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DISCLAIMER

Spherical Resorcinol-Formaldehyde Synthesis by Inverse Suspension Polymerization

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Abstract

Base catalyzed sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde by inverse suspension polymerization leads to the formation of uniform, highly cross-linked, translucent, spherical gels, which have increased selectivity and capacity for cesium ion removal from high alkaline solutions. Because of its high selectivity for cesium ion, resorcinol-formaldehyde (R-F) resins are being considered for process scale column radioactive cesium removal by ion-exchange at the Waste Treatment and Immobilization Plant (WTP), which is now under construction at the Hanford site. Other specialty resins such as Superlig® 644 have been ground and sieved and column tested for process scale radioactive cesium removal but show high pressure drops across the resin bed during transition from column regeneration to loading and elution. Furthermore, van Deemter considerations indicate better displacement column chromatography by the use of spherical particle beads rather than irregularly shaped ground or granular particles. In our studies batch contact equilibrium experiments using a high alkaline simulant show a definite increase in cesium loading onto spherical R-F resin. Distribution coefficient (K_d) values ranged from 777 to 429 mL/g in the presence of 0.1$\underline{M}$ and 0.7$\underline{M}$ potassium ions, respectively. Though other techniques for making R-F resins have been employed, to our knowledge no one has made spherical R-F resins by inverse suspension polymerization. Moreover, in this study we discuss the data comparisons to known algebraic isotherms used to evaluate ion-exchange resins for WTP plant scale cesium removal operations.

INTRODUCTION

The Savannah River Site (SRS), a Department of Energy (DOE) nuclear facility, has produced more than 130 million gallons of highly radioactive waste by-products from nuclear materials processing since 1954. While these wastes generally are high alkaline and contain nearly all the elements of the periodic table, most of the radioactivity is generated by the decay of cesium-137 and strontium-90 isotopes. Strontium-90 is found predominately in the sludge phase while cesium-137 is present primarily in the supernate. Moreover, these wastes are carefully managed and safely stored underground in million gallon carbon steel tanks until they can be immobilized by vitrification into borosilicate glass for long-term storage and disposal. Currently, researchers are actively searching for ways to remove the cesium from tank supernates to blend it with concentrated slurries and sludges for vitrification.

The University of South Carolina Chemistry and Biochemistry Department, in collaboration with Savannah River Site researchers, is investigating the synthesis of spherical resorcinol-formaldehyde (RF) polymers by inverse suspension polymerization. It has previously been demonstrated that RF resins show increased cesium selectivity and are kinetically suitable for displacement column process cesium removal by ion-exchange technology. Moreover, in this paper we discuss the synthesis approach taken and make data comparisons to known algebraic isotherms used to evaluate ion-exchange resins for WTP plant scale cesium removal operations.

EXPERIMENTAL

The resorcinol-formaldehyde resins were synthesized using the Bibler recipe. Resorcinol-catalyst-water molar ratios were 1:1:55.7, respectively. Formaline was added in excess. The resorcinol-catalyst solution was cooled to 0 ^{o}C before adding the formaline. Prior to starting the reaction, the solution was cooled to 0 ^{o}C to inhibit polymerization until the experiment was ready to begin.

A glass column reactor was fabricated to polymerize RF miscrospheres. The polymer solution was pumped through a jet nozzle designed to create microsphere droplets in an immiscible oil. The oil was housed in the reactor with the injector knozzle at the top. The reaction was carried out at 95 ^{o}C as the microspheres were injected into the oil. The RF microspheres were suspended in the oil and descended the length of the reactor until they were fully polymerized in the collector flask. After 13 hours all the polymer solution had been injected into the reactor. The beads were cured in the oil in the collector flask for another 11 hours at the reaction temperature. After the curing step, the beads were thoroughly washed free of oil using isopropyl alcohol (IPA) and tetrahydrofuran (THF), respectively. The fines were decanted and the resin was converted to the acid form using 100 mM sulfuric acid. The beads were stored in the acid form under nitrogen awaiting equilibrium and kinetics testing.

Batch contact equilibrium tests were carried out using the simulant in Table 1. Approximately 100 mg of resin (wet weight) was contacted with 10 mL of simulant for 72 hours using a mechanical shaker. The solution was filtered through a 0.22 mm disc filter. The filtrate was characterized for cesium using a DX-500 electrochemical/conductivity detector. Instrumental conditions are as follows: Dionex DX-500 ion chromatograph, Dionex CG-16 5x50mm guard column, Dionex CS-16 5x250mm separator column, 45mM methane sulfonic acid eluent, isocratic pumping at 1.2 mL/min, DS3 conductivity flow through cell, cation self-regenerating suppressor (recycle mode), 58.5 uL sample loop.

