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Preparation and Preliminary Evaluation of an Agglomerated Zirconia Based Anion Exchange Packing for Ion Chromatography

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ABSTRACT

The synthesis of novel, agglomerated zirconia based anion exchange packing is described. The packing consists of two regions. A surface-sulfonated cross-linked polyethylstyrene-encapsulated zirconia (PES–ZrO₂) acts as the inert core. A mono-layer coating of low cross-linked quaternized dimethylethanolaminated polystyrene latex, which is permanently attached to the opposite charge, functionalizes the surface of the inert core. Physical characterization of an agglomerated zirconia based anion exchange packing shows that the average diameter of the 5% cross-linked latex is 91.5 nm, and the diameter of the zirconia particles used as substrate, is 5–15 μm. The exchange capacity of the agglomerated zirconia based anion exchange packing is 0.01 mmol/g. The major virtue of agglomerated zirconia based anion exchange packing, is

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that it is not only stable in high pH environment (pH 13) but also compatible with common reversed-phase solvents. It is useful for the separation of various inorganic and organic anions.

Key Words: Zirconia based packing; Agglomerated anion exchangers; Stability; Ion chromatography.

INTRODUCTION

Ion chromatography is one of the most common and most widely used techniques for the separation of various ionic compounds.^[1,2] Of all the elements in a chromatographic system, the stationary phase is the key.^[3] At present, most of the anion column packings are electrostatically, latex-coated low-capacity ion exchangers.^[3-5] The pellicular nature of these materials provides for excellent mass transfer properties and fast separation. Dionex has been successfully preparing a series of the electrostatic agglomerated resins useful for the separation of inorganic and organic anions, as well as biomolecules such as amino acids and proteins,^[5-7] but the polymeric substrate can swell or shrink as the mobile phase changes. This results in loss of efficiency or unacceptable pressure drops across the column.^[8] So, many attempts have been taken to improve the quality of silica and other inorganic oxide packings. Recently, for example, polymer-coated silicas were used as supports of ion exchanger by Kurganov et al. for the separation of nucleotides and polypeptides,^[9] but silica-based and bonded-silica phase supports can be stable only in the range of pH 2-9.^[10,11] Polymer coating of silica has been used to extend its working pH range, but it is still unstable at extreme pH.^[12]

Zirconia has recently attracted interests as an alternate support material to silica for column packing because of its extraordinary chemical, mechanical, and thermal stability, and does neither swell nor shrink as the mobile phase changes.^[13] These advantages will be very favorable for ion chromatography stationary phases, since acid or alkali are always used as mobile phase in ion chromatography. As ion exchangers, there were only a few zirconia or coated-zirconia supports reported.^[14-24] For example, McNeff reported the quaternized polyethylenimine-coated zirconia used for the separation of oligonucleotides and oligodeoxynucleotides;^[15] Zhao reported the quaternized trimethylaminated polystyrene-coated zirconia used to separate some inorganic anions and nucleotides,^[16] but the separation performance was not high enough (Fig. 1).

Here, we just combined the ideas of polymer-encapsulated packing and surface-agglomerated resins to prepare an alkali-stable (pH 13) and organic

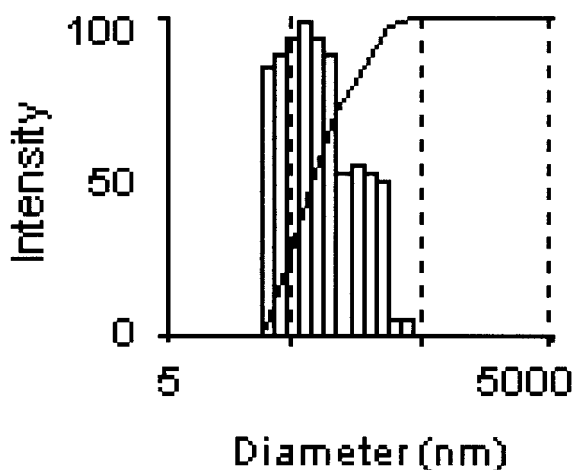


Figure 1. A chromatogram of the separation of inorganic anions on bonded quaternized trimethylaminated polystyrene-coated zirconia.^[16]

solvents-stable, agglomerated zirconia based anion column packing. This column packing uses polyethylstyrene-encapsulated zirconia (PES-ZrO₂) as substrate instead of polystyrene-divinylbenzene (PS-DVB) particles used in traditional commercial agglomerated resins. Unlike PS-DVB resins, zirconia based agglomerated anion exchange packing neither swells nor shrinks in organic solvents and it is still stable in high pH environment. Column evaluation tests show that it has good performance for use of separation of various inorganic and organic anions.

