Open-celled polymeric foam monoliths for heavy metal separations study

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Open-celled polymeric foam monoliths prepared by high internal phase emulsion polymerization (HIPE) are being investigated as improved materials for separation of heavy metals. In column flow studies, the foam monoliths have high flow rates and are durable up to at least 40 psi. A 4-vinylpyridine functionality has been incorporated into vinylbenzylchloride/styrene copolymer foams by graft-polymerization of vinylpyridine. The open structure of the foam and the flexible graft-polymerized ion-exchange chains result in improved kinetics in metal uptake. Iron uptake kinetics were greatly increased in the grafted foams over resin beads of similar structure. Plutonium uptake kinetics were moderately increased in the foams.

Introduction[+]

Polymeric resin beads are widely used for industrial metal ion separations as well as actinide and radionuclide separations and analytical techniques. Other uses include organic and inorganic chromatography, catalyst supports, adsorbents, and solid supported reagents for organic synthesis.[1–4] Open-celled polymer foam monoliths have the potential to provide improved separations and sorption/desorption kinetics. The open cell structure of the foams allows mass transport through a monolith to be mainly convective over the interior surfaces of the cells, minimizing diffusion. In conventional resin beads, most of the surface area available for solute sorption exists in the pores where the liquid medium is essentially stagnant so here diffusion is the dominant mechanism for mass transport. Diffusion is the slow step that causes elution curves of individual components to broaden and overlap, making separations difficult. Industry's solution to this problem has been to make smaller and more uniform sized resin beads. Smaller resin beads result in higher pressure drops across the column, lower throughput rates and increased chances of channeling. The open cell structure of foams also allows novel functionalization chemistry of the surface with ligands and ion-exchange groups that is not practical in resin beads. Porous polymer monoliths prepared using pore-forming solvents have been reported recently.[5,6] Pore diameters tend to be under 10 μm. We report here a method for preparing foam monoliths using high internal phase emulsion polymerization with cell sizes in the range of 2 μm–100 μm.

High aqueous flow rates through the foam monoliths can be obtained using this method. The interior of the foam structure is shown in Fig. 1.

The polymeric foams are fabricated to form rigid, durable monolithic columns using high internal phase emulsion polymerization (HIPE).[7–9] In this process, an emulsion is created in which the internal phase is comprised of small water droplets and the continuous oil phase is comprised of styrene and vinylbenzyl chloride monomers and divinylbenzene used as a crosslinking agent. The emulsion is shown schematically in Fig. 2. After formation of the emulsion, the monomers are polymerized and the water subsequently removed. The resulting material is a highly porous polymer monolith with cell sizes equivalent to that of the water droplets present in the original emulsion. The cell sizes can be varied from about 2 to 100 μm depending on the preparation conditions.
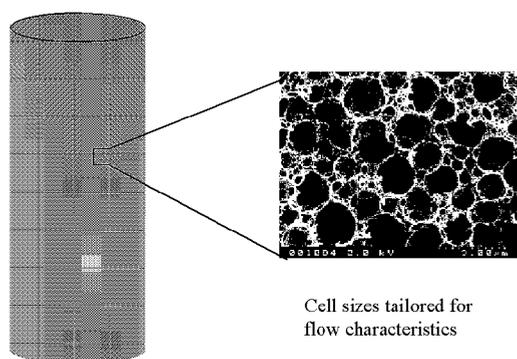

Cell sizes tailored for
flow characteristics

Fig. 1. Magnified view of foam interior
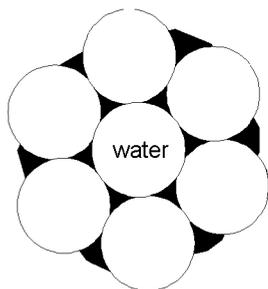
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Fig. 2. Representation of emulsion formed by high internal phase emulsion polymerization

In order to evaluate flow and structural properties, studies were performed on foam monoliths sealed into glass columns. Aqueous flow rates and pressure drops across the column were evaluated. Darcy's law was used to determine if pore closure or cell compression occurred under flow conditions.

