Ministry of Higher Education
and Seientific Research

University of Babylon

College of Science

Department of Chemistry

Perparation of Monolithic Material and Used for Analytical Applications

A thesis

Submitted to the Council of College of Science – University of Babylon
In Partial Fulfillment of the Requrirements for the Degree of Master of
in Chmistry

By

Ehab Fadhel Abed Hassan AL- Adely

M.Sc. University of Babylon – 2009

Supervised by Asst. Prof. Dr

Ahmed Ali Abdul- Sahib Al-karimi

2022 A.D **1443 A.H**

وزارة التعليم العالي والبحث العلمي

جامعة بابل /كلية العلوم

قسم الكيمياء

تحضير مادة مونوليثية و استخدامها في التطبيقات التحليلية

رسالة مقدمة

الى مجلس كلية العلوم – جامعة بابل

وهي جزء من متطلبات نيل درجة الماجستير في العلوم / الكيمياء

من قبل

ايهاب فاضل عبد حسن العادلي

بكالوريوس علوم كيمياء – جامعة بابل – ٢٠٠٩

بأشراف

الاستاذ المساعد الدكتور

احمد علي عبد الصاحب الكريمي

2022 م **١٤٤٣ هـ**

بسم الله الرحمن الرحيم

(قُلْ لَّآ أَقُولُ لَكُمْ عِنْدِي خَزَآئِنُ ٱللهِ وَ لَآ أَعْلَمُ ٱلغَيْبَ وَ لَآ أَقُولُ
لَكُمْ إِنِّي مَلَكٌ إِنْ أَتَّبِعُ إِلَّا مَا يُوحَىٰٓ إِلَيَّ قُلْ هَلْ يَسْتَوِي الْأَعْمَى
وَالْبَصِيرُ أَفَلَا تَتَفَكَّرُونَ)

صَدَقَ ٱللهُ ٱلعَلِيُّ ٱلعَظِيمُ

﴿الأنعام : ٥٠﴾

Supervisor Certification

I certify that this thesis was carried out under my supervision at the department of chemistryin College of Science at Babylon University, as a partial fulfillment of the Requirement for the degree of Master in Analytical Chemistry

Signature

Name. Dr. Ahmed Ali Abdulsahib Alkarimi

Scientific Order: Asst. Prof.

Address: University of Babylon / College of Science /Chemistry Department

Date: / /2022

Recommendation of Head of Chemistry Department

In view of the avilable recommendations, I forward this thesis for debate by the examining committee

Signature:

Name: Dr. Saadon Abdulla Aowda

Scientific order: Professor

Address: Head of Chemistry Department/ University of Babylon / College of Science

Date: / /2022

Acknowledgements

One Who Has Not Thanked the Creature Has Not Thanked the Creator

Praise be to Allah the Lord of the worlds and may the blessings and peace of Allah be upon the most honored of messengers our master Muhammad and upon all his family and companion.

I express my heartful thanks and deep regards to my supervisor (Asst. Prof. Dr. Ahmed Ali Abdul sahibAlkarimi) for his exemplary guidance, monitoring and constant encouragement throughout the course of this work.

I take this opportunity too to express my profound gratitude and deep regards to University of Babylon, College of Science/Chemistry Department, My colleagues graduate students, my family and all my friends

Ehab Fadhel Abed Hassan

Dedication

To those who were the reason for our survival ……. the martyrs of Iraq

To those who gave their lives for us ………..   my father and my mother

To whom I had the best deed ……...my wife, my brothers and my sisters

To those who fill my life with happiness ………. …………... my children

To those who stood with me in a time of trouble ……………my friends

I dedicate this work with all love and respect

Ehab Fadhel Abed Hassan

Table of Contents

Table of Figures

Table of Tables

Abbreviations

A.Am	Acryl amide
AIBN	2 , 2, - Azobisisobutyronitrile
ATRP	Atom Transfer Radical Polymerization
BET	Brunauer-Emmett-Teller
C°	Celsius
CCTP	Catalytic chain transfer polymerisation
CX	Cationic exchange
DEGDMA	Di(ethylene glycol) dimethacrylate
DMAP	2, 2-Dimethoxy-2-phenylacetophenone
EDMA	Ethylene glycol dimethacrylate
FESEM	Field Emission Scanning Electron Microscopy
GC	Gas Chromatography
GMA	Glycidyl methacrylate
h	Hours
HPLC	High Performance Liquid Chromatography
id	Internal diameter

LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantitation
min	Minute
NMP	Nitroxide mediated polymerization
od	Outer diameter
psi	Pressure per square inch
RAFT	Reversible addition−fragmentation chain-transfer
SAX	Strong anion exchange
SCX	Strong cationic exchange
TEGDMA	Triethylene glycol dimethacrylate
TEOS	Tetraethoxysilane
TMOS	Tetramethoxysilane
TSP	3 - (Trim ethoxysilyl) propyl methacrylate
TSP	3- (Trimethoxysilyl) propyl methacrylate
UV	Ultraviolet light
WAX	Weak anion exchange
WCX	Weak cation exchange

Summery

Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic column was manufactured as strong cation exchange column. A borosilicate tube (60 mm in length) with 1.5 mm, and 3.0 mm (i.d and o.d respectively) was used for insitu copolymerization using U.V light source.

The polymerization mixture was prepared by mixing monomers (glycidyle metharcrylate and acryl amide) (GMA) and crosslinker (ethylene dimethacrylate) (EDMA) and initiator (2, 2-dimethoxy-2-phenyl acetophenone) (DMPA) was dissolved in porogenic solvent consisting of 1-propanol and 2-butanol. The time taken to form the polymer inside the borosilicate column in the irradiation cabin was 4 minutes.

Various techniques were used such as FTIR, ^{1}HNMR, BET, and FESEM, to prove the formation of the polymer and also study the properties of the polymer such as pore size and surface area. Some properties of the prepared monolith have been investigated such as irradiation time, the distance between the irradiation source and the monolith column, Permeability of the monolith, chelating capacity for monolith column, Porosity calculation and Swelling measurement. The epoxy ring in glycidyle methacrylate was opened to form diol group Thus, the formation of a cation exchange column is by pumping 0.2 M HCl for 3 hours at a flow rate of 20 $\mu L.min^{-1}$ The monolith column used to remove some heavy metal has a direct relationship with the environment pollutants and with living organisms such as copper, lead and nickel by using ion exchange techniques.

Standard and wastewater solutions are used to investigate column efficiency in separation and two techniques were used for the determination of that separated heavy metals, atomic absorption spectrophotometer to determine copper, lead and nickel, and spectrophotometric method by using selective neocuproine reagent to determine copper. Beers' Lambert law was applied to constrict the calibration curve in the range (0.5-28 mg.$^{L-1}$), with LOD and LOQ 0.129 mg.L^{-1}, 0.353 mg.L^{-1} respectively. It was found arang validity of the prepared columnwas 70 days.

الخلاصة

تم تصنيع عمود مونوليثي من Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide وتم تعديله كعمود تبادل كتايوني قوي تم استخدام انبوب من البوروسلكيت (بطول ٦٠ ملم وبقطر داخلي ١،٥ملم وقطر خارجي ٣ ملم) لغرض البلمرة باستخدام مصدرللاشعة الفوق بنفسجية .

تم تحضير خليط البلمرة باستخدام المونمرات غليسيديل ميثاكريلات (GMA) (glycidyle metharcrylate) وأكريل أميد (A.Am) (acryl amide) ورابط متشابك (EDMA) (ethylene dimethacrylate) وبادئ (2,2-dimethoxy-2-phenyl acetophenone)

(DMPA) وتم اذابة الخليط باستخدام مذيب بروجيني يحتوي على 1-propanol و2- butanol وكان الزمن المستغرق لتكون البوليمر ٤ دقيقة داخل كابينة التشعيع.

تم استخدام عدد من التقنيات وهي طيف الاشعة الحمراء (FTIR),الرنين النووي المغناطيسي لبروتون الهيدروجين (^{1}HNMR), وتحليل (BET) ،والمجهر الالكتروني الماسح (FESEM)

لاثبات تكون البوليمر وايضا لدراسة بعض خصائص البوليمر مثل حجم المسام والمساحة السطحية كذلك تم دراسة بعض خصائص البوليمر مثل وقت التشعيع ،المسافة بين مصدر التشعيع وعمود البوليمر ،نفاذية عمود البوليمر ،المسامية ،السعة المخلبية للعمود ،الانتفاخية .

تم فتح حلقة الايبوكسي في غليسيديل ميثاكريلات لتكوين مجاميع الدايول وبالتالي تكوين عمود تبادل كتايوني قوي وذلك عن طريق ضخ 0.2M من حامض الهيدروكلوريك لمدة ثلاث ساعات وبمعدل تدفق $20\mu L.m^{-1}$.تم استخدام عمود التبادل المحضر لازلة بعض العناصر الثقيلة والتي لها علاقة مباشرة مع البيئة المحيطة وبالتالي مع الكائنات الحية مثل النحاس ،الرصاص والنيكل باستخدام تقنية التبادل الايوني

استخدمت محاليل قياسة ومحاليل للمياة العادمة لاختبار كفاءة العمود في الفصل ،تم استخدام نوعين من تقنيات التقدير لتقدير الايونات المزالة تقنية الامتصاص الذري حيث تم تقدير كل من النحاس ،الرصاص والنيكل بالاضافة الى تقنية الامتصاص الطيفي لتقدير النحاس باستخدام كاشف متخصص وهو كاشف النيوكروبين ،تم تطبيق قانون لامبريت بيرت بمدى (0.5-28ppm) وبحد كشف $0.129mg.L^{-1}$ وحد قياس كمي $0.353mg.L^{-1}$.تم حساب عمر العمود وكان ٧٠ يوما .

Chapter one

Introduction

1. Introduction

1.1. General introduction

Robert Synge[1] a Nobel laureate in the 1950s, was the first to postulate the existence of structures similar to what are now called monoliths[2] However, he noticed that these structures containing these soft materials would collapse under stress because they were primitive structures and were not designed to withstand high pressures. This is what Kubín et al [3]. Confirmed after 15 years when 2-hydroxyethyl methacrylate hydrogel monolith was prepared and tested where the permeability was very low.

Despite the creation of a polyurethane monolith that was more successful and through which a decent separation was obtained in GC and LC However, these early technologies did not last long and the modern era of monolithic columns began later [4-6].

In the mid-1980s, Belenky et al [7] studied the chromatography of proteins with a variety of chemical and column engineering groups at that time, they used stationary phases in rinsing method and this discovery resulted in what is known as the short saperation. Excessive over filling has made the creation of these layers of micro- sorbent materials extremely difficult, so a new generation of stationary phase- monoliths must be born [8].

The origin of the preparation of the highly bonded monolithic material is through a polymerization mixture consisting of monophenyl and diphenyl methacrylate monomer, a free-radical initiator, and a porogenic solvent in a flat or tubular mold that yielded a sheet or cylinder, then the prepared polymer is cut into strips in the form of discs after it has been removed from the mold, and used in chromatographic separation, hence, after continuous research a polymeric monolith was invented within typical columns as well as extended monomers used to styrene, divinylbenzene, acrylate and their derivatives[9].

At that time, Hjertén and his colleagues developed a cross-linked gel by polymerizing aqueous solutions of N, N-methylene bisacrylamide and acrylic acid in the presence of salt, usually ammonium sulfate, the gel was filled inside the column cross section after compressing its original volume to a small fraction and it showed good flow permeability despite the high pressure generated[10]. Tanaka et al. [11] found their inspiration in the inorganic aggregate, which is widely used in silica- chromatography [12].

