



Fabrication of zeolitic imidazolate framework-8-methacrylate monolith composite capillary columns for fast gas chromatographic separation of small molecules



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ABSTRACT

A composite zeolitic imidazolate framework-8 (ZIF-8) with a butyl methacrylate-co-ethylene dimethacrylate (BuMA-co-EDMA) monolithic capillary column (33.5 cm long \times 250 μ m i.d.) was fabricated to enhance the separation efficiency of methacrylate monoliths toward small molecules using conventional low-pressure gas chromatography in comparison with a neat butyl methacrylate-co-ethylene dimethacrylate (BuMA-co-EDMA) monolithic capillary column (33.5 cm long \times 250 μ m i.d.). The addition of 10 mg mL⁻¹ ZIF-8 micro-particles increased the BET surface area of BuMA-co-EDMA by 3.4-fold. A fast separation of five linear alkanes in 36 s with high resolution ($R_s \geq 1.3$) was performed using temperature program. Isothermal separation of the same sample also showed a high efficiency (3315 plates m⁻¹ for octane) at 0.89 min. Moreover, the column was able to separate skeletal isomers, such as iso-octane/octane and 2-methyl octane/nonane. In addition, an iso-butane/iso-butylene gas mixture was separated at ambient temperature. Comparison with an open tubular TR-5MS column (30 m long \times 250 μ m i.d.) revealed the superiority of the composite column in separating the five-membered linear alkane mixture with 4–5 times increase in efficiency and a total separation time of 0.89 min instead of 4.67 min. A paint thinner sample was fully separated using the composite column in 2.43 min with a good resolution ($R_s \geq 0.89$). The perfect combination between the polymeric monolith, with its high permeability, and ZIF-8, with its high surface area and flexible 0.34 nm pore openings, led to the fast separation of small molecules with high efficiency and opened a new horizon in GC applications.

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1. Introduction

For more than a century, chromatography has been one of the most important analytical techniques, particularly column chromatography, which is considered the most public chromatographic technique. The stationary phase within the columns in column chromatography has experienced continuous development since the first *Tswett* calcium carbonate column in 1901. The aim of the development is to achieve faster separation with high efficiency. Monolithic capillary columns are one of the newest types of chromatographic columns. The high permeability of capillary monolithic columns allows for faster separations; moreover, they are characterized by easy fabrication and modification, low

backpressure and the ability to work at the miniaturization scale due to a capillary size that reduces the consumption of carrier gas [1]. The two most popular types of monolithic columns are: inorganic silica and organic polymeric monoliths. Silica based inorganic monoliths have the ability of fast separation of small molecules, whereas polymeric monoliths are more efficient in separating macro-molecules. One of the most convenient methods used to enhance the separation of small molecules using polymeric monoliths is the incorporation of various nano- and micro-particles into the monolithic matrix. Several attempts have successfully been made using this technique, including carbon nanotube (CNT) [2–5], graphene oxide (GO) [6], C₆₀-fullerene [7], sporopollenin [8], and metal-organic frameworks [9–11].

Metal-organic frameworks (MOFs) were first introduced in 1995 by Yaghi et al. to describe the youngest group of porous materials [12]. In parallel, the main concepts were proposed by Kitagawa [13] and Férey et al. [14]. MOFs are highly ordered and precisely controlled crystalline systems that are composed of an inorganic

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metal-containing unit that is self-assembled with an organic ligand. MOFs crystalline structures can be selected through the precise selection of its components (metal cation and ligand) and rely on the wide choice of metal cations and organic linkers available. The main advantages of MOFs compared with the conventional inorganic porous frameworks are their almost unlimited diversity, very high surface area, ability for post-synthetic modifications and designable structures. The outstanding properties of MOFs have made them a successful candidate for many applications, such as gas storage for energy purposes, supercapacitors, catalysis, sensing, drug delivery, and chromatography [15].

Over the last decade, chromatography has become an application of interest for metal-organic frameworks. Chromatographic separations generally depend on the adsorption nature and strength of the stationary phase and its surface area. Hence, the high absorbability and high surface area of MOFs make them attractive targets as stationary phases for chromatographic applications. Our research group recently published a review entitled “Metal organic frameworks in chromatography” which summarized the applications of MOFs in chromatography among other excellent reviews [16–18].

Although using MOFs in chromatography has already given promising and surprising results, the use of MOFs incorporated with polymers (MOF-polymer) to form a composite stationary phase is still very limited [9–11]. The composite material combines the advantages of the MOF stationary phase and the monolithic organic stationary phase and avoids their disadvantages. The advantages gained from MOFs are the controlled pore size and shape, the high pore volume, higher surface area, the desired functionality and control of the apolar character, whereas the advantages of monolithic polymers are represented in the high permeability obtained while eliminating the low surface area problem of organic monoliths.

Recently, UiO-66 incorporated in a polymethylacrylic acid-co-ethylene dimethacrylate (MAA-co-EDMA) monolithic stainless steel conventional column (7 cm long \times 4.6 mm i.d.) was fabricated by Fu et al. for HPLC applications [9]. The (UiO-66)-(MAA-co-EDMA) composite successfully enhanced the separation of polycyclic aromatic hydrocarbons with efficiency (28,000 plates m^{-1} for 2,6-dimethylphenol). Huang et al. presented the first capillary monolithic column incorporated with MOF material [10]. They prepared an MIL-101(Cr)-(BuMA-co-EDMA) composite capillary column for electrochromatography (CEC) and nano-liquid chromatography (nano-LC). The prepared columns exhibit a satisfactory performance (52,000 in CEC and 24,000 plates m^{-1} in nano-LC) in comparison to previous reports on MOF packed columns. HKUST-1 nanoparticles were also examined to enhance the performance of glycidyl methacrylate-co-ethylene dimethacrylate capillary monolithic columns in liquid chromatography [11]. The efficiency of the separation increased for all comparable analytes separated in the conventional column of Fu et al.

