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Inorganic polymers as novel chromatographic stationary phase media

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Abstract

Aluminosilicate inorganic polymers (geopolymers) can be cheaply and readily prepared from dehydroxylated kaolinite clay and have been successfully demonstrated as a new type of stationary phase in the chromatographic separation of a mixture of three model aromatic compounds (a trisubstituted benzene, an ester and a pyrrole). Grinding and sieving to 105 μm produced powders with a similar particle size distribution and morphology to standard chromatographic silica, although smaller particle sizes and other morphologies can readily be produced. Three compositions of geopolymers were studied here and their performance was compared with conventional chromatography column packing media typically used for simple open-column and flash separations (silica and aluminas). Although the geopolymers were prepared under highly alkaline conditions, washing with acid to bring them to neutral pH before use was found to be unnecessary. The results obtained with the as-prepared geopolymer of standard composition showed it to possess a significantly greater number of plates/meter than any of the other column materials, including acidic and neutral aluminas and silica, and although more of the ester adsorbed to this column than on silica, in all other important respects the behavior of the geopolymer was comparable to silica and alumina. All the geopolymers were shown to be chemically stable to strong solvents such as ethanol, by comparison with conventional media such as silica and alumina, which were decomposed by ethanol; this suggests that unlike conventional silica, the geopolymer media may be cleaned with a strong solvent between runs without being degraded, and re-used. These results indicate that geopolymers represent a promising substitute for the commonly-used silica or alumina chromatography stationary phases, being simpler and cheaper to produce, more stable to strong solvents and showing comparable or better separation characteristics.

Keywords: A. Powders: chemical preparation; D. Clays; E. Functional applications; Column chromatography media

1. Introduction

Column chromatography is a ubiquitous technique for separating and purifying mixtures of chemical compounds. The mixture is placed on a stationary phase packed in a column and eluted with solvents of varying polarity that separate the components of the mixture and carry them out of the column [1]. The development of modern HPLC has placed increasing demands on the performance and chemical stability of the stationary phase, resulting in the development of new types of column material. These include metal oxides such as ZrO_2, TiO_2 and Al_2O_3, chosen for their good chemical stability [2], although there is some disagreement in the literature regarding the efficiency of using these metal oxides as stationary phases for HPLC due to problems with their surface chemistry [2,3]. The mesoporous silicas represent another class of materials that have attracted recent interest as stationary phases for advanced applications of HPLC. Surface modification of MCM-41 [4] and SBA-15 [5] with organic compounds or silanizing agents have been used to tailor the properties of these materials for specific separations [4,5]. An aluminosilicate version of MCM-41 calcined at 500 °C has also been investigated as a stationary phase for HPLC, and proved suitable for the separation of acid, neutral and basic compounds [6]. The multi-step synthesis of these modified mesoporous silicas is expensive and has led to an alternative approach, the silanization of chromatographic silica itself, for example with phenyl-containing silanes or fluorinated silanes [7]. The resulting materials can be tailored for specific separations, and are more stable to solvent dissolution than silica itself, especially if subjected to microwave treatment [7], but they are considerably more expensive than chromatography grade

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silica gel and moreover, the bonded-phase can be mechanically damaged thereby revealing a naked silica surface through active phase “bleeding” [8]. Additionally, basic compounds such as amines can be degraded by, or irreversibly bind to, the acidic silanol groups present on the stationary-phase surface thereby reducing its wide applicability for all functional group classes [9].

Since all these new stationary phases require expensive multi-step syntheses and have other drawbacks, silica gel remains one of the most commonly used stationary phases for column chromatography, especially for simple open-column separations, despite suffering from several drawbacks, one of the most serious being its behavior in highly polar solvents such as 100% ethanol, which strips out the silica and destroys the column material. Although silica gel is sufficiently cheap for one-time use, contamination of the eluted sample with silica can be a serious problem. For this reason, the most polar solvent that can practically be used with silica is approximately 20% methanol in 80% dichloromethane. A column packing medium suitable for use with more polar solvent mixtures containing up to 50% methanol would be more appropriate for many separation procedures.

Alumina is another relatively cheap column packing medium which can be obtained in acidic, neutral or basic forms, depending on its manufacturing conditions and the supplier. For this reason, its performance in a chromatographic column tends to be variable, even though it is chemically more robust to polar solvents than silica gel [1].

