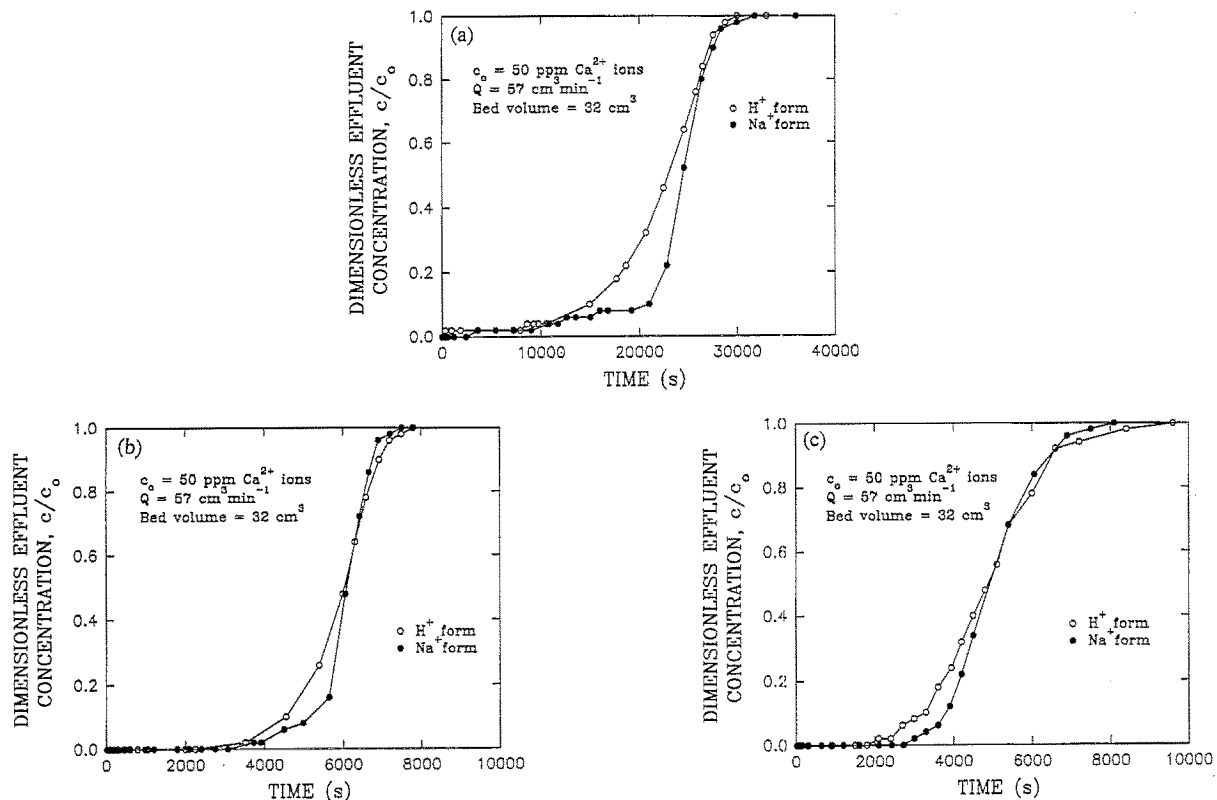


Fig. 7. (a) Effluent profiles from beds of strong acid cation exchange resin. (b) Effluent profiles from beds of sulphonated Puroilite resin beads. (c) Effluent profiles from modules of sulphonated polyhipe polymer.

Table 3  
Capacities of sulphonated polyhipe compared with commercial resins

Material (form)	Degree of sulphonation (%)	Challenge concentration (ppm)	Feed flux ( $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$ )	Total capacity ( $\text{g Ca}^{2+} / \text{g resin}$ )	Apparent capacity ( $\text{g Ca}^{2+} / \text{g resin}$ )
Polyhipe ( $\text{H}^+$ )	44	250	3.58	0.0478	0.0442
Polyhipe ( $\text{H}^+$ )	44	50	1.74	0.0478	0.0441
Polyhipe ( $\text{Na}^+$ )	44	50	1.74	0.0478	0.0450
Strong acid resin <sup>a</sup> ( $\text{H}^+$ )	98	250	3.58	0.1065	0.0845
Strong acid resin <sup>a</sup> ( $\text{H}^+$ )	98	50	1.74	0.1065	0.0894
Strong acid resin <sup>a</sup> ( $\text{Na}^+$ )	98	50	1.74	0.1065	0.0973
Purolite beads <sup>b</sup> ( $\text{H}^+$ )	20	50	1.74	0.0217	0.0138
Purolite beads <sup>b</sup> ( $\text{Na}^+$ )	20	50	1.74	0.0217	0.0141

<sup>a</sup> Amberlite IR-120;

<sup>b</sup> IP 5300.

resins in the hydrogen form exchange would yield hydrogen ions, increasing their concentration in the surrounding solution and therefore increasing the acidity of the solution locally. As local pH levels inside an ion exchanger can be very different from the bulk solution the equilibrium of the exchange reaction (Eq. (3)) may be pushed towards the adsorption of hydrogen ions reducing the amount of calcium ions adsorbed onto the resin.