To the best of our knowledge, MOF-polymer composites have not been used as a monolithic stationary phase in gas chromatography to date. The extraordinary properties of MOFs may bring more attention to the utilization of monolithic columns in GC, which is one of the less common applications, particularly for methacrylate monoliths [1,19–21]. The present research presents a novel composite stationary phase by incorporating a capillary methacrylate monolithic column with ZIF-8 [$Zn(2\text{-methylimidazole})_2$] micro-particles for GC applications using a conventional low-pressure GC instrument. ZIF-8 was explored for GC applications as a packed column [22] and as an open tubular column [23,24]. The most significant features reported for the ZIF-8 chromatographic separation are its unique molecular sieving nature of branched alkanes from linear alkanes through flexible pore openings and its apolar character, which enhanced the high resolution GC separation

of linear alkanes series. Zeolitic imidazolate framework-8 (ZIF-8) is characterized by its stable structure, high surface area (1500–1600 $m^2 g^{-1}$), uniform flexible narrow six-membered ring pore windows (0.34 nm) and large pores (1.14 nm) and very high chemical and thermal stability (380–550 $^{\circ}C$) [25]. Thus, ZIF-8 was used in a different percentage with butyl methacrylate-co-ethylene dimethacrylate to investigate its effect on the separation efficiency of nonpolar alkanes, polar organic solvents, isomers, gases and a thinner sample from the local market via conventional low pressure gas chromatography. The selected analytes are small enough to fit into the flexible ZIF-8 pores. A comparison with a conventional open tubular capillary column and with a ZIF-8 coated capillary column from a previous study revealed the superiority of the prepared columns for separating small molecules.

2. Experimental

2.1. Reagents and materials

2-Methylimidazole zinc salt (ZIF-8) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and produced by BASF under the commercial name of Basolite[®]Z1200. Polyimide-coated 250 μm i.d. fused silica capillaries were purchased from Restek (Bellefonte, USA). 3-(trimethoxysilyl) propyl methacrylate (TMSM) and azobisisobutyronitrile (AIBN) were purchased from Fluka (Buchs, Switzerland). Butyl methacrylate (BuMA) and ethylene dimethacrylate (EDMA) were obtained from Sigma-Aldrich (St. Louis, MO, USA). The gases (methane, helium, hydrogen, nitrogen and air), all of high-purity grade (99.9999%), were purchased from SIGAS (Riyadh, Saudi Arabia). For the comparative study, the TR-5 MS column, 30 m length and 250 μm inner diameter was purchased from Thermo Scientific (Waltham, MA, USA).

2.2. Instrumentation

All experiments were performed using a conventional Thermo Scientific gas chromatograph (Trace GC Ultra, USA). The system used a split/splitless injector, an oven with a temperature range of 50–400 $^{\circ}C$, a heating rate of up to 14.5 $^{\circ}C s^{-1}$ (870 $^{\circ}C min^{-1}$), programmability of 3 ramps/4, a flame ionization detector (FID) with a 1:10 hydrogen/air mixture as the flame fuel and an acquisition rate of 300 Hz. The sample was injected manually into the instrument. Both the injector and the detector were adjusted to 190 $^{\circ}C$. Data analysis was performed using the Chrom-Card data handling software package. The carrier gas was dried, high-purity helium.

Thermal stability of the prepared materials was measured using a Mettler-Toledo TGA/DSC Stare system (Schwerzenbach, Switzerland). The sample was heated from 25 to 400 $^{\circ}C$ at a heating rate of 10 $^{\circ}C min^{-1}$.

2.3. Preparation of ZIF-8-butyl methacrylate monoliths

The monolithic capillaries were prepared according to a previously described method [21] with some changes. The polymerization mixture consisted of 30% monomers (70% BuMA, 30% EDMA) and 70% porogen (50% 1-propanol, 50% 1,4-butanediol). ZIF-8 was dispersed and homogenized in the polymerization mixture under sonication for 10 min and was then purged with helium for 5 min. Four batches columns were prepared to examine the effect of adding ZIF-8 in different percentages ZIF-8-(BuMA-co-EDMA)-0, ZIF-8-(BuMA-co-EDMA)-1, ZIF-8-(BuMA-co-EDMA)-2, ZIF-8-(BuMA-co-EDMA)-3 with 0, 5, 10 and 15 $mg mL^{-1}$ ZIF-8, respectively. The empty fused silica capillary tubing (250 μm i.d.) has been activated with 1.0 $mol L^{-1}$ NaOH solution for 5 min and soaked for 10 min, then it rinsed with water and dried. The column was then flushed with 1.0 $mol L^{-1}$ HCl for 2 min and dried with

air. Finally, the capillary tubing was rinsed with toluene for 10 min and flushed with a 10% 3-(trimethoxysilyl) propyl methacrylate (TMSM) in toluene solution for 10 min and soaked for 2 h for modification. It was then flushed with toluene for 5 min and dried with air for 5 min.

After activation and modification with TMSM, 40 cm long \times 250 μm i.d. empty capillaries were filled with the polymerization mixture and thermally polymerized at 55 $^{\circ}\text{C}$ for 16 h. The relatively low polymerization temperature and the low cross-linker percentage were intended to increase the pore size of monoliths to make them more reliable for low pressure gas chromatography. The column length was adjusted to 33.5 cm and was washed with acetonitrile over night to remove the unreacted materials and porogenic solvents. The columns were fitted into a U-shaped stainless tube before polymerization to avoid any deformation of the polymer during connection (Fig. S1).

