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Poly(glyceryl monomethacrylate-co-ethylene glycol dimethacrylate) monolithic columns with incorporated bare and surface modified gluconamide fumed silica nanoparticles for hydrophilic interaction capillary electrochromatography

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ABSTRACT

This research article presents the preparation and characterization of monolithic capillary columns with incorporated bare fumed silica nanoparticles (FSNPs) and surface coated gluconamide FSNPs and their subsequent use in hydrophilic interaction capillary electrochromatography (HI-CEC) of small relatively polar solutes. The monolithic support was based on the in situ polymerization of glyceryl monomethacrylate (GMM) and ethylene glycol dimethacrylate (EDMA) yielding the poly(GMM-co-EDMA) monolith for the incorporation of bare and gluconamide-FNSPs. The poly(GMM-co-EDMA) monolith functioned as a true "support" for both types of polar FSNPs "stationary phases". In other words, monolithic capillary columns with "FSNPs stationary phases" were obtained in the sense that the contribution of the monolith proper to solute' retention was at its minimum. The gluconamide-FSNPs were obtained by reacting the FSNPs with the polar organosilane *N*-(3-triethoxysilylpropyl) gluconamide either by a pre- or on-column approach yielding p-gluconamide-FSNPs or o-gluconamide-FSNPs, respectively. While the p-gluconamide-FSNPs was coated by an oligosiloxane gluconamide layer as revealed by thermogravimetric analysis, the o-gluconamide-FSNPs are thought to be covered with a monomeric layer of gluconamide ligands as was manifested by the higher plate number obtained on the latter than on the former gluconamide-FSNPs incorporated monolithic columns. In the on-column modification process of FSNPs, the reaction was performed in a closed system whereby atmospheric water vapor are not available to cause the polymerization of the trifunctional organosilane *N*-(3-triethoxysilylpropyl)gluconamide. Also, the fact that the o-gluconamide-FSNPs incorporated monoliths were made from bare-FSNPs incorporated monoliths may indicate that the bare FSNPs were better dispersed into the monolithic matrix than the p-gluconamide-FSNPs, a condition that might have further contributed to the lower plate count obtained on p-gluconamide- than o-gluconamide-FSNPs incorporated monolithic columns. Overall, o-gluconamide-FSNPs stationary phases and to a lesser extent bare-FSNPs stationary phases proved useful in HI-CEC of small polar solutes, including DMF, formamide, thiourea, some phenols and nucleobases.

1. Introduction

Due to their relatively high surface-to-volume ratio and unique surface adsorption properties, nanomaterials have favored efficient mass transfer in chromatographic analyses and yielded different separation selectivities, respectively [1,2]. Among other things, both characteristics have facilitated the rapid exploitation of nanomaterials in the field of separation science [3–5] as well as in other fields of the life sciences [6,7] during recent years. To exploit nanomaterials in flow systems such as HPLC and CEC, good support media with favorable flow characteristics are required which can securely hold the nano sized particles to be used as nano-doped stationary phases in chromatographic and electrochromatographic separations. In this regard, polymeric monoliths can be viewed as ideal support matrices for the incorporation of nano-entities as they can be conveniently prepared by in situ polymerization in columns and channels of all sizes, which have favorable flow characteristics, using readily available monomers and crosslinkers [5,8–10].

Abbreviations: ACN, acetonitrile; AIBN, 2,2′-azobis(isobutyronitrile); DMSO, dimethyl sulfoxide; EDMA, ethylene glycol dimethacrylate; FSNPs, fumed silica nanoparticles; GMM, glyceryl monomethacrylate

