



Agglomerated carbon based phases for anion exchange chromatography

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ABSTRACT

Carbon-clad zirconia particles have been converted into ion exchange media through addition of charged latexes after covalent modification of the carbon surface. A variety of methodologies were investigated to introduce a negative charge to the carbon surface in the form of either sulfonate or oxygen containing functionalities (e.g. hydroxyl or carboxylate). Short analytical sized columns (35 mm × 4 mm I.D.) were packed with modified 2 μm nonporous carbon clad zirconia. Addition of the latex particles after the initial packing produced almost double the efficiency for the system compared to adding the latexes before packing. The optimized system could separate mixtures of common inorganic anions with efficiencies greater than of 41,000 plates/m and retention reproducibility of <2% RSD.

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1. Introduction

Agglomerated materials for IC were first reported and patented by Small and Stevens in 1975 [1–3]. These phases revolutionized the analysis of inorganic anions such as fluoride, chloride, nitrate and sulfate. The early agglomerated phases were based on 15–40 μm polystyrene divinylbenzene particles whose surface were made anionic by sulfonation. To make the phases anion-exchanging, polycationic latexes were electrostatically bound to the anionic surface. The quaternary amine functionality of the latexes act as the anion exchange sites. Since latexes can be made easily, cheaply and homogeneously in large scale, this insures that reproducible columns can readily be manufactured [4]. Agglomerated columns provide higher efficiencies than microporous exchangers due to reduced resistance to mass transfer [5].

Although more than 25 years have elapsed since the original patent, agglomerated polymeric particle based ion exchangers still comprise a significant portion of the stationary phases used in modern IC. Other polymer and latex compositions have been introduced to modify selectivity [5–7]. Also, the cross-linking within the polymer core particle has been increased from 2–5% to ≥50% to increase the mechanical strength of the particles and reduce their swelling in organic solvents [8]. This increased mechanical strength has enabled reduction of the agglomerated particle size to 7 μm to improve efficiency. However, such particles are still much larger and of lower efficiency than the silica-based chromatographic particles used in RPLC and other HPLC modes (2–5 μm).

Thus, IC columns are long (≥15 cm) compared to RPLC, resulting in slower speed of separation.

Standard silica based stationary phases typically have greater efficiency and mechanically stability than polymers for small molecules. To convert silica bonded phases into ion exchange phases, columns can be dynamically coated with cationic [9] and amphoteric [10] surfactants. However, the columns are typically greater than 15 cm in length, resulting in analysis times of ≥30 min. In contrast, Pelletier and Lucy separated 7 ions in less than 1 min using a 1.3 cm × 4.6 mm I.D. column coated with the cationic surfactant didodecyldimethylammonium bromide (DDAB) [11]. As particle size is proportional to efficiency as governed by the van Deemter equation [12], 1.8 μm C₁₈-silica particles were utilized to increase efficiency, and thus reduce the length of the column needed to separate the analytes. A very short column (≤2 cm) was also required to maintain an operating pressure that a regular HPLC pump could handle (<4.1 × 10⁴ kPa, 6000 psi). To reduce the back-pressure requirements, separations have also been performed on surfactant coated silica monoliths in both the capillary [13,14] and analytical formats [15–18].

Although surfactants provide a cheap and easily prepared dynamic coating, surfactant coated columns require a significant break-in period and experience gradual losses in column capacity [19]. Also, organic additives cannot be added to the eluent since they can remove the surfactant from the column.

As an alternative to charged surfactants, ionic polymers [20] and ionic latexes [21,22] have been added to silica media to create IC columns. The combination of the silica backbone with latexes yields highly efficient separations, with a quick start-up time and highly reproducible retentions. However, silica column degrade at high pH (>8) due to silica dissolution [23]. As a result, silica based columns

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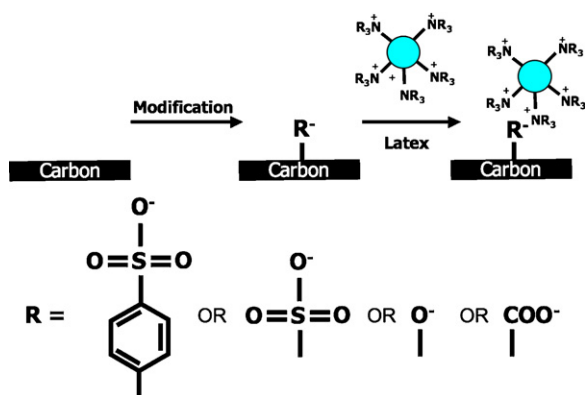


Fig. 1. Preparation of agglomerated phases for IC using carbon-clad zirconia.

are limited to weak organic acid eluents that produce higher backgrounds and yield poorer detection limits than IC eluents such as carbonate/bicarbonate and hydroxide.