2.4. Hydrodynamic properties calculations

The column's porosity (ϵ_T) was determined using HPLC with uracil as an unretained material by the following equation:

$$\epsilon_T = \frac{Ft_0 - V_e}{V_g} \quad (1)$$

where F is the volumetric flow-rate, t_0 is the retention time of an unretained marker, V_e is the extra-column volume (void volume) and V_g is the geometric volume. The modified Darcy's equation was used to calculate the permeability (K^o) of the prepared columns [19]:

$$K^o = \frac{u\eta L}{\Delta P j'} \quad (2)$$

where $\Delta P = P_i - P_o$ (P_i and P_o are the pressures of the carrier gas at the inlet and outlet of the column, respectively), j' is the Halasz compressibility correlation factor ($j' = 3(P^2 - 1)(P + 1)/4(P^3 - 1)$), where P equals P_i/P_o , L is the column length, and η and u are the carrier gas (helium) viscosity ($2.533 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ at 150 $^{\circ}\text{C}$ and 1 MPa) and the mean velocity, respectively.

The average diameter of the monolith channels (R) was estimated using the Hagen–Poiseuille equation [26,27]:

$$u = \frac{\Delta P R^2}{8\eta L} \quad (3)$$

The dead time in GC was determined experimentally using methane gas as an unretained material under different conditions (Table S1).

3. Results and discussion

3.1. Characterization and hydrodynamic properties

ZIF-8 micro-particle dispersibility within BuMA-co-EDMA monolithic matrix was investigated using energy dispersive X-ray spectrometry (EDS) by detecting the distribution of Zn atoms of the ZIF-8 structure. Polymerization was performed in 2 mL vials under the same polymerization conditions, monomer ratios and porogen percentage as inside the columns with 10 mg mL^{-1} and 15 mg mL^{-1} ZIF-8. Three samples of each vial were removed from the surface, from the middle and from the bottom of the vial. The EDS results showed an excellent homogeneity in the vial with 10 mg mL^{-1} ZIF-8 with 5.25 mass% in the surface, 6.36 mass% in the middle and 6.62 mass% in the bottom for Zn (Figs. S2–S4). In contrast, an accumulation of ZIF-8 micro-particles was observed in the vial with 15 mg mL^{-1} ZIF-8, with 0.94 mass% in the surface, 1.69 mass% in the middle and 26.76 mass% in the bottom (Figs. S5–S7). The density of ZIF is larger than that of the rest of the polymerization mixture.

Therefore, it is likely that the ZIF sediments during polymerization. Since the addition of ZIF can also affect the rate of polymerization, the large amount of ZIF slows the polymerization and the time for sedimentation is longer. Hence, the large difference between top and bottom for the 15 mg mL^{-1} experiment.

The SEM results of the control column with neat monolith BuMA-co-EDMA and a ZIF-8-(BuMA-co-EDMA)-2 composite column with 10 mg mL^{-1} ZIF-8 showed a significant change in the monolith morphology (Fig. 1). ZIF-8 micro-particles agglomerated on the surface of the monolith to form large clusters with a rough surface in the ZIF-8-(BuMA-co-EDMA)-2 column (Fig. 1C and D). The agglomeration of 4.9 μm particle size ZIF-8 on the inner surface of the macropores led to decreased average pore size, as calculated using the Hagen–Poiseuille equation, from 10.22 μm in the control column to 4.48 μm in ZIF-8-(BuMA-co-EDMA)-2 column (Table S2). The decrease in the average pore size resulted in lower permeability from $1.76 \times 10^{-11} \text{ m}^2$ to $3.39 \times 10^{-12} \text{ m}^2$, while the total porosity almost did not change (from 76% to 74%) indicating the higher percentage of micropores and macropores in the composite column than in the control column (Table S2).

Incorporation of 10 mg mL^{-1} ZIF-8 provided the BuMA-co-EDMA monolith with extra surface area, increasing its BET surface area from $16.66 \text{ m}^2 \text{ g}^{-1}$ to $56.8 \text{ m}^2 \text{ g}^{-1}$. The TGA plot for both the neat monolith BuMA-co-EDMA and for the ZIF-8-(BuMA-co-EDMA)-2 composite shows degradation beginning at 210 $^{\circ}\text{C}$ but with lower degradation rate for the composite material (Figs. S8 and S9). The rate of degradation is lower because ZIF-8 micro-particles have a higher thermal stability, but the parent polymer is degrading at the same temperature.

3.2. Chromatographic performance

To evaluate the effect of adding ZIF-8 to BuMA-co-EDMA monoliths with different ratios for separating small molecules, a mixture of pentane and hexane was separated isothermally at 150 $^{\circ}\text{C}$, the inlet pressure was 1 MPa and with a split injection (Fig. 2a). The ZIF-8-(BuMA-co-EDMA)-2 column with 10 mg mL^{-1} ZIF-8 showed the best performance with fast and complete separation ($R_s = 1.8$), whereas the control column with no ZIF-8 and the ZIF-8-(BuMA-co-EDMA)-1 column with 5 mg mL^{-1} ZIF-8 showed poor separation. In contrast, the extra ZIF-8 of 15 mg mL^{-1} in the ZIF-8-(BuMA-co-EDMA)-3 column resulted in broad peaks with a relatively long retention time at the same conditions; hence, the former column represents the perfect combination ratio of ZIF-8 and BuMA-co-EDMA due to its homogeneity observed in the EDS results and its chromatographic performance. An excellent fast separation of a linear alkanes mixture (pentane, hexane, heptane, octane and nonane) was performed using ZIF-8-(BuMA-co-EDMA)-2 (33.5 cm long \times 250 μm i.d.) in approximately 0.6 min (36 s) with a temperature program (130–200 $^{\circ}\text{C}$, 120 $^{\circ}\text{C min}^{-1}$) (Fig. 2b). The significant improvement of the linear alkanes separation was due to van der Waals interactions with the apolar inner surfaces of the ZIF-8 pores. Additionally, the rapid separation arises from the high permeability provided from the BuMA-co-EDMA monolithic matrix.