Early studies shown that the organic polymeric and inorganic polymeric silica-based aggregates have low return pressure and high flow rates, these features make it widely used in the separation of large and small particles like proteins and nucleic acids [7,13,14]

1.2 Monolithic materials

A monolith can be defined geologically as a single rock of different shapes interspersed with holes, the word monolith consists of two terms (mono), and (lithos), which means (one) and (stone) respectively, the examples of these rocks are those used by the Chinese to build palaces. The monolithic rock is shown in Figure 1.1[15].

Figure 1.1 Photograph of the porous monolith erected at the entrance of the Summer Palace Park, Beijing , China. [15]

Monolithic separations media have become in recent decades singificant separation media duo to them have many advantages. For example, they have low backe pressure and high flow rate because they contain a large number of connected channels in addition to the ease of preparation using homogeneous or heterogeneous materials within matrix [16-18].

By compareing the monolithic separation media with traditional packed columns, special advantagescan be noted for homogeneous separation media because it consists of one piece with high permeability [19-21] .The traditional packing Columns contain rather large voids, even in the ideal columns. 30%

of the volume is voids, and this is a natural result of filling, and this percentage is considered large, so that a large part of the column volume is not used for separation (Figure 1.2 a). Thus, the only way to improve the separation efficiency is to reduce the porous particle size and lengthen the diffusion path (Figure 1.2 b). Despite this improvement, thire a problem with permeability it will low and backe pressure will be high therefore, it is preferable use a monolith in the separation because it is characterized by high permeability and low back pressure (Figure 1.2 c) [22].

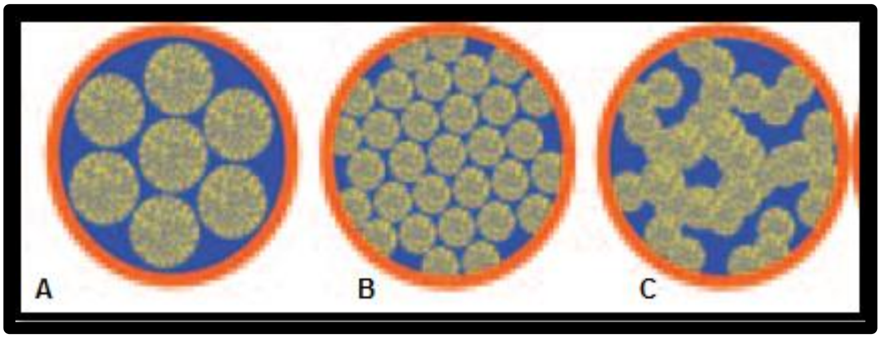


Figure 1.2 Evolution of columns from (a) highly permeable and less-efficient packed columns to (b) less-permeable and highly efficient packed columns to (c) highly permeable and highly efficient monolithic columns

1.3 Types of monoliths

1.3.1 Organic-based monoliths

Hjerten et al. [10] is one of the attempts to prepare the organic monolith in the late 1980s. This type can be prepared by mixing the monomer, crosslinker, porogenic solvent and an initiator [23]. There are three types of monomers that are commonly used in organic polymer monoliths; methylacrylates [24] styrene [25], and acrylamides [26].

The reason for choosing these monomers is that they have individual properties that make them widely used in the organic monoliths. For example, styrene is chosen because of the aqueous nature of its aromatic ring, while methyl acrylate is chosen because of its methoxy ring [26].

In this type of monoliths, 1-propanol and 1, 4-butanol are often used as porogenic solvents to help mix the components homogeneously in addition to controlling the porosity of the column. Also, these solvents help in the growth of monolith in one direction, as a result of homogeneous mixing [27].

The organic monolith Figure (1.3) has some special properties such as moderate back pressure and operates in a wide range of pH [28,29]. The organic polymer consists of three types, the first type is in the form of a column, where the polymerization takes place inside the column whose length is 30-60 mm, the second type is in the form of a plate or a thin disk of 3 mm in size, and the last type is polymerized inside capillary tubes and is used in separation applications on a large scale [30,33] table (1.1) shows some of the types of organic monolith used in different types of separation.

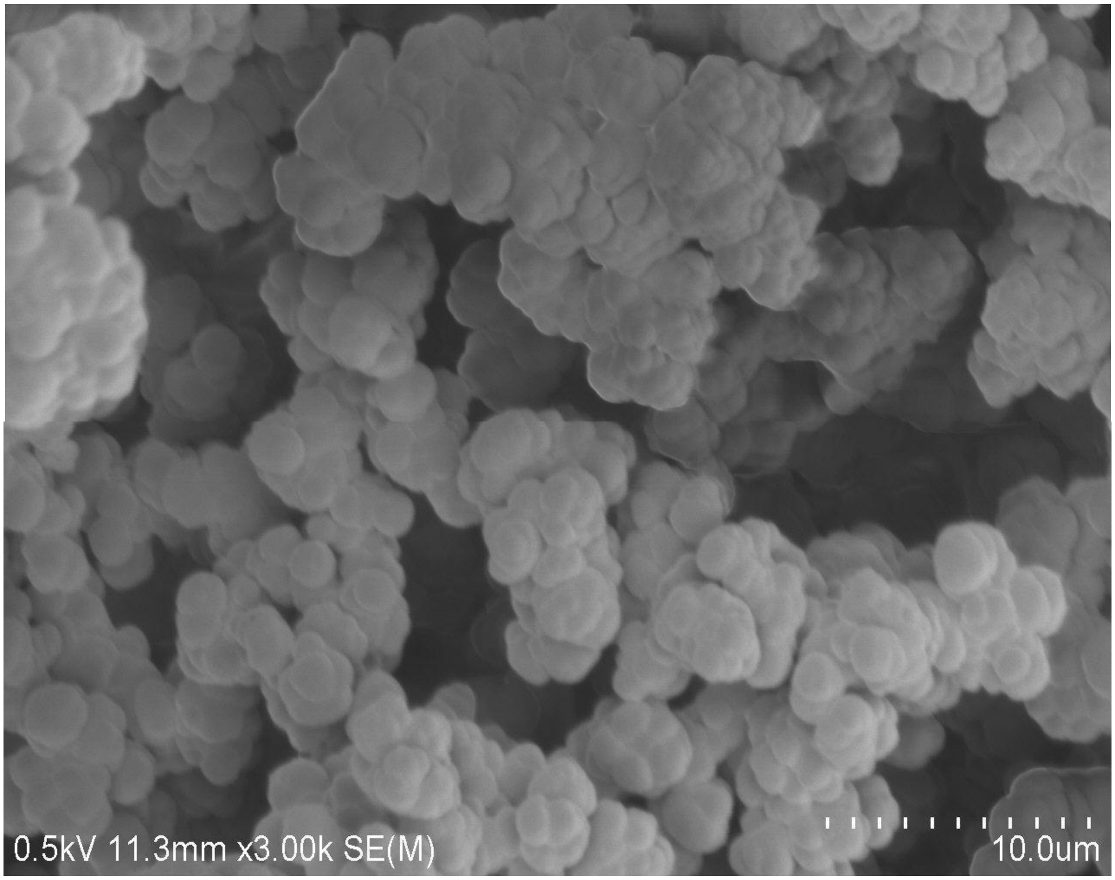


Figure 1.3 Organic-based monoliths [38]

In Table 1-1, we will review some types of organic monoliths, which are considered as previous studies of this type.

Table 1-1 types of organic monoliths

Monoliths	Technique	Sample	Reference
(AAm-Mann-Monomerco-Bis) glycomonolith	Affinity bioseparation	Concanavalin A	[34]
(dimethylacrylamide) with attached phage	Affinity chromatography	Particulate containing feeds	[35]
Poly(GMA-co-EDMA) monolith, RNA aptamer functionalized	Affinity chromatography	Lysozyme in egg white solution	[36]
oly(HEMA-co-PEGDA) cryogel monolith	Anion exchange	Immunoglobulin G	[37]
llulose grafted with GMA	chromatography	IgG	[38]
(AHA-co-PMA-co-EDMA) monolith	hydrophilic and cation exchange	Proteins	[39]
(IL-co-C12-co-TMPTAco-EDMA)	Ion Exchange	Lysozyme	[40]
(VER-co-EDMA) monolith	Anion exchange	human plasma	[41]
Poly(styrene-co-DVB)	Reverse Phase Chromatography	Protein	[42]

1.3.2 Inorganic-based monoliths

Inorganic monolith can be prepared using a variety of materials such as silica, alumina, zirconia, iron and other materials. These columns (most of which are silica) contain a large number and variety Pores that are used to separate molecules [43].

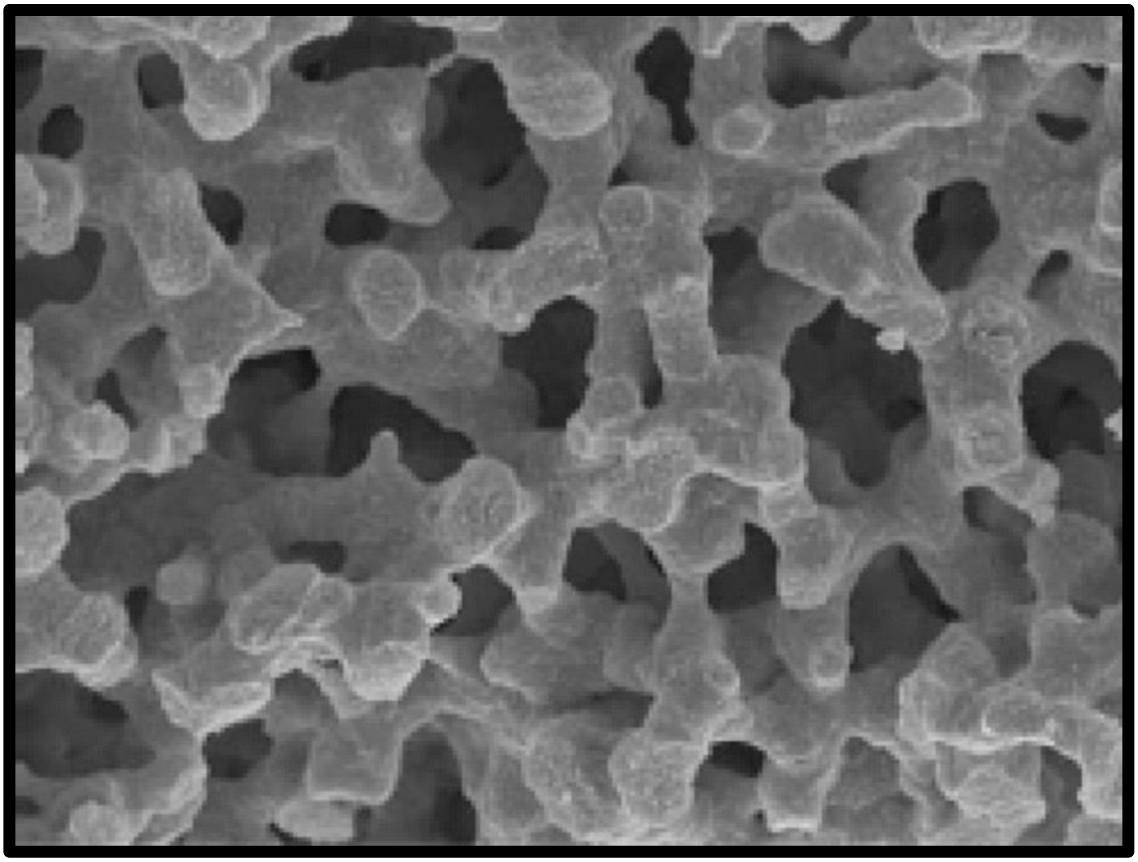


Figure 1.4 Inorganic-based monoliths [44]

Nakanishi and Suga [12].(50 years old) were among the first used silica in the preparation of inorganic homogeneous stones. They used tetraethyl orthosilicate (TEOS), (TMOS), respectively as basic materials in the preparation of silica monolith. TEOS and TMOS are hydrolyzed and then condensed in the presence of polyethylene glycol, thus forming a large compact mass and then treated with ammonia to create pores on the silica structure, the resulting silica monolith often needs further chemical derivation with functional groups such as poly(4-vinylphenylboronic acid-co-MBAA)) for example [45].