The aim of the present work was to develop a simple, inexpensive stationary phase as a substitute for open-column or flash separations where silica or alumina would commonly be used, with comparable or superior chromatographic performance and more chemical stability to polar solvents than silica. The materials chosen for this study were aluminosilicate inorganic polymers, also known as geopolymers, which can be cheaply and readily synthesized and may display the best properties of silica and alumina media. These materials are X-ray amorphous compounds consisting of randomly organized three-dimensional arrangements of tetrahedral silicate and aluminate units joined through common oxygen atoms [10]. Charge balance in the tetrahedral aluminate units is achieved by the presence of (usually) monovalent alkali ions [10]. Geopolymers are readily prepared by mixing a solid aluminosilicate such dehydrated kaolin clay with an alkali metal silicate under highly alkaline conditions [10], with the mixture setting to a hard mass at ambient temperatures. The setting properties of aluminosilicate geopolymers are dependent on their composition, particularly their SiO_2/Al_2O_3 molar ratio, which is normally stated to have an optimum value of about 3, although geopolymers with both higher and lower silica contents have been shown to be viable [11]. In the present study, three geopolymer compositions, normal, high-silica and high-alumina were used. Since the as-prepared materials are highly alkaline, the experiments were conducted on geopolymers that had been brought to approximately neutral pH by titrating with acid, with the non-neutralized materials included for comparison.

In the present work, the material properties of the inorganic polymers (particle morphology and particle size distribution) were tailored to correspond closely to the bulk chromatography-grade silica and alumina for which they were intended to substitute, but much smaller particle sizes and other particle shapes can readily be produced by varying the grinding procedure. The performance of both the neutralized and as-prepared inorganic polymers as stationary chromatography phases was compared with commercial chromatography-grade silica and both acidic and neutral chromatographic alumina on the basis of the separation of three model compounds, a benzenoid (1,3,5-tribromobenzene), an ester (ethyl cinnamate) and a pyrrole (indole).The chemical and physical characteristics of chromatographic media exert a large effect on their performance, since their chemistry dictates the degree of binding of the analyte and therefore its retention, while the particle morphology influences the packing characteristics and flow of the solvents through the column. The aim of the present study was to develop a silica substitute as a batch chromatography stationary phase for open-column or flash separations, rather than for more advanced HPLC applications where these features are of greater importance. In this study, the physical, chemical and chromatographic characteristics of several inorganic polymers of differing composition pre-washed in a very polar solvent (ethanol) were determined, and their chemical stability in ethanol was measured by analysis of the silica and alumina stripped out by the solvent.

2. Experimental

2.1. Sample preparation

The sodium geopolymers were prepared from New Zealand 1:1 layer lattice halloysite clay (Imerys Premium Grade) dehydroxylated at 600 °C overnight. This was mixed with an aqueous solution of NaOH (BDH reagent grade) and sodium silicate solution (FERNZ Chemical Co, Type D, $Na_2O/SiO_2=0.48$, solids content = 41.1 mass %) to give a “normal” geopolymer composition shown in Table 1. The high-silica composition (Table 1) was obtained by the incorporation of additional silica (fine silica fume), while the high-alumina composition (Table 1) was obtained by the addition of amorphous ρ-alumina (Alphabond 300, Alcoa). After thorough mixing, the geopolymers were cured in covered plastic molds at 80 °C for 6 h, then uncovered and oven-dried at 40 °C overnight. The hardened blocks were broken into pieces and ground in a vibratory mill (Bleuler, Switzerland) fitted with a tungsten carbide pot and milling rings and sieved to pass a 105 µm mesh. 50 g aliquots of each of the geopolymer powders were washed with 0.1 M HCl (5 mL), calculated on the basis of separate titration experiments to bring the pH to neutral, filtered through a Buchner funnel, washed thoroughly with ethanol and dried. The geopolymer powders were again sieved before being used in the chromatography experiments.

Table 1
Molar compositions of the inorganic polymers studied here.

Geopolymer type	SiO_2/Al_2O_3	Na_2O/SiO_2	H_2O/Na_2O
Normal	3.54	0.36	10.76
High-silica	6.40	0.35	10.08
High-alumina	1.31	0.67	10.37

For comparison, chromatography-grade silica (Silicycle Quebec, SilicaFlash grade F60, 40–63 μm), acidic alumina (Merck 150, Type T) and neutral alumina (Brockman Grade 1) were also run.

2.2. Sample characterization

The particle size distributions of all the samples were determined using a Malvern Mastersizer Model 2000 and the particle morphologies were determined by SEM (Quanta 450) at an operating voltage of 30 kV. The formation of the geopolymers and the effect of acid treatment was determined for all the samples by X-ray powder diffraction (Philips PW1700 computer-controlled diffractometer with a graphite monochromator using Co K_α radiation) and both ^{27}Al and ^{29}Si solid-state MAS NMR at a magnetic field of 11.7 T using a Bruker Avance III 500 spectrometer operating at a ^{27}Al frequency of 130.24 MHz and a ^{29}Si frequency of 99.29 MHz. Since well-prepared geopolymers are X-ray amorphous, the NMR experiments are essential to determine any changes in the state of the aluminate and silicate units caused by exposure to the chromatography solvents. The 11.7 T ^{27}Al solid-state spectra were acquired using a 4 mm Doty MAS probe with a silicon nitride rotor spun at 10–12 kHz, a 1 μs pulse and a 1 s recycle time, the spectra referenced with respect to $Al(H_2O)_6^{3+}$. The ^{29}Si spectra were acquired with a 5 mm Doty MAS probe and a zirconia rotor spun at ~6 kHz. The excitation pulse for ^{29}Si was 7 μs with a recycle time of 30 s and the spectra were referenced with respect to tetramethyl silane (TMS).