A mixture of polar organic solvents consisting of diethyl ether, acetone, dichloromethane, chloroform and tetrahydrofuran was used to detect the separation power of the composite ZIF-8-(BuMA-co-EDMA)-2 monolithic column compared with the control BuMA-co-EDMA monolithic column for polar samples at the same conditions (isothermal at 100 $^{\circ}\text{C}$, inlet pressure 1 MPa, split injection). The elution order of the polar sample in both columns and the separation temperature, which is much higher than their boiling points (b.p.) demonstrated that the separation is dependent not only on the boiling points but also on the polarity of the probes. Diethyl ether (b.p. = 34.6 $^{\circ}\text{C}$, dipole moment = 1.15 D) was the first eluent, followed by

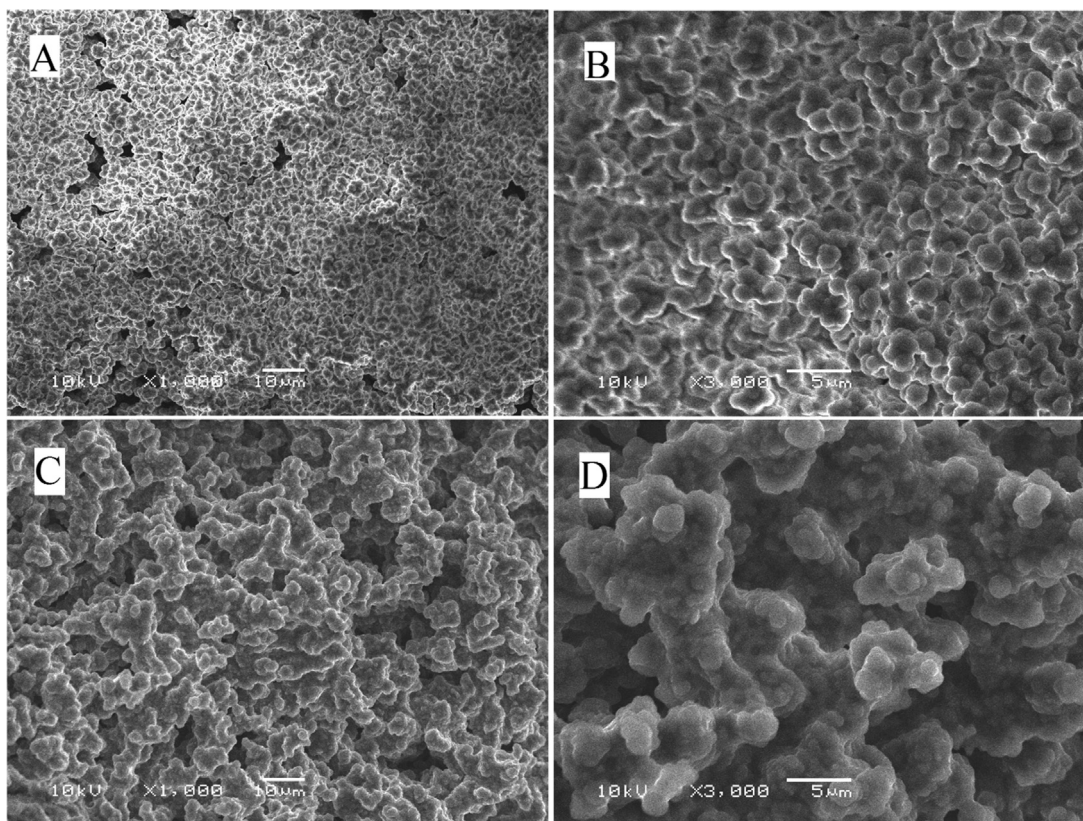


Fig. 1. SEM images of (A, B) poly (BuMA-co-EDMA) monolith and (C, D) ZIF-8-(BuMA-co-EDMA) composite monolith with incorporation of 10 mg mL⁻¹ ZIF-8.

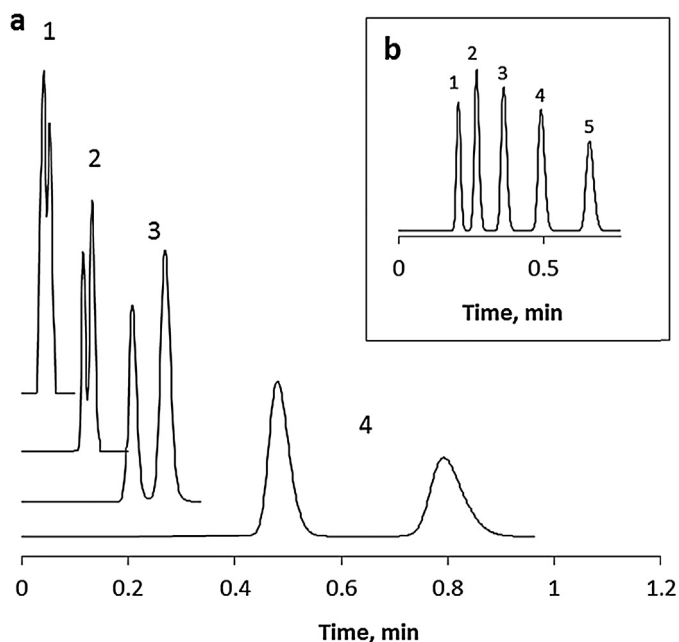


Fig. 2. (a) Chromatograms of pentane and hexane separated using four ZIF-8-(BuMA-co-EDMA) composite monolithic capillary columns with different ZIF-8 concentrations; control (1), 5 mg mL⁻¹ ZIF-8 (2), 10 mg mL⁻¹ ZIF-8 (3), and 15 mg mL⁻¹ ZIF-8 (4). Conditions: isothermal at 150 °C; inlet pressure 1 MPa; split injection. (b) Fast separation of linear alkane series using ZIF-8-(BuMA-co-EDMA)-2 column with 10 mg mL⁻¹ ZIF-8. Conditions: temperature program 130–200 °C, 120 °C min⁻¹; inlet pressure 1 MPa; split injection. Peaks: pentane (1), hexane (2), heptane (3), octane (4), nonane (5).

