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Naturally Occurring Montmorillonite-Based Polymer Monolith Composites as Stationary Phases for Capillary Liquid and Gas Chromatography

Ahmad Aqel [1,*], Munir Obbed [1,2], Ayman A. Ghfar [1], Kareem Yusuf [1], Ameen M. Alsubhi [1] and Ahmed Badjah-Hadj-Ahmed [1]

[1] Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[2] Department of Chemistry, College of Science, Hadhramout University, Mukalla P.O. Box 50512, Yemen
* Correspondence: aifseisi@ksu.edu.sa; Tel.: +966-11-4676009

Abstract: This work is associated with the preparation of capillary chromatographic columns containing inorganic-organic composites comprised of naturally occurring montmorillonite (MMT) clay mineral and polymethacrylate monolithic material. The prepared composites combine the best qualities of both constituents, offering desirable properties for use under the disparate conditions of both GC and HPLC at the same time. The stationary phases were investigated by scanning electron microscopy (SEM), the specific surface area, and thermogravimetric analysis (TGA) and examined in terms of various conditions utilized for GC and HPLC methods. The prepared columns demonstrated an excellent permeability and stability against common chromatographic conditions, such as the eluent type, flow rate, pressure, and temperature. The results confirmed that the addition of small amounts of MMT into the monolith induced significant improvement in the specific surface area, which contributed to the formation of more active sites and enhanced the retention of analytes. The registered column backpressures did not exceed 980 kPa and 16,500 kPa for the prepared GC and HPLC columns, respectively. The prepared columns were subjected to the separation of various interesting compounds possessing different chemistries and polarities, including alkanes, alkylbenzenes, polycyclic aromatic hydrocarbons (PAHs), alcohols, ketones, phenols, some common organic solvents, and isomeric mixtures. Under the optimal conditions, the efficiency of the columns fell between 4900–38,500 plates m^{-1} for GC and 3400–58,800 plates m^{-1} for capillary HPLC applications. In all cases, the measured chromatographic resolution was more than 1.38, with excellent an peak symmetry and low tailing factors. In comparison with the most commonly used commercial columns, the polysiloxane open tubular column for GC and silica-based C_{18} packed column for HPLC, the prepared GC columns demonstrated a faster separation with a higher efficiency, comparable resolution and tailing factors, and lower consumption of carrier gas. Regarding the capillary columns prepared for HPLC, the chromatographic experiments exposed a much lower run time with a comparable efficiency and resolution and drastically lower consumption of mobile phase solvents and samples. The results demonstrate that the MMT-based polymethacrylate monolith composites are applicable as novel and promising separation media for analyzing various mixtures of interest in different fields, such as petrochemical and environmental samples.

Keywords: stationary phase; separation column; clay mineral; montmorillonite; monolith; polymethacrylate

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1. Introduction

To date, GC and HPLC techniques have been developed in many fields and have become the most attractive systems for the purification, isolation, separation, and analysis of a wide range of chemicals [1–3]. On the other hand, most science and technology disciplines are always evolving, growing, becoming more complex, and encountering

new and continuous difficulties. As a result, to analyze more substances in complex environments while reducing the costs, time, and waste associated with the analysis, it has become increasingly necessary to develop powerful separation methods or to improve the efficiency and sensitivity of current approaches. In any GC or HPLC method, the separation of the sample components occurs in columns consisting of an appropriate stationary phase material. Therefore, the development of a successful analytical procedure is very closely associated with the creation of effective separation columns, which are mostly dependent on the preparation of high-performance stationary phases.

The overall quality of the separation column is dependent on many interrelated characteristics, such as the type of the base material, its geometry, and its surface chemistry. The physical and chemical properties of the stationary phases, as well as their mechanical stability and permeability, are crucial for effective separation and analytical methods. However, the separation columns have seen significant advancements and inventions in different directions, and today, many types of stationary phases with a wide variety of characteristics are available on the market. The chromatographers, then, should be able to select the desired characteristics and decide whether the column type is suitable for a particular separation.

Nonetheless, recognizing modern chromatographic column trends is very important, since the separation column continues to develop quickly, leading to new products with different properties and performances [4,5]. One of the main benefits is the extraordinary flexibility of GC and HPLC technologies, particularly the separation columns, which may be enhanced to meet the analytical requirements in the development stages. This work is concerned with the preparation of novel and promising stationary phases that may simultaneously be employed as column-packing materials for GC and HPLC applications.

Monoliths represent a relatively new and creative form of separation media for quick chromatographic analysis. In principle, monolithic columns have been proposed as an alternative to conventional particulate-packed columns [6]. Monoliths are made from a continuous single piece of block materials composed of porous rods of different sizes, providing a unique porosity and permeability, especially for large-sized chemicals, typically synthetic polymers, microorganisms, and biological compounds such as peptides, proteins, and glycoproteins [7–11]. The performance of various monolithic materials has been examined for the separation of several samples. Typically, two basic types of monolithic media have been developed and used in chromatographic techniques as stationary phase materials: organic-based polymer monoliths, prepared by a molding process, and inorganic silica-based monoliths, synthesized by the sol-gel approach [12,13]. However, a hybrid inorganic-organic structure consisting of both basic types has also been developed by several procedures [14,15].

According to the literature, polymer-based monolithic stationary phases are mainly synthesized from organic monomers such as acrylate, methacrylate, acrylamide, and styrene derivatives [16–20]. The typical solutions used for the synthesis of the polymer-based monoliths should consist of at least one monomer, a crosslinker, and a suitable solvent, which can easily be poured into an empty column. The polymer monolithic structure is then formed using a thermal polymerization process or other methods [6–8]. The bare polymer-based monoliths essentially consist of interconnected non-porous micro-globules, and their porous structure is formed of mainly large macropores and lacks mesopores. The absence of the small mesopores in the stationary phase structure comes at the cost of the surface area and the number of interaction sites that are needed to improve the retention of small compounds [7–22]. However, several methods have been developed to modify the bare monolithic structures and enhance their retention abilities and adsorptive efficiency [7–22].

In the present work, we propose the naturally occurring MMT clay mineral as an embedded material for polymethacrylate monoliths for the first time to improve the separation performance of the stationary phase in GC and HPLC applications. Clay minerals such as MMT, kaolinite, illite, and chlorite have been widely utilized in many applications

due to their considerable abundancy and versatility, low cost, high surface area-to-volume ratio, environmentally friendly nature, high thermal and chemical stability, applicability to a wide range of pH values, and ease of modification or functionalization [23,24]. MMT is one of the most representative clay minerals. Their particles are formed by stacking mineral layers, in which silica is the dominant constituent of this clay. The structure of MMT is a 2:1 mineral layer, with every layer composed of two tetrahedral silica sheets and one octahedral alumina sheet in a sandwich-like structure with a 9.6 Å thickness [25,26].

The bare MMT particles are naturally hydrophilic. Hence, the embedding of MMT into the polymer monolithic materials is expected to enhance the retention properties of the final stationary phase, especially for polar compounds. However, the modification or functionalization of the MMT surface to develop it into a hydrophobic material is also possible, which opens up opportunities for different retention abilities. On the other hand, the structure of MMT contains not only external but also internal surfaces. Thus, the retentive properties of the polymer-based monoliths containing MMT are expected to be improved accordingly. Thus, the lack of interaction sites may be overcome through the introduction of MMT particles into the porous structure of the normal polymer monolithic channels. Based on the structure of the selected materials, this hybrid structure is expected to have intermediate characteristics of the organic polymethacrylate monolith and the inorganic MMT medium. The combination of the impressive properties of the organic polymer monoliths and MMT natural clay minerals, such as the high surface area, good thermal and mechanical stability, and fast mass transfer between phases, makes this combination a strong candidate material for use as a stationary phase in chromatography for both GC and HPLC columns.

2. Materials and Methods

2.1. Chemicals and Reagents

The naturally occurring clay mineral MMT K 10 powder was purchased from Sigma-Aldrich (Steinheim, Germany). Acetic acid, sodium hydroxide, hydrochloric acid, and formic acid, in addition to all of the alkanes, alkylbenzenes, PAHs, alcohols, organic solvents, ketones, phenols, and isomers used in the present work, were purchased from BDH (Lutterworth, UK), Acros Organics (Morris County, NJ, USA), and Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol dimethacrylate (EDMA), glycidyl methacrylate (GMA), azo-bis-isobutyronitrile, and 3-(trimethoxysilyl)propyl methacrylate were acquired from Aldrich (Steinheim, Germany). HPLC-grade acetonitrile, methanol, ethanol, and acetone were supplied by Fisher Scientific (Leicestershire, UK). Ultrapure water was prepared using the Millipore system, Milli-Q, Millipore S.A.S. 67,120 (Molsheim, France), and then filtered with 0.20 µm nylon membrane filters from Whatman (Maidstone, UK).

2.2. Preparation of the Columns

Polyimide-coated untreated fused silica tubing (250 µm i.d. for GC and 100 µm i.d. for HPLC) was purchased from Restek (Bellefonte, PA, USA). The capillary tubing was rinsed with acetone and then with a 0.20 mol L^{-1} NaOH solution for 30 min and soaked in the same solution for 1.0 h, before being rinsed with water and dried in a stream of N_2 for 10 min. The capillary was then flushed with 0.20 mol L^{-1} HCl for 1 h, rinsed with water, and dried in a stream of N_2 for 10 min. The tubing was rinsed with ethanol for 10 min and flushed with 25% 3-(trimethoxysilyl)propyl methacrylate solution in ethanol for 30 min and left with the same solution overnight, then rinsed with ethanol for 10 min and dried with a stream of N_2 for 10 min. The activated capillary was then cut with a razor blade into pieces about 220 and 320 mm in length for the GC and HPLC columns, respectively.