Column studies were carried out in a 1.43 cm i.d. graduated, jacketed glass column. The temperature was maintained at 25 ^{o}C using a water circulator. A 10.4764 g aliquot of the resin was conditioned overnight in 50 mL of 0.5M NaOH. The resin slurry was added to the jacketed column with tapping and further conditioned with 5 bed volumes (BV) of 0.25M NaOH. The resulting bed height was 7.6 cm. The simulant feed was pumped through the resin bed at an average rate of 2.4 BV/hr using an HPLC dual piston gradient pump. All effluent from the column was collected at ~0.5 BV intervals in 10 mL vials using an ISCO fraction collector.

Table 1. Batch Contact Simulant

	Mass Added	Final Volume	Cesium Concentration
K2CO3	6.9490g	1L	0.85mM
NaOH	68.0817g		
Na2SO4	71.0763g		
NaCOOCH3	82.0092g		
NaNO2	138.0198g		

Table 2. Feed Simulant

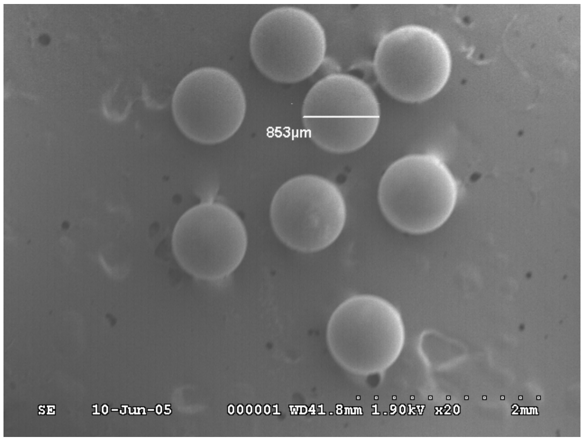
	Mass Added	Final Volume	Cesium Concentration
K2CO3	27.8984g	4L	0.53mM
NaOH	272.4202g		
Na2SO4	284.3799g		
NaCOOCH3	329.7713g		
NaNO2	551.8994g		

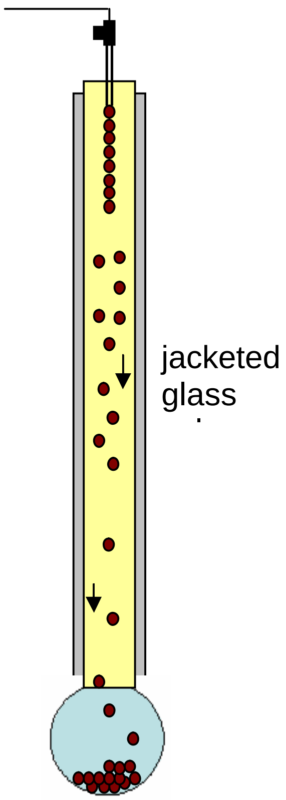
RESULTS

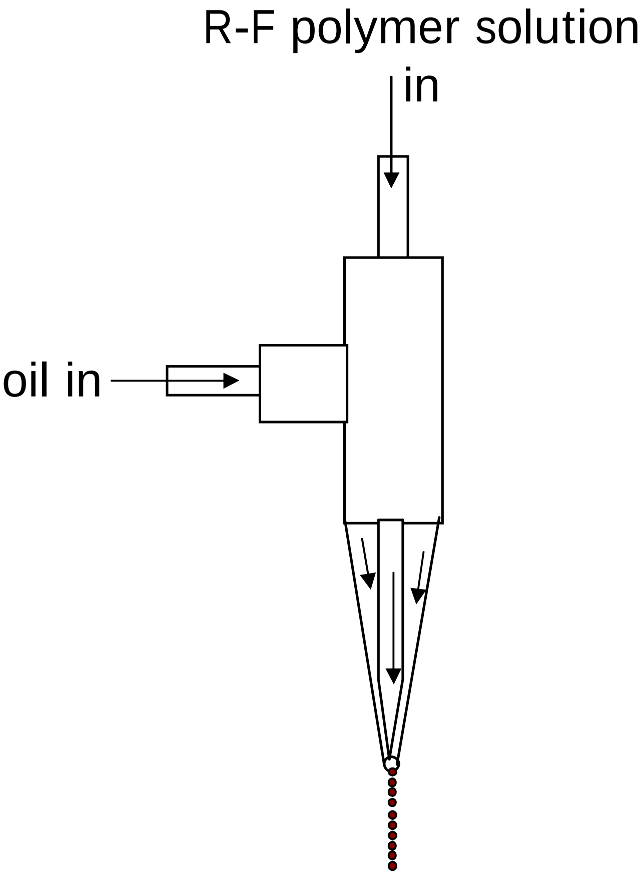
Base catalyzed sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) with formaldehyde by inverse suspension polymerization leads to the formation of uniform, highly cross-linked, translucent, spherical gels (shown in figure D below), which have increased selectivity and capacity for cesium ion removal from high alkaline solutions. Inverse suspension polymerization of resorcinol with formaldehyde allows consistent particle size control of R-F beads without bead agglomeration.