The effect of a highly polar solvent (ethanol) on all the stationary media was determined by magnetically mixing 1 g of the solid with 6.6 mL of the solvent for 3.5 h, these conditions being chosen to mimic the typical conditions to which the stationary phase is subjected in the present chromatography experiments. The liquid was then centrifuged off, filtered through a 0.5 μm microfilter, diluted 100 times with deionised water and analyzed for Si and Al by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using a modified version of method 3120B.

2.3. Chromatography

The chromatographic behavior of the ethanol-washed geopolymers, chromatographic silica and chromatographic alumina, was determined by separating a mixture of three model aromatic compounds, a benzenoid (1,3,5-tribromobenzene, Aldrich), an ester (ethyl cinnamate, BDH) and a pyrrole (indole, J.T. Baker) on a self-packed column. All solvents used for chromatography were HPLC-grade (Fisher Scientific). All solvents and test compounds were used as received without further purification. Standard mixtures of the three test compounds were prepared containing 20 mg 1,3,5-tribromobenzene in 20 mL hexane, 20 mg ethyl cinnamate in 2 mL hexane and 10 mg indole in 2 mL of hexane. The chromatography was carried out using a mixture of 1 mL of each of these solutions diluted by adding 2 mL of hexane to give final concentrations of 0.2, 2 and 1 mg/mL of 1,3,5-tribromobenezene, ethyl cinnamate and indole, respectively.

The chromatography was carried out using a model 1120 compact liquid chromatograph (Agilent Technologies) fitted with an unheated stainless steel column (250 mm x 4.6 mm ID) and equipped with a single-wavelength UV detector set to 287 nm and controlled by E/Z Chrom Elite software (Agilent Technologies). The stationary phase was introduced into the column as a slurry and allowed to pack under gravity before being pressurized to ensure full packing of the column. The instrument was programmed to start the experiment by injection of 20 μL of the test mix onto the column that was being eluted (flow-rate of 1 mL/min) with 100% hexane, changing over 17 min. to 50% ethyl acetate for 5 min, followed a rapid return to 100% hexane for the remainder of the 30 min run to allow column re-equilibration. Each experiment was performed in triplicate, and establishment of compound identity was achieved by comparison of the retention times of the standards run separately. Calculation of column efficiency (plates/meter), peak resolution, asymmetry and retention factors were calculated automatically using the US Pharmacopeia algorithms in the E/Z Chrom Elite software for performing data analysis. The retention time of the 1,3,5-tribromobenzene was used as an unretained compound marker.

3. Results and discussion

3.1. Characteristics of the materials

A selection of typical XRD traces of the powders is shown in Fig. 1. The as-prepared normal and high-silica geopolymers (Fig. 1a and b) all show the broad background amorphous feature typical of a well-formed geopolymer [10] with two sharp reflections arising from the crystalline silica polymorphs quartz and cristobalite present as impurities in the original clay. By contrast, the high-alumina geopolymers (Fig. 1c) are composed of crystalline $Na_2Al_2Si_{1.85}O_{7.75}.H_2O$ (JCPDS file no. 38-241) together with a small amount of amorphous geopolymer phase and the residual quartz and cristobalite reflections. The formation of crystalline phases in high-alumina geopolymers has previously been reported and is suggested to arise from modification to the structure to accommodate the violation of Lowenstein's Rule in these compositions [11]. The XRD patterns of all these geopolymers are unchanged by washing with acid. The XRD trace of the neutral chromatography alumina (Fig. 1d) indicates that this is solely γ-alumina (JCPDS file no. 10-425), whereas the acidic alumina also contains small amounts of other transition aluminas, in addition to γ-alumina. The XRD trace of the chromatography silica (Fig. 1e) shows this to be totally amorphous. The XRD traces of all these samples remained unchanged after the chromatography experiments (data not shown).

Typical solid-state ^{27}Al and ^{29}Si MAS NMR spectra are shown in Figs. 2 and 3, respectively. The chemical shifts of the Al spectra indicate the coordination number of the aluminum, which in well-formed geopolymers is solely 4; this is the case for the normal and high-silica geopolymers, in both the as-prepared and acid-treated forms (Fig. 2d), in which the chemical shift is representative of a typical tetrahedral chemical environment [12].