Functionalized foams were prepared by graft-polymerization of 4-vinylpyridine to the surface. Vinylpyridine was chosen because it is a similar functionality to that in the polyvinylpyridine (PVP) resin, Reillex™ 425. A similar resin, Reillex™HPQ is useful for actinide processing.[10,11] Reillex™HPQ is an N-methylated version of the 425 resin. The foam was treated with sodium thiosulfate to introduce free-radical initiation sites on the vinylbenzyl chloride groups. Vinylpyridine polymerizes readily from these sites upon exposure to UV light, resulting in grafted polymer chains that extend out into the foam cell. This preparation is shown in Fig. 3. A grafted copolymer of 4-vinylpyridine and a bis(2-chloroethyl) vinylphosphonate was also prepared. Pendant polymer chains of this type are sometimes referred to as tentacles.[12] The functionalized foams were batch tested for uptake of iron in 10N hydrochloric acid and plutonium in 7M nitric acid. Distribution coefficients were determined at various times of exposure.
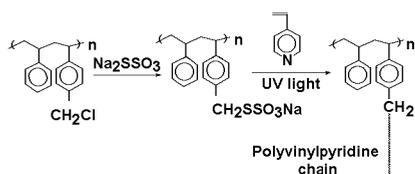

Fig. 3. Graft polymerization of vinylpyridine to foam

Experimental

Foam preparation

An oil phase and an aqueous phase were prepared before foam formation. In a typical preparation, the oil phase consists of 10.64 g vinylbenzyl chloride (mixed

isomers), 6.67 g styrene, 2.83 g divinylbenzene (mixed isomers) and 8.73 g sorbitan monooleate. 2,2'azobisisobutyronitrile (100 mg) was added and stirred until dissolved shortly before foam preparation. All materials were used as received. The aqueous phase consists of water containing 500 mg/l sodium sulfate. The two phases were pumped through three 15 μm filters in series. The oil phase was pumped at 50 ml/min and the aqueous phase was pumped at 425 ml/min, joining prior to going through the three 15 μm filters. The foam emulsion was pumped into 1.8 cm diameter glass tubes, closed at one end with a stopper. The other end was capped prior to polymerization. The tubes were placed in a vented convection oven at 60 °C for 24 hours. Both ends of the tubes were then opened and the foams removed by running water through the tubes. The foams were soxhlet extracted with 2-propanol for 18 hours to remove the surfactant, sorbitan monooleate, and dried at 60 °C.

Preparation of foam columns

A piece of 1.8 cm diameter foam prepared in a glass column was cut into sections 14.5 cm long. The foam was centered in a glass chromatography column and sealed to the glass using a polyester fiberglass resin. The resin was allowed to cure overnight.

Flow studies on foam columns

Aqueous flows through the columns were provided by a high pressure stainless steel feed reservoir filled with water and pressurized from a compressed air cylinder equipped with a pressure regulator. Pressure gauges before and after the column were used to measure the pressure drop across the column. A multiple flowmeter panel was used to measure flow rates.

Graft polymerization

The 1.8 cm diameter foam monoliths were cut into approximately 7 cm sections and placed in 400 ml N,N-dimethylformamide. Sodium thiosulfate (26 g) was added and the mixture was heated at 80 °C for 2.5 hours with slow stirring using a magnetic stir bar. The foam pieces were rinsed in water and stirred slowly for 24 hours in 1 liter of water with 4 changes of water. The foam pieces were then air dried and wrapped in aluminum foil for storage. A section of foam weighing approximately 0.5 g was then placed in a glass tube equipped with a 45/50 ground joint. 15 ml of freshly distilled 4-vinylpyridine was added. The vinylpyridine was immediately soaked up by the foam. The tube was evacuated and backfilled with nitrogen three times and kept under a positive pressure of nitrogen. The foam/vinylpyridine was illuminated by a high intensity

long range UV lamp at a distance of about 7 cm. The foam began to develop a green-blue color with 5 minutes. The foam pieces were exposed to the UV light for various periods of time ranging from 45 minutes to 17.5 hours. After polymerization, the foam pieces were soxhlet extracted with 2-propanol for 18 hours, dried, and the amount of grafting determined by weight gain.

Batch testing - iron in 10N HCl

Weighed pieces of foam (approximately 125 mg) were placed in vials. The foam pieces were broken up with a spatula to approximate the size of the resin beads (18–5 mesh). Some pieces were larger than resin beads and some pieces were smaller. 20 ml of 10^{-3}M iron nitrate in 10N HCl was placed in the vial with the foam. The vial was placed in a shaker for various periods of time. A similar amount of Reillex™ 425 resin beads was treated in like manner for comparison testing. The iron in solution was measured by UV absorption at 362 nm using an 8452 HP diode array spectrometer.