For the GC columns, the composition of the monomeric mixture used for the preparation of the columns, by weight percentage, was 14% GMA, 8% EDMA, 77% porogen (mixture of propanol/1,4-butanediol = 50/50, v/v), and 1% of an azo-bis-isobutyronitrile initiator. On the other hand, the composition of the monomeric mixture used for the capillary columns prepared for HPLC applications, by weight percentage, was 24% GMA,

16% EDMA, 59% porogen (mixture of propanol/1,4-butanediol = 50/50, *v*/*v*), and 1% of an azo-bis-isobutyronitrile initiator.

The monomeric mixtures were mixed with vortex into a homogenous solution and then sonicated and purged with N_2 for 10 min. Each capillary column was then filled with the corresponding mixture and both ends were plugged with a piece of rubber. The polymerization was performed in an oven at 70 °C for 15 h. The prepared columns were then washed with acetonitrile to remove the unreacted materials and porogenic solvents. After washing, about 1.0 cm was cut from both capillary ends to obtain a final length of 30 and 20 cm for each GC and HPLC column, respectively. Twelve capillary columns, including six columns for each GC and HPLC application, were prepared with different MMT contents, as described in Table 1. The columns without incorporated clay were prepared using the same procedure. Prior to the chromatographic experiments, the prepared columns were washed with acetonitrile and methanol at a flow rate of 0.50 μL min^{-1} until a constant column backpressure was observed.

Table 1. MMT content of the prepared columns. Porosity and permeability values of the prepared capillary GC and HPLC columns.

Column	MMT (mg mL^{-1})	MMT (%)	Porosity (%)	Permeability (m^2)		
				Helium [a]	Acetonitrile [b]	
C_{G1}	0.0	0.0	88	8.49×10^{-12}	4.79×10^{-13}	GC columns 30 cm long × 250 μm i.d.
C_{G2}	1.0	0.1	86	3.72×10^{-12}	3.73×10^{-13}	
C_{G3}	2.0	0.2	85	3.35×10^{-12}	3.14×10^{-13}	
C_{G4}	3.0	0.3	82	2.57×10^{-12}	1.05×10^{-13}	
C_{G5}	4.0	0.4	80	1.84×10^{-12}	9.61×10^{-14}	
C_{G6}	5.0	0.5	79	1.57×10^{-12}	9.33×10^{-14}	
C_{L1}	0.0	0.0	77	5.89×10^{-13}	6.53×10^{-14}	HPLC columns 20 cm long × 100 μm i.d.
C_{L2}	1.0	0.1	75	4.95×10^{-13}	6.10×10^{-14}	
C_{L3}	2.0	0.2	74	3.15×10^{-13}	5.21×10^{-14}	
C_{L4}	3.0	0.3	72	1.27×10^{-13}	3.03×10^{-14}	
C_{L5}	4.0	0.4	71	8.86×10^{-14}	1.44×10^{-14}	
C_{L6}	5.0	0.5	67	ND [c]	9.73×10^{-15}	

[a] Measured by GC at 1.0 mL min^{-1}. Helium flow rate and 100 °C column temperature. [b] Measured by nanoLC at a 5.0 μL min^{-1} acetonitrile flow rate and 30 °C column temperature. [c] The pressure value exceeded 1000 kPa (145 psi) (maximum allowable working pressure in the normal GC systems).

2.3. Characterization of the Stationary Phase Materials

The prepared columns and synthesized materials were subjected to a scanning electron microscope (SEM), thermogravimetric analysis (TGA), and specific surface area characterization. The SEM images were obtained using a Jeol JSM-6380LA (Tokyo, Japan) analytical scanning electron microscope at 20 kV. The thermal stabilities were measured using TGA with a Mettler-Toledo TGA/DSC Stare system (Mettler-Toledo, Schwerzenbach, Switzerland). The samples were heated from room temperature to 500 °C at a ramp rate of 10 °C min^{-1}. The Brunauer–Emmett–Teller (BET) technique was used to obtain the surface area of the prepared materials using a Gemini VII 2390 Micromeritics surface area analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) at 77 K. The synthesized materials were ground and degassed at 150 °C before the data acquisition.

2.4. Capillary Gas Chromatography

To evaluate the performance of the prepared columns for GC applications, various mixtures, including alkane, alkylbenzene, and alcohols series, common organic solvents, and isomers, were subjected to GC separation in both the isothermal and temperature programming modes. All the GC separations were carried out using a commercial gas chromatography system equipped with a flame ionization detector (FID) at an acquisition rate of 300 Hz (Trace GC Ultra, Thermo Scientific, Waltham, MA, USA). In all cases, the separation conditions were optimized in terms of the carrier gas flow rate, oven temperature, injection volume in the split/splitless modes, and injector and detector temperatures. High-purity He was used as the carrier gas, and a H_2/air mixture (1:10) was used as the FID flame fuel.

2.5. Capillary Liquid Chromatography

The performance of the prepared columns was investigated through liquid-phase separations on a capillary scale. For this purpose, several groups of chemical compounds of different sizes and polarities were investigated. All analyses were performed using Dionex Ultimate 3000 RSLC nanoLC system (Thermo Scientific, Sunnyvale, CA, USA) equipped with an ultra-violet detector with a 3 nL wavelength detection cell volume. The chromatographic conditions for all the mixtures were optimized in terms of the mobile phase solvents and flow rate, column temperature, and detection wavelength. In all cases, the sample injection volume was fixed at 4 nL using a Vici Valco external injector (VICI, Houston, TX, USA). For the comparison with the conventional column, the analyses were accomplished using a Shimadzu LC-20AD liquid chromatograph (Shimadzu, Kyoto, Japan).

3. Results and Discussion

3.1. Capillary Columns' Preparation

This work relates to the preparation of a new and promising separation media for various GC and HPLC applications. Natural occurring MMT particles were added to organic polymers, particularly poly(GMA-co-EDMA), for the synthesis of innovative composite materials, which were then used as stationary phases for capillary-scale HPLC and GC. In this composite, the polymer monolith acts as the matrix that provides the body, shape, and bulk that holds the material together. On the other hand, MMT particles serve as fillers that determine the internal structure and modify the physical and chemical properties of the composite.

The structure of MMT is characterized by 2D sheets of corner-sharing SiO_4 tetrahedra or AlO_4 octahedra [25,26]. However, bare MMT particles are small and present with a wide range of diameters, usually ranging from micrometer- to millimeter-scale particles. To prepare efficient separation columns, a uniform particle size, shape, and distribution are preferred. For this purpose, MMT particles were sieved using a sonic sifter separator in the range between 5 and 10 μm. Then, the fine powders were transferred to the oven and dried at 100 °C for 2 h to remove any moisture from the clay interlayers. Before being packed into the capillary columns, the resulting clay particles were mixed thoroughly with the monomeric mixture by vertex and sonication to maintain a homogenous solution inside the columns, as shown in Figure 1A. While maintaining a stable suspension, the mixture was poured into the capillary columns, and the polymerization was carried out in the oven at 70 °C for 15 h. Control columns, the columns without incorporated MMT, were prepared by the same procedure with the same monomeric mixtures.

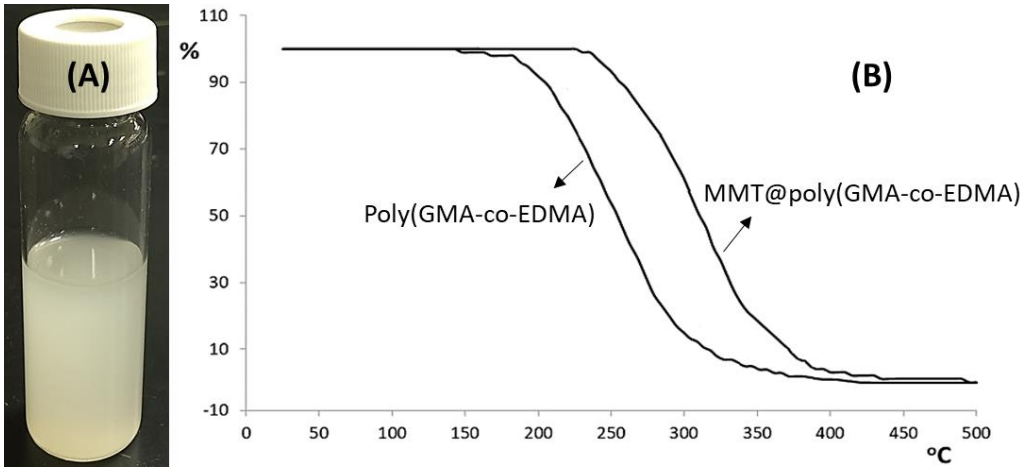

Figure 1. (**A**) Suspension of MMT in the porogenic solvents. (**B**) Thermal behavior of the poly(GMA-co-EDMA) monolithic polymer before and after the incorporation of MMT (3.0 mg mL^{-1} MMT). The samples were heated from 25 to 500 °C at a heating rate of 10 °C min^{-1}.

3.2. Characterization and Stability of the Stationary Phases

The morphology of the MMT and the prepared columns was investigated using SEM micrographs. The SEM images indicated that MMT possessed irregular shapes with a particle size distribution of about 1.02–4.82 µm, as displayed in Figure 2A. The cross-section SEM image of the MMT@poly(GMA-co-EDMA) capillary column shown in Figure 2B demonstrates that the preparation of the composite inside the column rendered a permeable medium with a uniform structure that was well attached to the surface of the capillary tube. The bulk region SEM images of the bare monolith poly(GMA-co-EDMA) (Figure 2C) and the MMT@poly(GMA-co-EDMA) composite (Figure 2D) corresponding to 3.0 mg mL^{-1} MMT showed a significant change in the stationary phase morphology. Clay mineral particles are distributed on the polymer monolith, forming a rough surface in the MMT@poly(GMA-co-EDMA) column. The distribution of the MMT on the inner surface of the monolith macropores led to a decrease in the average pore size of the final stationary phase.