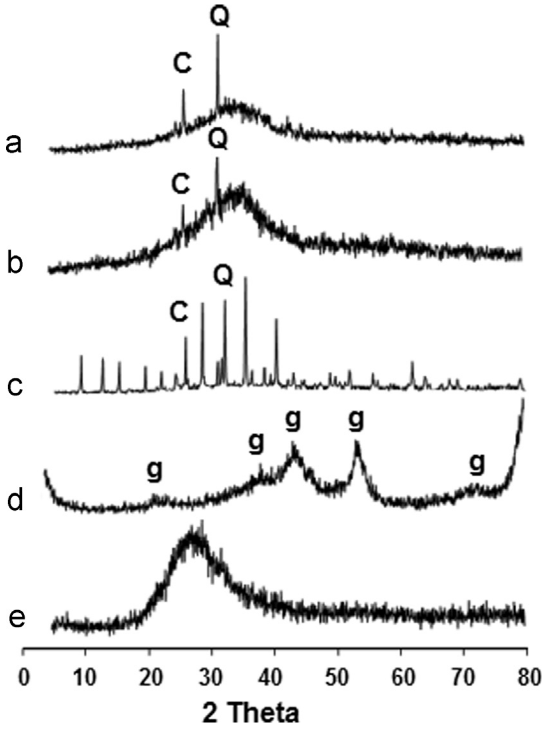

Fig. 1. Representative XRD traces for the ethanol-washed geopolymers and chromatography silica and alumina. (a) normal geopolymer, as-prepared and acid-washed, (b) High-silica geopolymer, as-prepared and acid-washed, (c) High-alumina geopolymer, as-prepared and acid-washed, (d) neutral chromatography alumina, (e) chromatography silica. Key: Q=quartz (JCPDS file no. 33-1161), C=cristobalite (JCPDS file no. 11-695), g=gama-alumina (JCPDS file no.10-425). Unmarked peaks in pattern (c) are from $Na_2Al_2Si_{1.85}O_{7.75} \cdot H_2O$ (JCPDF file no. 38-241).

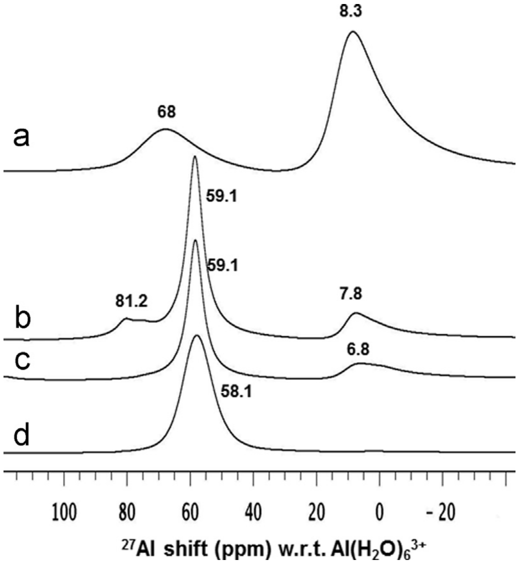

Fig. 2. Representative 11.7 T ^{27}Al MAS NMR spectra. (a) Neutral chromatographic alumina, (b) High-alumina geopolymer as-prepared, (c) High-alumina geopolymer acid-washed, (d) Normal and high-silica geopolymers, both as-prepared and acid-washed.

By contrast, the high-alumina geopolymers (Fig. 2 b and c) contain, in addition to the major tetrahedral resonance at about 59 ppm, a smaller, broader octahedral resonance at 7–8 ppm, corresponding to residual octahedral aluminum resulting from incomplete geopolymer formation. The as-prepared high-alumina geopolymer also contains evidence of additional tetrahedral sites at 81 ppm (Fig. 2b), corresponding to small amounts of impurity phases that are removed by acid treatment (Fig. 2c). The neutral and acidic chromatography aluminas contain two broad Al resonances (Fig. 2a), with the octahedral sites at 8.3 ppm predominating; this spectrum is typical of γ-alumina and the transition aluminas [12].

The ^{29}Si MAS NMR spectra of the as-prepared and acid-treated geopolymers (Fig. 3d) show a single broad resonance typical of these amorphous materials [12], whereas this resonance in the high-alumina samples is much narrower (Fig. 3c), consistent with their greater crystallinity. The high-silica samples (Fig. 3b) contain, in addition to the geopolymer resonance at about −88ppm, another resonance at about −92 ppm, indicating the presence of other species richer in silica; this is as expected for a silica-rich composition. The spectrum of chromatographic silica (Fig. 3a) contains the resonance of pure silica at −111 ppm, together with another smaller resonance at about −102 ppm indicating the presence

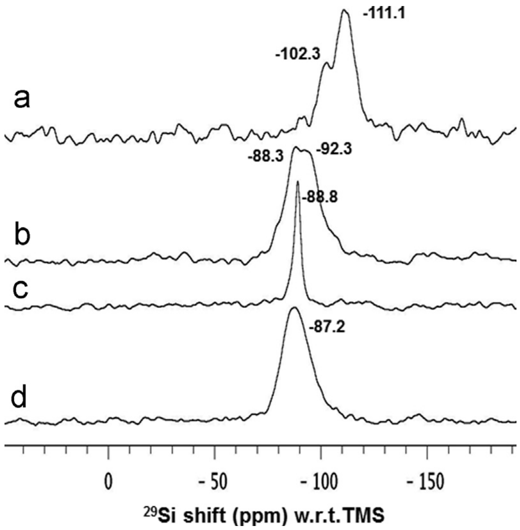

Fig. 3. Representative 11.7 T ^{29}Si MAS NMR spectra. (a) Chromatographic silica, (b) high-silica geopolymer, as-prepared and acid-washed, (c) High-alumina geopolymer, as-prepared and acid-washed, (d) Normal geopolymer, as-prepared and acid-washed.