Carbon-clad zirconia is a phase that is mechanically strong and that allows the use of eluents that span the entire pH range (0–14). Our lab has demonstrated the use of surfactant coatings on carbon based particles [24]. Pure carbon packings lacked mechanical strength [24], although this instability may have derived from poor column packing by the manufacturer [25]. However, carbon-clad zirconia was shown to be a promising new support for IC. Surfactant coatings provided good separations, but experienced long break-in times and gradual capacity loss. Covalent introduction of arylamine anion exchange sites to carbon-clad zirconia phases yielded stable retention in IC, but were incompatible with hydroxide eluents and exhibited low capacity [26].

Herein agglomerated phases are explored as a means of introducing ion exchange characteristics to carbon-clad zirconia. The first step in preparing an agglomerated carbon clad zirconia is to introduce a negatively charged functionality (R^-) onto the carbon surface (Fig. 1). Diazonium chemistry and other techniques are explored. Positively charged latexes are then added to convert the particles into agglomerated anion exchangers (Fig. 1).

2. Experimental

2.1. Materials and reagents

Methanol (Fisher Scientific, Ottawa, ON, Canada) and tetrahydrofuran (EMD Chemicals, Gibbstown, NJ, USA) were of HPLC grade. Dichloromethane (Fisher) and chloroform (Fisher) were of Optima grade. Pyridine (Fisher) and 1,2-dichloroethane (Fisher) were of analytical grade. Anhydrous ethanol (Fisher), concentrated nitric acid (Caledon Chemicals, Georgetown, ON, Canada), chlorosulfonic acid (99%, Sigma–Aldrich, Oakville, ON, Canada), sulfanilic acid monohydrate (Sigma–Aldrich) and potassium permanganate (Sigma–Aldrich) were used as received. All water was 18 M Ω nanopure water (Nanopure Water System, Barnstead, Chicago, IL, USA) and was filtered through 0.22 μ nylon membrane filters (Millipore, Bedford, MA, USA) prior to use. All non-aqueous solvents were filtered through 0.2 μ m Fluoropore filters (Millipore). All inorganic chemicals were reagent grade or better. Iodide (BDH, Toronto, ON, Canada), sulfate (BDH), nitrite (99.9+%, Sigma–Aldrich), bromide (Sigma–Aldrich), fluoride (Sigma–Aldrich), chloride (EMD) and nitrate (EMD) were used as their sodium salts. Molecular sieves (8–12 mesh, Acros Organics, NJ, USA) were heated to 250 °C in a moisture free oven overnight prior to use. A suspension of latex particles (polyvinylbenzylammonium-

divinylbenzene, AS12A, Dionex, Sunnyvale, CA, USA) was used as received.

Carbon-clad zirconia particles (3 μ m, porous (30 m²/g, batch #65-175 and #69-119); 2 μ m, non-porous (0.7 m²/g, batch #70-250); ZirChrom, Anoka, MN, USA) were used as received. The carbon-clad zirconia particles were kept in their original container in a desiccator until just prior to use. The 3 μ m carbon-clad zirconia particles were from batch #65-175, used unless otherwise stated.

2.2. Reaction vessel cleaning

Glass vials (28 mm \times 57 mm, Fisher) used to contain the modification reactions were cleaned with piranha (1 part 30% H₂O₂, 3 parts sulfuric acid), rinsed with an abundance of filtered 18 M Ω nanopure water, dried in a moisture free oven (≥ 140 °C), and allowed to cool before use. A new, clean vial with a new screw cap top was used for every modification. The reactions involving nitric acid used 200 mL round-bottom flasks, cleaned with copious amounts of water, ethanol and methanol, dried in a moisture free oven, and allowed to cool before use.

2.3. Diazonium modification of carbon-clad zirconia

Carbon-clad zirconia was modified using *in situ* generated diazonium ions as described previously [26]. In brief, sulfanilic acid and two equivalents of HCl were dissolved in 8 mL of 36% ethanol and sonicated for 10 min. Then, 0.1 g of carbon-clad zirconia particles and a magnetic stir bar were added. The contents of the vial were stirred, sonicated for 10 min, and the vial placed into a 60 °C oil bath with stirring. An equivalence of an aqueous sodium nitrite solution was added dropwise over 1 min, darkening the solution yellow and producing bubbles (**Caution:** nitrogen gas is evolved rapidly). The vial was capped and the contents of the vial were allowed to react. The vial was then placed on an ice bath. The particles were collected on a 0.22 μ m nylon filter and washed with a series of solvents ranging in polarity – specifically water, ethanol, THF, acetone, methanol and then with various water/methanol blends. Washing continued until the filtrate was clear and colorless. The particles were transferred to a clean vial and rotovapped. The vial was placed into a sonic bath for a few seconds to free the particles from the vial walls prior to being sent for analysis. Scale up of the synthesis was accomplished by increasing the solvent and reaction components 20-fold, with care taken during the sodium nitrite addition.