(3) Hydrogen bonding effects would be expected between the hydrogen counter ions and the oxygen atoms of the sulphate groups. Hydrogen bonding would be in addition to any electrostatic effects, leading to stronger binding of the hydrogen ions onto the  $-\text{SO}_3^-$  groups and making their replacement by calcium ions more difficult.

### 3.3. Capacity from dynamic tests

A value for the apparent capacity of each resin (for  $\text{Ca}^{2+}$  ions) can be estimated from the effluent profiles by calculating the area between the adsorption curve and a line representing the concentration of the feed solution (shown as shaded regions I and II in Fig. 8). Using the given axes, the area represents the mass of challenge ions adsorbed onto one gram of resin material. Breakthrough occurs when the concentration of the effluent stream rises above zero and so the 'breakthrough capacity' can be estimated from region I on the graph. The ratio of area I to the total shaded area represents the degree of column utilisation for the particular bed of resin operating under the conditions of a given experiment. High values of the degree of column utilisation indicates that the resin bed is performing more efficiently.

A higher flow rate and a greater ion concentration in solution causes the degree of column utilisation for both the strong acid resin and sulphonated polyhipe to decrease only slightly. In these tests, increasing the feed concentration of  $\text{Ca}^{2+}$  ions to 250 ppm produced a more definitely defined step change in the effluent profiles. A higher feed concentration tends to increase the apparent capacity of a resin (at lower flow rates) as the equilibrium of Eqs. (3) and (4) is pushed to the right. However, at the higher flow rate, these

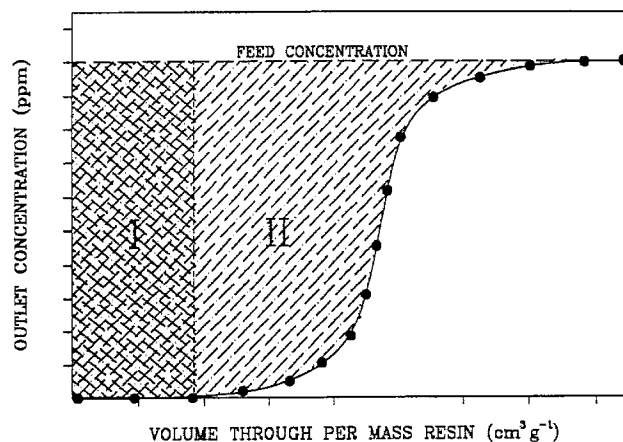


Fig. 8. Adsorption capacity from effluent profiles.

effects are masked (in the strong acid cation exchange resin) by the faster passage of fluid through the resin producing an overall reduction in capacity.

Figs. 9 and 10 show the effluent profiles for modules of sulphonated polyhipe and beds of strong acid resin being challenged at differing flow rates. Ion breakthrough occurs earlier at a higher flow rate. A reduction in breakthrough capacity results in a drop in the degree of column utilisation.

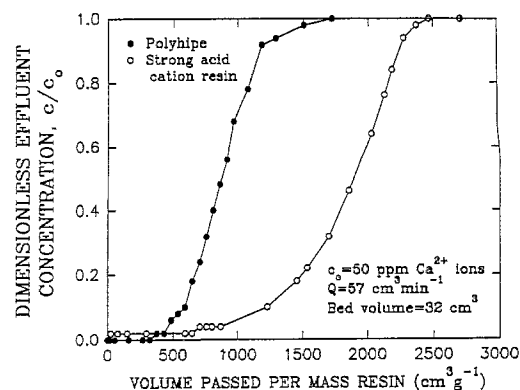


Fig. 9. Effluent profiles from a bed of strong acid cation exchange resin and a sulphonated polyhipe module challenged at normal feed rate and feed concentration conditions.