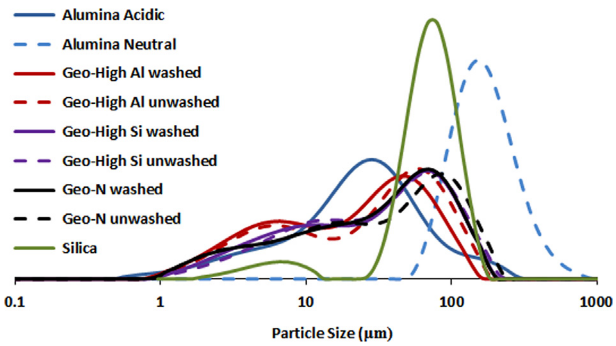

Fig. 4. Particle size distributions of the geoplymers, chromatographic silica and alumina.

of silanol groups [12]; this is not unexpected in view of the method of synthesis for these silicas.

The particle size analyses (Fig. 4) show all the geopolymer samples have similar bimodal size distributions to the chromatographic silica and acidic alumina, the maximum in the distribution curve occurring at ~70 μm, whereas the neutral alumina particle size is slightly larger (~140 μm).

A selection of representative SEM micrographs of the powders is shown in Fig. 5. The as-prepared geopolymer of normal composition (Fig. 5a) shows larger particles with rounded edges resulting from the grinding process, decorated on the surface with much smaller grinding debris. Washing these with acid leaves the morphology unchanged, and similar morphology is observed after the chromatography experiment. Similar larger grains decorated with small particles of grinding debris are seen in both the high-silica and high-alumina geopolymers (Fig. 5 b and c respectively). The smaller particles in the geopolymer samples are responsible for the tails in the bimodal particle size distributions (Fig. 4). By contrast, the chromatography-grade silica (Fig. 5d) consists of particles with faceted edges, suggestive of a dried gel, whereas both the chromatography aluminas are composed of more rounded particles (Fig. 5e and f), especially the neutral alumina (Fig. 5f) of which the particles are also larger and more uniform, confirming the particle size analysis results (above). Since the morphology of the column packing material is an