Plutonium in nitric acid

Pieces of foam weighing 125 mg were contacted with 6 ml of a 7 N nitric acid solution containing 18 mg of plutonium (IV). The foam pieces were broken as above. Aliquots were removed at 30 minutes, 2 hours and 6 hours. A multi-channel gamma spectrometer with a high purity germanium detector was used for distribution coefficient determinations.

Results and discussion

Flow studies

Aqueous flow rates through the foams were rather high. The flow rates could be tailored by varying the cell structure to be comparable to those achieved with columns containing 185 μm–400 μm resin beads in a column of similar size. The foams also withstood pressure drops of 40 psi with no sign of foam compression or structural failure. A linear relationship between pressure drop across the column and flow rate was obtained as predicted by Darcy's law, $Q = (-\kappa A \Delta P)/\mu l$. Deviation from a linear response would indicate foam compression or structural failure, where Q is the fluid flow rate, κ is the permeability, A is the cross sectional area, ΔP is the pressure drop, μ is the fluid viscosity, L is the column length.

Graft polymerization

Weight gains ranging from 29% to 220% of the original foam piece were obtained by the graft polymerization. The weight gain showed little

dependence on UV exposure time as can be seen from the Table 1. These results are contrary to what was expected from similar grafting polymerizations where methyl methacrylate was grafted onto vinylbenzyl chloride polymers.[13] These earlier experiments were performed in solution and the degree of grafting increased with irradiation time. High degrees of grafting were obtained within 15 minutes. Explanations may be that the foams were thiosulfated non-uniformly or the vinylpyridine distribution was non-uniform, but other explanations are possible. The free radical initiation sites introduced by thiosulfate are stable when stored in the dark. Thiosulfated foams aged for several weeks showed as high or sometimes higher weight gains from the grafting reaction.

Table 1. Weight gain of grafted foams at various UV exposure times

Weight gain, % of original foam weight	Exposure time, hour
220	1.50
194	17.50
143	3.50
108	6.00
92	2.00
88	6.00
29	0.75

Iron uptake in 10N HCl

The vinyl pyridine grafted foams showed significantly enhanced uptake kinetics compared to PVP resin beads for iron uptake in 10N HCl. The lower the amount of grafting, the faster the uptake kinetics and the higher the final distribution coefficient. The increased uptake kinetics in the foams with lower amounts of grafting may be due to reduced pore clogging by the grafted polymer. Although the cells are very large compared to the polymer chain length, some of the interconnecting pores may be sufficiently small to be blocked by the grafted polymer. Another explanation could be that the chains stiffen and have reduced mobility as metal binding occurs. The high distribution coefficient of the samples with low amounts of grafting may be explained by the fact that the maximum metal uptake is reached very quickly. The other samples may eventually reach the same value if left long enough. The tests were performed in iron concentrations well below the capacity of the resins. Desorption using 1N HCl was complete in 20 minutes in the case of both the foams and beads. The vinylpyridine/vinylphosphonate ester grafted foam at a level of 40% weight gain showed the highest distribution coefficient and also very fast uptake kinetics. This sample may be showing a synergistic effect between the phosphonate and the vinylpyridine. The resin beads had the lowest distribution coefficient and the slowest uptake kinetics, as shown in Fig. 4.
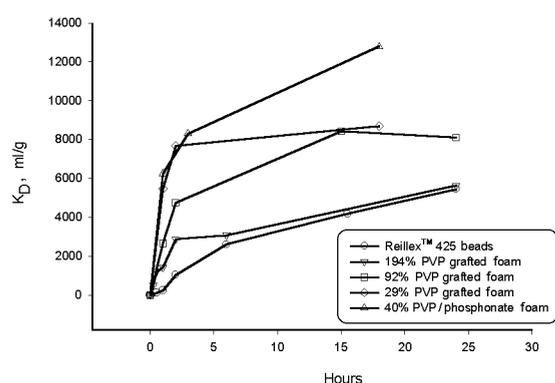
Fig. 4. Distribution coefficient of several foams and Reillex™ resin measured at various contact times

Table 3. Distribution coefficients of grafted foams and resin for plutonium uptake from 7N nitric acid. K_d for the foams is based on the weight of PVP, styrene and divinylbenzene