Silica monolith has many advantages and characteristics, including that it possesses a very specific network of large and medium pores (Figure 1.4) and as a result, the surface area is relatively large (often 200–300 $m^2 . g^{-1}$) the pore size and surface area can also be controlled by adjusting the preparation parameters. Also, one of the properties of the silica monolith is that it is stable at high temperatures (more than 750 degrees Celsius) and does not swell or shrink upon contact with various solvents [46, 47].

There are limitations when using the inorganic aggregate, including the dissolution of its external structure consisting of silica when using solutions with a pH higher than 8, so it is recommended to use solutions with a pH of less than 8 in addition, the alkoxide precursors is insoluble in water, which must be dissolved to obtain the proportion of silica - water suitable for complete hydrolysis and this problem can be overcome by using solvent agents such as alcohol [48]. There are many different types of inorganic monoliths that are used in a wide range of fields. Some of them are presented in Table (1.2).

Table 1-2 Some types of inorganic monolith

Monoliths	Technique	Sample	Reference
Sol-Gel with rSPA immobilized on it	chromatography	antibodies	[49]
Trypsin-functionalized silica and titania monolith	Chromatography.	oligonucleotides	[50]
aluminosilica monoliths	Adsorption	proteins	[51]
Pepsin-functionalized silica monolith	electrochromatography	Nefopam	[52,53]
CuAAC silica	chromatography	Glycoprotein	[53]
Trypsin-functionalized silica and titania monolith	Mass spectrometry	Lysozyme	[54]
Sol-Gel modified with C18 and –CN Mesoporous	Reverse phase chromatography	Peptides	[55]

1.3.3. Hybrid monoliths (Organic – Inorganic)

In recent years, a new class of monoliths has emerged, called the hybrid monolith, which combines its characteristics between organic and inorganic monoliths. Thus, the hybrid monolith consists of two main parts, the first of which contains the inorganic silica part (HSM), and the other contains the organic polymer part (HPM) [56].This is done by distributing the organic matrix evenly through the inorganic matrix [57]. As a result of this combination of the two types; we get new characteristics such as increased biocompatibility [58] increased thermal stability, which leads to increased lifespan [59] and finally increased mechanical force [60].

1.4. Polymerization process

Vinyl polymerization is a significant method in the process of creating polymers and is of considerable importance in numerous sectors of life, whether photopolymerization or thermal polymerization, after preparing the polymerization mixture, which consists of monomers, initiator, cross-linker, and organic solvents, the polymerization process begins, which is either thermal polymerization or photopolymerization, although photopolymerization is the most often used polymerization. This is accomplished by employing a UV source with a wavelength of about (365nm) The photopolymerization process is mostly dependent on the generation of free radicals[61,62].

1.4. 1.Thermal polymerization

In this process, heat is used to generate free radicals, where the polymerization mixture is injected into the column or disc and placed in a water bath. In most cases, isobutyl is used as an initiator in the thermal polymerization process [63].

Thermal polymerization was first used in 1992, when Svec and Frechet[63] published a paper on the manufacture of continuous sticks (called monolith columns at this time) using glycidyl methacrylate as monomer and ethylene glycol dimethacrylate as a cross-linker and using cyclohexanol and dodecanol as pyrogenic solvents and the initiator was AIBN[64]. The temperature must be controlled to obtain a porous structure that can be repeated regularly at high temperatures, the decomposition of the initiator and the diffusion rate is large, accompanied by a large growth in the size of the nuclei, and thus the size of the pores becomes very small at low temperatures, the decomposition of the initiator is very little. Therefore, moderate temperatures must be used to achieve it as a balance between the size of the pores and the degree of decomposition of the initiator required [65].

The choice of initiator may also affect the features of the porous structure obtained. For example, the replacement of 2, 2, 9-azobisisobutyronitrile (AIBN) by 2, 2, 9-azobis- (2, 4-dimethyl) valeronitrile (ADVN) in the preparation of poly (glycerol dimethacrylate) monolith, while keeping the other reaction parameters constant, lead to a decrease in population of mesopores and to formation of more macropores that, in turn, resulted in a decrease in the total surface area from 143 to 93 $m^2.g^{-1}$ [66].

1.4.2. Photopolymerization

The term photopolymerization means the use of light as an energy source in the formation of polymers, where this energy is used to form new chemical bonds. Photopolymerization usually takes place at a temperature of (10-41) C°, but most of the time photopolymerization takes place at room temperature. Photoinitiators absorb energy in the visible and ultraviolet (250-450) nm region in contrast to thermal polymerization. Solvents with low boiling points can be used such as ethanol, tetrahydrofuran, acetonitrile, propanol, chloroform, butanol, ethyl acetate, and hexane [66, 67].

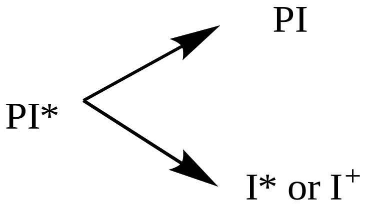
For light to be absorbed by the initiator the emission line from the light source must overlap the initiator's absorption band. In this case, the photoinitiator (IP) is raised to the state of electronic excitation (by upgrading the electron to a higher energy orbital) and is symbolized by (PI*) as in Eq [68].

$$\mathbf{PI + Light \longrightarrow PI^*} \qquad \mathbf{1.1}$$

The life time of PI is very short and then it goes through two phases

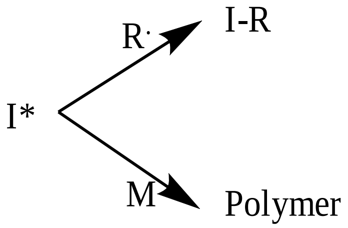
1- Decay and return to PI with the generation of heat and light.

2- It undergoes a chemical reaction, and this phase results in reactive intermediate I* or I^+:



1.2

The reactive intermediate, for example, I* in turn may react with another radical R that initiates the polymerization of the monomer M:



1.3

Photopolymerization takes less time than thermal polymerization and is affected by the intensity of the bright light and the concentration of the initiator. Khimich et al. [69] investigate the photopolymerization of poly (GMA-co-EDMA) monomers using (Darokur-1173) as an initiator and cyclohexanol as an organic solvent, it was discovered that using 1 % of the weight of the initiator yields an 80 % yield after 20 minutes of irradiation with ultraviolet rays with a wavelength of 320 nm, but increasing the weight of the initiator from 1 % to 2 % by weight yields a return of 96 % while maintaining homogeneous polymer units.

1.5. Free radical polymerization

Free radical polymerization is one of the polymer formation processes in which the polymer grows by successive addition of monomer units. This process occurs by breaking the double bonds and converting them to an active free radical [70]. Free radical polymerization is one of the most widely used polymerization processes. In addition to its recent applications in the separation processes in chemistry, it is also used in the industrial field, as is the case in the manufacture of safety glass using poly (methyl methacrylate) and the manufacture of coffee cups from polystyrene foam to polymerize free radicals. Several advantages, including the following; [71]

1- Relative sensitivity to impurities
2- Their reactions require moderate temperatures
3- Allow multiple polymerization processes

The mechanism of free radicals is well understood, and the extension of its concept to new monomers is clearly visible. The mechanism of free radicals can be summarized in the following diagram;

$$\text{Initiator} \longrightarrow 2R^{1*} \qquad \text{Initiator}$$

$$2R^{1*}+M \longrightarrow R_1^{*} \qquad \text{Chain Initiation}$$

$$R_1^{*}+nM \longrightarrow R_n^{*} \qquad \text{Propagation}$$

$$R_n^{*}+AB \longrightarrow R_nA+B^{*} \qquad \text{Transfer}$$

$$\left.\begin{array}{ll} R_m^{*}+R_n^{*} \longrightarrow P_{m+n} & \text{Combination} \\ R_m^{*}+R_n^{*} \longrightarrow P_M+P_n & \text{Disproportionation} \end{array}\right\} \text{Termination}$$

$R^{1}*$ represents a free radical capable of initiating propagation; M denotes a molecule of monomer; Rm* and Rn* refer to propagating radical chains with degree of polymerization of m and n, respectively; AB is a chain transfer agent; and Pn + Pm represent terminated macromolecules [71]. Free radical polymerization is used in the preparation of many polymers such as poly (vinyl chloride), polystyrene and its copolymers (with acrylonitrile, butadiene, etc.), polyacrylates, polyacrylamide; poly (vinyl acetate), poly (vinyl alcohol) and fluorinated polymers comprise the most important of these materials. However, no pure block copolymers and essentially no polymers with controlled architecture produced by conventional radical polymerization [72].

1.6. Monomers

1.6.1. Glycidyl methacrylate (GMA)

There are many monomers that are used in the production process of monolith, but one of the most famous and widely used of these monomers, is glycidyl methacrylate (GMA) [73-75] duo tothat its structure contains an epoxy group, which is an effective group that can be modified according to the required reaction (Figure 1.5).

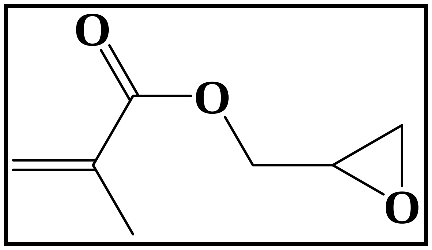


Figure .1.5. Glycidyl methacrylate (GMA)

the properties of monomers contribute to determining the solvents used in the polymer formation process, and therefore they also play a role in the formation of the porous structure of the polymer. For example, when preparing poly (GMA-co-EDMA) with a pore size of 1mL, that needs 20% of dodecanol solvent and 80% of cyclohexanol, while when preparing 2-hydroxyethyl methacrylate (HEMA) with the same pore size we need a larger amount of dodecanol solvent [75]. Merhar et al. [75,76] combine nine monomers, including GMA, initially alone, and the second time combined the nine monomers with EDMA, they observed that the pore radius decreased with the increase of hydrophobicity with respect to GMA, while the total porosity of the monomers prepared from different monomers under similar conditions were very similar, here the effect of EDMA appears, and through this study, they were able to explain the effect of the structure of the monomers on the overall porosity of the polymer.

1.6.2. Acrylamide (A.Am)

It is a white crystalline compound soluble in water, aceton and alcohol but insoluble in benzene. Infrared and Raman spectra studies showed that the entire acrylamide molecule is flat and that the structure of acrylamide is compatible with that of the amide [77].