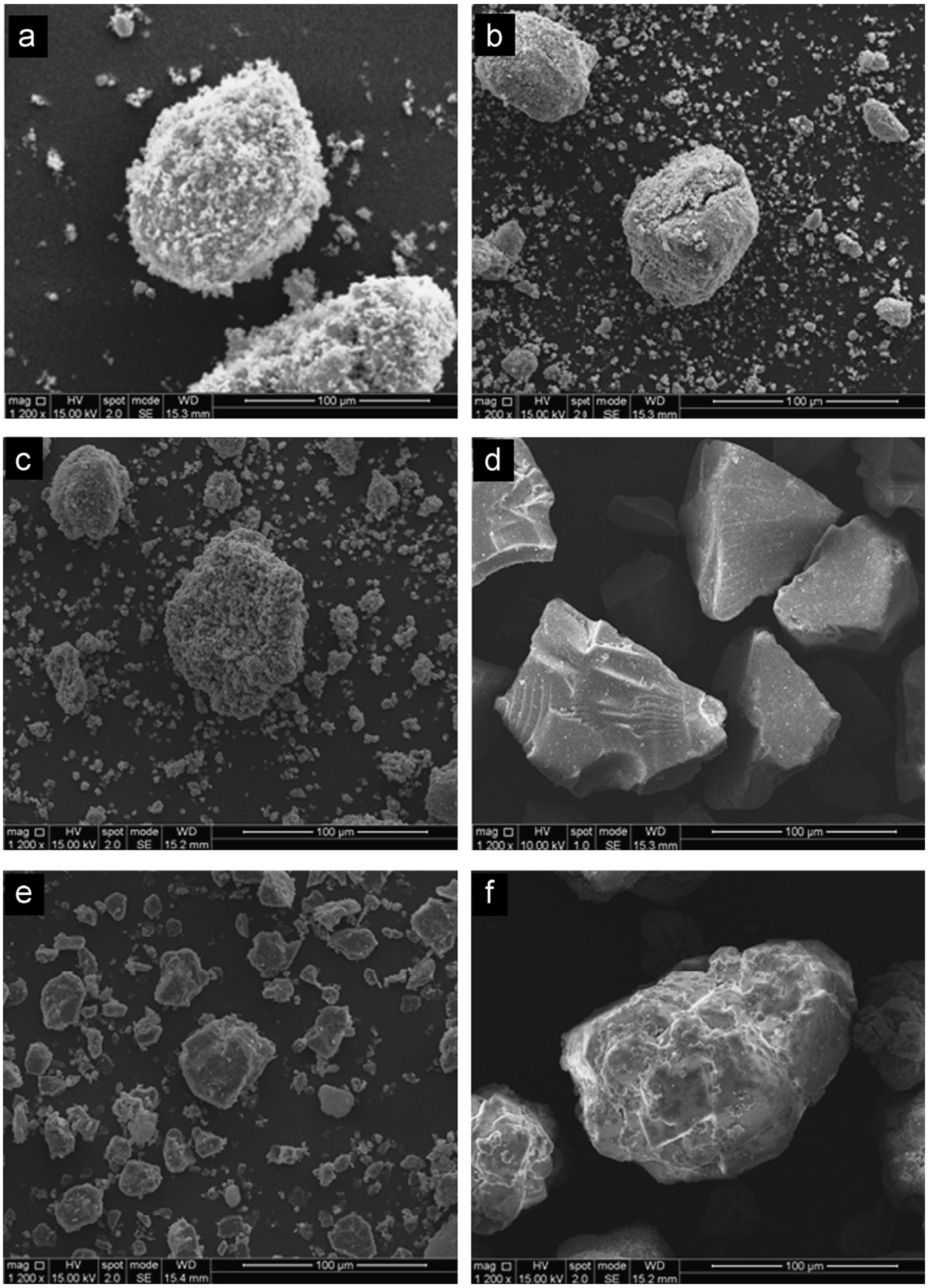

Fig. 5. Representative SEM micrographs of the geopolymers and chromatographic silica and alumina. (a) as-prepared normal geopolymer, (b) as-prepared high-silica geopolymer, (c) as-prepared high-alumina geopolymer, (d) silica, (e) acidic alumina, (f) neutral alumina.

important factor in determining the path of the solvent through the column, the similar angular morphology of the geopolymers to that of chromatographic silica, and the presence of smaller particles which fill the voids between suggests that in terms of solvent retention, these materials should behave similarly, whereas the rounded morphology and regular size distribution of the aluminas should permit a more direct passage of solvent through the column.

3.2. Chromatography

Representative chromatograms testing the various stationary phases (Fig. 6) show that the as-prepared ethanol-washed geopolymer column packing material of normal composition (Fig. 6a) gives comparably good separation of the three model compounds as the conventional column packing materials alumina (Fig. 6b) and silica (Fig. 6c). Similarly good separation was obtained with the ethanol-washed high-silica and high-alumina geopolymers, in both the as-prepared and acid-washed forms.

Greater detail about the comparative performance of the column packing materials was extracted from the numerical parameters from the chromatograph, shown graphically in Fig. 7. The parameter of plates/meter shown in Fig. 7(a) is of particular note; this is significantly greater for the as-prepared geopolymer than for the other geopolymers, and most importantly, chromatography silica and the two aluminas. Acid-treatment of the geopolymers degrades their performance in terms of this parameter, particularly in the case of the normal geopolymer. This is an important result from a practical point of view, as it suggests that one of the steps in the preparation procedure is unnecessary.

The area of the analyte peaks (Fig. 7b) is another parameter of interest since it provides an indication of the degree of irreversible absorption of the analytes to the column stationary phase. In this case, silica performs better than all the geopolymers, which show