EXPERIMENTAL

Reagents

Zirconium oxychloride (Jiaozuo Chemical factory, Jiaozuo, China) was technical grade, vinyltriethoxysilane (Tianjin No. 1 Chemical Reagent Factory, Tianjin, China) was chemical reagent grade, divinylbenzene (Gaoqiao Chemical Factory, Shanghai, China) was technical grade, and stored at 5°C. Divinylbenzene consists of 55% meta and para isomers, 45% ethyl styrene. It was washed with an aqueous solution of 10% sodium hydroxide and followed by deionized water to remove the inhibitor. 4-Vinylbenzyl

chloride (90%, ACROS ORANGICS, New Jersey) was technical grade, dimethylethanolamine (Shanghai San'aisi Chemical Co. Ltd. Shanghai, China) was chemical reagent grade. All the anions were obtained from analytical reagent-grade salts in deionized water. Sodium fluoride and sodium bromide were made at Tianjin No. 3 Chemical Reagent Factory, China. Sodium chloride and sodium nitrite were made at Tianjin No. 2 Chemical Reagent Factory, China. Sodium nitrate was made at Dalian Inorganic Chemical Factory, China. Potassium phosphate monobasic was made at Beijing Hongxing Chemical Factory, China. Sodium sulfate was made at Tianjin Dagang Chemical Factory, China. Lactic acid was made at Tianjin No. 6 Chemical Reagent Factory, China. Malic acid was made at Beijing Chemical Reagent Company, China. Propandioic acid and maleic acid were made at Tianjin No. 2 Chemical Reagent Factory, China. Tartaric acid was made at Tianjin No. 1 Chemical Reagent Factory, China. Oxalic acid was made at Xi'an Chemical Reagent Factory, China.

Apparatus

A scanning electron microscope, model X-650 (Hitachi Corporation, Japan), was used to record the electron micrograph. A photon correlation spectrometer, model INNOVA 300 BI 9000AT, was used to determine the latex size distribution. A Dionex-120 ion Chromatograph with a SRS-ULTRA suppressor and a conductivity detector was used to obtain the chromatograms.

Zirconia Substrate Particles

The diameter of 5–15 μm Zirconia particles, synthesized by an oil emulsion^[25] method, were used as the substrate of the column packings. Synthesis of cross-linked polymer-modified zirconia was according to the method reported by Zuo.^[26] Zirconia microspheres (15 g) were mixed with 20 mL vinyltriethoxysilane in toluene using *p*-toluenesulfonic acid as the catalyst. After refluxing for 7 hr, the mixture was filtered and washed and the vinyl-siliconyl-bonded zirconia was obtained. Then, under a nitrogen atmosphere, 10 g vinylsiliconyl-bonded zirconia microspheres and 5 mL divinylbenzene were added to a 100 mL round-flask using acetonitrile as solvent and azodiisobutyronitrile as initiator. The mixture was heated at 70°C for 8 hours, and the polyethylstyrene–divinylbenzene-encapsulated zirconia were obtained. The C% of the polymer-encapsulated zirconia is 23% by elemental analysis. The surface-sulfonated polymer-encapsulated zirconia was obtained using sulfuric acid to an exchange capacity of 8 $\mu\text{mol/g}$.

Ion Exchange Latex

The ion exchange latex used in this work was synthesized by copolymerization of 5% divinylbenzene with 95% vinylbenzyl chloride using emulsion polymerization techniques according to the method reported by Chong and Berni,^[27] and then quaternized with three tertiary amines: trimethylamine (TMA), triethylamine (TEA), dimethylethanolamine (DEMA), respectively.