2.4. Chlorosulfonic acid modification of carbon-clad zirconia

A known amount of carbon-clad zirconia (0.1 or 2.0 g) was added to a cleaned vial containing a stir bar and 10 mL of either chloroform, dichloromethane, 1,2-dichloroethane or pyridine. The vial was then sonicated for 10 min and stirred for 20 min. A known amount of chlorosulfonic acid (0.1–0.5 mL) was added slowly using a syringe (**Caution:** chlorosulfonic acid reacts violently with water). The reaction was allowed to proceed for a set period of time (15 min to 30 h). The particles were collected on a 0.2 μ m Fluoropore filter and washed with the reaction solvent, water, water/methanol blends, ethanol, THF and acetone. The particles were periodically agitated with fine streams of solvent during filtration. If the filter became stained during filtration, the particles were transferred to another Fluoropore filter and rinsed with methanol and water. Washing continued until the filtrate was clear and colorless. The particles were transferred into a clean vial using methanol, sonicated, decanted, and then placed on a roto-vap (35 °C) to remove residual methanol. To ensure the particles were free from the vial walls, the vial was sonicated for a few seconds before particles were sent for analysis. Scale up of the synthesis was accomplished by increasing the solvent and reaction

components 20-fold with care taken during the chlorosulfonic acid addition.

2.5. Nitric acid modifications of carbon-clad zirconia

0.1 g of 2 μm non-porous carbon-clad zirconia were added to a cleaned 250 mL round bottom flask. A stir bar was added and the flask was placed into a thermostated oil bath. 50 mL of concentrated nitric acid was added and the contents were refluxed (140 °C) for a set amount of time (15 min to 10 h) and then placed in an ice bath. With stirring, 10 M NaOH solution was added until the solution was $\text{pH} \geq 7$. The particles were collected on a 0.22 μm nylon filter and washed with methanol and water, and handled as in Section 2.4.

2.6. Apparatus

IC separations were performed with an ICS-3000 chromatography system (Dionex) consisting of an ICS-3000 DP pump, an ICS-3000 DC temperature housing unit, an ICS-3000 EG eluent generator (KOH), an ASRS-300 2 mm anion-suppressor in recycle mode, and an ICS-3000 CD conductivity detector. Data acquisition and control were performed using Chromeleon version 6.8 SP3 software (Dionex).

Slurry packing was performed with an air-driven liquid pump with lower pressure air modification (DSF-122-87153, Haskel, Burbank, CA, USA). Additionally, a packing trial was performed using two ProStar LC pumps (Varian, Palo Alto, CA, USA). Polyether etherketone (PEEK) column jackets 35 mm \times 4 mm I.D. (Dionex) were used. Two grams of modified carbon-clad zirconia were slurried in 35 mL of filtered water and sonicated for 20 min prior to packing. The particles were placed in an 80 mL holding reservoir (Lab Alliance, State College, PA, USA) and packed in the downward direction using water as the driving solvent. The pressure was increased from 0 kPa (0 psi) to 4.5×10^4 kPa (6500 psi) over 1 min and then held at 4.5×10^4 kPa until at least 300 mL of water had passed through the column. The columns were then quickly fitted with end fittings (0.5 μm polymer frits) and flushed with copious amounts of water. The columns were then capped and left overnight in a thermostated environment (30 °C) to allow packing bed expansion before use.

An AXIS ULTRA X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Wharfedale, Manchester, UK) system was used for XPS analyses. A CHNS-O EA1108 elemental analyzer (Thermo Scientific, Waltham, MA, USA) was used for elemental analysis. The precision was 0.001%w/w and 0.05 at.% for elemental analysis and XPS in the modes utilized. Method blanks on both instruments were performed for all experiments.