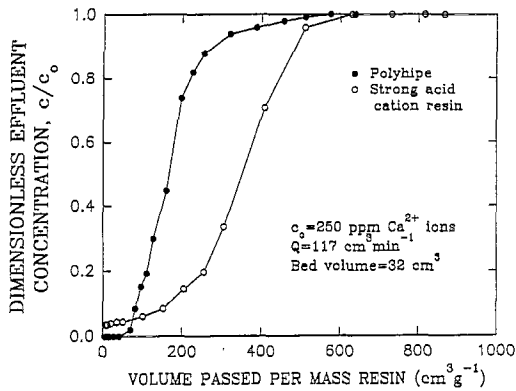


Fig. 10. Effluent profiles from a bed of strong acid cation exchange resin and a sulphonated polyhipe module challenged by a high concentration of  $\text{Ca}^{2+}$  ions at a high feed rate.

The drop in degree of column utilisation was less in the case of polyhipe, and the polyhipe was not affected as much as the strong acid resin by the increase in flow rate. This can also be seen when examining the apparent capacities of the two exchangers in Table 3. The apparent capacity of the strong acid resin falls as the flow rate is increased, from 84% of its total capacity to 79%, but the apparent capacity of the polyhipe remains similar at the two flow rates at around 92% of its total capacity. The very slight increase in apparent capacity in the polyhipe module was due to the higher feed concentration used in the increased flow rate tests. The total capacities shown in Tables 3 and 4 were calculated from the results of titrimetric analysis assuming that the number of ionic sites required to exchange with a  $\text{Ca}^{2+}$  ion was double of that required to exchange with a  $\text{Na}^+$  ion.

By noting the volume at which breakthrough occurred (when the effluent concentration became greater than zero) the capacity at breakthrough could be calculated. Under ideal conditions the breakthrough capacity should be equal to the apparent capacity which in turn should equal the total capacity. However, under normal working conditions the total capacity > apparent capacity > breakthrough capacity. Table 4 shows the difference that occurred in breakthrough capacity when the form of the resin was changed from  $\text{H}^+$  to  $\text{Na}^+$ . Higher throughput volumes were reached before breakthrough occurred when the resins were in the sodium form, indicating again that better adsorption took place using this form of resin.

Table 4  
The breakthrough capacity of various resins challenged with a 50 ppm  $\text{Ca}^{2+}$  solution at a flux of  $1.74 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$

Material	Breakthrough volume ( $\text{cm}^3/\text{g resin}$ )		Breakthrough capacity ( $\text{g Ca}^{2+}/\text{g resin}$ )	
	$\text{H}^+$ form	$\text{Na}^+$ form	$\text{H}^+$ form	$\text{Na}^+$ form
Sulphonated PHP	350	513	0.0175	0.0256
Strong acid resin	19	247	0.0009	0.0123
Purolite beads	136	160	0.0068	0.0080

Table 5  
The degree of column utilisation of various resins

Material	Degree of column utilisation			
	Breakthrough capacity			
	Total capacity		Apparent capacity	
	$\text{H}^+$ form	$\text{Na}^+$ form	$\text{H}^+$ form	$\text{Na}^+$ form
Sulphonated PHP	0.366	0.536	0.397	0.569
Strong acid resin	0.008	0.115	0.010	0.126
Purolite beads	0.313	0.368	0.493	0.567

Values of the degree of column utilisation are shown in Table 5; the  $\text{Na}^+$  form of the polyhipe resin proved showed the highest degree of column utilisation, indicating that it was the most efficient at removing the challenge species. However only about 57% of the available total capacity of the polyhipe was used before breakthrough occurred; greater column utilization could be expected at lower feed fluxes.

### 3.4. Polyhipe as an ion exchange material

The above discussion presents the results in terms of an adsorber, which does not take account of the concentration–valence effect; the effect of the solution normality on selectivity is important for polyvalent/monovalent ion exchange such as the systems considered in this work ( $\text{Pb}^{2+}$  or  $\text{Ca}^{2+}$  against  $\text{H}^+$  or  $\text{Na}^+$ ). With this in mind it is pertinent to look at the results also in terms of the normalised ion fraction, which tends to enhance the selectivity aspect of the resin rather than the total capacity. The ion exchange equivalent of the Langmuir isotherms is the so-called ‘constant separation factor’, defined for the systems in this paper as:

$$\alpha_{\text{H}}^{\text{Pb}} = \frac{y_{\text{Pb}}}{x_{\text{Pb}}} \bigg/ \frac{y_{\text{H}}}{x_{\text{H}}} \quad (3)$$

where  $y_i$  and  $x_i$  are respectively the ion fractions of species  $i$  in the resin and in the solution. The polyhipe and strong acid data shown in Figs. 4 and 5 are presented in terms of ion fractions in Fig. 11. The improvement of effectiveness of

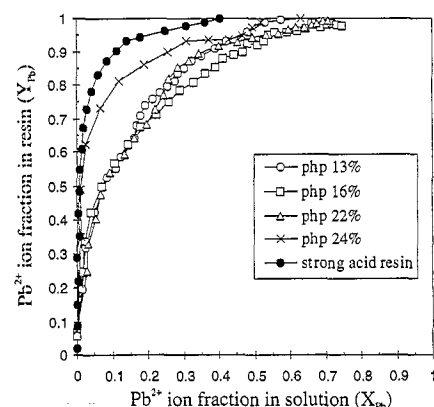


Fig. 11. The data reported in Figs. 4 and 5 replotted in terms of ion fractions.