Agglomerated Zirconia Based Anion Exchange Packing

Diluted quaternized latex (20 mL), synthesized as above, was added to a 100-mL round-flask. Then, a slurry mixture of 10 g surface-sulfonated polyethylstyrene–divinylbenzene-encapsulated zirconia microspheres and 50 mL deionized water was added drop by drop. After 1 hr of reaction by stirring vigorously, the mixture was left to stand for half an hour. After dumping the excess latex, the particles were washed with deionized water, three times, till the excess latex was removed completely. The exchange capacity of this stationary phase is 0.01 mmol/g.

RESULTS AND DISCUSSION

This study shows that the latex diameter influences the column capacity; the diameters of the latex used are commonly in the range from 50 to 500 nm.^[6] Figure 2 shows a particle size distribution (PSD) result of the DEMA functionalized latex we prepared, the average diameter is 91.5 nm, as can be seen in the figure. Different quaternary ammonium latexes show different selectivity of the separations, especially for inorganic anions. The three tertiary amines we used to quaternize the latex represent a range of hydrophilicity and molecular size. For the separation of the seven inorganic anions, the DMEA quaternized latex showed the best performance. Details will be discussed in our further research.

An SEM micrograph of latex agglomerated polymer-encapsulated zirconia particles is shown in Fig. 3. The photograph indicates that coverage of the sulfonated zirconia based core microsphere by the anion exchanger latex is nine tenths, and is a mono-layer coverage. It has been reported, that the column efficiency is most strongly effected by the size of the substrate particles,^[6] and the structure of the polymer-coated on the surface of the zirconia particles can also influence the separation. The cross-linked polymerization method we used can obtain a polymer film of the thickness of 1–10 nm.

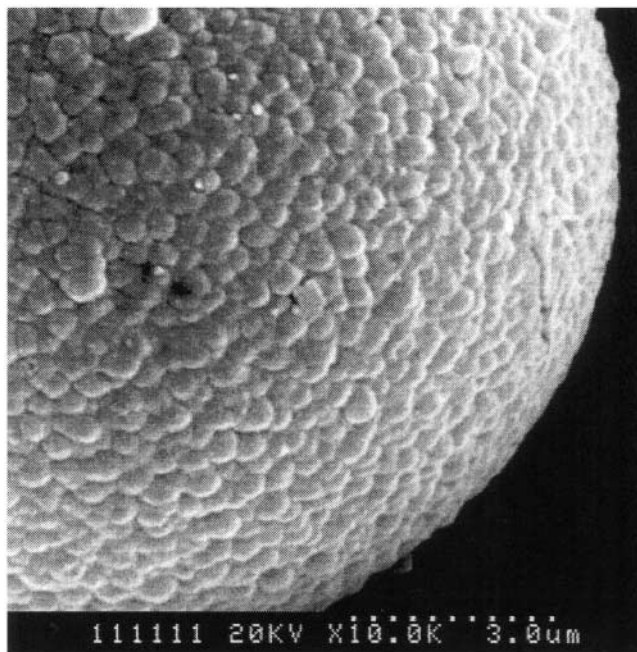


Figure 2. PSD of the quaternized polystyrene latex.