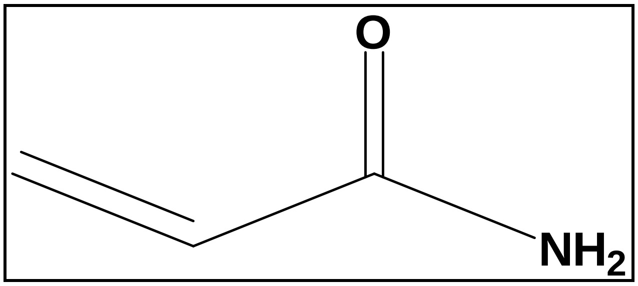


Figure .1.6. Acrylamide (AAm)

The structure of acrylamide Figure (1.6) its contained double bond is one of the features that led to its frequent use in the polymerization of free radicals, whether polymerizing acrylamide alone or with other monomers as well as containing functional groups that can be used after polymerization in various chemical applications such as separation, affinity and other applications [78,79].

1.7. Crosslinkers

Although there are many crosslinkers (Table 1-3), the most famous of them is ethylenedimethacrylate (figure 1-7), where it forms rigid polymers with methacrylate polymers are often copolymerized with butyl methacrylate, glycidyl methacrylate, and hydroxyethyl methacrylate [80-83].

Table 1-3 Some Crosslinkers use in preparation monoliths

Crosslinker	Scientific symbol	Reference
Diethylene glycol dimethacrylates	DEGDMA	[74]
triethylene glycol dimethacrylates	TEGDMA	[84]
trimethylolpropane trimethacrylate	TRIM	[75]
glycerol dimethacrylate	GDMA)	[85]
1,4-butanediol dimethacrylate	BDDMA	[85]

Courtois et al. [74] used a mixture of crosslinkers to prepare monolith methacrylate and these are (DEGDMA) and (TEGDMA), which are characterized by their structure containing chains of diethylene glycol or triethylene glycol which gives the crosslinker a good flexibility which in turn helps to avoid material failure during polymerization due to internal stress pH, and organic solvent contents [86].

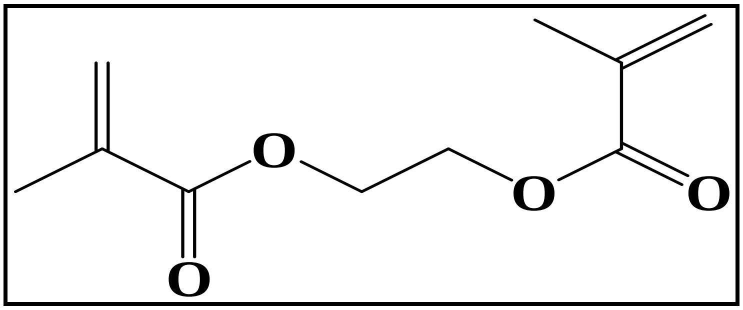


Figure 1.7 Ethylene glycol dimethacrylate

Binghe GU and co-workers [87] were able to prove the effect of crosslinker factors on the final product of the polymer by conducting a study on the poly (PEGMEA-co-EDMA) monolith, which shown great adsorption force and when EDMA was replaced with polyethylene glycol dimethacrylate (PEGDA) with more hydrophilicity than EDMA donot appear any adsorption.

Tennikova et al [8] he manipulated the crosslinker ratios and monitored the flow pressure of the poly (GMA-co-EDMA) monolith, where it was found that 75% of EDMA gave a permeability of 0.8 - 1 and at 60%. It was found that the permeability was 22.4 and in 50% the permeability was 40.0, Thus, the ratio of 50% or the proportions close to it became the optimal condition for the preparation of the polymer.

1.8. Porogenic solvents

It previously knewn that the crosslinker affects the formation and hardness of the monolith, and to a small extent on the formation of pores, but porogens are considered one of the strongest factors that affect the formation of the geometric structure of the pores; therefore, the change of porogen only affects the porous structure of the polymer; therefore, a solvent must be chosen so that it is a good solvent for the monomers and a poor solvent for the final polymer, and this is limited by the solubility parameter(ð) [88,89] for both the monomer and the solvent, for example d is 8.5 for DEGDMA and (ð) is (9.9H),(9.1H),(8.4H),(9.1H) for solvents (acetone, THF, ethyl propionate, and ethyl acetate) respectively; therefore, these solvents are a good solvent for the DEGDMA polymer, so they were excluded from use. So must choose from the solvent (methanol, ethanol, 2-propanol, and tert-butanol), which have values of (ð) (14.5 H, 12.7 H, 11.5 H, 10.5 H) respectively. Indeed, methanol was chosen in the preparation of the polymer (DEGDMA)[90-92].

1.9. Post-polymerization modifications to the epoxy ring in GMA

GMA is an interesting monomer and is commonly used to prepare PGMA in an easy and inexpensive way by free radical polymerization. Figure (1.8) .GMA contains a highly tensioned triple ring, which makes its stay in this triple form a very short period, so such rings are easy to modify in many reactions [64,93-96].

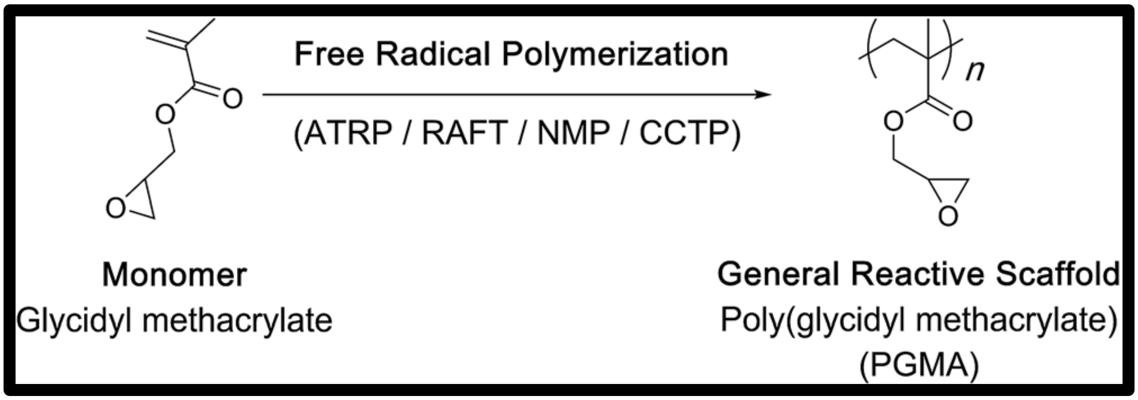


Figure 1.8 Synthesis of polyglycidyl methacrylate by free radical Polymerization methods [97]

Although the epoxy ring in glycyl methacrylate is a ternary ring that is stressful in nature, it needs an acidic or alkaline catalyst which is necessary for the ring opening reaction [98].Modification of polymers after their formation is an important way for functional polymer, which allows their development within the polymer family. There are many chemical reactions that epoxy ring enters, such as functionalisation with amines [99,100] functionalisation with thiols[101,102] functionalization with azide [103] ,functionalization with carboxylic acid [104-106] and functionalisation with water[107,108] (Figure 1.9) .

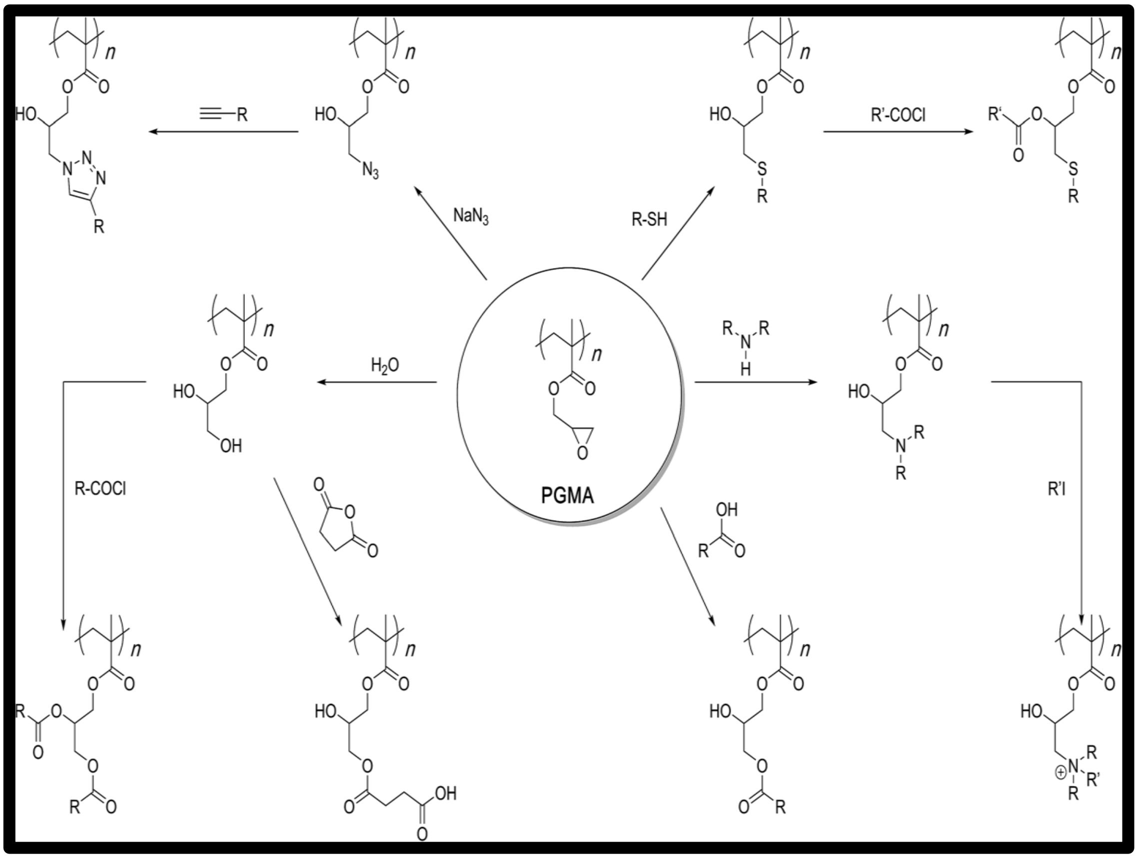


Figure 1.9 Post-polymerisation modification reactions of polyglycidyl methacrylate

1.10. Chromatography [109]

Chromatography is a technique used to separate and quantify molecules. The principle of chromatography depends on where the mixture is applied to the surface or in the solid and the stationary phase is separated from each other with the help of the mobile phase. Some components of the mixture remain for a long time in the stationary phase and move slowly in the chromatographic system, while others pass quickly into the mobile phase and leave the system quickly and this is determined by matters related to adsorption (solid-liquid) and partition (liquid-liquid) and based on this, the basic components can be divided for the chromatographic system as follows;

1-Stationary phase; this stage consists of a solid phase or layer of liquid adsorbed on the surface of a solid.

2- Mobile phase; this phase is always in the liquid state or gaseous component

3-Separated molecules; include a lot of materials to be separated such as ions, proteins, nucleic acids, etc., Chromatography are divided into many types such as [110].