acetone (b.p. = 56 °C, dipole moment = 2.91 D), dichloromethane (b.p. = 39.6 °C, dipole moment = 1.6 D), tetrahydrofuran (b.p. = 66 °C, dipole moment = 1.63 D) and finally chloroform (b.p. = 61.5 °C, dipole moment = 1.15 D). The BuMA-co-EDMA monolith is mainly apolar, but it is more polar than silicate stationary phases [28–30], which led to a faster elution of the more polar acetone than the less polar dichloromethane, despite the lower b.p. of the latter. This was also true for the elution of tetrahydrofuran before chloroform. The control column without ZIF-8 micro-particles demonstrated excellent separation for the five solvents in 9 s with high resolution ($R_s = 1.09$ – 1.96) under the mentioned conditions (Fig. 3a). The ZIF-8-(BuMA-co-EDMA)-2 composite monolithic column showed a much longer separation time than the control column (≈ 1.4 min) (Fig. 3b); however, the efficiency of separation markedly increased as we will see later. Although ZIF-8 leads to more apolar character for the BuMA-co-EDMA monolith, the overall apolarity did not affect the elution order, whereas ZIF-8 addition increased the efficiency of separation through its high surface area and lower porosity, resulting in less diffusion of the separated species.

Skeletal isomers separation is another application of ZIF-8-(BuMA-co-EDMA) monolithic columns. A high resolution separation of an octane and iso-octane mixture ($R_s = 1.8$) in less than 0.6 min was achieved using a ZIF-8-(BuMA-co-EDMA)-2 column at inlet pressure of 1 MPa and with a split injection at isothermal conditions of 150 °C, which is higher than the boiling points of either molecule, indicating that the different boiling points are not the cause of separation (Fig. 4a). The main reason for separation in this case is the molecular sieving phenomenon of ZIF-8, which assists in separating branched alkanes from their linear isomers. The bulkier branched iso-octane did not fit into the small pores of the ZIF-8 micro-particles, despite its flexibility, whereas the linear octane was retained because of its longer pathway through the ZIF-8 pores. A successful separation of a 2-methyl octane and nonane

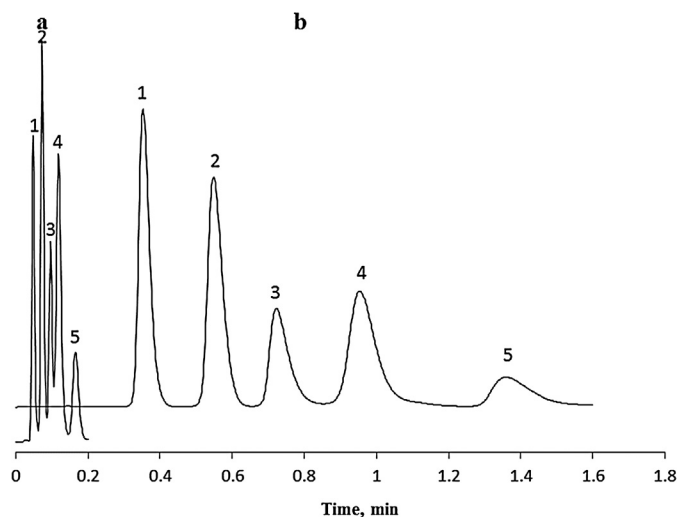


Fig. 3. Separation of polar organic solvents mixture using control column (a), and ZIF-8-(BuMA-co-EDMA)-2 column (b). Conditions: isothermal 100 °C; inlet pressure 1 MPa; split injection. Peaks: diethyl ether (1), acetone (2), dichloromethane (3), tetrahydrofuran (4), and chloroform (5).

mixture was also performed under the same previous conditions with good resolution ($R_s = 1.1$), whereas the control column with no ZIF-8 failed to separate the mixture (Fig. 4b).

In a promising experiment, a ZIF-8-(BuMA-co-EDMA)-2 column proved its ability to separate gases under ambient temperature (conditions: isothermal at 30 °C; inlet pressure 1 MPa; splitless injection). Iso-butane/iso-butylene, a gas mixture of industrial significance, was separated with high resolution ($R_s = 1.4$) at room temperature in approximately 0.5 min (Fig. 5). The perfect combination between the high surface area apolar ZIF-8 and the high permeable BuMA-co-EDMA monolith was responsible for the unusually good separation at room temperature because the polymeric monolithic column alone was unable to separate the mixture.

3.3. Column efficiency

Fig. 6 shows the height equivalent of theoretical plates (HETP) versus the flow rate of the carrier gas in a van Deemter curve for ZIF-8-(BuMA-co-EDMA)-2 composite column. The van Deemter curves for octane and nonane using both the control column and ZIF-8-(BuMA-co-EDMA)-2 composite column were plotted over a range of different pressures (0.5–1 MPa), where the flow rates were measured manually using a flowmeter and at