The specific surface area of the bare monolith poly(GMA-co-EDMA) and the MMT@poly (GMA-co-EDMA) composite corresponding to 1.0, 3.0, and 5.0 mg mL^{-1} MMT were measured using liquid nitrogen physisorption based on the BET and Langmuir methods. In a typical case, the BET method gave a specific surface area of 13.43 m^2 g^{-1} for the naked monolith poly(GMA-co-EDMA). On the other hand, the measured specific surface areas were 21.15, 47.17, and 52.68 m^2 g^{-1} for the MMT@poly(GMA-co-EDMA) composites corresponding to 1.0, 3.0, and 5.0 mg mL^{-1} MMT, respectively. The addition of MMT increased the Langmuir surface area of the neat monolith from 25.52 to 83.60 m^2 g^{-1} for the MMT@poly(GMA-co-EDMA) composite corresponding to 5.0 mg mL^{-1} MMT. The N_2 adsorption and desorption isotherms of the poly(GMA-co-EDMA) and MMT@poly(GMA-co-EDMA) are provided in the Supporting Information (Figure S1A,B). Clearly, the results confirmed that the addition of small amounts of clay minerals into the monolith induced significant improvements in the specific surface area, which contribute to the formation of further active sites and enhance the retention of analytes.

The thermal stability of the stationary phase is a very important characteristic, especially for GC applications. The thermal stability of the bare monolith poly(GMA-co-EDMA) and MMT@poly(GMA-co-EDMA) composite materials was investigated using the TGA method. The typical TGA plots in Figure 1B demonstrate that the degradation began at about 180 °C for the neat monolith. The MMT@poly(GMA-co-EDMA) composite corresponding to 3.0 mg mL^{-1} MMT, on the other hand, did not show any significant thermal degradation below 240 °C, which then enabled the use of higher operation temperatures for the columns. Furthermore, the degradation rate of the MMT@poly(GMA-co-EDMA) com-

posite was lower than the degradation rate of the neat monolith poly(GMA-co-EDMA) due to the high thermal stability of the MMT. TGA plots of the MMT@poly(GMA-co-EDMA) composites corresponding to 1.0 and 5.0 mg mL^{-1} MMT are provided in the Supporting Information, Figure S2A,B.

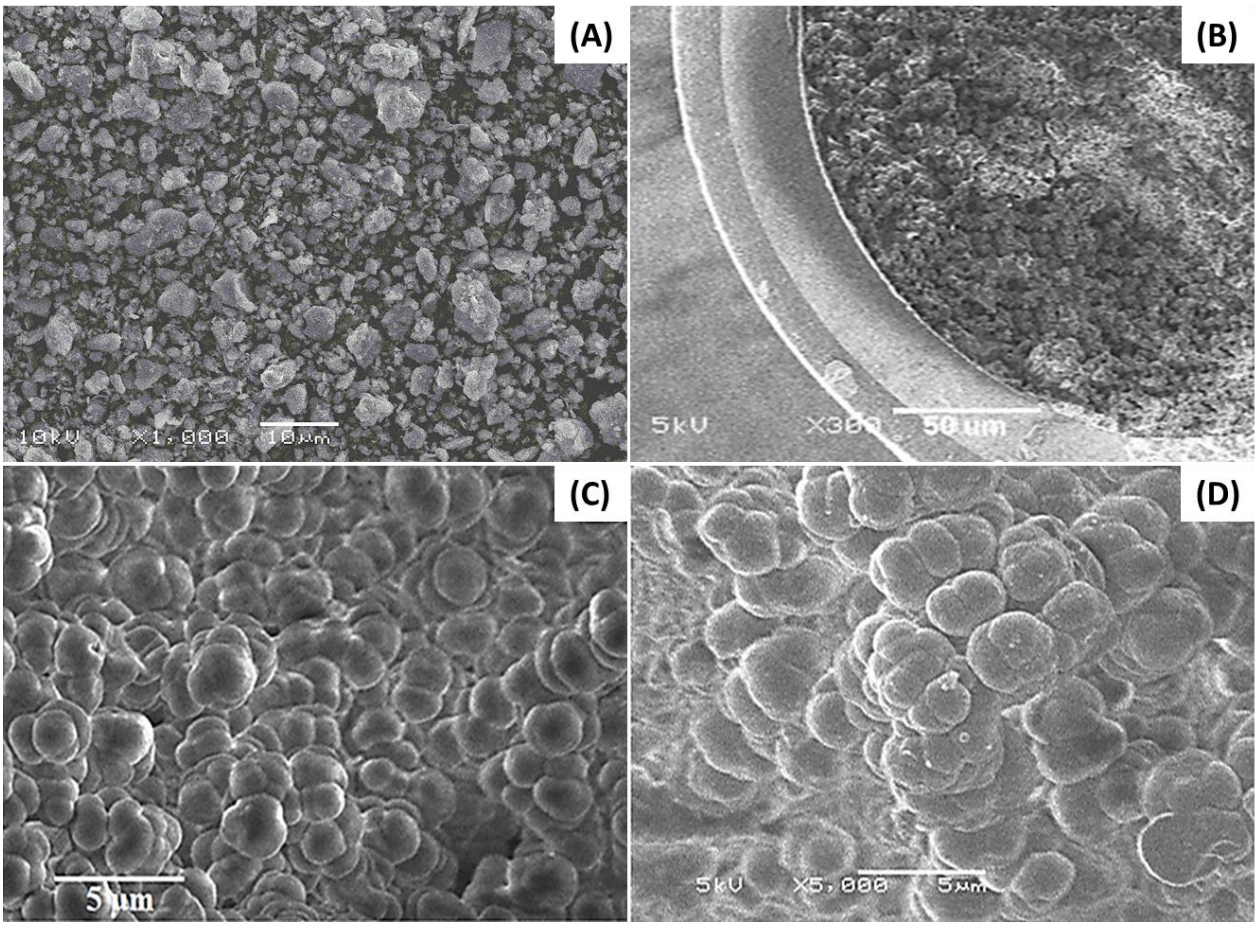

Figure 2. (**A**) SEM image of the MMT after sieving. (**B**) Cross-section SEM image of C_{G1} column. (**C**) Bulk region SEM image of the C_{L1} column. (**D**) Bulk region SEM image of the C_{L4} column.

The stability of the stationary phases inside the columns was also examined. Figure 3A illustrates the relationship between the helium flow rate, as a carrier gas, and the columns' backpressure in GC at 150 °C for the control column and some of the columns prepared with MMT. Figure 3B shows the relationship between the acetonitrile flow rate, as mobile phase, and the columns' backpressure in HPLC at 30 °C for the poly(GMA-co-EDMA) columns with and without MMT. As expected, the columns prepared with MMT exhibited higher backpressures in both tests. The capillary columns prepared with MMT@poly(GMA-co-EDMA) composite stationary phases exhibited backpressures in the ranges of 100–980 kPa in GC and 50–21,600 kPa in HPLC. These reasonable backpressures are vital to extending the lifetime of the prepared column. The backpressure of the columns increased linearly, as shown in Figure 3A,B, over the applied flow rate ranges of 0.10–2.25 mL min^{-1} for helium gas in GC and 0.50–10 μL min^{-1} for the acetonitrile solvent in capillary HPLC. The linear relationships between the backpressures of the prepared columns and eluent flow rates with regression factors between 0.9990 and 0.9996 indicate the good mechanical stability and permeability of the eluents inside the columns.