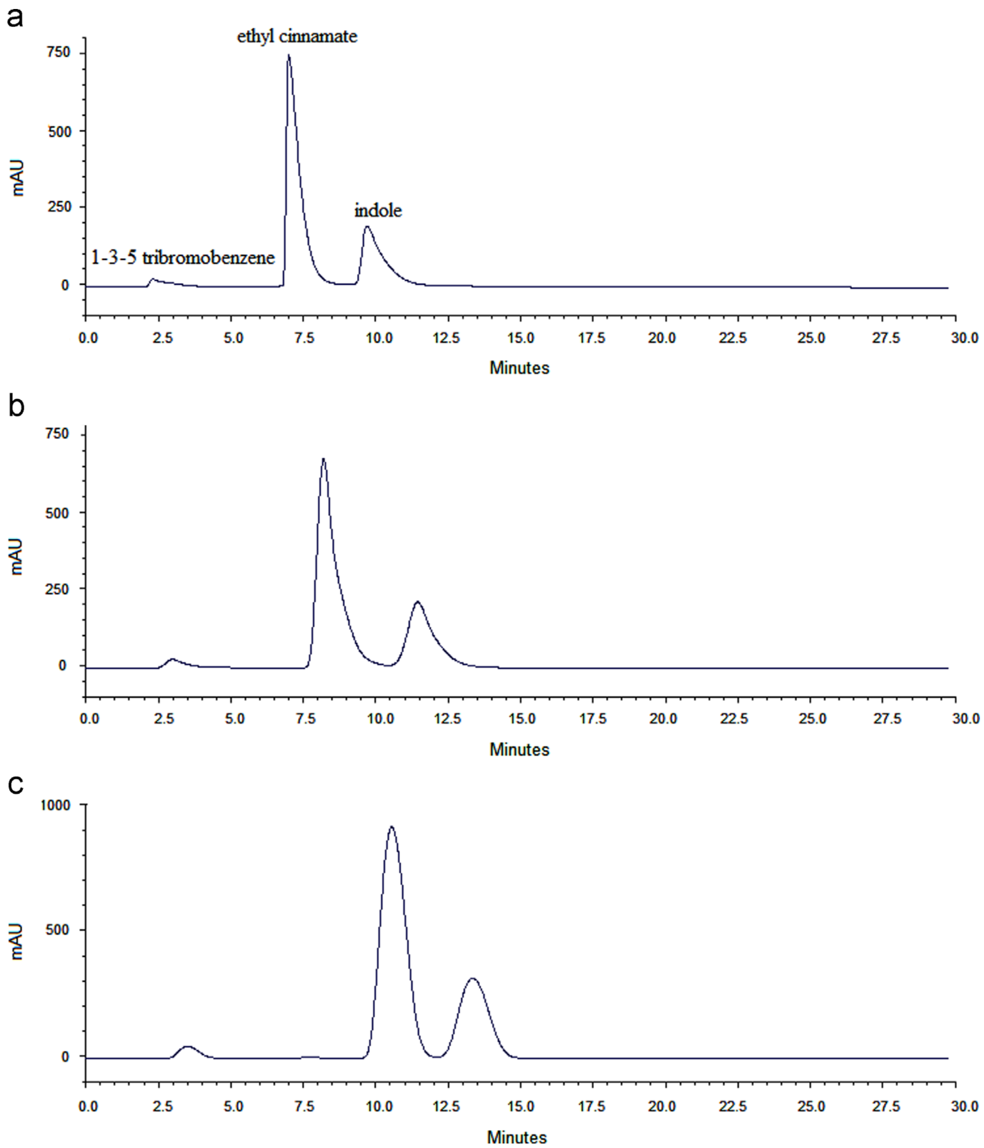

Fig. 6. Representative chromatograms for the three model compounds separated using different column packing materials. (a) normal geopolymer, as-prepared, (b) acidic alumina, (c) silica.

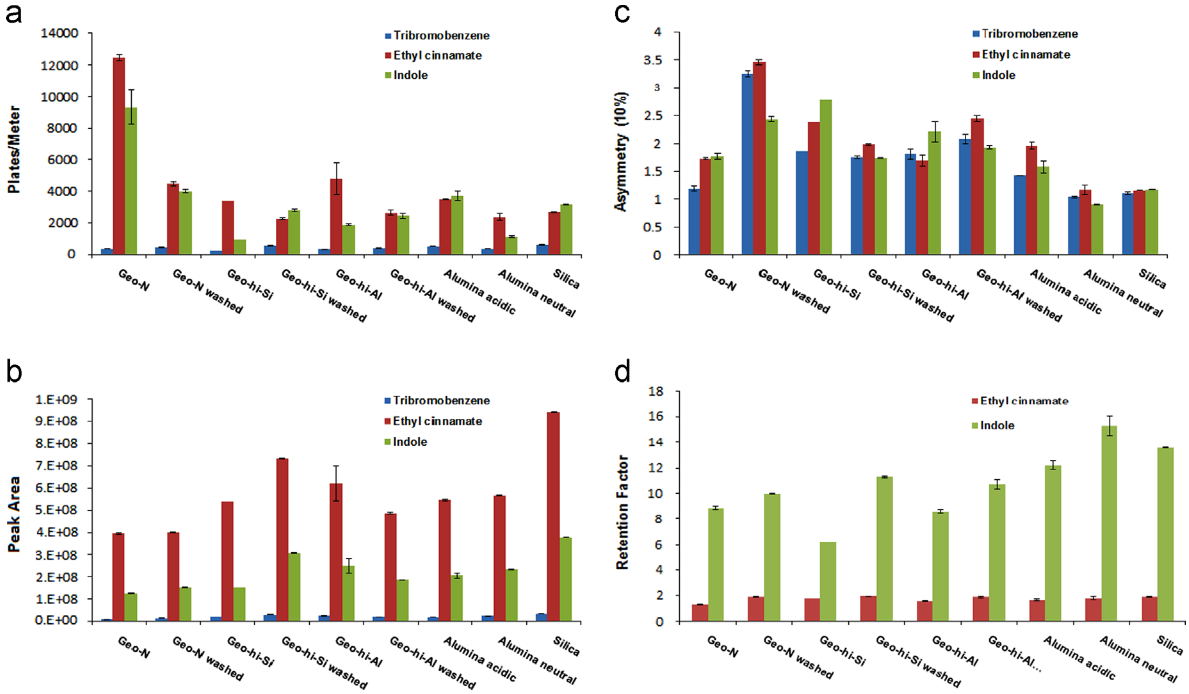

Fig. 7. Graphical representation of the chromatographic parameters for the three model compounds separated on the various column packing materials. (a) number of plates/meter, (b) retention time, (b) peak area, (c) peak asymmetry and (d) retention parameter *k*.

an approximately similar degree of absorption to the aluminas, apart from the acid-washed high-silica geopolymer which displays more silica-like behavior (Fig. 7b).