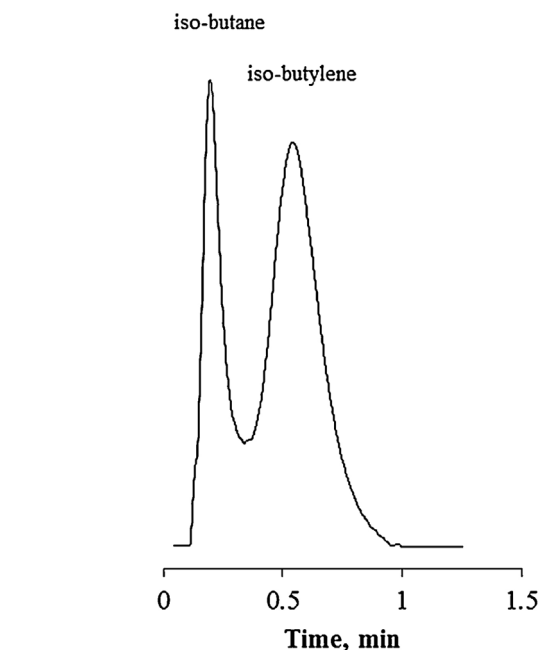


Fig. 5. Separation of iso-butane-iso-butylene gas mixture using ZIF-8-(BuMA-co-EDMA)-2 column. Conditions: isothermal at 30 °C; inlet pressure 1 MPa; splitless injection.

constant temperature of 120 °C. The optimal values of the HETP from the van Deemter curves showed that the incorporation of ZIF-8 into the monolithic matrix increased the column efficiency. HETP improved from 0.79 mm (1296 plates m^{-1}) for octane and 0.67 mm (1500 plates m^{-1}) for nonane using control column to 0.56 mm (1770 plates m^{-1}) for octane and 0.61 mm (1647 plates m^{-1}) for nonane using ZIF-8-(BuMA-co-EDMA)-2 composite column. The van Deemter curves proved the superiority of the composite column over the neat polymeric control column.

One of the benefits of monolithic phases in GC is the reduced C term (interphase mass transfer) indicating by shallow van Deemter plots which allow to perform faster separations without losing too much efficiency. That is to say there is no significant change in efficiency when increasing the flow rate to exceed the optimum value using monolithic columns other than packed columns or open tubular columns [31–33]. The incorporation of ZIF-8 microparticles into methacrylate monolith did not affect the mentioned advantage of the monolithic phase allowing for even faster separation with almost the same efficiency (Fig. 6).

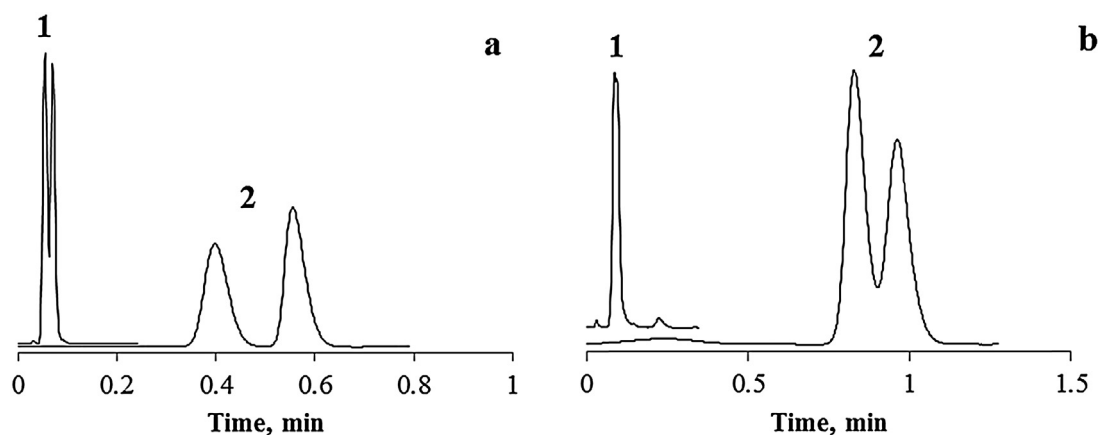


Fig. 4. Separation of structural isomers using control column (1), and ZIF-8-(BuMA-co-EDMA)-2 column (2). Conditions: isothermal 150 °C; inlet pressure 1 MPa; split injection. Peaks: iso-octane and octane, respectively, as eluted (a), 2-methyl octane and nonane, respectively, as eluted (b).

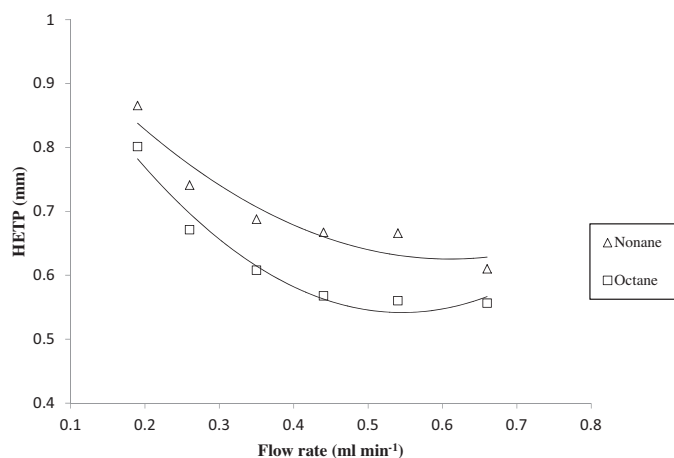


Fig. 6. The van Deemter plots relating height equivalent of theoretical plate (HETP) and flow rate of the carrier gas (helium) for ZIF-8-(BuMA-co-EDMA)-2 composite column. At constant temperature 120 °C and at a pressure range of 0.5–1 MPa. Solutes: octane and nonane.

van Deemter plots for polar solutes also showed an improvement in the efficiency using the composite column over the control column. For instance, the plate number per meter for dichloromethane separation increased from 1500 plates m^{-1} (HETP = 0.66 mm) using control column to 2721 plates m^{-1} (HETP = 0.36 mm) using ZIF-8-(BuMA-co-EDMA)-2 composite column.