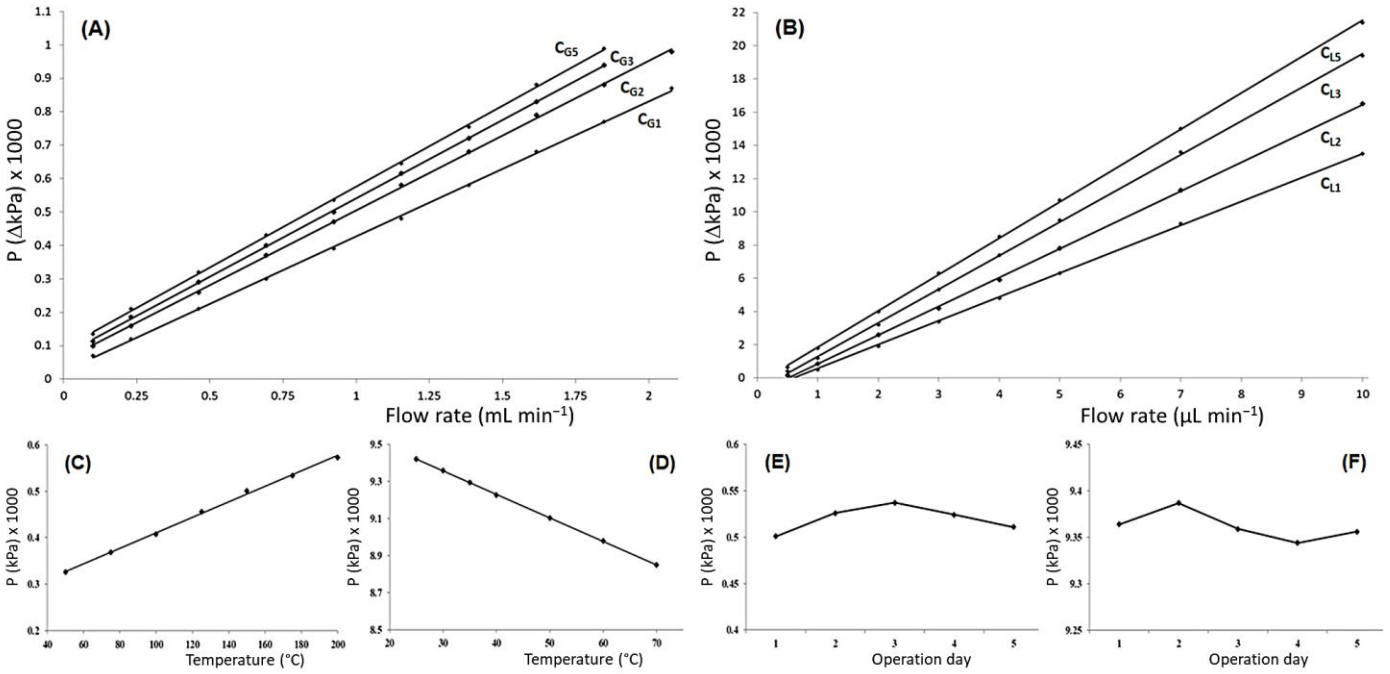

Figure 3. (**A**) Graph illustrating a plot of the pressure drop versus flow velocity using helium as a carrier gas in GC at 150 °C for the poly(GMA-co-EDMA) columns with/without MMT. (**B**) Graph illustrating a plot of the pressure drop versus flow velocity using an acetonitrile as mobile phase in nano-HPLC at 30 °C for the poly(GMA-co-EDMA) columns with/without MMT. (**C**) Pressure drop versus column temperature curve of helium as carrier gas at a flow rate of 0.926 mL min^{-1} for the MMT@poly(GMA-co-EDMA) column. (**D**) Pressure drop versus column temperature curves of acetonitrile as mobile phase at a flow rate of 5.0 μL min^{-1} for the MMT@poly(GMA-co-EDMA) column. (**E**) Graph illustrating plots of the pressure drop versus operation days as helium passed through the MMT@poly(GMA-co-EDMA) column at a 0.926 mL min^{-1} flow rate. (**F**) Graph illustrating plots of the pressure drop versus operation days as acetonitrile passed through the MMT@poly(GMA-co-EDMA) column at a 5.0 μL min^{-1} flow rate.

Based on the previous methods [27,28], the values of the permeability and total porosity were measured at a 0.926 mL min^{-1} helium flow rate and 100 °C isothermal temperature for the GC columns and a 5.0 μL min^{-1} acetonitrile flow rate and 30 °C for the HPLC columns. The results confirmed the decrease in the average pore size of the monolith channels. The decrease in the pores was caused by the lower permeability, decreased from 8.49 × 10^{-12} m^2 (88% total porosity) for the control column to 1.57 × 10^{-12} m^2 (79% total porosity) for the column corresponding to 5.0 mg mL^{-1} MMT for the GC columns. The same behavior was noted for the capillary HPLC columns, with permeability values decreasing from 6.53×10^{-14} m^2 (77% total porosity) for the control column to 9.73 × 10^{-15} m^2 (67% total porosity) for the column corresponding to 5.0 mg mL^{-1} MMT. The porosity and permeability values of the prepared columns are provided in Table 1.

The stability of the prepared columns was also investigated in terms of the column temperature and operation days. As revealed in Figure 3C, for the C_{G4} column corresponding to 3.0 mg mL^{-1} MMT, a directly proportional linear relationship was obtained for the temperature vs. the pressure drop curve using helium as carrier gas at a 0.926 mL min^{-1} flow rate over a temperature range from 50 to 200 °C. The C_{L4} column, on the other hand, demonstrated an inversely proportional linear relationship for the temperature vs. the pressure drop curve using acetonitrile as a mobile phase at a 5.0 μL min^{-1} flow rate over a temperature range from 25 to 70 °C, as shown in Figure 3D. A linear dependence with an R^2 better than 0.9993, in both cases, indicated the excellent stability of the columns at the applied temperatures. The stability of the prepared columns against the flow rate was also studied over five consecutive days. The curves in Figure 3E,F exhibit the excellent stability

of the columns' backpressure ($\leq \pm 46$ kPa) over the operating days at a 0.926 mL min^{-1} flow rate for GC and a 5.0 µL min^{-1} flow rate for the HPLC column. In conclusion, the stability tests proved that there was no degradation or bleeding of the stationary phases under the applied GC and HPLC conditions.

3.3. Gas Chromatography Applications

Mixtures of standard alkanes, alkylbenzenes, alcohols, some organic solvents, and isomers were used to evaluate the performance of the prepared columns for GC separation. The separation processes were developed using various chromatographic conditions, including the carrier gas flow rate, oven temperature, thermal mode, injection temperature and volume, and detector temperature. Sample volumes of 1.0 µL were injected with split ratios ranging between 1:200 and 1:500. Table 2 summarizes the peak parameters for the studied mixtures expressed in terms of t_R, H, R_s, and A_s under the optimal conditions.

Table 2. Peak parameters for the separation of the studied mixtures using the C_{G4} and C_{L4} columns expressed in terms of t_R, H, R_s, and A_s under the optimal conditions.

C_{G4} Column					**C_{L4} Column**				
Solute	**t_R (min)**	**H (mm)**	**R_s**	**A_s**	**Solute**	**t_R (min)**	**H (mm)**	**R_s**	**A_s**
pentane	1.73	0.151	-	1.13	benzene	0.38	0.081	-	1.13
hexane	3.27	0.110	2.82	0.94	toluene	0.58	0.052	2.17	1.05
heptane	4.82	0.069	3.41	0.96	ethylbenzene	0.85	0.034	3.19	1.09
octane	7.25	0.065	4.54	1.07	propylbenzene	1.19	0.043	3.85	1.13
nonane	10.92	0.054	5.58	1.02	butylbenzene	1.86	0.044	4.73	1.14
benzene	0.38	0.078	-	1.06	pentylbenzene	2.94	0.057	6.52	1.07
toluene	0.67	0.066	1.87	1.13	hexylbenzene	4.65	0.066	8.19	1.25
ethylbenzene	0.83	0.059	2.62	1.10	heptylbenzene	7.52	0.044	11.73	1.28
propylbenzene	1.38	0.031	4.03	1.15	naphthalene	4.38	0.020	-	1.15
butylbenzene	2.15	0.027	5.94	1.14	acenaphthylene	5.14	0.017	2.36	1.23
pentylbenzene	3.47	0.028	7.37	1.04	phenanthrene	5.71	0.031	2.02	1.31
hexylbenzene	5.57	0.029	9.27	1.05	anthracene	6.28	0.022	1.85	1.27
heptylbenzene	9.16	0.049	11.93	1.24	pyrene	7.31	0.018	2.28	1.08
methanol	0.30	0.044	-	1.12	chrysene	9.14	0.042	4.35	1.24
ethanol	0.51	0.034	1.38	1.18	dibenzo(*a*,*h*)anthracene	11.74	0.035	5.83	1.26
propanol	0.78	0.026	2.69	1.05	acetone	6.52	0.293	-	1.37
butanol	1.49	0.061	5.98	1.13	cyclohexanone	9.23	0.171	1.54	1.24
pentanol	2.83	0.066	7.27	1.18	acetophenone	14.64	0.102	2.96	1.38
diethyl ether	0.44	0.063	-	1.06	butyrophenone	20.10	0.095	2.39	1.37
dichloromethane	0.76	0.092	4.19	1.10	4-aminophenol	1.62	0.268	-	1.35
acetone	1.03	0.117	1.92	1.14	*p*-cresol	2.46	0.270	1.51	1.42
chloroform	1.38	0.094	2.86	1.18	4-nitrophenol	4.13	0.132	2.38	1.26
tetrahydrofuran	1.75	0.081	3.81	1.27	4-chlorophenol	5.84	0.185	1.82	1.47
isooctane	0.26	0.086	-	1.13	2-naphthol	9.75	0.253	3.20	1.39
octane	0.34	0.062	2.19	1.26					
p-xylene	2.13	0.205	-	1.07					
m-xylene	3.90	0.181	2.98	1.28					
o-xylene	5.75	0.120	2.37	1.16					
isopropanol	0.16	0.051	-	1.19					
propanol	0.19	0.040	1.69	1.26					

t_R: retention time, H: height equivalent to a theoretical plate, R_s: chromatographic resolution, and A_s: asymmetry factor measured at the 10% peak height.

3.3.1. Separation of Alkanes

The prepared columns were used for the separation of five linear alkanes (pentane, hexane, heptane, octane, and nonane) using different experimental conditions. Figure 4A,B shows the GC separation of the alkane series at the same carrier gas flow rate of 1.0 mL min^{-1} with a temperature program (110–180 °C, 50 °C min^{-1}) using the poly(GMA-co-EDMA) and MMT@poly(GMA-co-EDMA) columns. While the poly(GMA-co-EDMA) column showed a poor separation with a chromatographic resolution (R_s) $\leq$ 1.16 (Figure 4A), the MMT@poly(GMA-co-EDMA) column allowed for a full separation of solutes, with an $R_s \geq 2.82$, in approximately the same run time, which was about 12 min (Figure 4B). By measuring the efficiency of the columns, the presence of MMT showed a marked improvement in the column efficiency by the increase in the plate number (N) by a factor between 3.4 times for hexane and 6.6 times for nonane (Table 2). As an example, the measured N value for the octane injected into the poly(GMA-co-EDMA) column was 2100 plates m^{-1}, compared with 15,400 plates m^{-1} for the MMT@poly(GMA-co-EDMA) column using the same chromatographic conditions.