- Column chromatography
- Ion-exchange chromatography
- Gel-permeation (molecular sieve) chromatography
- Affinity chromatography
- Paper chromatography
- Thin-layer chromatography
- Gas chromatography
- Dye-ligand chromatography
- Hydrophobic interaction chromatography
- Pseudoaffinity chromatography
- High-pressure liquid chromatography

1.11. Ion- exchange chromatography

The basis of the work of ion exchange chromatography is the electrostatic interactions between the charged groups of the materials to be separated and between the supporting groups present in the column, provided that the charges are opposite, that is, if the material to be separated is positively charged, the charge of the supporting groups inside the column must be negative and vice versa, after that the material is separated from the column either by the concentration of ionic salts and the ionic strength of the buffer solution or by changing the pH value [111].

There are two types of ion exchangers, positively charged ion exchangers, called anion exchangers, and negatively charged ion exchangers, called cation exchangers Figure(1.10)[112].

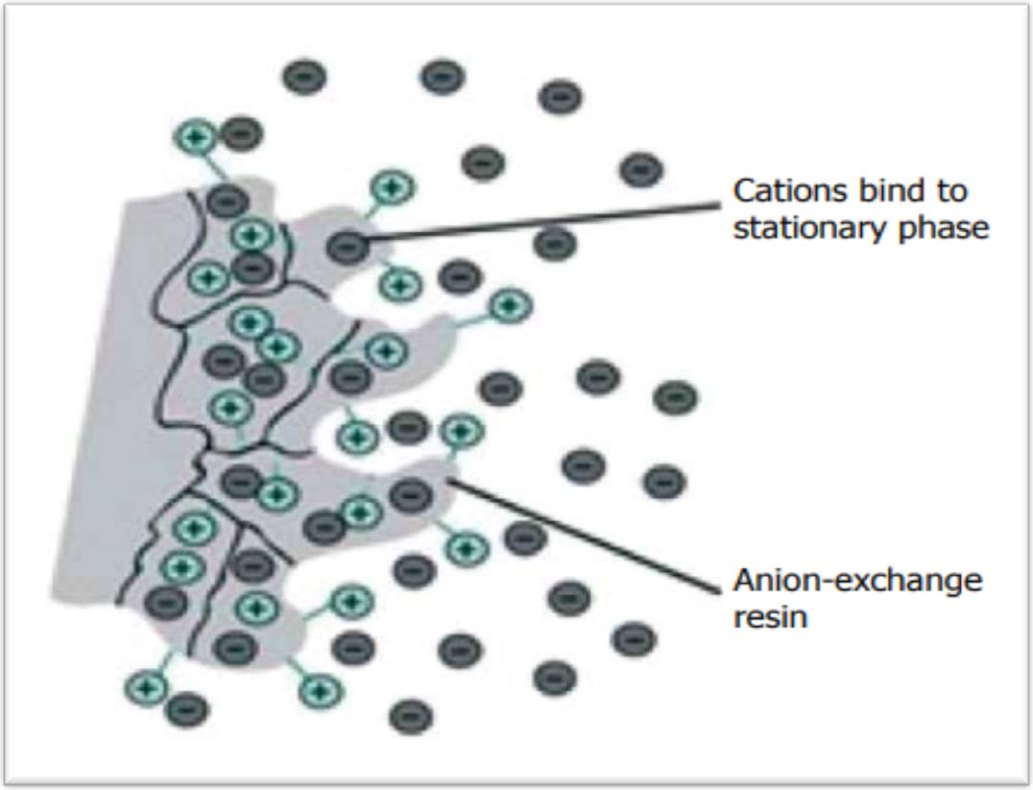


Figure (1.10) Two types of ion exchangers

1.12. Ion-exchange materials

The ion exchange columns, are widely and commercially available today, which are based on the basis of molecular media, that includes the use of both polymeric and silica supports, and can be classified into more than eight types, which are different based on the nature of their manufacture, and some of them are more popular than others.At the present time due to this difference or preference, it depends on the modification being made to them. The modification may be, for example, by adding silane reagents to silica, grafting the support surfaces with polymeric chains, encapsulating polymeric supports in a polymer film, or electrostatic conduction of colloidal particles [113].

Both silica and polymer supports are used in ion exchange techniques, but polymeric supports are preferred nowadays in most cases due to the stability of polymer supports at high pH, especially in ion exchange applications that require high alkaline rinses, and this condition is not fulfilled when using silica supports for this reason, polymeric supports are so popular in ion exchange applications [114].

1.13. Polymeric monoliths as ion exchang

The introduction of polymeric materials in ion exchange techniques is very important due to the advantages that polymeric materials have some properties, such as mechanical stability, and as mentioned previously, their tolerance to high levels of pH[115].

The process of developing new ion exchangers has been still as the focus of researchers' attention and is considered one of the most challenging research objectives. This development is linked to a number of general trends, including; [116].

1- The continuous increase in its ion exchange capacity, as this trend is linked when starting to design any ion exchanger.

2- Another important trend is to improve the efficiency of the column, by which;

- ❖ Using smaller particle ion exchangers.
- ❖ Improving the surface chemistry or using homogeneous porous columns, which in turn leads to a change in the shape of the column

3- Reducing the diameters of the separation columns is one of the other trends that must be taken into consideration when starting to design ion exchange columns, and there is a tendency to design robust and efficient capillary ionic chromatography.

4- Changes in bonding chemistry by introducing new functional groups to separate anions, cations, or both, or by improving the water and thermal stability of ion exchangers and thus expanding the range of applications [117-119].

It is noticeable that the monolith material achieves the above-mentioned trends in a large proportion and become preferred over the traditional packed columns in terms of some concepts such as the concept of interstitial tension between the two phases as well as the absence of dynamic forces as well as the possibility of introducing specialized functional groups other than the functional groups found in the beads that are packed in the traditional columns and on the other hand, the use of monolith materials made it possible to control the pore size by selecting the porogenic solvents, or by controlling the percentage between the crosslinker on the one hand, the monomer phases and the porogenic solution on the other[120].

1.14. Heavy metals

With the fast rise of industrialisation in recent years, contamination of land, water, and air has increased. Heavy metal pollution has created a surge in sudden environmental contamination occurrences, resulting in heavy metals entering the environment in high concentrations in a short period of time, causing significant harm [121].

Heavy metal elements are metal elements with densities more than 4.5 g.cm^{-3} Cd, Cr, Hg, Pb, Cu, As, and other heavy metal pollutants are common. Heavy metals are extensively spread in the atmosphere, water, and soil, and they are difficult to biodegrade and poisonous, making them one of the most deadly contaminants. It is mostly caused by heavy metal mining and processing, as well as the discharge of industrial and vehicle pollutants into rivers or penetrated into the soil by rains. Excessive heavy metal pollution in the natural environment will enter the food chain by inhalation, ingestion, or skin contact, and then re-accumulate in the body, posing a severe hazard to public health [122].

Carcinogenesis, deformity, and mutation are the most common symptoms. The following are the primary dangers of typical heavy metals: Hg enters the liver shortly after eating, causing severe harm to the brain, nerves, and eyesight; Cd can cause high blood pressure, cardiovascular and cerebrovascular illnesses, bone, liver, and kidney damage, among other things. Lead can harm the fetus' neurological system and cause congenital mental impairment. As well as causing systemic disorders, mostly skin damage [123].

Heavy metals monitoring is both a necessity and a critical component in preventing and controlling heavy metal pollution. In the actual application of environmental pollution monitoring, it is mainly concerned with the spatial analysis of continuous regions rather than the precise content of pollutants at a given position in space. As a result, rapid and accurate detection of heavy metal elements, as well as understanding of the spatial distribution pattern and characteristics of regional heavy metal pollution, are critical for heavy metal pollution assessment and management, as well as geographic pollution essential for the prevention [124].

1.14.1. Copper

Copper is one of the important elements that playing significant role in the daily life, for example developing of red blood cells, bones, and many biological processes in human beings [117]. In addition, it is required in a sufficient amount to avoid fatigue, slowed growth, iron insufficiency, brittle bones, and a weakened immune system due to copper deficiency. Whereas, high levels of copper will lead to big issue for human health [126].

Copper is a commonly available metal that is used for electrical wiring, plumbing, air conditioning tubing, and roofing. Copper has excellent electrical and thermal conductivity, strong corrosion resistance, simplicity of fabrication and installation, a beautiful appearance, easy availability, and high recyclability, which makes it appropriate for various applications.

Furthermore, copper, a vital component for humans and other living forms, and is biocidal to some species [127].

However, copper(II) is one of the most poisonous heavy metals to living beings and one of the most common heavy metal pollutants in the environment. Metal cleaning and plating baths, pulp, paper board mills, wood pulp manufacture, and the fertilizer sector are all possible sources of copper in industrial effluents. As a result, the wastewaters from these sectors include significant quantities of copper (II) ions, necessitating treatment before removal in effort to reduce water contamination [127].

1.14.2. Lead

Lead is one of the most poisonous metals, has an accumulative impact, and is a high-priority contaminant in the environment, the detrimental consequences of lead pollution on human health are well-known, and among them are reduced enzyme activity, renal function, and neuromuscular issues, lead has been categorized as a Group B2 (likely) human carcinogen by the United States Environmental Protection Agency (EPA) there are now legislative controls on the discharge of lead into the environment nonetheless, it is employed as a raw ingredient in industries such as car batteries, ceramics, and ink. Furthermore, lead is a byproduct of various industrial processes used to manufacture fertilizers and insecticides. In both circumstances, it might have been released into the environment as a result of an insufficient production method or as a result of an accident [128,129].

The usage of gasoline antiknock chemicals with paint pigments causes major environmental and health issues, as a result, the World Health

Organization (WHO) has set the maximum acceptable level for lead in drinking water at 10($mg.L^{-1}$)as a result, it is critical to monitor the lead level in the ambient sample [130,131].

1.14.3. Nikel

Nickel is the fifth most abundant element on Earth, behind iron, oxygen, silicon, and magnesium. This metal is widely distributed in the environment because it is a key element of almost 100 minerals that have several industrial and commercial applicationsIt's primarily found in minerals including pentlandite, garnierite, millerite, niccolite, and ulmannite. Nickel is frequently found in two ore types: sulphide and laterite. Baron Axel Frederich Cronstedt, a Swedish scientist, extracted nickel from an ore in 1751, the majority of the world's nickel supply is now mined in Canada, Cuba, the former Soviet Union, China, and Australia [132].

(Ni) is a trace metal that is widespread in the environment due to both natural and anthropogenic activity. The release of (Ni) into the environment, especially its deposition in agricultural soils, is a major problem. The naturally occurring concentrations of (Ni) in soil and surface waters are generally less than 100 mg/kg and 0.005 mg/L, respectively however, anthropogenic activities such as the use of fossil fuels for power generation, mining, smelting, car emissions, the disposal of domestic, municipal, and industrial waste, steel manufacture, and the cement industry all contribute to the increased release of Ni into the soil [133].