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Silica nanoparticles in the form of fumed silica nanoparticles (FSNPs) have distinctive properties including high surface area, good adsorption capabilities and mechanical stability which facilitated the development of FSNPs incorporated monolithic stationary phases [3,11]. In addition, these FSNPs possess silanol groups on their surface through which various ligands can in principle be covalently bonded to the FSNPs surface to yield a variety of chromatographic stationary phases. In fact, both unmodified and surface modified FSNPs have been recently introduced for the successful preparation of polymeric monolithic stationary phases with incorporated nanoparticles. For instance, Aydoğan and El Rassi have recently developed a poly(glyceryl monomethacrylate-co-ethylene glycol dimethacrylate) stationary phase with incorporated bare FSNPs for hydrophilic interaction liquid chromatography (HILIC) [3]. In addition, these researchers have prepared polymethacrylate based monolithic columns with covalently incorporated modified octadecyl FSNPs for reversed phase chromatography. The FSNPs were first modified with 3-(trimethoxysilyl)propylmethacrylate to yield a "hybrid" methacryloyl FSNPs monomer (MFSNP) and subsequently they were in situ copolymerized with glyceryl monomethacrylate (GMM) and ethylene glycol dimethacrylate (EDMA) in the presence of a binary porogenic solvent composed of cyclohexanol and 1-dodecanol. The monolith thus obtained was grafted with octadecyl ligands by reacting the silanols of the incorporated FSNPs with octadecyldimethylchlorosilane. A wide range of analytes including alkylbenzenes, aniline derivatives, phenolic compounds and six standard proteins were separated on the prepared monolithic column [4]. Furthermore, a novel boronic acid-FSNPs incorporated hybrid monolithic stationary phase has been prepared by the in situ copolymerization of MFSNPs, 3-chloro-2-hydroxypropyl methacrylate and EDMA in a binary porogenic solvent mixture consisting of cyclohexanol and dodecanol. The hydrophobic/affinity interactions of the prepared monolithic column have been examined by nano-liquid chromatography in the separations of alkylbenzenes, proteins and glycoproteins [11]. As it has been described in the just-mentioned references, the incorporation of bare or modified FSNPs yielded promising monolithic columns which concurrently utilize the unique properties of both the FSNPs and the monolithic support matrix.

This paper focuses on the development of polymethacrylate based monolithic stationary phases with incorporated bare (i.e., unmodified) and surface modified FSNPs with a polar organosilane, namely *N*-(3-triethoxysilylpropyl)gluconamide, for use in hydrophilic interaction-capillary electrochromatography (HI-CEC). The surface modification of the FSNPs was carried out either by pre-column or on-column functionalization reactions with *N*-(3-triethoxysilylpropyl)gluconamide to yield the so-called p-gluconamide-FSNPs or o-gluconamide-FSNPs, respectively, where the notations p- and o- refer to pre- and on-column modifications, respectively. The FSNPs used in this study, are commercially available under the trade name of AEROSIL® 200, which are amorphous, highly dispersed, nonporous and hydrophilic in nature. They have an average primary particle size of ~ 12 nm and S_{BET} of 200 ± 25 m^2/g [12]. Poly(glyceryl monomethacrylate-co-ethylene glycol dimethacrylate) monolith which is referred to as poly(GMM-co-EDMA) was originally found to be an ideal support matrix by Mayadunne and El Rassi for the incorporation of hydroxyl functionalized multi walled carbon nanotubes [5]. This same poly (GMM-co-EDMA) monolith was selected in the current study as the support matrix for preparing the monolithic capillary columns with incorporated bare and surface modified FSNPs. To the best of our knowledge, this study demonstrated for the first time, the successful separation of the polar solutes under HI-CEC conditions using monolithic capillary columns incorporated with bare and surface modified gluconamide-FSNPs.