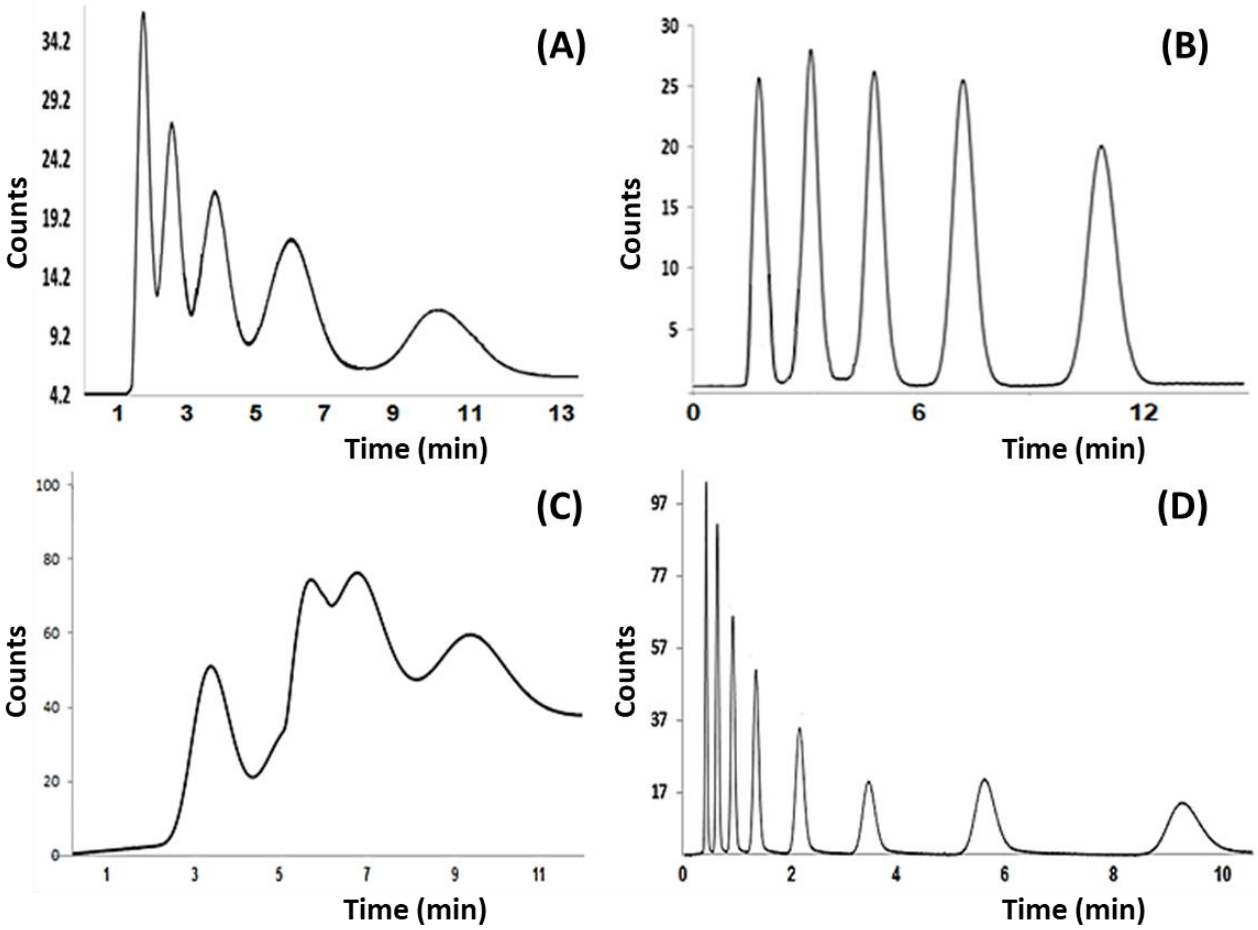

Figure 4. GC separation of alkane series under the optimal conditions using GMA (**A**) and MMT@poly(GMA-co-EDMA) (**B**). Conditions: flow rate: 1.0 mL min^{-1}, injector temperature: 200 °C, temperature program: 110–180 °C, 50 °C min^{-1}, detector temperature: 200 °C. Compounds in order of elution: pentane, hexane, heptane, octane, and nonane (20%, v/v% for each compound). GC separation of alkylbenzene series under the optimal conditions using GMA (**C**) and MMT@poly(GMA-co-EDMA) (**D**). Conditions: flow rate: 0.4 mL min^{-1}, injector temperature: 200 °C, oven temperature: 160 °C isothermal, detector temperature: 200 °C. Compounds in order of elution: benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, and heptylbenzene (12.5%, v/v% for each compound).

3.3.2. Separation of Alkylbenzenes

In the present application, the columns were tested for the separation of eight alkylbenzenes (benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, and heptylbenzene) under different experimental conditions. Again, while the poly(GMA-co-EDMA) column was unable to resolve the alkylbenzene series, as shown in Figure 4C, the MMT@poly(GMA-co-EDMA) column was successfully used to separate the eight alkylbenzenes in about 10 min, as displayed in Figure 4D, with R_s values ranging between 1.87 and 11.93 under isothermal GC conditions at 160 °C and a 0.40 mL min^{-1} flow rate. The efficiency obtained for the MMT@poly(GMA-co-EDMA) column was in the range between 12,800 plates m^{-1} for benzene and 37,000 plates m^{-1} for butylbenzene under the optimal conditions, as displayed in Table 2. The results indicate that the incorporation of MMT into the monolith stationary phases does not greatly affect the retention of either alkane or alkylbenzene mixtures because of the hydrophilic character of the MMT, while the model solutes are relatively nonpolar.

3.3.3. Separation of Alcohols

Five consecutive homologous alcohols, ranging from methanol to n-pentanol, were tested under different isothermal and isobaric conditions or by programming the oven temperature in order to obtain the best resolution in the shortest time. Figure 5A,B demonstrates the GC separation of the alcohol series under the optimal conditions (120–180 °C, 15 °C min^{-1} temperature program, at a 0.50 mL min^{-1} flow rate) using the poly(GMA-co-EDMA) and MMT@poly(GMA-co-EDMA) columns, respectively. Although methanol and ethanol were partially resolved, with R_s = 0.62, the poly(GMA-co-EDMA) column showed a good resolution of the remaining alcohols after about 3 min. On the other hand, the MMT@poly(GMA-co-EDMA) column provided a better separation, with $R_s \geq 1.40$, after a slightly longer run time. The plate number ranged between 15,200 and 38,500 plates m^{-1} for the MMT@poly(GMA-co-EDMA) column in comparison with 2800–4000 plates m^{-1} for the poly(GMA-co-EDMA) column. As we observed in the case of the n-alkanes, a marked peak broadening was noticed in the case of the alcohols separated on the poly(GMA-co-EDMA) column. This result could be explained by the high porosity of the naked monoliths. The higher retention times of the alcohols using the incorporated column refer to the hydrophilic character of the MMT in the modified columns.

3.3.4. Separation of Organic Solvents

A mixture of common organic solvents was used to evaluate the separation power of the prepared columns. Figure 5C presents the separation of the mixture using the MMT@poly(GMA-co-EDMA) column. The elution order of the solvents in both columns was as follows: diethyl ether was the first to be eluted, followed by dichloromethane, acetone, chloroform, and tetrahydrofuran, as shown in Figure 5C. The elution order demonstrates that the separation clearly depends on the volatility and the polarity of the studied solvents. However, a complete separation of the five probes was accomplished in about 1.80 min, with $R_s \geq 1.92$, at a 1.1 mL min^{-1} carrier gas flow rate using a temperature program mode (100–160 °C, 8 °C min^{-1}). Under the optimal conditions, the plate number of the studied solvents fell between 8500 plates m^{-1} for acetone and 15,900 plates m^{-1} for diethyl ether, as demonstrated in Table 2.

3.3.5. Separation of Isomers

To explore the capability of the prepared columns to differentiate between structural isomers, investigations were carried out on three isomeric mixtures. The separation chromatograms of the isooctane and octane mixture, shown in Figure 5D (180 °C, isothermal, 1.1 mL min^{-1}), *p*-, *m*-, and *o*-xylenes mixture, shown in Figure 5E (100–160 °C, 8 °C min^{-1}, 1.0 mL min^{-1}), and isopropanol and propanol mixture, shown in Figure 5F (110 °C, isothermal, 1.3 mL min^{-1}), using the MMT@poly(GMA-co-EDMA) column showed that an excellent and fast separation of the three isomeric mixtures was implemented, with a

chromatographic resolution ≥1.69 in all cases. Under the optimal conditions, the best performance was registered for propanol, with a plate number of 25,000, followed by isopropanol, with a plate number of 19,600. The higher performance and plate number values for both the alcoholic isomers, compared with the alkanes and xylenes, confirm the interaction efficiency of MMT for polar compounds.