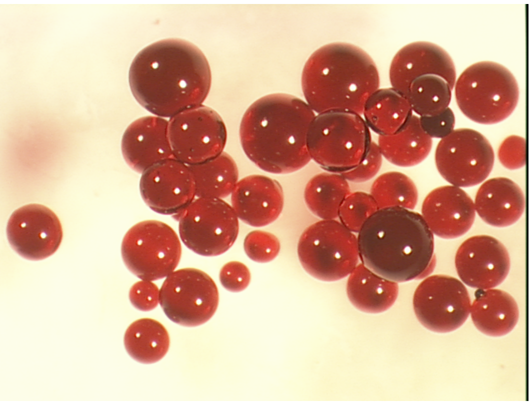
In our synthesis approach we mechanically control the size of R-F microsphere particles by an injection nozzle used to introduce the polymer solution into a hot oil as illustrated in Figure A below. The RF microspheres are created in the nozzle by break up with a sheathed-flow of silicone oil as illustrated in Figure B below. The silicone oil flows over the outside of the needle and sweeps aqueous polymer microspheres off the end of the needle as they are formed. As the aqueous microspheres are swept off the end of the needle, they are encapsulated in the silicone oil of like density and streamed out through the injector orifice into the reactor where they are polymerized (as illustrated in Figures A and C). As the RF microspheres are polymerized they descend the length of the reactor into the collector flask, which is also kept at reaction temperature.

The microspheres are aqueous polymer droplets encapsulated in the silicone oil. Because of the difference in the hydrophobic-lypophilic balance (HLB), the polymer solution forms a miscele droplet (microsphere) in the oil. The polymerization (polycondensation) reaction takes place in each individual capsule, where the water of the reaction is trapped. We believe the trapped water aids in the cross-linking process, resulting in an increase in cesium ion capacity and selectivity. Microscopic images of beads produced by this approach show these beads to be perfectly spherical.