2.7. Formation of agglomerated particles

Dionex AS12A latex particles are 140 nm in diameter, functionalized with alkyl quaternary ammonium groups and provided as a suspension. Two procedures were used to form agglomerated IC columns. First, columns (35 mm \times 4 mm I.D.) containing modified, non-latexed carbon-clad zirconia particles were pre-rinsed with at least 10 column volumes of filtered water. The coating solution was a 15-fold aqueous dilution of the latex stock. With the suppressor detached, the diluted suspension was pumped through the column until breakthrough was detected using the conductivity detector. The columns were then flushed with an additional 10 column volumes of suspension, and finally with copious amounts of deionized water. The pump was then thoroughly rinsed before any analysis.

Alternatively, before packing, 4 mL of a 4-fold diluted AS12A suspension were added to 2.0 g of modified particles. The mixture was manually agitated and sonicated for 10 min. The particles were collected on a 0.22 μm nylon filter; washed with methanol, ethanol,

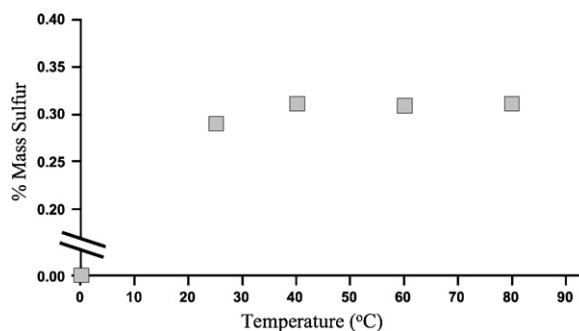


Fig. 2. Effect of temperature on sulfur loading using *in situ* generated sulfanilic acid diazonium ions. Experimental conditions: 0.10 g of 3 μm porous carbon-clad zirconia; 1 mmol sulfanilic acid in 33% EtOH/water; 1 equiv. NaNO_2 ; 2 equiv. HCl; $n = 3$. Error for each reading is equal to or smaller than the size of each point.

water and THF; transferred into a clean vial with methanol; sonicated and decanted; and then placed on a rotovap (35 °C) to remove any remaining methanol.

3. Results and discussion

3.1. Introduction of a negative charge to carbon-clad zirconia

3.1.1. Diazonium modification of particles

To prepare an anion-exchange agglomerated particle, positively charged latexes are electrostatically bound to a negatively charged particle. We previously demonstrated that carbon-clad zirconia stationary phases for IC can be prepared using diazonium chemistry [26]. As a result, a brief set of optimization trials were performed using *in situ* thermal deposition of an arylsulfonate onto the particles. The effects of time, temperature and sulfanilic acid concentration on particle modification were probed.

Reaction of 0.1 g of 3 μm carbon-clad zirconia particles with sulfanilic acid (4-aminobenzene sulfonic acid) for greater than 15 min yielded a constant 0.31%w/w sulfur modification of the particles. Reaction times above 4 h produced the most reproducible amount of sulfur modification (RSD < 1%). Fig. 2 shows the effect of temperature on the amount of sulfur loaded onto the particles. At 0 °C no sulfur loading was observed. Temperatures of ≥ 25 °C yielded a significant and essentially equivalent sulfur loading of 0.31%w/w. The greatest reproducibility was achieved at 60 °C (1.3% RSD). This temperature was utilized for all further modifications.

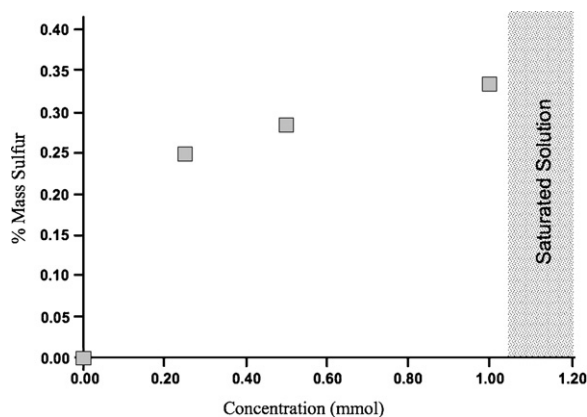


Fig. 3. Effect of sulfanilic acid concentration on surface modification. Experimental conditions: 0.10 g of 3 μm porous carbon-clad zirconia; 1 mmol sulfanilic acid in 33% EtOH/water; reaction temperature = 60 °C; 1 equiv. NaNO_2 ; 2 equiv. HCl; $n = 3$. Error for each reading is equal to or smaller than the size of each point.

Increasing the sulfanilic acid concentration increases the functionality of the surface (Fig. 3). However, the solubility of sulfanilic acid is limited to 1 mmol in the optimized solvent (33% EtOH in water) [27]. A modification performed above the saturation point (1.25 mmol) yielded the same level of sulfur modification as the 1 mmol trial. Thus, 1 mmol was utilized for all future experiments.