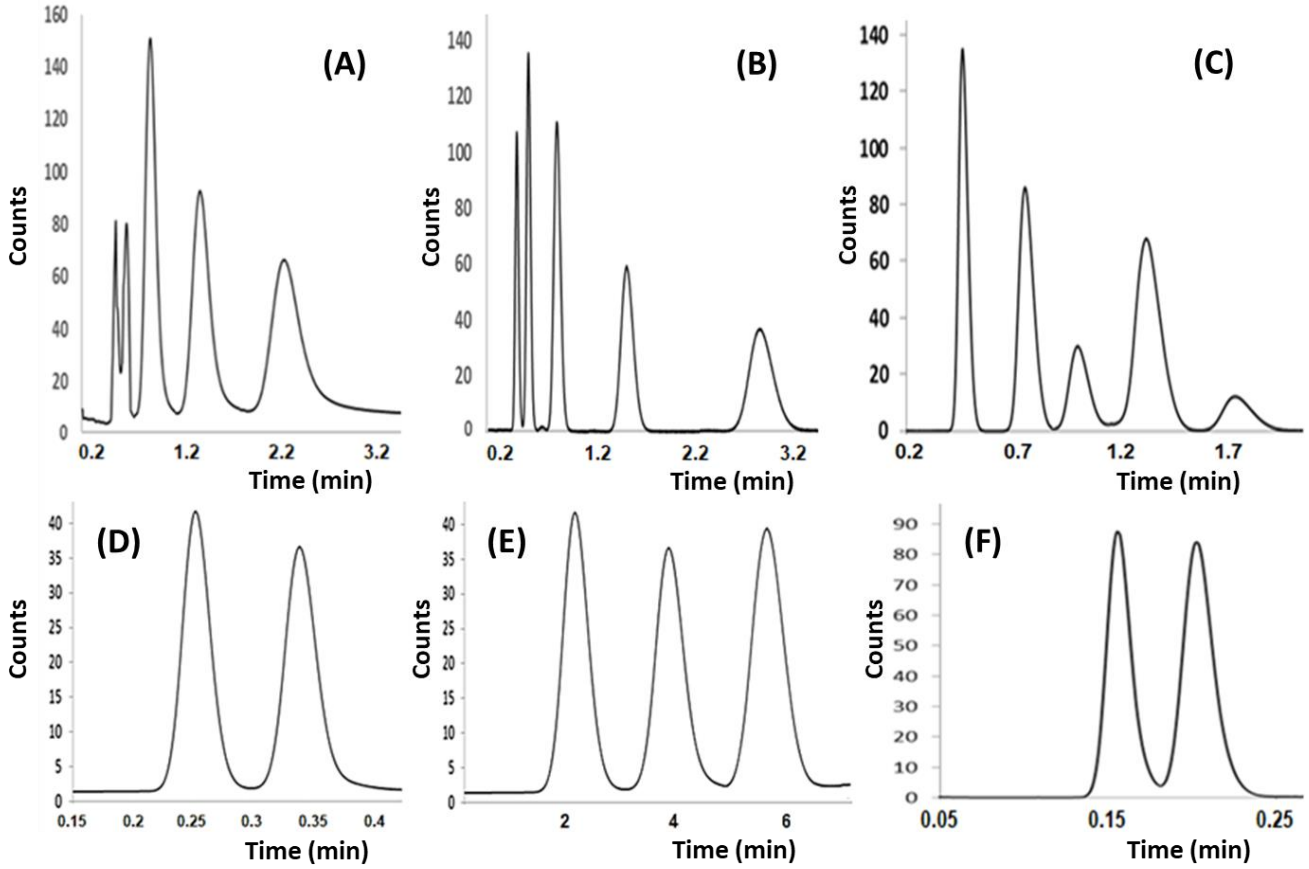

Figure 5. GC separation of the alcohol series under the optimal conditions using GMA (**A**) and MMT@poly(GMA-co-EDMA) (**B**). Conditions: flow rate: 0.5 mL min^{-1}, injector temperature: 250 °C, temperature program: 120–180 °C, 15 °C min^{-1}, detector temperature: 250 °C. Compounds in order of elution: methanol, ethanol, propanol, butanol, and pentanol (20%, *v*/*v*% for each compound). GC separation of some organic solvents using the MMT@poly(GMA-co-EDMA) column (**C**). Conditions: flow rate: 1.1 mL min^{-1}, injector temperature: 200 °C, temperature program: 100–160 °C, 8 °C min^{-1}, detector temperature: 200 °C. Compounds in order of elution: diethyl ether, dichloromethane, acetone, chloroform, and tetrahydrofuran (20%, *v*/*v*% for each compound). GC separation of some isomeric mixtures using the MMT@poly(GMA-co-EDMA) column, (**D**) isooctane and octane (50%, *v*/*v*% for each compound). Conditions: flow rate: 1.1 mL min^{-1}, injector temperature: 200 °C, oven temperature: 180 °C isothermal, detector temperature: 200 °C. (**E**) *p*-, *m*-, and *o*-Xylenes (33.33%, *v*/*v*% for each compound). Conditions: flow rate: 1.0 mL min^{-1}, injector temperature: 200 °C, temperature program: 100–160 °C, 8 °C min^{-1}, detector temperature: 200 °C. (**F**) Isopropanol and propanol (50%, *v*/*v*% for each compound). Conditions: flow rate: 1.3 mL min^{-1}, injector temperature: 250 °C, oven temperature: 110 °C isothermal, detector temperature: 250 °C.

3.4. Capillary Liquid Chromatography Applications

Mixtures of standard alkylbenzene series, some PAH compounds, phenols, and ketones were tested to investigate the efficiency of the prepared columns for capillary HPLC applications. The separation conditions were optimized in terms of the mobile phase solvents, flow rate, column temperature, injection volume, and detection wavelength. The

chromatographic parameters for the studied mixtures expressed in terms of t_R, H, R_s, and A_s under the optimal conditions are presented in Table 2.

3.4.1. Separation of Alkylbenzenes

In this test, the effect of MMT's incorporation into the monoliths was investigated for the separation of eight homologous alkylbenzenes using the columns prepared for capillary-scale HPLC. While the naked monoliths failed to separate the model solutes (Figure 6A), the MMT@polymethacrylate monoliths allowed for a total separation of the eight compounds in approximately 8.0 min, with $R_s \geq 2.17$, using a binary acetonitrile/water (50:50, v/v%) as a mobile phase at a flow rate of 1.5 μL min^{-1}, as shown in Figure 6B. The UV detector was fixed at a 260 nm detection wavelength. By varying the mobile phase flow rate, the best efficiency under the optimum conditions was obtained for ethylbenzene at a 1.0 μL min^{-1} flow rate, which corresponded to 29,400 theoretical plates m^{-1}. As revealed through the GC applications, the incorporation of MMT into monolith stationary phases does not greatly affect the retention of alkylbenzene mixtures because of the hydrophilic nature of the MMT structure.

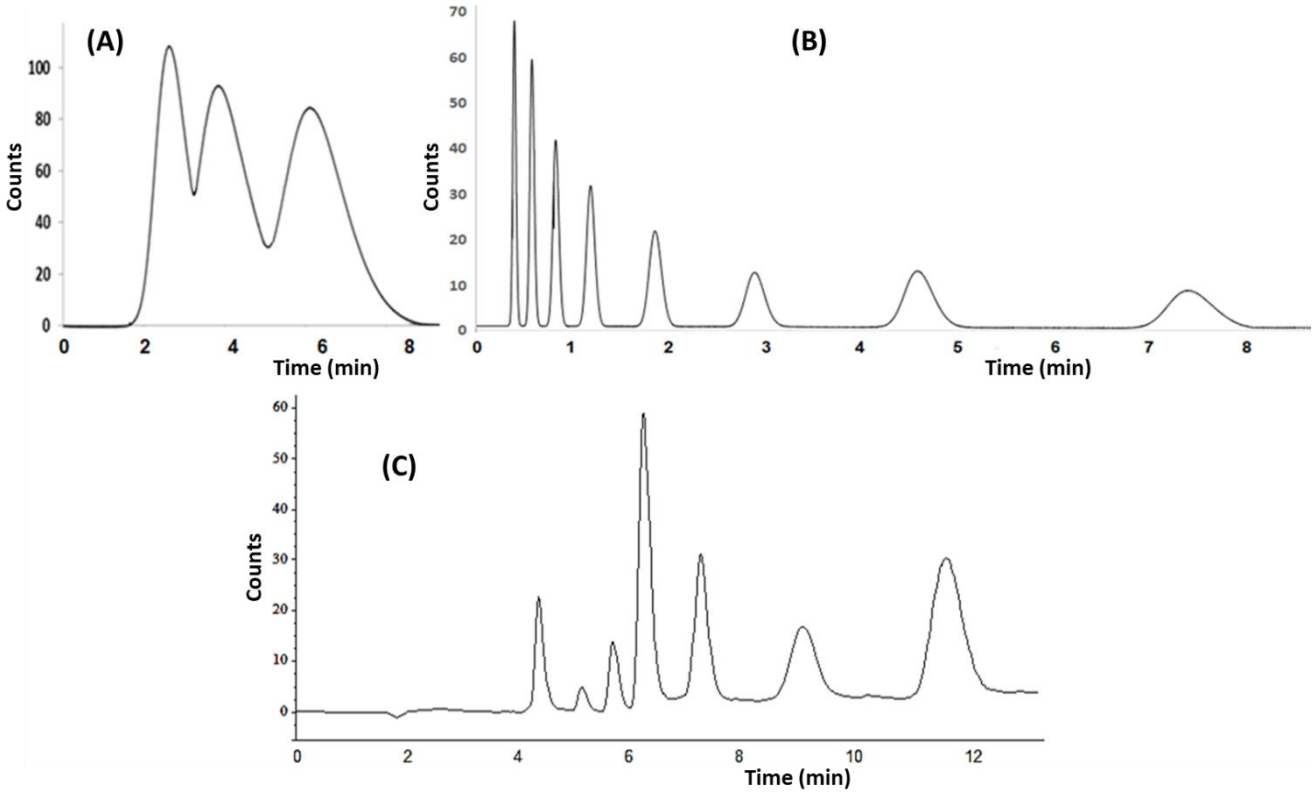

Figure 6. HPLC separation of the alkylbenzene series under the optimal conditions using GMA (**A**) and MMT@poly(GMA-co-EDMA) (**B**). Conditions: flow rate: 1.5 μL min^{-1}, detection wavelength: 260 nm, mobile phase: ACN/H_2O (50:50, v/v), column temperature: 30 °C. Compounds in order of elution: benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, and heptylbenzene (10 μg mL^{-1} for each compound). HPLC separation of PAH mixture under the optimal conditions using MMT@poly(GMA-co-EDMA) (**C**). Conditions: flow rate: 0.5 μL min^{-1}, detection wavelength: 230 nm, mobile phase: 0 → 3 min; 40% acetonitrile, 3 → 13 min; linear gradient 40% → 90% acetonitrile, column temperature: 50 °C. Compounds in order of elution: naphthalene, acenaphthylene, phenanthrene, anthracene, pyrene, chrysene, and dibenzo(*a*,*h*)anthracene (10 μg mL^{-1} for each compound).