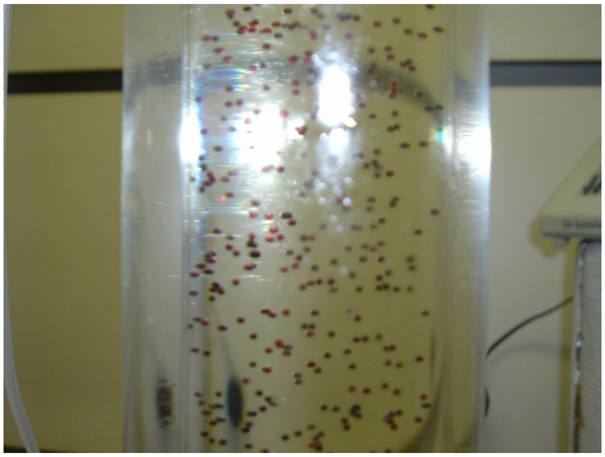
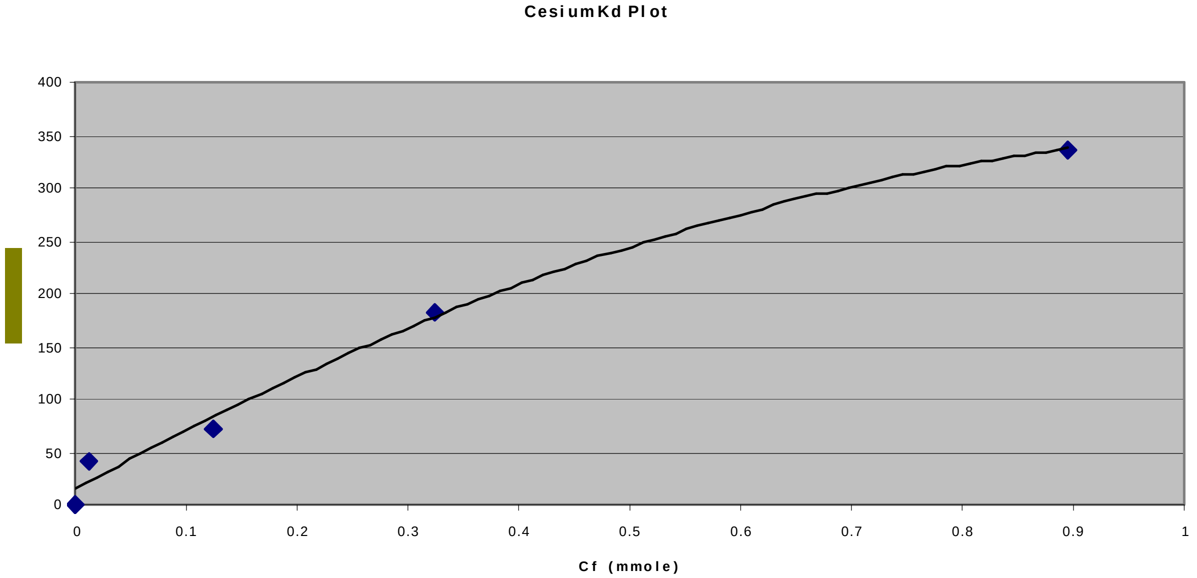
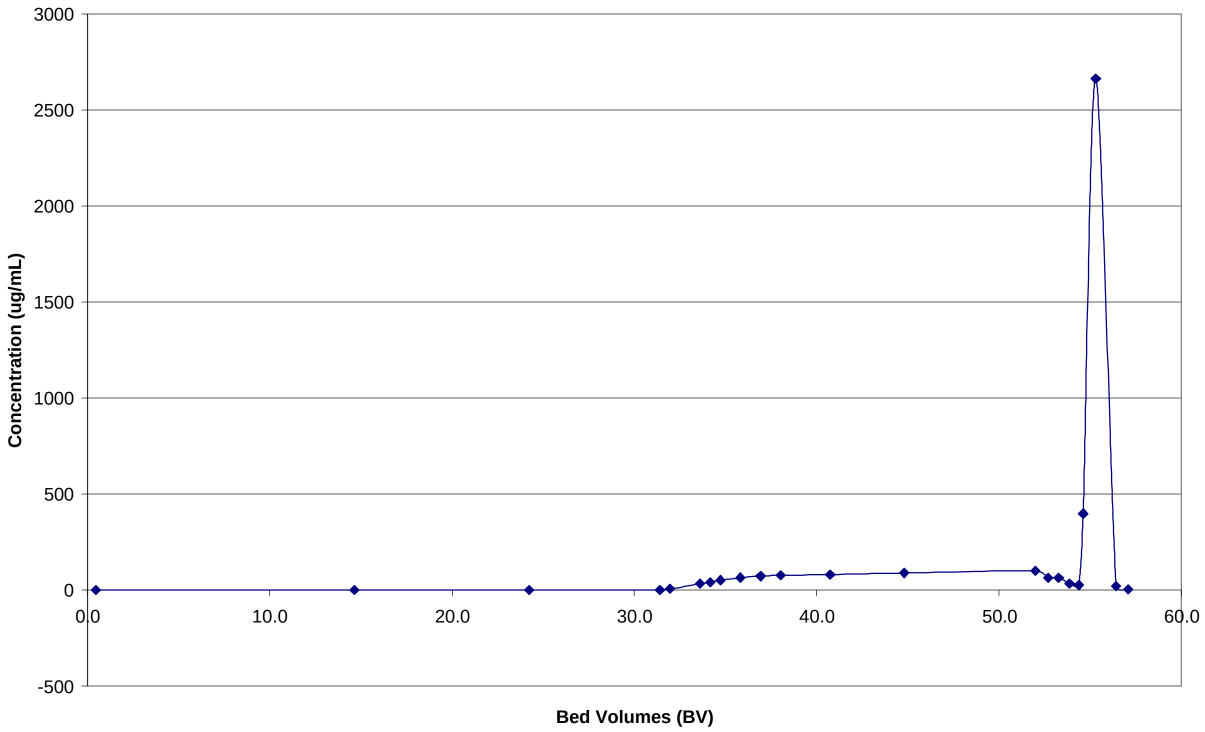