The asymmetry of the peaks (Fig. 7c) shows that the most symmetrical peaks are those from the silica column and neutral alumina; the asymmetry of the as-prepared normal geopolymer is similar to that of acidic alumina, whereas all the peaks of other geopolymers are relatively less symmetric. The peak asymmetry is a less important parameter in the present case, since all the peaks are sufficiently resolved that they are not interfered with by this tailing effect. It should be noted that no attempts were made to optimize the particle shape and size distribution of the geopolymers and therefore peak asymmetry is to be expected in this study, and should be less important in further development of the stationary phases.

A further parameter defining the behavior of the stationary phases is the peak retention factor k ($k=[t_{(r)}-t_{(m)}]/t_{(m)}$ where $t_{(m)}$ is the unretained retention time and $t_{(r)}$ is the retention time of a species) of the column stationary phase since this includes a number of factors related to the column dimensions, packing density, etc. in addition to the properties of the stationary phase. In the present experiments, the time at which the 1,3,5-tribromobenzene appears is taken as $t_{(m)}$. The behavior of k for the other two analytes on each of the column packing materials is shown in Fig. 7d. Values of k of 5–10 represent the best trade-off between time spent adsorbed to the stationary phase and the length of time required for the full separation of the analytes. Fig. 7d shows that all the column packing materials fall within this range for the separation of indole, but all, including silica and the aluminas, have k values >5 for ethyl cinnamate. Thus, the separation characteristics of all the stationary phases as reflected in their retention factors are similar.

Table 2
Al and Si contents of ethanolic solutions after exposure to the stationary phases, determined by ICP-OES.

Sample	Al concentration (mg/L)	Si concentration (mg/L)
Normal geopolymer	nd*	nd
Normal geopolymer acid-washed	nd	nd
High-Si geopolymer	nd	nd
High-Si geopolymer acid-washed	nd	nd
High-Al geopolymer	nd	2.0
High-Al geopolymer acid-washed	nd	2.2
Silica	nd	2.7
Alumina neutral	nd	2.4
Alumina acidic	3.6	nd

*nd–denotes below the level of detection of this method (0.5 mg/L for Al and 2.0 mg/L for Si).

3.3. Chemical stability of the media in a strong solvent (ethanol)

The Si and Al contents of ethanolic solutions resulting from exposure of the various column materials to ethanol are shown in Table 2. Although the need to dilute the ethanolic solutions in water for ICP-OES measurements resulted in limits of detection of 0.5 mg/L for Al and 2.0 mg/L for Si, the results show that within these limits, the normal and high-silica geopolymers are unaffected by ethanol, whereas some Si is removed from the high-alumina geopolymers, possibly reflecting their atypical crystalline structure. By comparison with the "normal" geopolymers, significant leaching of Si from the silica occurs, and also from the neutral alumina, suggesting the presence of a silica impurity in this material. Acidic alumina is even less stable to ethanol, being the only material in this group to lose Al (Table 2). Thus, the most promising of the new stationary phases (as-prepared "normal" geopolymer) is superior to both conventional silica and alumina in its greater chemical stability to a strong polar solvent.

4. Conclusions

Aluminosilicate inorganic polymers (geopolymers), cheaply and readily prepared from dehydroxylated kaolinite clay, were compared with chromatographic stationary phases (silica and two aluminas) commonly used for simple and open-column separations. For comparative purposes, the geopolymers were processed to possess similar particle size distributions and morphologies to the commercial chromatography silica and aluminas used here, but in future applications they can readily be prepared in smaller particle sizes and shapes. Additionally, although they were synthesized under highly alkaline conditions, they did not require washing with acid to bring them to neutral pH before use. Three compositions of geopolymers were studied here; those containing high concentrations of silica and high amounts of alumina behaved more poorly than a "normal" geopolymer composition in the chromatographic separation of a mixture of three aromatic test compounds. The results obtained with the as-prepared "normal" geopolymer washed in a polar solvent before use (ethanol) showed a significantly greater number of plates/meter than any of the other column materials, including the acidic and neutral aluminas and silica, and although more of the ester was irreversibly adsorbed on this column than on silica, in all other important respects the behavior of the geopolymer was comparable to silica and alumina. In addition, all the geopolymer media show greater chemical stability to strong polar solvents (ethanol) than the commercial silica and alumina, suggesting their suitability for multiple uses after cleaning with a strong solvent between runs. All these results indicate that geopolymers represent promising substitutes for silica and alumina, performing as well or better than the conventional stationary phases in the applications for which they are commonly used (open-column or flash separations). Geopolymers also have the advantages of being simpler and cheaper to synthesize than silica, or the more complex bonded-stationary phases being developed for advanced HPLC, therefore combining some of the best attributes of alumina and silica.

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