3.4.2. Separation of PAHs

A mixture of seven PAHs (naphthalene, acenaphthylene, phenanthrene, anthracene, pyrene, chrysene, and dibenzo(*a*,*h*)anthracene) was tested under different conditions to obtain the best resolution in the shortest time. As an example, the PAHs were completely resolved in about 12 min, with $R_s \geq 1.85$, using the MMT@poly(GMA-co-EDMA) column under gradient elution conditions with an acetonitrile/water binary mixture (0 → 3 min; 40% acetonitrile, 3 → 13 min; linear gradient 40% → 90% acetonitrile) and a flow rate of 0.5 μL min^{-1} at a column temperature of 50 °C, as illustrated in Figure 6C. The detector wavelength was set as 230 nm. The performance, in terms of the plate number, for the columns prepared with no MMT exhibited an efficiency not exceeding 6500 plates m^{-1}. On the other hand, the measured efficiency of the MMT@monolith ranged between 23,800 plates m^{-1} for chrysene and 58,800 plates m^{-1} for acenaphthylene under the optimal conditions. The obtained results show that the MMT@monolith columns are reliable as routine tools for the analysis of these contaminants, which are very toxic for humans and living organisms.

3.4.3. Separation of Ketones

The prepared columns were also applied for the separation of a mixture of four ketones, namely acetone, cyclohexanone, acetophenone, and butyrophenone, using different HPLC conditions. The effect of the presence of MMT was very noticeable in the retention of ketonic compounds. Figure 7A,B demonstrates the separation of the ketone mixture under the optimal conditions using poly(GMA-co-EDMA) and MMT@poly(GMA-co-EDMA), respectively. At all the studied flow rates, the four ketones were partially separated, with a resolution of less than 0.82 in all cases, using the unmodified column. Using the same chromatographic conditions (1.0 μL min^{-1} of a mobile phase consisting of acetonitrile/water (30:70, *v*/*v*) with 1% formic acid, 254 nm detection wavelength), the separation of ketones was complete on the MMT@poly(GMA-co-EDMA) column, indicating a remarkable increase in the retention times, with better resolutions of $R_s \geq 1.54$. The plate numbers were then calculated for each ketone at different flow rates. The presence of MMT induced an improvement in the column efficiency, with plate numbers ranging from 3400 plates m^{-1} for acetone to 10,500 plates m^{-1} for butyrophenone under the optimal conditions.

3.4.4. Separation of Phenols

A mixture of five substituted phenols, consisting of 4-aminophenol, *p*-cresol, 4-nitrophenol, 4-chlorophenol, and 2-naphthol, was used to evaluate the prepared columns using different separation conditions. Under the optimized conditions, the phenolic compounds were successfully separated by the MMT@poly(GMA-co-EDMA) column in less than 12 min, as shown in Figure 7C, using a binary methanol/water (60:40, *v*/*v*) with a 1% formic acid mobile phase at a flow rate of 1.5 μL min^{-1} and a detection wavelength of 254 nm, with the column temperature fixed at 30 °C. The performance, in terms of the column plate number, was in the range between 3700 plates m^{-1} for *p*-cresol and 7600 plates m^{-1} for 4-nitrophenol under the optimal conditions using the MMT@monolith column. In all cases, the R_s values of the five peaks were not less than 1.51 under the mobile phase flow rate fluctuating from 0.5 to 2.0 μL min^{-1}.

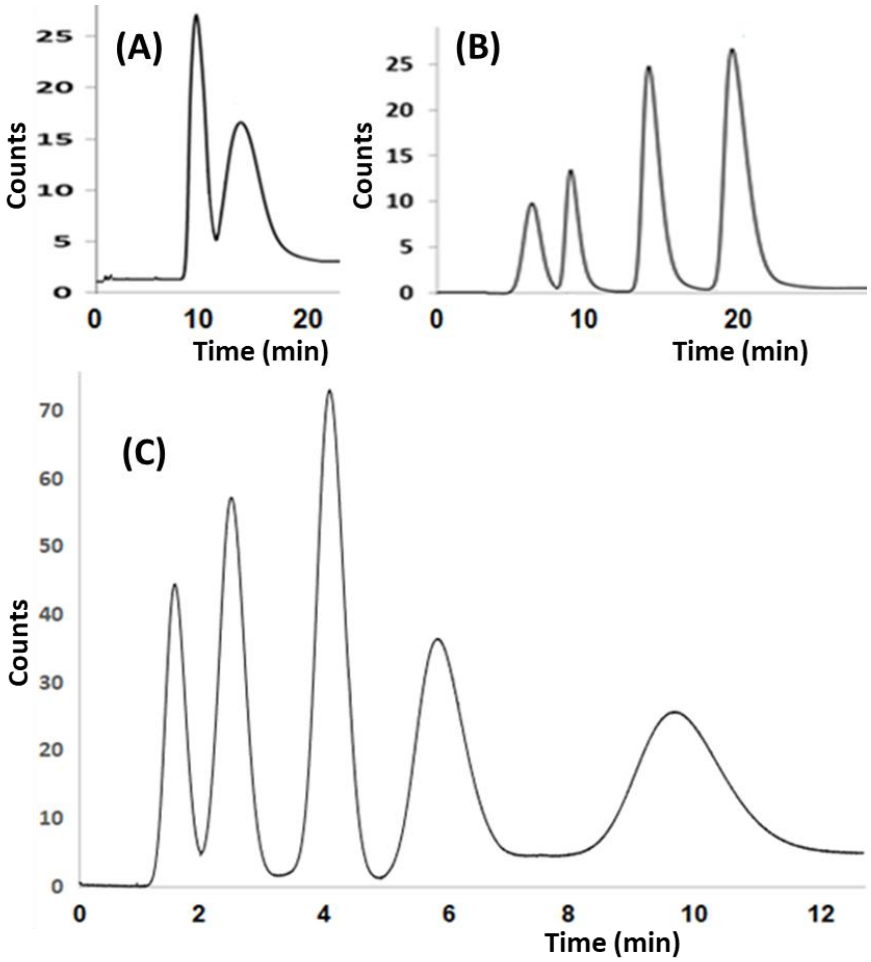

Figure 7. HPLC separation of the ketone mixture under the optimal conditions using GMA (**A**) and MMT@poly(GMA-co-EDMA) (**B**). Conditions: flow rate: 1.0 μL min^{-1}, detection wavelength: 254 nm, mobile phase: ACN/H_2O (30:70, *v*/*v*) with 1% formic acid, column temperature: 30 °C. Compounds in order of elution: acetone, cyclohexanone, acetophenone, and butyrophenone (5 μg mL^{-1} for each compound). HPLC separation of the phenol mixture under the optimal conditions using MMT@poly(GMA-co-EDMA) (**C**). Conditions: flow rate: 1.5 μL min^{-1}, detection wavelength: 254 nm, mobile phase: MeOH/H_2O (60:40, *v*/*v*) with 1% formic acid, column temperature: 30 °C. Compounds in order of elution: 4-aminophenol, *p*-cresol, 4-nitrophenol, 4-chlorophenol, and 2-naphthol (10 μg mL^{-1} for each compound).

3.5. Repeatability and Reproducibility Study

The repeatability and reproducibility of the methods and the prepared columns were investigated. For this purpose, two compounds, ethylbenzene and propylbenzene, were studied using C_{G4} and C_{L4} columns in terms of the %RSD of four chromatographic parameters: t_R, H, A, and R_s. The repeatability and reproducibility tests were accomplished by estimating the run-to-run and day-to-day repeatability of the separation methods and column-to-column reproducibility of the prepared columns. The %RSD values based on the run-to-run injections were ≤1.96% for the C_{G4} column and ≤2.55% for the C_{L4} column (n = 5). Based on the day-to-day injections, the %RSD levels were ≤3.19% for the C_{G4} column and ≤3.99% for the C_{L4} column over five successive days. The injection of ethylbenzene and propylbenzene into each of the five C_{G4} and C_{L4} columns prepared by the same procedure and the same monomeric mixtures showed a lower reproducibility. In all cases, for the two columns, the measured values of the %RSD fell between 3.00% for the R_s values and 21.52% for the H values. The results exhibited an excellent repeatability using the same column and a slightly lower reproducibility using columns prepared in

different batches. This could be clarified by the presence of many variables and several preparation steps. The complete results are given in Table 3.

Table 3. Repeatability and reproducibility study of the C_{G4} and C_{L4} columns expressed as %RSD under the optimal conditions in terms of the t_R, H, A, and R_s parameters.

	C_{G4}							C_{L4}						
	Ethylbenzene			Propylbenzene				Ethylbenzene			Propylbenzene			
	t_R (min)	H (mm)	A ($\times 10^4$)	t_R (min)	H (mm)	A ($\times 10^4$)	R_s	t_R (min)	H (mm)	A	t_R (min)	H (mm)	A	R_s
1	0.84	0.077	106.16	1.38	0.050	128.82	4.01	0.85	0.045	85,485	1.18	0.051	64,719	3.84
2	0.83	0.079	105.95	1.38	0.052	129.63	4.04	0.85	0.045	85,206	1.19	0.054	65,027	3.85
3	0.81	0.080	106.88	1.37	0.052	128.04	4.03	0.85	0.044	85,851	1.19	0.054	64,529	3.86
4	0.83	0.078	107.08	1.38	0.050	127.59	4.03	0.85	0.044	85,830	1.20	0.052	64,833	3.86
5	0.83	0.079	106.62	1.38	0.051	128.07	4.02	0.84	0.044	85,639	1.19	0.052	64,963	3.85
Avg.	0.83	0.079	106.54	1.38	0.051	128.43	4.03	0.85	0.044	85,602	1.19	0.053	64,814	3.85
%RSD	1.32	1.45	0.45	0.32	1.96	0.63	0.28	0.53	1.23	0.31	0.59	2.55	0.31	0.22
1	0.82	0.074	106.34	1.36	0.052	123.76	4.03	0.85	0.043	25,832	1.19	0.055	65,723	3.84
2	0.82	0.073	105.14	1.36	0.054	128.55	4.07	0.82	0.045	26,482	1.16	0.052	64,368	3.83
3	0.84	0.077	108.47	1.34	0.054	122.01	4.04	0.82	0.047	26,074	1.15	0.051	64,632	3.86
4	0.82	0.073	106.67	1.34	0.055	118.54	4.03	0.82	0.046	25,886	1.17	0.055	63,769	3.85
5	0.84	0.074	107.40	1.33	0.051	126.84	4.02	0.84	0.043	25,730	1.15	0.054	64,488	3.85
Avg.	0.83	0.074	106.80	1.35	0.053	123.94	4.04	0.83	0.045	26,001	1.16	0.053	64,596	3.85
%RSD	1.32	2.21	1.16	1.00	3.09	3.19	0.48	1.70	3.99	1.14	1.44	3.40	1.10	0.30
1	0.83	0.074	106.80	1.35	0.053	123.94	4.04	0.83	0.045	26,001	1.16	0.053	64,596	3.85
2	0.73	0.063	113.92	1.27	0.046	141.63	3.83	0.85	0.061	24,207	1.20	0.050	63,762	3.92
3	0.86	0.061	100.64	1.38	0.049	118.35	3.94	0.85	0.069	22,750	1.22	0.078	65,501	3.98
4	0.84	0.085	122.87	1.21	0.067	127.82	4.08	0.78	0.072	25,381	1.11	0.061	67,142	3.76
5	0.82	0.068	107.04	1.38	0.071	109.27	3.82	0.88	0.047	22,152	1.18	0.047	58,472	4.07
Avg.	0.82	0.070	110.25	1.32	0.057	124.20	3.94	0.84	0.059	24,098	1.17	0.058	63,895	3.92
%RSD	6.16	13.79	7.69	5.71	19.48	9.65	3.00	4.42	21.05	6.85	3.59	21.52	5.13	3.04