3.4. Repeatability, reproducibility and stability

A repeatability study was performed on ZIF-8-(BuMA-co-EDMA)-2 using pentane and nonane as testing solutes to inspect the stability of the composite stationary phase (Table 1). The run-to-run repeatability for 10 successive injections at 150 °C isothermal condition and 1 MPa inlet pressure was very good with a relative standard deviation (RSD %) of 0.02 for pentane and 0.09 for nonane with respect to the retention factor. The RSD % of the efficiency in terms of the HETP was 0.21 for pentane and 0.02 for nonane. The 1 week day-to-day repeatability demonstrated good repeated results, with a very small retention factor error of 0.03 RSD % for pentane and 0.11 RSD % for nonane. The efficiency of the column was sustained over the 7 days, with 0.03 RSD % for the HETP for pentane and 0.02 RSD % for the HETP for nonane.

To investigate the column-to-column reproducibility, pentane and nonane were separated using nine different columns prepared

Table 1
Repeatability and reproducibility study for the ZIF-8-(BuMA-co-EDMA)-2 column.

Column	Run to run				Day	Day to day				Batch	Column to column			
	Pentane		Nonane			Pentane		Nonane			Pentane		Nonane	
	k^a	H^b (mm)	k	H (mm)		k	H (mm)	k	H (mm)		k	H (mm)	k	H (mm)
ZIF-8-(BuMA-co-EDMA)-2	0.79	0.50	6.86	0.32	1	0.78	0.41	6.67	0.32	a	0.86	0.53	6.89	0.59
	0.79	0.50	6.65	0.31	2	0.80	0.41	6.81	0.26		0.91	0.76	6.94	0.32
	0.84	0.76	6.85	0.33	3	0.74	0.53	6.54	0.33		0.92	1.05	6.66	0.49
	0.83	0.32	6.88	0.31	4	0.86	0.38	6.88	0.29	b	0.77	0.93	6.35	0.54
	0.77	0.94	6.67	0.34	5	0.81	0.44	6.80	0.28		0.90	0.35	6.82	0.24
	0.79	0.60	6.79	0.31	6	0.78	0.42	6.74	0.32	c	0.76	0.36	6.22	0.39
	0.81	0.58	6.88	0.32	7	0.78	0.49	6.63	0.31		0.85	0.66	6.91	0.57
	0.79	0.41	6.81	0.31							0.96	0.94	6.70	0.36
	0.75	0.52	6.77	0.37							0.72	1.09	6.49	0.30
		0.77	0.94	6.66	0.36									
Average	0.79	0.60	6.78	0.32		0.79	0.44	6.72	0.30		0.85	0.74	6.66	0.42
RSD% ^c	0.02	0.21	0.09	0.02		0.03	0.05	0.11	0.02		0.08	0.28	0.26	0.13

^a Retention factor.

^b Height equivalent of theoretical plate.

^c Relative standard deviation %.

Table 2

Comparison between an open tubular commercial column and the ZIF-8 incorporated monolithic column at the optimal isothermal conditions and at the same carrier gas (helium) flow rate of 0.6 $mL\ min^{-1}$.

Columns	TR-5 MS ^a			ZIF-8-(BuMA-co-EDMA)-2		
	t_R (min) ^b	N (m^{-1}) ^c	H (mm) ^d	t_R (min)	N (m^{-1})	H (mm)
Alkanes^e						
Pentane	2.79	537	1.96	0.21	2640	0.38
Hexane	2.92	554	1.81	0.27	2580	0.39
Heptane	3.21	590	1.69	0.38	2991	0.33
Octane	3.67	558	1.79	0.57	3315	0.30
Nonane	4.67	377	2.65	0.89	3282	0.31
Polar solvents^f						
Diethyl ether	3.31	Not separated		0.27	1296	0.77
Acetone	3.31			0.37	1692	0.59
DCM	3.47	2475	0.40	0.46	2199	0.45
THF	4.22	4090	0.24	0.57	2310	0.43
Chloroform	4.10	2307	0.43	0.74	2640	0.38

^a Commercial open tubular column (3000 cm long \times 250 μm i.d.).

^b Retention time.

^c Number of theoretical plates.

^d Height equivalent of theoretical plates.

^e Alkanes mixture as a non-polar sample.

^f Polar solvents mixture as a polar sample.

from three separate polymerization batches (Table 1). Reproducibility study showed that ZIF-8-(BuMA-co-EDMA) composite columns are reliable with a retention factor RSD % of 0.08% for pentane and 0.26% for nonane and with HETP RSD % of 0.28% for pentane and 0.13% for nonane.

3.5. Comparison with an open tubular capillary column

A TR-5MS (5% phenyl methylpolysiloxane) column (3000 cm long \times 250 μm i.d.) was chosen as an example of a commercially available open tubular capillary column for comparison with the ZIF-8-(BuMA-co-EDMA) (33.5 cm long \times 250 μm i.d.) composite monolithic capillary column (Table 2) because of its predominant non-polarity with slight polarity from the added 5% phenyl groups, which is similar to the ZIF-8-(BuMA-co-EDMA) stationary phase. The separation was optimized using isothermal condition for both columns at the same flow rate of 0.6 $mL\ min^{-1}$ which is the optimum gas flow for the composite column extracted from the van Deemter plot. A linear alkane mixture (pentane, hexane, heptane, octane and nonane) was separated using the TR-5MS column in 4.67 min at 100 °C and in 0.89 min at 150 °C using

ZIF-8-(BuMA-co-EDMA)-2. The separation efficiency increased 4–5 times when using the ZIF-8-(BuMA-co-EDMA)-2 column, as shown in Table 2. Moreover, the analysis time was reduced 80–92% and the resolution between pentane and hexane was 1.46 using TR-5MS column and 1.85 using ZIF-8-(BuMA-co-EDMA)-2 column. On the other hand, TR-5MS column has a superior thermal stability (370 °C), also the optimum carrier gas flow for this column is around 1.0 mL min⁻¹ at which the efficiency will be improved, however we have fixed the flow rate at 0.6 mL min⁻¹ to compare the two columns at the same gas consumption level. The use of a more thermally stable polymer other than methacrylate will indeed overcome the thermal stability problem and the utilization of high pressure GC will allow for higher flow rate and even faster separation. ZIF-8-(BuMA-co-EDMA)-2 was also superior to the ZIF-8 coated capillary column (2000 cm long × 250 μm i.d.) from a previous publication [23]. The height equivalent of theoretical plates for hexane was improved approximately 192 times from 73 mm to 0.39 mm, and the analysis time decreased from 1.5 min to 0.89 min.