3.1.2. Chlorosulfonic acid modification of carbon-clad zirconia

The most common sulfonation agent is chlorosulfonic acid [28–32]. However, a variety of solvents have been utilized in the literature without justification. Herein chloroform, dichloromethane, and 1,2-dichloroethane along with pyridine, a common organic solvent, were explored.

Reactions of 0.1 g of 3 μm carbon-clad zirconia with 0.1 mL chlorosulfonic acid at 25 °C yielded 0.29%w/w sulfur when performed in chloroform, dichloromethane or 1,2-dichloroethane. Drying the solvents with molecular sieves improved the yields slightly (0.30%w/w). Reactions in dry pyridine yielded only 0.18%w/w sulfur, and so were not pursued further. The reproducibility (RSD) of sulfur loading was 2.3% with dry 1,2-dichloroethane and 1.5% with dry chloroform or dichloromethane. Only chloroform and dichloromethane were probed further.

Optimization of the reaction temperature was limited by the low boiling points of chloroform (61 °C) and dichloromethane (40 °C) [33]. Therefore, reactions were performed at ≤ 30 °C. At 25 °C, reactions in the two solvents yielded 0.29%w/w. Below 25 °C, the sulfur loading was always lower than that at 25 °C. Use of 30 °C gave only minor gains in capacity (0.30%w/w) but poor reproducibility was observed ($\geq 4\%$ RSD). As a result, 25 °C was utilized in all further studies.

The volume of chlorosulfonic acid added had minimal effect on the sulfur loading. Using 0.05 mL of chlorosulfonic acid yielded 0.26%w/w sulfur, while 0.1–0.5 mL of chlorosulfonic acid yielded 0.29%w/w sulfur. Reaction times of 0.5–4 h yielded 0.29%w/w, whereas 20–30 h yielded 0.58%w/w. Twenty hours was utilized in all further experiments.

Under similar experimental conditions, chlorosulfonic acid yields comparable sulfur loadings to diazonium based modification (0.29%w/w vs. 0.31%w/w). As chlorosulfonic acid is cheaper and more suited to an industrial setting, specifically for mass production, chlorosulfonic acid was used for the remainder of the experiments.

3.1.3. Effects of particle composition

The carbon loading on carbon-clad zirconia can vary from batch to batch. To test the effect of carbon loading on the modification, a special batch of 3 μm porous carbon-clad zirconia was obtained containing 5–6 monolayers of carbon vs. the normal 2–3 monolayers. Samples (0.1 g) of each batch were modified using the optimized chlorosulfonic acid conditions (0.1 mL chlorosulfonic acid, 20 h, and 25 °C). The sulfur loading was 0.18%w/w on the high C particle vs. 0.29%w/w on the normal particles. XPS analysis shows the same atomic percentage of sulfur ($\sim 3.7\%$) exists on the surface of both particles using either the thermal deposition or chlorosulfonic acid methods. Thus, the carbon loading does not affect the efficiency of the surface reaction. Rather, the lower sulfur loading is probably due to reduced surface area within the pores (Fig. 4). In an extreme case, the pores may become inaccessible due to carbon covering the entrance [34]. The lower accessible surface and the pore blockage are the reasons that carbon-clad zirconia is normally provided with 2–3 monolayer coverage [34]. However, some zirconia remains exposed at this coverage. To minimize the effect of carbon loading, all other experiments used particles from a specific batch.

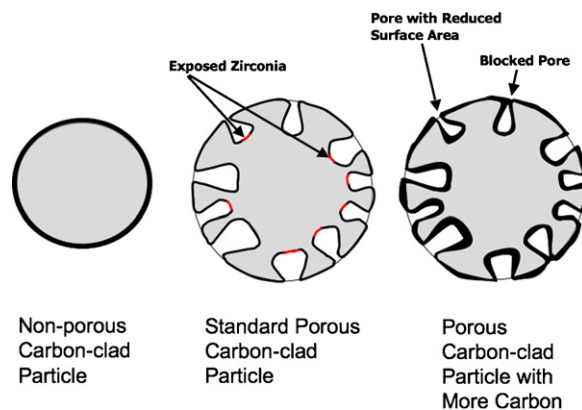


Fig. 4. Pores of carbon-clad zirconia material.

3.1.4. Oxidative modification of carbon-clad zirconia

Oxidation of graphitic carbon yields hydroxyl, carboxylate and ketonic functionalities [35]. Previous studies used permanganate to alter the retentive characteristics of graphitic carbon [35]. However, under all conditions studied (reaction times of 0.5–2 h and > 5 mM potassium permanganate), the potassium permanganate removed almost all the carbon ($< 6\%$ remaining) from the carbon-clad zirconia particles (both 2 μm nonporous and 3 μm porous) leaving essentially a zirconia phase, which is unsuitable for preparing agglomerated phases.