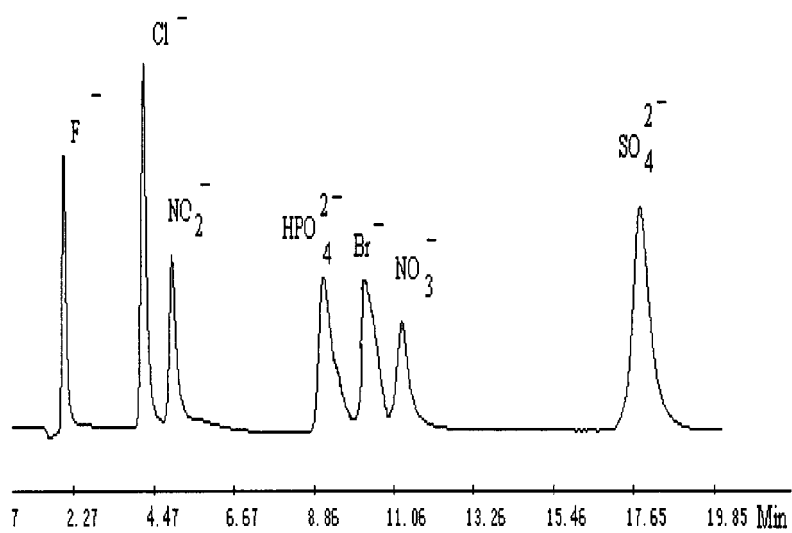


Figure 3. SEM micrograph of an agglomerated zirconia microsphere.

Figures 4 and 5 are the chromatograms of the separation of seven inorganic anions and the separation of some organic acids. The chromatograph column (250 × 4.6 mmol i.d.) was filled with the DEMA quaternized latex agglomerated zirconia based packings, under a pressure of 35 MPa by a high-pressure pump, model 6752B-100 (Beijing Analytical Instruments Technical Company, Beijing, China). The mixture of seven anions and the mixture of the organic acids were made from analytical reagent-grade salts or acids in deionized water. The solutions were filtered through a 0.45 μm filter prior to use. Seven inorganic anions were separated effectively on the column, as shown in Fig. 4. The retention time, resolution, and column efficiency are given in Table 1. These are comparable with the commercial polymer resins Dionex AS-14^[7] and better than bonded zirconia based anion exchange material^[16] (Fig. 1). Six organic acids, commonly contained in fruit juice and beverage were also well separated on this column (Fig. 5).

The alkali-stability of agglomerated zirconia based anion exchanger, which we believe to be a major advantage of zirconia based over silica-based phases, was performed using 0.1 mol/L NaOH as the rinsing eluent. After rinsing for 1000 column volumes, the retention time and column

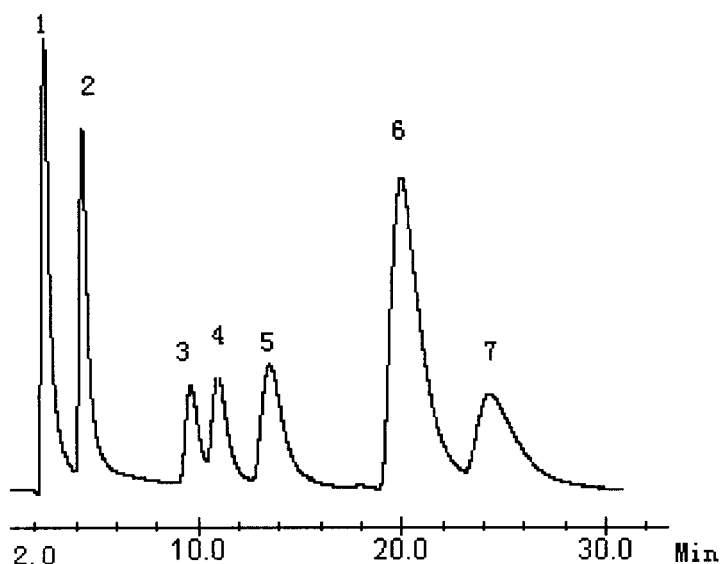


Figure 4. Separation of seven anions. F^- , 5 mg/L; Cl^- , 10 mg/L; NO_2^- , 15 mg/L; Br^- , 20 mg/L; NO_3^- , 25 mg/L; HPO_4^{2-} , 30 mg/L; SO_4^{2-} , 30 mg/L. Mobile phase, a mixture of 5.5 mmol/L Na_2CO_3 and 2.5 mmol/L $NaHCO_3$; flow rate, 1.05 mL/min; injection volume, 50 μL; test temperature, 25°C; column pressure, 1.0×10^7 Pa.