1.15. Literature review

1.15.1. Summary of the data from previously reported research about using monolith as ion-exchange to ions separation

Table1.4 previously reported research about using monolith as ion-exchange to ions separation

NO.	Type of monolith	Mode of Chromatography	Sample	Reference
1	BMA-co-EDMA-co-AMPS monolith modified with latex nanoparticles	SAX	I^-,Br^-,NO_3^- ,NO_2^-	**[119]**
2	GMA-co-EDMA monolith sulphonate using sodium sulphat and modified with latex nanoparticles	SAX	I^-,Br^-,NO_3^- ,NO_2^-	**[118]**
3	GMA-co-EGDMA-co-MMA functional with pentaerythritol tetrakis(3mercaptopropionat) and THIOLS	SCX	Heavy metals	**[134]**
4	Lcys- poly(GMA-MAA-EDMA)	SCA	Cr^{3+}	**[135]**
5	GMA-co-EDMA-co-A.Am	SCX	Cu^{2+},Pb^{2+},Ni^{2+}	

1.15.2. Summary of the data from previously reported research about using monolith as ion-exchange to molecules separation

Table1.5 previously reported research about using monolith as ion-exchange to molecules separation

NO	Type of monolith	Mode of Chromatography	Sample	Reference
1	Ion-exchange GMA-co-EDMA, the GMA was modified using diethylamine.	HPLC	Proteins	[136]
2	Ion-exchange GMA-co-EDMA, GMA was grafted with poly(2-acrylamido-2-methyl-1-propanesulfonic acid	HPLC	Proteins	[137]
3	CIM QA	SAX	Purification of tomato mosaic virus Separation of immunoglobulin M from immunoglobulin G	[138]
4	GMA-co-DVB Grafting	WAX	Separation of oligonucleotides	[139]
5	SAX GMA-co-DVB, GMA was modified with diethylamine followed by alkylation with diethyl sulfate	µLC	Nucleotides and oligonucleotides	[140]
6	GMA-co-DVB	SAX	Separation of nucleotides and Oligonucleotides	[140]

7	pAAm cryogel	WAX	Purification of DNA	[141]
8	pAAm cryogel	SAX	Purification of DNA	[141]
9	pAAm cryogel Coating	SAX	Purification of DNA	[141]
10	Commercially available CIM DEAE	WAX	Protein fractionation prior to MALDI TOF MS, water-soluble barley proteins	[142]
11	CIM QA	SAX	Removal of human serum albumin from human plasma	[143]
12	CIM EDA	WAX		[144]
13	GMA-co-EDMA	WAX, SAX	Adsorption of plasmid DNA isolated from E. coli	[145]
14	GMA-co-EDMA	SAX	Purification of plasmid DNA from E. coli clarified lysate	[146]
15	NBE-co-DMN-H6	SAX	Separation of oligodeoxythymidylic acids	[147]
16	Poly(DPEPA-co-POSS) monolith	Reverse phase chromatography	Standard proteins, egg white proteins and BARD1 BRCT domains protein	[148]
17	CIM QA	SAX	Isolation of bacteriophage	[149]
18	UNO-Q	SAX	Purification of enzyme	[150]

19	ProSwift SAX-1S	SAX	Determination of anions in seawater	[151]
20	GMA modified with diethylamine	Weak ion exchange column	bovine serum albumin (BSA), thyroglobulin, plasmid DNA	[152]
21	SPMA-co-PEGDA	Strong cation exchange chromatography	Protein Standard and peptides	[153]
22	WAX GMA-co-EDMA, GMA was functionalized using trimethylamine	CE	Five inorganic anions	[154]
23	(CEA-co-PEGDA)	Weak cation exchange without hydrophobicity	Proteins and peptides	[155]
24	WAX GMA-co-EDMA, GMA was modified with diethyl amine	HPLC	Ligodeoxythymidilic and DNA	[156]
25	Poly(TEPIC-co-TAEA) epoxybased monolith	Weak anion exchange mode	Glycoproteins	[157]
26	Poly(HEMA-co-PEGDA) cryogel monolith, DMAEMAgrafted	Anion exchange Chromatography	Immunoglobulin G in bovine milk whey	[37]
27	Poly(GE 100-co-EDA) epoxybased monolith	Ion exchange and hydrophobic interaction	Standard proteins	[158]
28	Poly(MAA-co-EGDMA-co-PEGDA)) monolith, GMA grafted, sodium sulfite or diethyl amine processed	Ion exchange chromatography	BSA, lysozyme	[159]
29	Poly(MAA-co-EGDMA-co-PEGMA cryogel monolith, DEAE introduced	Weak anion exchange adsorbent with high binding capacity	BSA	[160]
30	Poly(IL-co-C12-co-TMPTAco- EDMA	Ion Exchange Chromatography	Lysozyme in egg white	[40]

31	Sulfoalkylated Poly(HEMA-co- GMA-) cryogel monolith	Strong cation exchange chromatography	Standard proteins	[161]
32	Hydrophobic poly(BMA-*co*-EDMA) with grafted AMPS	Strong cation exchange chromatography	11 intact proteins and then protein digests	[162]
33	Quaternary amine-modified Poly(GMA-co-EDMA) monolith	Strong anion exchange chromatography	Standard proteins, virus-proteins mixture	[163]
34	Sulfonated Poly(GMA-co-EDMA) monolith	Strong cation exchange chromatography	Standard proteins	[164]
35	Poly(GMA -co- EDMA) and poly(styrene-*co*-DVB)	Separation using anion exchange and reverse phase chromatography	Tandard Proteins and E Coli. Lysate	[165]

1.16. Aim of stady

This study aims the preparetion and investigates new monolithic columns depending on glycidyl methacrylate as the major component combined with other monomers that have different properties to be used for ion exchange chromatography. The monoliths produced should have a high efficiency in the separation.

Glycidyl methacrylate monomer has been chosen to prepare the copolymers due to the significant ability of pendent epoxide groups to participate in many chemical reactions and modifications for numerous applications. Therefore, these properties were used to prepare and investigate monolithic columns as ion exchange columns, which can be used to separate the largest number of ions process.

Chapter two

Experimental Part

2. Experimental

2.1. Instruments

Ther are several techniques were using in this current study; most of them are listed in table (2-1).

Table (2.1) Instrument used in this research

No.	Device name	The manufacture company
1	Electronic analytical balance with four decimal places	Denever Instrument Germany TP-214
2	heater	Heidolph RM Hei-standard
3	HPLC pump (Varian Prostar system)	kd Scientific Holliston,MAU.S.A
4	Iirradiation Cabinate(220V-50HZ)	Home made
5	UV-Visible spectrophotometer (double-beam)	Japan (shimadzu)(UV-1700)
6	Sonicater	ultra sonic bath India
7	FT-IR 380 spectra	Bruker
8	Syringe pump	Bioanalytical System Inc., USA
9	stirrer VWR	West Chester, PA, USA
10	Field Emission Scanning Electron Microscopy (FESEM)	TESCAN, Model: Mira3, Czech Republic
11	Brunauer-Emmett-Teller (BET)	BEL, Model: BELSORP MINI II, Japan
12	Proton nuclear magnetic resonance(^{1}HNMR)	Model: Innova 5 Concole with an Oxford 500 Magnet, Country: United state
13	pH-meter	WTW
14	Oven	Jlabtech, Korea
15	Atomic Absorption Spectroscopy	SHIMADZU AA-6300

2.2. Chemicals

The chemical materal used in this study are shown in table (2-2).

Table (2-2) Materals usedin the study, purity and manufacture company

No.	Chemical name	Chemical formula	Purity	The manufacture company
1	Glycidyl methacrylate	$C_7H_{10}O_3$	98%	Sigma-Aldrich, Poole, UK
2	Acrylamide	$CH_2CHCONH_2$	98%	Sigma-Aldrich, Poole, UK
3	Ethylene dimethacrylate	$C_{10}H_{14}O_4$	98%	Sigma-Aldrich, Poole, UK
4	3-(trimethoxysilyl) propylmethacrylate	$H_2C{=}C(CH3)CO_2(CH2)3Si(OCH_3)_3$	98%	Sigma-Aldrich, Poole, UK
5	2, 2-dimethoxy-2-phenyl acetophenone	$C_6H5COC(OCH_3)_2C_6H_5$	98%	Sigma-Aldrich, Poole, UK
6	1-Propanol	C_3H_8O	97%	G.C.C
7	2-Butanol	$CH_3CH_2CH(OH)CH_3$	97%	G.C.C
8	Hydrochloric acid	HCl	Analar	G.C.C
9	Sodium hydroxid	NaOH	99%	BDH
10	Nitric acid	HNO_3	97%	G.C.C
11	Copper(II) nitrate	$Cu(NO_3)_2\cdot 3H2O$	98%	BDH
12	Neocuproine	$C_{14}H_{12}N_2$	98%	Merck
13	nikel (II) nitrate	$Ni(NO_3)_2.6H_2O$	98%	BDH

14	lead (II) nitrate	$Pb(NO_3)_2$	98%	BDH
15	Ethanol	C_2H_5OH	94%	G.C.C
16	Methanol	CH_3OH	96%	G.C.C

2.3. Preparation stock solutions.

2.3.1. Preparation of (0.2 M) of hydrochloric acid

This solution was prepared by taking 1.7 mL of concentrated hydrochloric acid (that percentage of purity 35% (w/w) and specific gravity 1.18 $g.mL^{-1}$) and added to 100mL volumetric flask containing water and then completed the volume to the mark.

2.3.2. Preparation (0.2 M) of sodium hydroxide

This solution was prepared by taking (0.8 g) of sodium hydroxied in dry and clean beaker and added (50 mL) distilled water and when the dissolved done the solution transferred to (100 mL) volumetric flask and then completed the volume to the mark.

2.3.3. Preparation of (200 $mg.L^{-1}$) Copper (II) nitrate

0.1900 g from Copper (II) nitrate where taking in dry and clean beaker and added 50 mL from distilled water and when the dissolved done the solution transferred to (250 mL) volumetric flask and then completed the volume to the mark with distilled water after that, a series of solutions were prepared with different concentrations from the original solution.

2.3.4. Preparation (200 $mg.L^{-1}$) Nickel (II) nitrate

0.2476 g from Nickel (II) nitrate where taken in dry and clean beaker and added 50 mL from distilled water and when the dissolved done the solution transferred to (250 mL) volumetric flask and then completed the volume to the mark with distilled water after that, a series of solutions were prepared with different concentrations from the original solution.

2.3.5. Preparation (200 mg.L^{-1}) lead (II) nitrate

0.0799 g from lead (II) nitrate where taken in dry and clean beaker and added 50 ml from distilled water and when the dissolved done the solution transferred to (250 mL) volumetric flask and then completed the volume to the mark with distilled water after that, a series of solutions were prepared with different concentrations from the original solution.

2.4. Preparation of reagents

2.4.1. Preparation Neocuproine reagent (100 mg.L^{-1})

0.01 g from Neocuproine where taking in in dry and clean beaker and added (5 mL) from ethanol and when the dissolved done the solution transferred to (100 mL) volumetric flask and then completed the volume to the mark with distilled water.

2.5. Preparation of the polymerization mixture [166]

The polymerization solution is prepared by mixing 450μL (GMA) with 481.5 mg (A.Am) and 50 μL (EDMA) as cross-linker. (DMPA) with 1% from the weight of the monomers which was used as an initiator. The porogenic solvent (1000μL1-propanol + 650μL 2-butanol) was used to dissolve the monomers, crosslinker and initiator. The polymerization mixture was mixed well for 10 min using a magnetic stirrer. followed, nitrogen gas was passed over the polymerization mixture to expel the oxygen, and then the formed mixture was degassed by ultra-sonication for about 10 min.