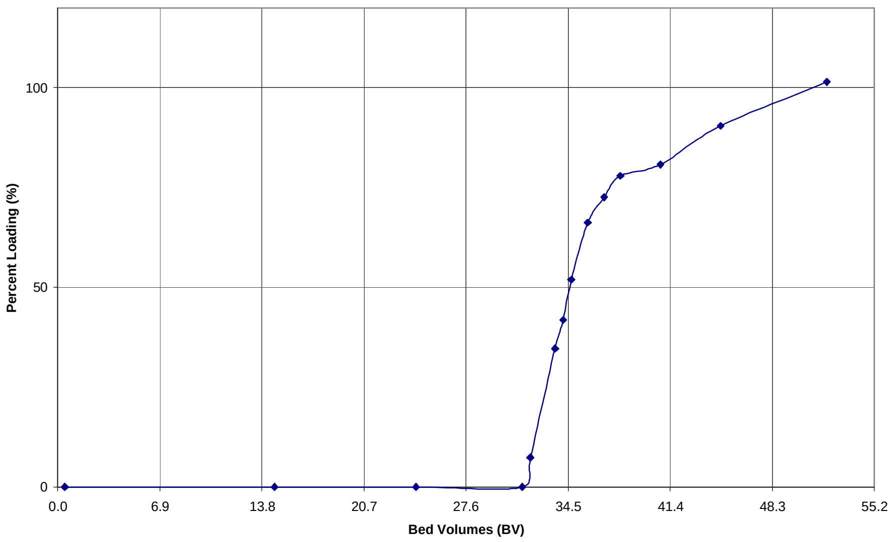
Table 3. Batch Contact Equilibrium Study

Test ID	Wet Weight (g)	Dry Resin Wt. (g)	F-factor	Phase Ratio	[Co] ug/mL	[Cf] ug/mL	[S] ug/g	Kd mL/g
9-9-RF-1	0.3414	0.0993	0.291	101	56.5	<2	<5488	<2740
9-9-RF-2	0.3417	0.0994	0.291	101	113	16.5	9708	588
9-9-RF-3	0.3410	0.0992	0.291	101	282.5	43	24143	561
9-9-RF-4	0.3420	0.0995	0.291	100	565	119	44824	377

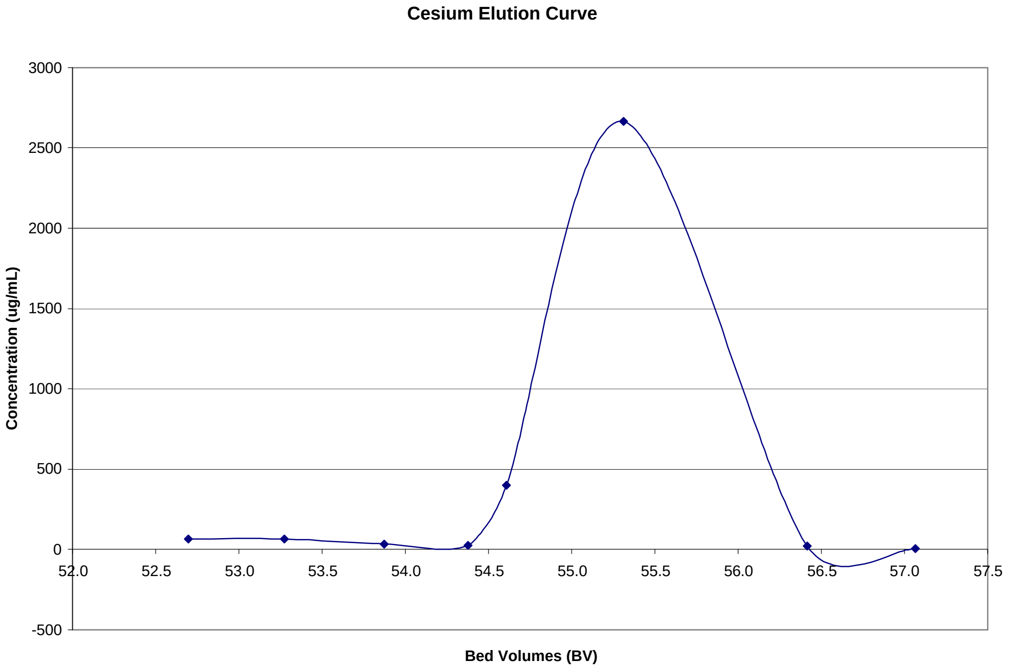




Cesium Loading and Elution



Cesium Loading Curve


Cesium Elution Curve
Concentration (ug/mL)
3000
2500
2000
1500
1000
500
0
-500
52.0
52.5
53.0
53.5
54.0
54.5
55.0
55.5
56.0
56.5
57.0
57.5
Bed Volumes (BV)

References:

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