2. Experimental

2.1. Instruments

CEC experiments were performed on an HP ^{3D}CE system from Hewlett-Packard (Waldbronn, Germany) equipped with a photodiode array detector. Electrochromatograms were recorded with a PC running an HP ChemStation software package and the data were processed by OriginPro v8.5.1 from Origin Lab Corp. (Northampton, MA, USA). The in situ polymerization of the monolithic capillary columns was carried out in a Model 105 Isotemp water bath from Fisher Scientific (Fairlawn, NJ, USA). The hot water circulating Tygon tubing jacket used in the on-column modifications was thermo regulated by VWR Scientific water bath Model 1162 from PolyScience (Niles, IL, USA). Model-45 solvent delivery system from Waters Associates (Milford, MA, USA) was used in conditioning the pre-polymerized capillary columns. An automated syringe pump from kdScientific (Holliston, MA, USA) Model KDS101 legacy nano-liter infusion pump was used to pass the reagents through the fused silica capillary when silanizing its inner walls and to condition the monolithic capillary column with the mobile phase. An ultrasonic cleaner Model 1510R-MTH from Branson Ultrasonic Cooperation (Danbury, CT, USA) was used for low power sonication and a Model F50 sonic dismembrator from Fisher Scientific (Waltham, MA, USA) was used for high power sonication. In characterizing the surface modified FSNPs, Fourier transform infrared (FTIR) analyses were carried out at the attenuated total reflectance mode using a Nicolet IS50 FT-IR machine from Thermo Scientific company (Waltham, MA, USA). A Model Q-50 thermogravimetric analyzer from TA instruments (New Castle, DE, USA) was used to perform the thermogravimetric analyses (TGA) in which bare and surface modified FSNPs were heated from 25 °C to 750 °C at a heating rate of 20 °C/min under a 40 mL/min of continuous nitrogen gas flow.

2.2. Reagents and materials

Fused silica capillaries having 100 μm internal diameter (i.d.) and 360 μm outer diameter (o.d.) were purchased from Polymicro Technologies (Phoenix, AZ, USA). FSNPs, AEROSIL® 200, having an average primary particle size of ~ 12 nm and S_{BET} = 200 ± 25 m^2/g (for more detailed characteristics see the bulletin [12]) were gifted by Evonik Corporation (Parsippany, NJ, USA). Glyceryl monomethacrylate (GMM) was purchased from Monomer-Polymer and Dajac Labs (Trevose, PA, USA). Ethylene glycol dimethacrylate (EDMA), 3-(trimethoxysilyl)propylmethacrylate, cyclohexanol, 1-dodecanol, thiourea, uracil, adenine and cytosine were purchased from Sigma Chemical Co. (St. Louis, MO, USA). 2,2′-Azobis(isobutyronitrile) (AIBN) was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). Thymine was from Nutritional Biochemical Corporation (Cleveland, OH, USA). *N,N*-Dimethylformamide (DMF) and formamide were obtained from EM Science (Gibbstown, NJ, USA). ACS grade acetonitrile (ACN), toluene, acetone and glacial acetic acid were purchased from Pharmco-AAPER (Brookfield, CT, USA). Phenol, resorcinol and 4 Å effective pore sized molecular sieves were purchased from Fisher Scientific Co. (Fairlawn, NJ, USA). Pyrogallol was from Baker Chemical Co. (Phillipsburg, NJ, USA). Ammonium acetate, ammonium hydroxide and dimethyl sulfoxide (DMSO) were obtained from Spectrum Quality Products Inc., (Gardena, CA, USA). *N*-(3-Triethoxysilylpropyl)gluconamide (50% in ethanol) were purchased from Gelest Inc., (Morrisville, PA, USA).

2.3. Silanization of the capillary walls

The inner walls of a 45 cm × 100 μm i.d. fused silica capillary were pre-treated using an automated syringe pump, by first passing water for 2 min, then 1 M NaOH for 30 min followed by 0.1 M HCl for 30 min and water again for 30 min at a flow rate of 1 mL/h. Subsequently, the inner walls of the fused silica capillary were silanized in the presence of a solution of 50% (v/v) 3-(trimethoxysilyl)propylmethacrylate in acetone for 6 h at room temperature at a flow rate of 33.3 μL/h. Next, the capillary was rinsed with methanol for 10 min at a flow rate of 1 mL/h and was dried with a stream of nitrogen gas for another 10 min.