Alternatively, concentrated nitric acid at room temperature for 2 h did not oxidize the particles. Even 6 h reaction at 25 °C provided less than a 6% increase in oxygen content by XPS. Reacting the carbon-clad zirconia in boiling nitric acid (140 °C) resulted in a significant introduction of oxygen to the surface. Unfortunately, the XPS instrumentation available could not distinguish between hydroxyl, carboxylate and ketonic oxygen. Therefore, the surface oxidation was monitored indirectly, based on the adsorption of latexes to the surface. To ensure that the AS12A latex was strongly bound to the oxidized surfaces, the particles were then subjected to the stringent washing procedure used for diazonium modified particle. Direct XPS analysis of nitrogen was not possible as the strong static repulsion between these particles necessitated the use of charge suppression techniques, which significantly broadened the charged N1s peak at 404–406 eV assigned to the quaternary ammonium groups on the charge latexes. As a result, the amount of latex loading onto the particles was determined by monitoring the change in carbon loading by XPS before and after the addition of the latexes to the particles. As shown in Fig. 5, there is a rapid oxi-

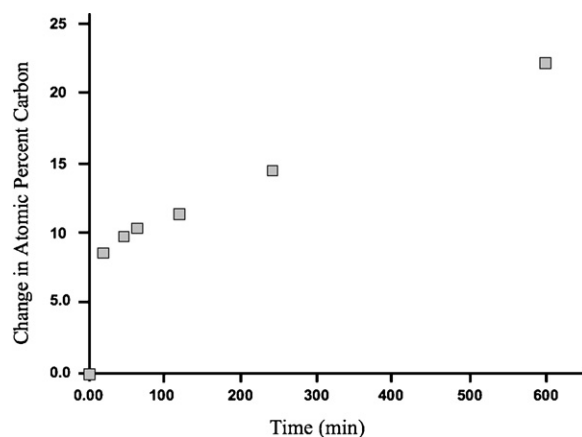


Fig. 5. Change in carbon content of modified particles after latex coating. Experimental conditions: 0.1 g of 2 μm carbon-clad zirconia particles; 50 mL HNO_3 ; 140 °C.

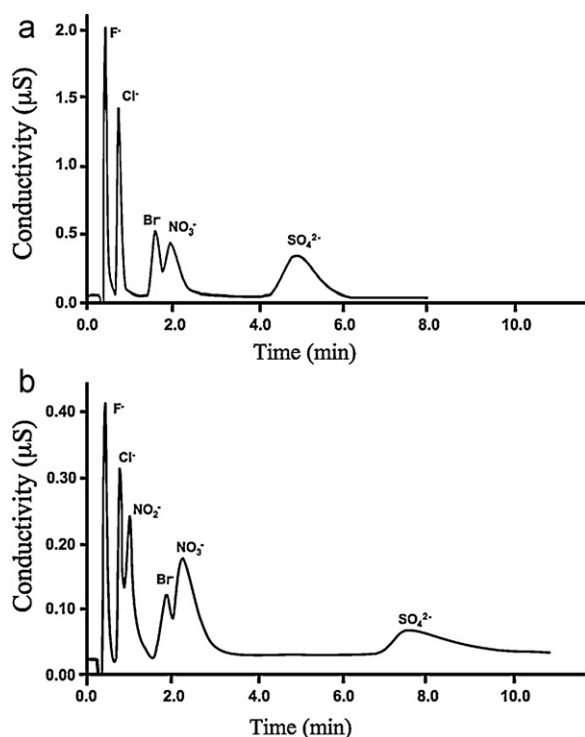


Fig. 6. Separations of ions on a chlorosulfonic acid modified column which was packed and then coated with latex. Experimental conditions: flow = 1.00 mL/min; pressure = ~2850 psi; eluent = 10 mM potassium hydroxide; sample volume = 10 μ L. (a) HPLC pump packed, analytes = 0.10 mM; (b) constant pressure pump packed, analytes = 0.025 mM.

dation of the carbon surface over the first 15 min in boiling nitric acid and, thereafter, a linear increase in the oxidation. However, after 2 h reaction, increasing amounts of zirconia were observed by XPS, indicating loss of the carbon cladding. Therefore, studies of agglomerated particles (Sections 3.2 and 3.3) were performed with carbon-clad zirconia that was treated with boiling nitric acid for 15–45 min.