The same composite column showed excellent separation efficiency for a polar organic solvents mixture (diethyl ether, acetone, dichloromethane, chloroform and tetrahydrofuran) compared with TR-5MS (Table 2). The latter column failed to separate diethyl ether and acetone at 60 °C, whereas the former successfully separated them at 130 °C with high resolution ($R_s \geq 1.92$). The total analysis time decreased from 4.10 min to 0.74 min, and the efficiency increased by 1.2–1.97 times except for THF it decreased. The elution order of the polar sample on TR-5MS changed to follow the boiling points order, except for acetone, which is the most polar eluent among the mixture, because this column is classified as a slightly polar column. The very fast separation provided from the monolithic butyl methacrylate high permeability and the high efficiency of small molecules separation due to the flexible apolar pores and high surface area of the incorporated ZIF-8 micro-particles opens a new horizon for GC separation.

3.6. Real sample analysis

To demonstrate the separation efficiency of the composite monolithic columns for real samples, a paint thinner sample from the local market was tested. Thinner is an ideal mixture to investigate the column performance because it normally contains a few organic solvents related to various chemical species, such as alkanes, alcohols, ketones and aromatics. Eight almost fully separated peaks, which represented the main composition of the thinner sample, were obtained using the ZIF-8-(BuMA-co-EDMA)-2 composite column with a temperature program of 40–45 °C, 5 °C min⁻¹ then 45–150 °C, 120 °C min⁻¹ and 1 MPa inlet pressure (Fig. 7). A quite satisfied separation was obtained for the paint thinner real sample with a good resolution ($R_s \geq 0.89$). The relative percentages of the composition were detected through the area percentages of the separated peaks as well as the retention times, resolution, boiling points and relative polarities (Table S3).

The elution order followed the boiling points elevation order as a primary separation factor; however, as discussed previously, polarity plays a significant role in separation. Methanol was eluted first, followed by acetone, hexane, 2-propanol, 2-butanone, benzene, propyl acetate and toluene, with a total separation period of 2.43 min. The polarity of methanol (relative polarity $E_T^N = 0.76$) overcame its boiling point to move it before the more volatile acetone, which has a lower polarity ($E_T^N = 0.636$) [34]. Similarly, 2-propanol ($E_T^N = 0.057$) eluted at 1.77 min, before more volatile components that have lower polarity, 2-butanone ($E_T^N = 0.33$) and benzene ($E_T^N = 0.11$), which eluted at 1.89 and 2.09 min, respectively. The ability of the novel ZIF-8-(BuMA-co-EDMA) composite

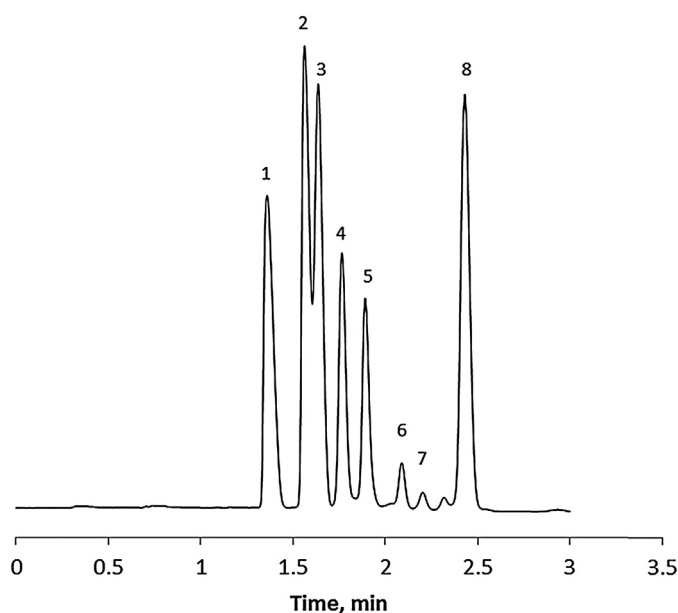


Fig. 7. Separation of a commercial thinner sample using ZIF-8-(BuMA-co-EDMA)-2 column. Conditions: temperature program 40–45 °C, 5 °C min⁻¹ then 45–150 °C, 120 °C min⁻¹; inlet pressure 1 MPa; split injection. Peaks: methanol (1), acetone (2), hexane (3), 2-butanone (4), 2-propanol (5), benzene (6), propyl acetate (7), and toluene (8).

monolithic column to separate complex samples with high efficiency gives it an additional advantage.

4. Conclusions

In summary, the fabricated ZIF-8-(BuMA-co-EDMA) composite column combined the advantages of the BuMA-co-EDMA monolithic matrix and the ZIF-8 micro-particles. The high permeability of the monolithic matrix along with its capillary size achieved a very fast separation with less gas consumption than the open tubular columns. The high surface area, flexible 0.34 nm pores and apolar interactions of ZIF-8 led to a highly efficient separation of various small molecules, such as linear alkanes, polar solvents, structural isomers, gas mixtures and even a complex real sample.

Although the incorporation of MOF particles into a monolithic matrix was explored in HPLC in two recent publications, to the best of our knowledge, this is the first investigation of this stationary phase in GC. We believe that MOF-monolithic polymer composite columns may bring more attention to monolithic columns in GC especially for high pressure GC.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.06.026>

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