Run-to-run | Day-to-day | Column-to-column

t_R: retention time, H: height equivalent to a theoretical plate, A: peak area, and R_s: chromatographic resolution.

3.6. Comparison Study

In this part of the study, the prepared composite capillary columns were compared with the commercial columns most commonly used in GC and HPLC techniques. For this reason, two columns were selected, a diphenyl dimethyl polysiloxane (5% phenyl + 95% methyl) open tubular capillary column with a 30 m length × 0.25 mm i.d. × 0.25 µm film thickness, purchased from Restek (Bellefonte, USA), for the GC application, and a silica-based BetaSil C_{18} (octadecyl)-packed column with a 15 cm length × 4.6 mm i.d. and 3 µm particle size, sourced from Thermo Scientific (Waltham, MA, USA), for the HPLC comparisons. Each column was operated under the optimum separation conditions to resolve the alkylbenzene mixture. The comparison was accomplished in terms of some of the important chromatographic parameters, including the analyte retention, number of theoretical plates, chromatographic resolution, peak symmetry, and the consumption of samples and mobile phases. Table 4 presents the peak parameters for the separation of the alkylbenzene mixture using commercial GC and HPLC columns. The typical separation chromatograms of the alkylbenzene series under the optimal conditions using a commercial open tubular capillary GC column and a commercial packed HPLC column are demonstrated in Figures S3 and S4, respectively (Supporting Information).

Table 4. Peak parameters for the separation of the alkylbenzene mixture using commercial GC and HPLC columns expressed in terms of the t_R, H, R_s, and A_s under the optimal conditions.

Solute	Commercial GC Column				Commercial HPLC Column			
	t_R (min)	H (mm)	R_s	A_s	t_R (min)	H (mm)	R_s	A_s
benzene	0.92	0.305		1.06	3.81	0.083		1.25
toluene	1.38	0.393	2.20	1.11	4.47	0.058	1.40	1.20
ethylbenzene	2.10	0.220	2.97	1.20	5.27	0.047	1.79	1.34
propylbenzene	3.17	0.114	4.38	1.22	6.46	0.043	2.74	1.22
butylbenzene	4.89	0.089	6.19	1.14	8.07	0.041	3.71	1.21
pentylbenzene	7.53	0.058	7.74	1.08	10.18	0.036	4.49	1.19
hexylbenzene	11.45	0.084	9.68	1.18	13.32	0.033	5.74	1.21
heptylbenzene	17.63	0.060	12.36	1.26	17.51	0.031	6.08	1.30

t_R: retention time, H: height equivalent to a theoretical plate, R_s: chromatographic resolution, and A_s: asymmetry factor measured at the 10% peak height.

3.6.1. Comparison with Commercial GC Column

Under the optimal isothermal separation conditions, for the prepared C_{G4} composite column and the commercial polysiloxane open tubular column, the results show that the prepared columns enabled the separation of the alkylbenzenes mixture much faster than the commercial column (only half the time of the run). However, both columns were successfully used to resolve the alkylbenzene series, with comparable resolution and asymmetry factors. In spite of their much shorter length (0.30 m compared to 30 m long for the commercial open tubular column; 100 times shorter), the prepared composite column showed better efficiency values, measured in terms of the plate number. The efficiency values of the prepared column ranged between 12,800 plates m^{-1} for benzene and 37,000 plates m^{-1} for butylbenzene, while the best efficiency was 17,200 plates m^{-1} for pentylbenzene, obtained with the commercial open tubular column.

The most important limitation for the prepared composite columns could arise from the restriction of applying high temperatures in the GC applications, being 220/240 °C compared to 300/320 °C for most polysiloxane-based columns. However, the enormous range of organic polymer-based materials and their characteristics could provide various innovative solutions to this drawback. The second obstacle is related to the maximum allowable working pressure in GC. All the current GC normal systems are candidates that can work under pressures not exceeding 1000 kPa, which are suitable for open tubular columns. In this regard, the composition of the monomeric mixture and the polymerization conditions should be optimized for purposes such as the control of the porosity and permeability of the prepared columns and prevention of high column backpressures, as suggested in this work, while providing enough performance for the separation of the intended mixture. Nevertheless, the comparison data demonstrate that the prepared columns allow for a faster separation with a higher efficiency and lower consumption of helium as a result of the use of lower flow rates of the carrier gas, i.e., 1.0 mL min^{-1} in comparison with 1.5 mL min^{-1} for the commercial open tubular column, operated under the optimal separation conditions.

3.6.2. Comparison with the Commercial HPLC Column

Regarding the separation of the alkylbenzene compounds in HPLC, each column was subjected to operation under the optimal conditions, achieved in an isocratic mode to manage the chromatographic resolution and run time. Again, the prepared MMT@polymer composite column exhibited a much lower run time (less than half the time of each run) due to the highly porous structure of the monolith. Additionally, the comparison results reveal that both columns allowed for the successful separation of the alkylbenzenes with comparable resolution and tailing factors. Using the prepared composite column, the measure efficiency values for the alkylbenzenes ranged from 12,300 plates m^{-1} for benzene to 29,400 plates m^{-1} for

ethylbenzene. On the other hand, the efficiency values using the commercially packed column fell between 12,000 plates m^{-1} for benzene and 32,300 plates m^{-1} for heptylbenzene. These comparable efficiency values of the prepared column compared with the 3 μm particulate packed column, along with their lower run time, proved the performance of this composite stationary phase for these types of chromatographic separations.

The preparation of HPLC columns on the capillary scale and smaller i.d. columns also contributes to a decrease in the mobile phase solvents and analyzed samples and consumption of stationary phase materials. This was obvious upon observing the mobile phase flow rate (1.5 μL min^{-1} compared to 0.40 mL min^{-1} for the conventional packed column) and sample injection volumes (4.0 nL in comparison with 5.0 μL for the conventional packed column). The capillary columns also require very small amounts of chemicals for their preparation compared with the conventional-scale columns. All these compensations contribute to significant reductions in the consumption of chemicals, thus reducing the amount of generated waste and the costs of the analysis. On the other hand, the capillary-scale columns are severely affected by additional volumes arising from the improper selection of tubings, connections, and fittings. Therefore, additional precautions are required to ensure the use of suitable volumes of the sample injections and detector cells, as well as the flow rate of the mobile phases.

4. Conclusions

As a novel and promising form of separation media, natural MMT@polymer monolith composites were successfully prepared, characterized, and used for various GC and HPLC applications. Using the same stationary phase for both GC and HPLC columns is highly innovative; however, this technique is very limited in the chromatography world. Various mixtures of chemicals with different chemistries and polarities, including alkanes, alkylbenzenes, PAHs, alcohols, some common organic solvents, phenols, ketones, and isomers, were used as model molecules to evaluate the separation performance of the prepared columns. The synthesized materials and prepared capillary-scale columns proved to be efficient, fast, stable, and reproducible for the separation of the studied chemicals under different chromatographic conditions. This work presents a new stationary phase that may open up promising opportunities for food, petrochemical, environmental, forensic, and pharmaceutical analyses, including those of isomeric compounds. However, the applications could be enlarged to many other research and industrial areas, since the materials and polymer chemistry are extremely rich in terms of the number options, and the hydrophilic nature of MMT can be modified or functionalized to create a more hydrophobic material, which opens up limitless opportunities for other applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations9120389/s1, Figure S1: the N2 adsorption and desorption isotherms of (A) poly(GMA-co-EDMA) and (B) MMT@poly(GMA-co-EDMA) composite; Figure S2: TGA plots of the MMT@poly(GMA-co-EDMA) composites corresponding to 1.0 mg mL^{-1} MMT (A) and 5.0 mg mL^{-1} MMT (B). The samples were heated from 25 to 500 °C with a heating rate of 10°C min^{-1}; Figure S3: Typical GC chromatogram of alkylbenzene series (12.5%, *v*/*v*% for each compound) at the optimal conditions using a commercial open-tubular capillary column. Compounds by order of elution: benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, and heptylbenzene; Figure S4: Typical HPLC chromatogram of alkylbenzene series (10 μg mL^{-1} for each compound) at the optimal conditions using a commercial packed column. Compounds by order of elution: benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene, and heptylbenzene.

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