Sample*	30 min K_d	2 hr K_d	6 hr K_d
194%	48	160	842
92%	63	106	224
29%	2.2	7.3	8.2
Reillex™ 425	32	132	362

* Sample designation refers to % weight gain of original foam weight due to grafting

Iron capacity from 10N HCl

The foam capacity of the 194% weight gain sample for iron in 10N HCl was slightly higher than the resin bead sample. The foams with lower amounts of grafting have lower capacities, as expected when the capacity is determined on a total weight basis. If the capacity is determined based on the amount of grafted polyvinylpyridine, the capacity is higher but tends to decrease as the percent grafting decreases. The foams with higher percent grafting would be expected to have longer chains. This result may indicate that the longer chains are more efficient in binding iron. Polyvinylpyridine chains have a theoretical capacity of 9.51 milliequivalents per gram assuming a 1:1 ratio of metal ion to ligand. The results are shown in Table 2.

Table 2. Foam and resin capacity for iron from 10N HCl

Sample	Capacity based on total weight, meq/g	Capacity based on grafted PVP only, meq/g
194%	4.45	6.75
144%	3.81	6.47
109%	3.26	6.25
92%	2.29	4.77
88%	2.68	5.73
Reillex™ 425	4.04	

Plutonium uptake

Plutonium distribution coefficients determined at various times for foam samples and Reillex™ 425 are shown in Table 3. The K_ds are based on the total weight of the grafted foams rather than on the grafted portion only.

The 194% polyvinylpyridine grafted sample showed faster uptake kinetics than the resin beads and also a higher overall distribution coefficient after 6 hours exposure. The 92% polyvinylpyridine grafted sample showed initially the fastest kinetics of all the samples but then slowed down. The final distribution coefficient after 6 hours was lower than in the 194% grafted foam. This observation my be explained by the fact that the plutonium concentration in the test solution is relatively high and is approaching the capacity of the grafted polyvinylpyridine. This effect is seen in the 29% polyvinylpyridine grafted sample where overall poor performance was seen due to the fact that the available plutonium exceeded the capacity of the foam. In the case of the iron uptake experiments the total amount of metal present was low, 1.1 mg iron versus 18 mg in the plutonium experiments for the same amounts of foam. It has been reported previously that comparison of K_d curves for different resins is only valid when quantities of plutonium per amount of resin are identical and that the K_d decreases with higher amounts of plutonium present per volume resin.[11] This means that a comparison of the efficiency of the grafted polyvinylpyridine to Reillex™ 425 beads is only valid if the amount of grafted polymer is the same as the amount of resin beads since the resin beads are pure polyvinylpyridine with a few percent of a crosslinking agent. The K_d therefore should be higher for the grafted foams if the sample weight is based on the grafted portion.

If the K_d is based on the amount of grafted polyvinylpyridine rather than on the total weight, the values increase as shown in Table 4. These results do not show the comparison for similar plutonium/polyvinylpyridine ratios for the beads and foams, but they do show that the 92% grafted foam has a higher K_d while the total amount of polyvinylpyridine is approximately half of that in the resin beads. The grafted polymer chains are evidently more accessible and efficient that traditional resin beads.

Table 4. Distribution coefficients of grafted foams and resin for plutonium uptake from 7N nitric acid. K_d for the foam is based on the weight of polyvinylpyridine only

Sample*	30 min K_d	2 hr K_d	6 hr K_d
194%	73	242	1276
92%	131	221	467
29%	9.8	32.4	36.4
Reillex™ 425	32	132	362

* Sample designation refers to % weight gain of original foam weight due to grafting

Conclusions

The foam monoliths showed good flow properties in column testing and are structurally sound at pressure differentials up to 40 psi. This demonstrates that the monoliths are suitable for a wide variety of column applications and will not collapse under normal operating pressures. The vinylpyridine graft-polymerized foams showed greatly enhanced kinetics for uptake of iron and enhanced distribution coefficients. These results indicate that foam monoliths will provide faster and more efficient separations. Vinylpyridine and vinylphosphonate grafted as copolymers appeared to show a synergistic effect for iron uptake. Synergistic effects through graft polymerization of comonomers look very promising for higher efficiency and need further investigation. The vinylpyridine graft-polymerized foams show enhanced distribution coefficients and uptake kinetics for plutonium at sufficiently high grafting levels. The increased accessibility of the grafted chains in the open cells is one of the factors contributing to the enhanced performance.

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