2.6. Silanization process of borosilicate tube [167]

This process was carried out in sequential stages. In the first stage, the borosilicate tube (figure 2.1) was washed with acetone to get rid of any contaminated organic matter, and then the tube was washed with distilled water to get rid of the acetone. Then the second stage, which is pumping 0.2 M sodium hydroxide solution into the inner surface of the tube using a syringe pump at a speed of (20 µL.m^{-1}), This process, is followed by a wash with distilled water. Then the hydrochloric acid was pumped as a third stage using the same pump and at the same speed. After that, it is washed with distilled water to get rid of acid residues, and then the tube is washed with ethanol to get rid of the distilled water, and then comes the fourth stage, which is rinsing with a solution (3-trimethoxysilyl) propyl methacrylate, finally, the glass tube was dried using nitrogen gas.

Figure 2.1 Photograph of borosilicate tube

2.7. Irradiation cabinet manufacture

The irradiation cabinet was manufactured locally using raw materials to be used in the polymerization process.

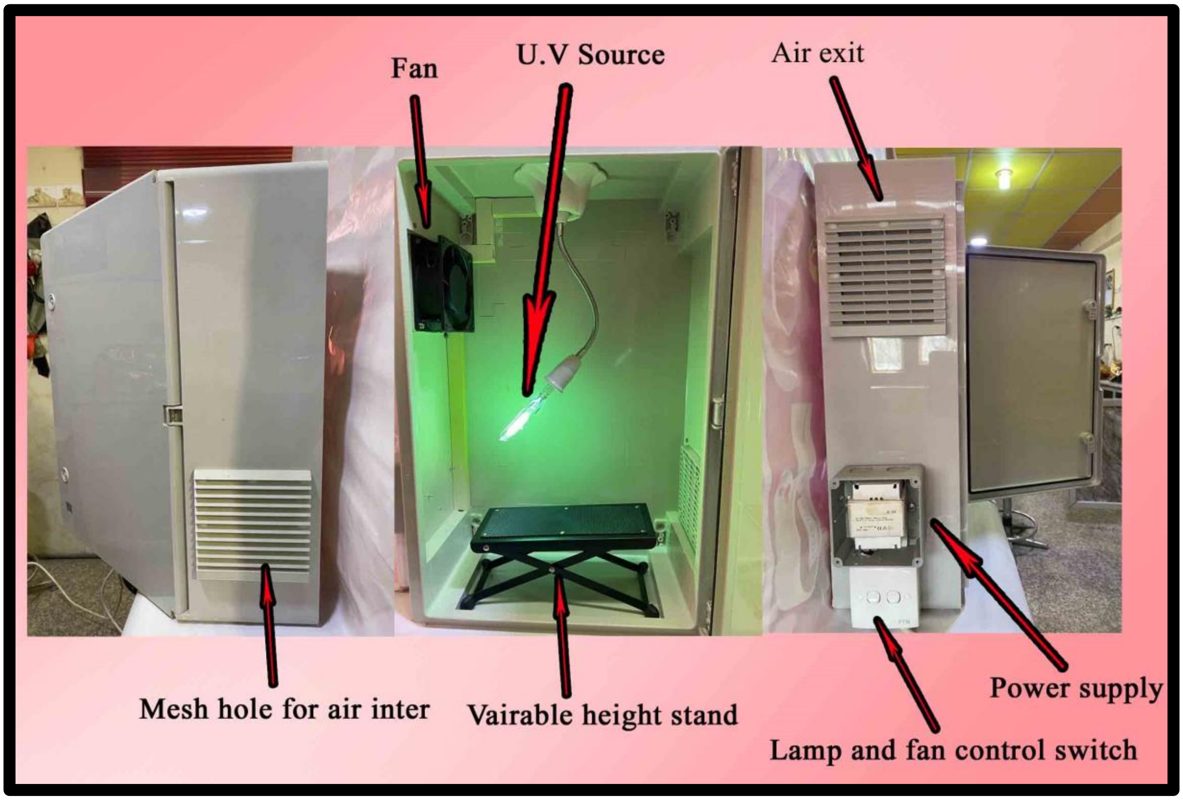


Figure 2.2 Photograph of Irradiation cabinet

2.8. Polymerization process [61]

After both the polymerization mixture in paragraph **(2.3)** has been prepared and Silanization process of borosilicate tube in paragraph **(2.4)** has been prepared, the polymerization mixture is carefully injected into the glass tube and transferred to the irradiation cabinet that was manufactured as mentioned in paragraph **(2.5)** to starting the polymerization process to form the polymer.

2.9. Investigation of the irradiation time [168,169]

The irradiation time was investigated for each column until the required irradiation time was reached, by given desired pore size and surface area.

2.10. Investigation of the distance between the irradiation source and the monolith column

The effect of the distance between the irradiation source and the monolith column was studied to reach the appropriate dimension. This process was carried out by using a variable height stand, as shown in the figure **(2.2).**

2.11. Characterization of the prepared polymer

2.11.1. Scanning electron microscope (SEM) [170,171]

(TESCAN, Model: Mira3, Czech Republic) Scanning electron microscope (SEM) was used to study the morphology of the polymer. Where the sample was coated with a thin layer of gold and platinum (the thickness of the layer is about 2 nm) by spray coating machine and then the images were obtained using an accelerating voltage (20 Kv) and a current of 100 pA in the high vacuum mode.

2.11.2. FT-IR spectroscopy [172]

The FT-IR spectra were studied using FT-IR 380 (Bruker) spectra where two samples were taken, purified, and dried well, and the first sample was taken directly for measurement after being triturated with KBr to prove the formation of the polymer. As for the second sample, the ring was opened as in paragraph **(2.13)** and then it was triturated with KBr and its IR spectrum was measured to prove the success of opening the ring through a comparison Its IR spectrum with the IR spectrum of the first sample.

2.11.3 Brunauer-Emmett-Teller (BET) analysis

(BEL, Model: BELSORP MINI II, Japan) was used to to studied the pore size and surface area of the prepared polymer. Where the monolith column was prepared as in paragraph (2.6), but by using an un Silanization borosilicate tube to remove the monolith easily, then the unreacted materials were removed by washing the monolith with ethanol and distilled water and then drying monolith in an electric oven at a temperature of 60 C°, then using the heat curve for nitrogen adsorption at a temperature of 77 K to obtain the surface area and average pore size of a monolith.

2.11.4. ^{1}H NMR spectroscopy [173,174]

^{1}HNMR Device, Model: Innova 5 Concole with an Oxford 500 Magnet, Country: United state where used to check the formation of the polymer by observing the displacements given in the test result.

2.12. Test Permeability of the monolith [136]

Column permeability was tested by using a HPLC pump with isocratic elution system (KD Scientific Holliston, MAU.S.A) where the distilled water was pumped at different flow rate and the back pressure was measured until the back pressure in pumping system was stable the pressure is recorded..

2.13. Ring opening by hydrolysis [175]

After polymer formation, the epoxy ring of the glycidyl methacrylate monomer was opened by pumping 0.2 M hydrochloric acid at 20 μL/min^{-1} for 3 hours to form the diol groups.

2.14. Calculation chelating capacity for monolith column [176]

The column capacity was calculated using the following equation:

$$\boldsymbol{Q = \frac{C \times V}{W}} \qquad \qquad (\mathbf{2-1})$$

Where **Q** is the adsorption capacity of the chelating monolith column, (mmol.g^{-1}), **V** is the volume of the eluate (L), **C** is the concentration of (M^{2+}) in the eluate (mmol.L^{-1}), **W** is the dry weight of monolith inside the column (g), where the amount of ions that the column can absorb was calculated.

2.15. Porosity calculation

By using Fletcher *et al*. method, the total porosity of the prepared monolith was calculated using the method of the scientist mentioned above, which states;

$$\boldsymbol{\emptyset t} = (\boldsymbol{WM} - \boldsymbol{WT}) / \boldsymbol{dLR2\pi} \qquad (\mathbf{2-2})$$

Where Øt is the porosity, WM the weight of the monolith while it is wet (i.e. Pumping water into the monolith column using a syringe pump for three hours, after which the monolith is weighed), WT it is the weight of a dry monolith column (i.e. The monolith does not contain any moisture inside the pores, only air), d is the density of water, L is the length of the monolithic column, and R is the cylindrical radius of the column,(d and R were measured using Digital Vernier Caliper).

2.16. Swelling measurement

A number of polar and non-polar solvents such as water, methanol, ethanol, benzen, and acetonitrile ... etc.were used to determine the extent of swelling of the monolith where specific weights of the polymer were taken and immersed in the above mentioned solvents and by observing the change in the weight of the monolith The porosity of the monolith was calculated.

2.17. Use Glycidyle methacrylate-co-ethylene dimethcrylate-co-acryl amide monolithic as as strong cation exchange column

Glycidyle methacrylate-co-ethylen dimethcrylate-co-acryl amide was used as astrong cation exchange column to separate**(Cu^{2+},Pb^{2+},Co^{2+})** ions after the epoxy ring has been opened and converted into groups of diol,

This process takes place in several steps, which are summarized as follows:

1- Load the solutions containing these ions into the column using a syringe pump at a flow rate of 20 $\mu L/min^{-1}$.

2- Washing the column using distilled water at the same flow rate to get rid of unreacted ions.

3- Pumping 2 M of nitric acid into the column to removing ions from the column and collecting the displacement solution that contains the displaced ions to use for detection and determintion.

4- Washing the column with distilled water to get rid of residual nitric acid inside the pores of the column.

Chapter Three

Results and discussion

3. Results and discussion

3.1. Preparation of the polymerization mixture

Preparation of the polymerization mixture was carried out by depending on the procedure published elsewhere with some modifications15 including monomers types according to the properties of a prepared monolith, in addition, the composition of porogenic solvent[166].

Two types of monomers were used in the preparation of the polymerization mixture; glycidyl methacrylate and acryl amide in a ratio of (50:50). The crosslinker and the initiator were EDMA and DMPA, respectively. There are some features that to use of these two monomersfor example, in GMA which participate in the double bond (methacrylic double bond) that could be photopolymerization reaction, as well as the epoxy group used in many post-polymerization reactions. Acrylamide contains the double bond and amide group that could be in many post-polymerization reactions.

The EDMA crosslinker was used in the preparation of the polymerization mixture because it is one of the most famous crosslinkers used in the preparation of polymers, especially with methacrylate monomers. It gives the polymer rigidity and increases the cohesion strength in addition to playing a major role in controlling the size of the polymer pores, where small percentages case of need for small pore size and large surface eara, vice versa, EDMA have an importance in avoiding material failure due to internal stress during the multiaging process, or osmotic shock when using gradients with a wide range of salt concentration, pH and organic solvent contents due to the flexibility it gives to the polymer structure.

2,2-dimethoxy-2-phenylacetophenone (DMPA) were used in the polymerization mixture because it gives the start of the polymerization process by attacking the double bonds and was preferred over other initiators such as2,2-azoisobutyronitrile (AIBN) because it gives a regular reaction and does not generate nitrogen gas during the polymerization process.

1-propanol and 2-butanol were used as aporogenic solvent for agood solvent for monomers, initiator and crosslinker and a poor solvent for the polymer. In addition, they give an appropriate pore size for the prepared polymer.

3.2. Silanization process of borosilicate tube [177,178]

The silanization process considered one of the crucial processes to form a monolith inside the columns due to prevention the monolith from slipping out of the column when high flow reats and high back pressures applied, reduce the effect of shrinkage during the polymerization process, preventing the interaction of the analyst with silanol group in samples especially if the samples are proteins.