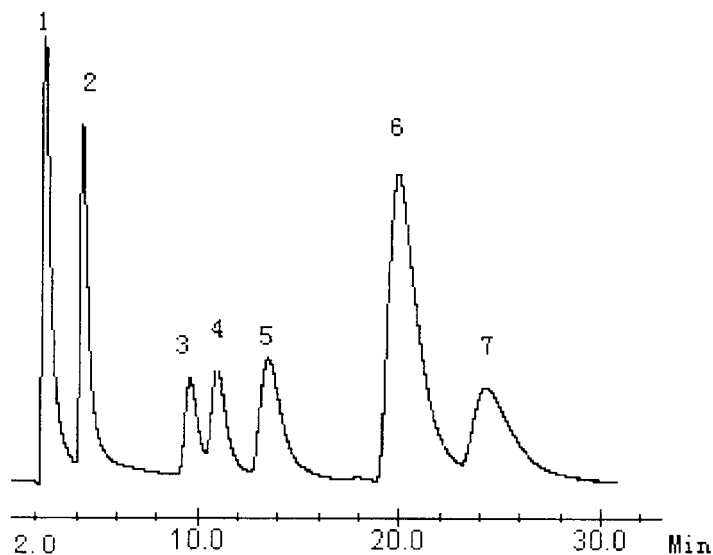


Figure 5. Separation of six organic acids and Cl^- . 1, 5 mg/L lactic acid; 2, 10 mg/L Cl^- ; 3, 15 mg/L malic acid; 4, 15 mg/L propandioic acid; 5, 15 mg/L tartaric acid; 6, 30 mg/L oxalic acid; 7, 20 mg/L maleic acid. Mobile phase, a mixture of 5.5 mmol/L Na_2CO_3 and 2.5 mmol/L NaHCO_3 ; flow rate, 1.05 mL/min; injection volume, 50 μL ; test temperature, 25°C; column pressure, 1.0×10^7 Pa.

Table 1. Resolution, retention time, and column efficiency of the seven inorganic anions.

	Anions						
	F^-	Cl^-	NO_2^-	HPO_4^{2-}	Br^-	NO_3^-	SO_4^{2-}
Concentration (mg/L)	5	10	15	30	20	25	30
Retention time (min)	3.06	5.28	6.10	10.42	11.23	12.40	18.52
Resolution (R_s)		7.3	2.1	8.0	1.2	1.8	8.2
Efficiency (plates/m)	3,484	5,744	5,652	6,804	8,864	9,458	10,120

Note: Efficiency was calculated by $N = 5.54(t_R/w_{1/2})^2$, where t_R and $w_{1/2}$ are the retention time and the width at half-height for corresponding ions.

Table 2. Base stability study of the column.

	Anions						
	F ⁻	Cl ⁻	NO ₂ ⁻	HPO ₄ ²⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻
Retention time a	3.06	5.28	6.10	10.42	11.23	12.40	18.52
Retention time b	3.04	5.24	6.15	10.39	11.09	12.49	18.50
Column efficiency a	3,484	5,744	5,652	6,804	8,864	9,458	10,120
Column efficiency b	3,476	5,766	5,694	6,774	8,832	9,450	10,118

Note: Retention time a and column efficiency a are obtained before rinsing with 0.1 mol/L NaOH, retention time b and column efficiency b are obtained after rinsing with 0.1 mol/L NaOH for 1000 column volume.

Table 3. Content of the anions in tap water.

	F ⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
Column 1 (we prepared)	0.71	105.66	23.93	176.98
Column 2 (Dionex AS-14)	0.69	107.79	24.41	176.43

efficiency of the seven inorganic anions were determined again; there are no obvious changes after rinsing, as can be seen in Table 2. The solvent-compatible properties were tested with methanol and acetonitrile as the eluents. After rinsing with methanol and acetonitrile for 1000 column volumes, respectively, retests of the separation of the anions gave results almost the same as that before the elution, indicating no damage to the column.

In addition, we tested the content of inorganic anions in tap water, the results were close to that tested by the commercial column Dionex AS-14 (Table 3), which shows that the column we prepared is useful to apply in practice.

In summary, we have successfully prepared alkali-stable and organic solvent-compatible agglomerated zirconia based anion exchange packing. We believe, that this new anion exchanger offers great utility to chromatographers for separation of various anions.

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