3.2. Formation of agglomerated carbon-clad zirconia particles and packing

The cationic latex instantaneously adsorb onto carbon-clad zirconia pretreated using the chlorosulfonic acid and nitric acid oxidation procedures described above. The latex-to-particle ratio was optimized by placing loose carbon-clad zirconia particles in solution with a suspension of latex and monitoring the absorbance at 400 nm (*i.e.*, turbidity from the latex). Agglomerated particles had a reduced settling rate. Pretreated 2 μ m zirconia particles settled within 2 h, whereas agglomerated particles required centrifugation. Also, dry agglomerated particles exhibit strong sorption to the walls of the glass vial and mutual electrostatic repulsion from each other.

Initial packing studies were performed on the chlorosulfonic acid pretreated particles. Constant pressure pumps can produce higher efficiency and more stable packings than alternate methods [36,37]. This was borne out in our studies. Packing was performed either: with two constant flow pumps using manual control of the flow rate to maintain constant pressure; or with a pneumatically actuated constant pressure pump. Extrusion of the stationary phase showed that the constant pressure pump produced a tighter packed column. It was also observed that slightly more material was required to pack the column using constant pressure. Similarly, as shown in Fig. 6, the chromatographic efficiency on the col-

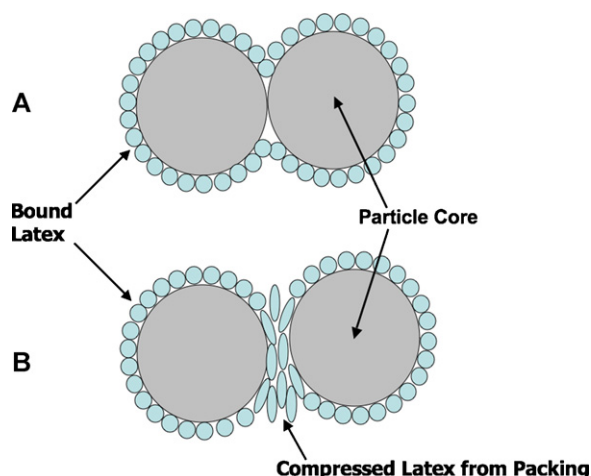


Fig. 7. Latex coatings of packed columns. (a) Column packed then latex added. (b) Latex added before column packing.

umn packed with the constant pressure pump (2.3×10^4 plates/m for bromide) was higher than the column packed with the constant flow pumps (1.5×10^4 plates/m). Columns packed with the constant pressure pump maintained efficiencies for over 3000 column volumes of flow and backpressures up to the 2.1×10^4 kPa (3000 psi) limit of the IC instrument.

Using nitric acid pretreated particles, the column was packed and modified using two different constant pressure methods. One method was latexing the particles and then packing the column. The second method was packing the column with the oxidized particles and then passing a latex suspension through the column. Fig. 7 illustrates the bed structure of both packing methods. When a stationary phase is suspended in solution and packed, the particles become, theoretically, as tight as possible. In the scenario where there is no latex attached to the particles before packing, the stationary phase particles butt up against one another. Thus, when the latex is added after packing, the latex attaches to the particles, but cannot adhere to the contact points (Fig. 7a). If the particles are coated in latex prior to packing, the latexes are compressed between the particles (Fig. 7b). As a result, the system will have a higher capacity, but the bed is not as stable and has increased backpressure. The performance of columns packed using these two procedures is discussed in Section 3.3.

Another consequence of adding the latex and then packing, is a slower packing process. Without latex, a 35 mm \times 4.6 mm column with 2 μ m non-porous particles, requires 1.5 h to pass 300 mL (6 reservoir volumes) of water using 4.5×10^4 kPa (6500 psi). Packing the same column with the same carbon to which latexes are bound, requires 20 h to pass the same volume of water.

3.3. Separations using the modified phases

Untreated carbon clad zirconia does not retain ($k \sim 0$) fluoride, chloride, nitrite, bromide, nitrate and sulfate. Addition of the latexes increases the capacity from 0 μ equiv./column to 5–9 μ equiv./column. Fig. 6a shows a separation of an ion mixture on a chlorosulfonic acid modified column which was packed and then latexed. The permeability of the column reduced by 16% upon addition of the latexes. Using KOH eluent, the separation efficiency and LOD for nitrate were 1.4×10^4 plates/m and 26 ppb, respectively. The retention time RSD was <1.2% over more than 1.0×10^4 column volumes. Fig. 6b shows a separation under the same conditions for a column packed with the constant pressure pump. As mentioned previously, the efficiency for