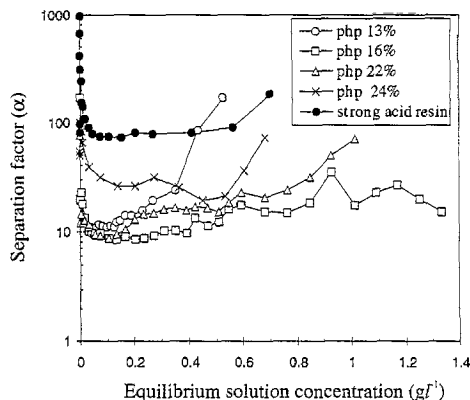


Fig. 12. The data reported in Figs. 4 and 5 replotted in terms of the separation factor.

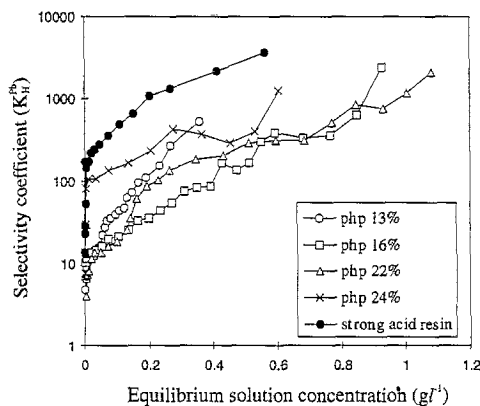


Fig. 13. The data reported in Figs. 4 and 5 replotted as the selectivity coefficient as a function of the solution concentration, indicating the effect of sulphonation on selectivity.

polyhipe as an ion exchange medium is apparent when the degree of sulphonation exceeds 22%. The separation factors for the same resins are shown on Fig. 12; although there is rather more scatter in the data, these generally show the greatest separation is provided by resins with higher degrees of sulphonation and all data show a variation of the separation factor with equilibrium solution concentration. (The reason for the 13% sulphonated PHP being inconsistent with the other data is unclear.)

An alternative way of presenting divalent/monovalent ion exchange data is by using the molar selectivity coefficient, defined as:

$$K_H^{Pb} \left( \frac{Q}{C_0} \right) = \frac{y_{Pb}(1-x_{Pb})^2}{x_{Pb}(1-y_{Pb})^2} \quad (4)$$

where  $Q$  is the total equivalent resin capacity and  $C_0$  the total equivalent solution capacity. The data interpreted in this way is plotted on Fig. 13, and shows similar trends to the data presented in the earlier plots. However, it is noted that the values for  $K_H^{Pb}$  tend to increase with solution concentration; at very low concentrations the values are similar to those expected for strong acid resins.

## 4. Conclusions

Polyhipe (PHP) foam structures are not easily sulphonated due to a combination of the small sizes of windows that connect the larger cells and the high viscosity concentrated sulphuric acid. The exchange capacity increases with the degree of sulphonation and it would be desirable to achieve a 100% sulphonated PHP. The extended surface area and high permeability, together with the low mass of adsorbent material that arises as a result of the cellular structure of the media, are properties that make PHP attractive as a potential adsorbent. Its exchange capacity is similar to existing commercial ion exchange media, and the results from this work suggest that the degree of column utilisation of a PHP medium is as good as or better than that from the commercial media.

Although the total capacity of the PHP was rather lower than that for the strong acid cation resin (Amberlite IR-120), the far superior hydrodynamics of the PHP structure ensured better contact between the adsorbent and fluid. This led to PHP being capable of treating larger volumes of liquid before breakthrough of ions at the downstream end of the bed, resulting in higher breakthrough capacities for the PHP even though its degree of sulphonation was much lower. It is worth summarising below the comparisons between PHP and the strong acid resin.

	Degree of sulphonation (%)	Total capacity (g Ca <sup>2+</sup> /g resin)	Breakthrough volume (cm <sup>3</sup> /g resin)	Breakthrough capacity (g Ca <sup>2+</sup> /g resin)
PHP	44	0.0478	513	0.0256
Amberlite IR-120	98	0.1065	247	0.0123

The potential of the PHP structure as an effective adsorbent is demonstrated, and would be enhanced if full sulphonation were achieved.

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