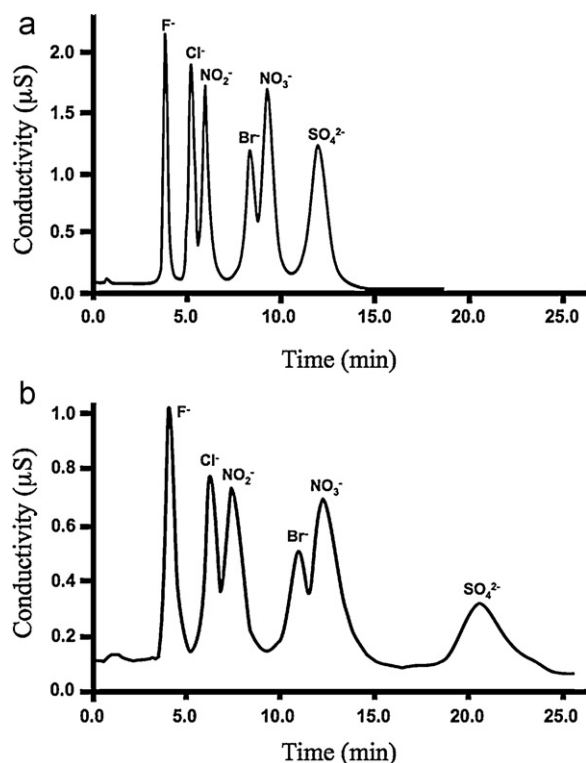


Fig. 8. Separations of ions on a nitric acid modified columns coated in latex. Experimental conditions: flow = 0.10 mL/min; pressure = 2930 psi; sample volume = 10 μL ; analytes = 0.025 mM; eluent = 20 mM KOH; boiling nitric acid 45 min; 2 μm non-porous carbon clad zirconia. (a) Particles packed then latexed. (b) Particles latexed then packed.

nitrate was 2.3×10^4 plates/m. The increased efficiency decreased the LOD to 14 ppb. The efficiencies of these carbon columns are lower than those observed for short silica monoliths [38] and short particle based silica columns [11]. However, the carbon columns show greater stability and can be used with hydroxide eluents.

Fig. 8 shows separations on nitric acid pretreated carbon-clad zirconia which was packed-then-latexed (Fig. 8a) or latexed-then-packed (Fig. 8b). The backpressure of the nitric acid treated columns was much greater than for the chlorosulfonic acid. The columns in Fig. 8 generated 1.9×10^4 kPa (2700 psi) and 2.0×10^4 kPa (2900 psi) at 0.10 mL/min, whereas the chlorosulfonic acid columns generated similar backpressure at 1.0 mL/min. The nitric acid treated particles coated with latexes before packing routinely resulted in $1.4\text{--}2.1 \times 10^3$ kPa (200–300 psi) higher backpressure than columns coated after packing.

Fig. 8b shows a minimum resolution of 1 and 2.4×10^4 plates/m for nitrate for the column latexed-then-packed. The packed-then-latexed column (Fig. 8a) has a minimum resolution of 1.15 and an efficiency of 4.6×10^4 plates/m. These efficiencies are an improvement over that of the chlorosulfonic acid column despite the longitudinal diffusion broadening caused by the low flow rate. Additionally, all peaks are less tailed (asymmetry factor = 1.1) than for the chlorosulfonic acid treated phases (asymmetry factor = 1.6, Fig. 7). The nitric acid columns are stable for >2500 column volume with a 1.5% RSD for retention time of sulfate using 5–75 mM hydroxide eluent. However, when ≥ 90 mM hydroxide was used, the retention of all peaks decreased by $\sim 3\%$ per hour, with the packed-then-latexed column showing somewhat better stability. Also, the backpressure of the system decreases by 30 psi/h when ≥ 90 mM hydroxide was used. Although, latex flowing through the lines was not observed by the conductivity detector, this loss in

pressure and capacity suggests a loss of the latexes from the column.

Reducing the nitric acid pretreatment time to 15 min resulted in lower latexing and lower flow resistance such that 0.3 mL/min could be used. Efficiencies were comparable to the chlorosulfonic acid columns (1.7×10^4 plates/m) but retention was lower ($k = 3.4$).

4. Conclusions

Modification of carbon-clad zirconia to be used as stationary phase supports for agglomerated anion-exchangers has been demonstrated using several methodologies. Diazonium chemistry and chlorosulfonic acid yielded the same capacity. Higher capacity agglomerated columns were produced using nitric acid pretreatment. Future work will explore the use of smaller cationic latexes to minimize the back pressure of agglomerated phases based on small support particles.

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