The silanization process Figure (1-3) involves the reaction of propyl methacrylate (3-trimethoxylyl) with silanol groups (Si-OH) on the inner wall of the borosilicate tube this reaction is carried out through a number of steps, taking place in a number of sequential steps, where the solutions were pumped in each step using a syringe pump at a flow rate of 5 µl. min^{-1} for one hour. In the first step, acetone was injected into the borosilicate tubes to remove any organic metal and then rinsed with distilled water to remove acetone residues and at the same time analyze the siloxan groups with water and increase the density of the silanol groups using a 0.2 M solution of sodium hydroxide, then wash with distilled water to remove the remaining sodium hydroxide and this is the second step.

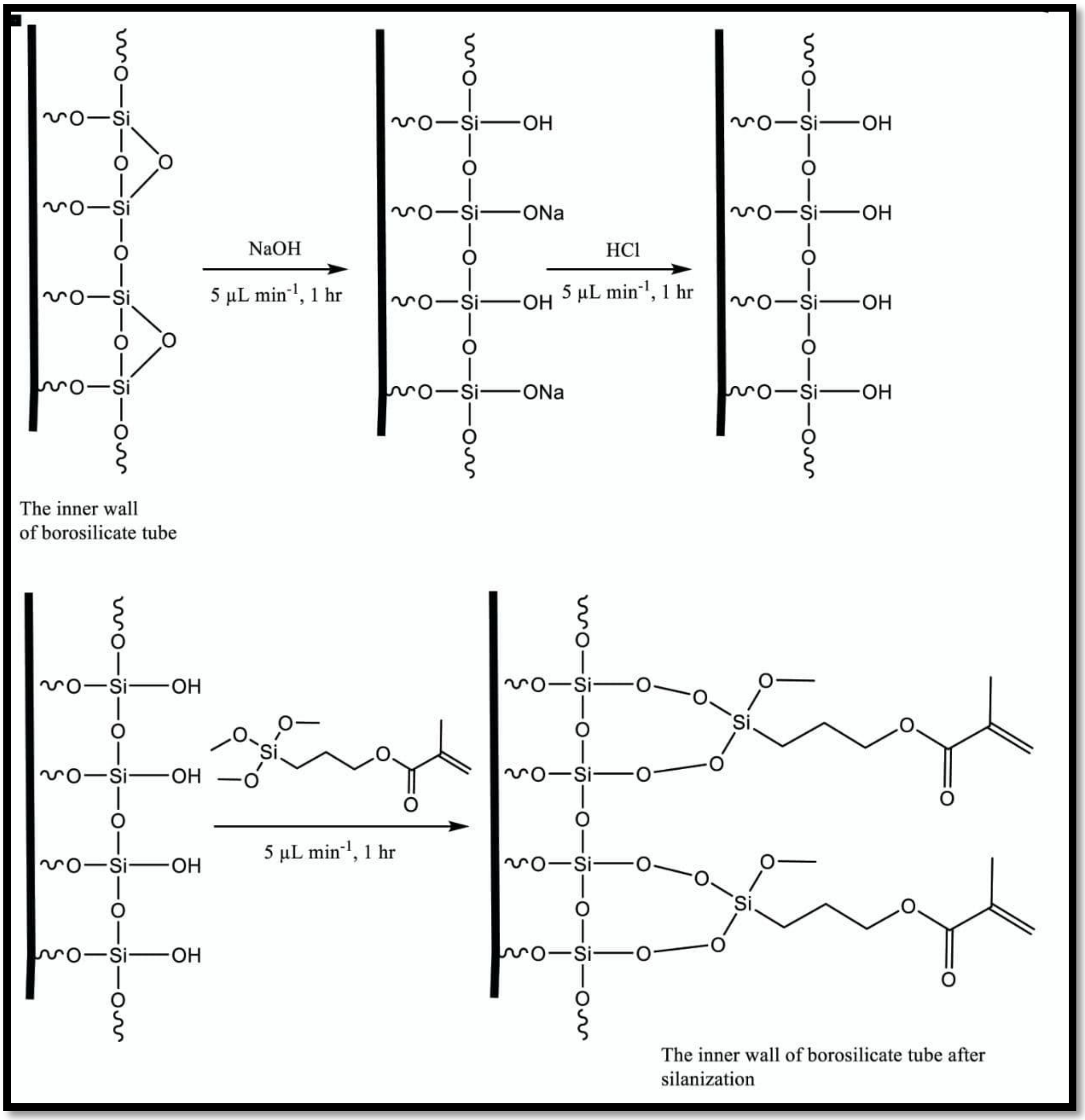


Figure 3.1 Silanization process of borosilicate tube

In the third step involves using a 0.2 M hydrochloric acid solution which is responsible for removing and neutralizing the remaining alkali metal ions, then the borosilicate tube is also rinsed with distilled water to remove the hydrochloric acid residue, followed by an ethanol rinse to remove the water residue finally, the fourth step begins, where (3-trimethoxysilyl) propyl methacrylate, which is a dual-functional reagent, was injected. The reaction time was given one hour; followed nitrogen gas was passed inside the tube for drying. Now the trimethoxysilane groups are attached to the silanol groups on the inner tube walls, and the monolith will be attached to the inner surface of the tube via methacrylate groups.

3.3. Polymerization process [61,179]

The polymerization process begins by injecting the polymerization mixture into the borosilicate tube, that silanized, It shoud be checked that no air bubbles are left inside the tube because O_2 is a scavenging the free radical, then the ends of the tube are blocked with rubber stoppers after that the tube is transferred to the irradiation cabinate, which was manufactured localy as shown in (2-2). Photopolymerization was used in the polymer preparation process as it has many advantages, including not requiring long time, avoiding high temperatures that lead to polymer cracking, controlling the size of pores by increasing or reducing the irradiation period and also controling the length of the polymeric chain. The photopolymerization process was carried out by using UV radiation, where the free radical polymerization process begins, which consists of several steps that can be summarized as follows;

1- Cleavage step, this step includes the formation of the benzoyl fraction by using ultraviolet light, which leads to the decomposition of the initiator (2, 2-dimethoxy-2-phenylacetophenone) to the acetal fraction as an inhibitor of the polymerization process Figure (3.2).

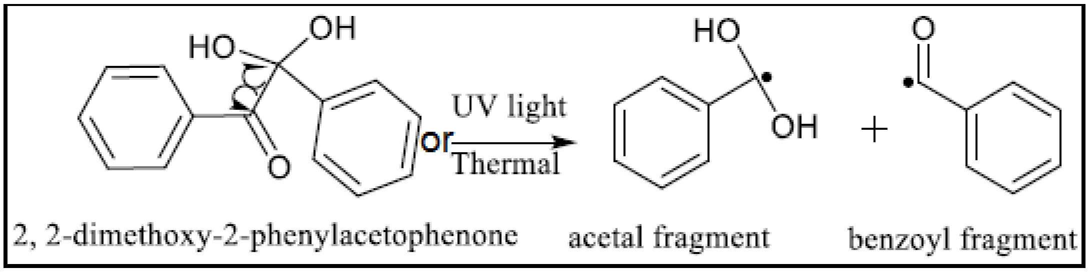


Figure 3.2 cleavage step

2- Initiation step, this step involves attacking the benzoyl portion formed from the first monomer step, specifically from the double bond to form new free radicals on the monomer figure (3.3)

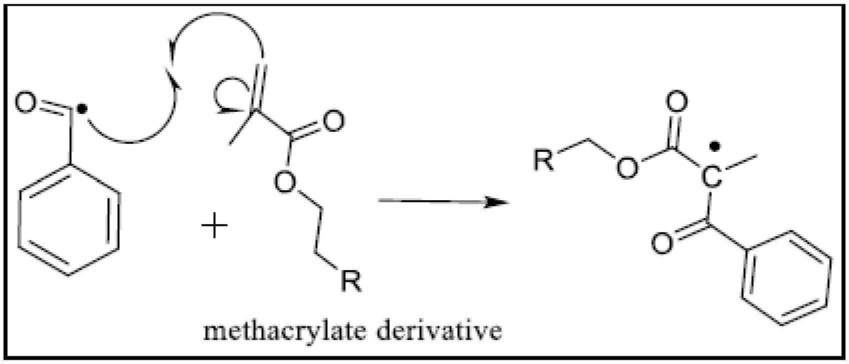


Figure 3.3 Initiation step

3- Propagation step, this step includes attacking the free radicals on the monomer that formed in the second step the cross-linker at the double bond to develop the polymer chain figure (3.4).

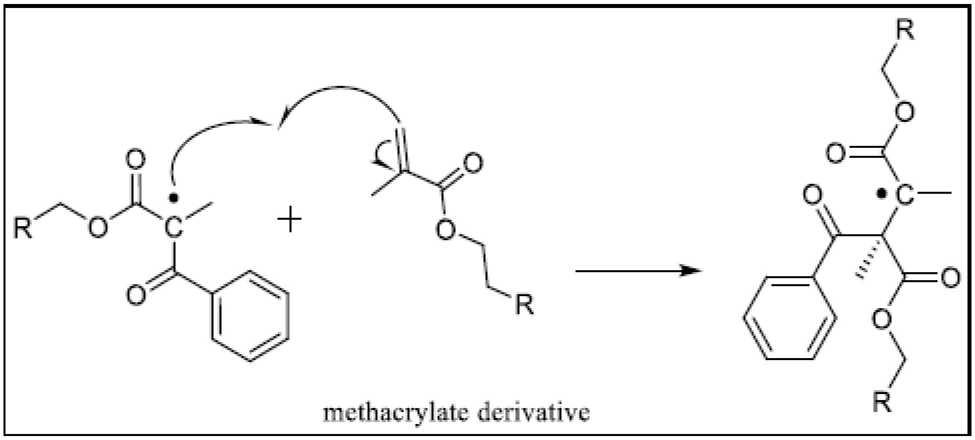


Figure 3.4 Propagation step

4- Termination step,, at this step, all the free radicals react with each other, and then the polymer is formed in the final form figure (3.5).

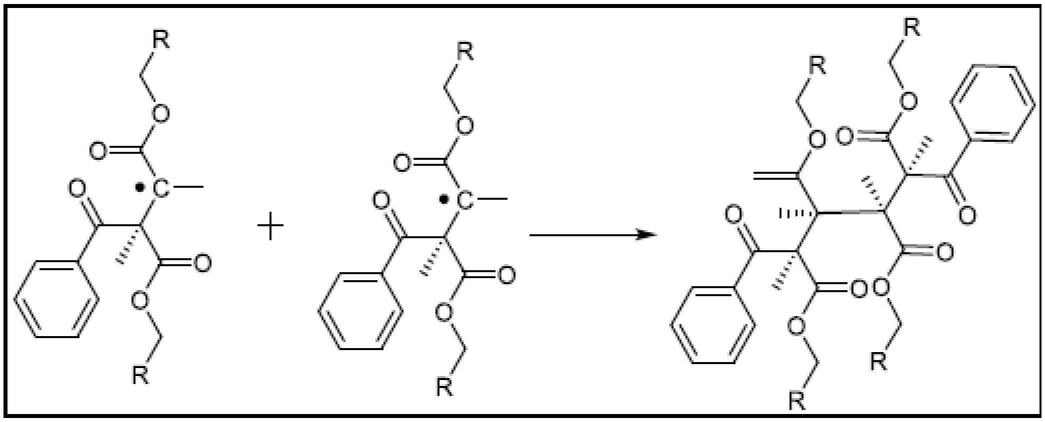


Figure 3.5 Termination step

Figure 3-6 shows the final formula of the polymer after the polymerization process is completed.

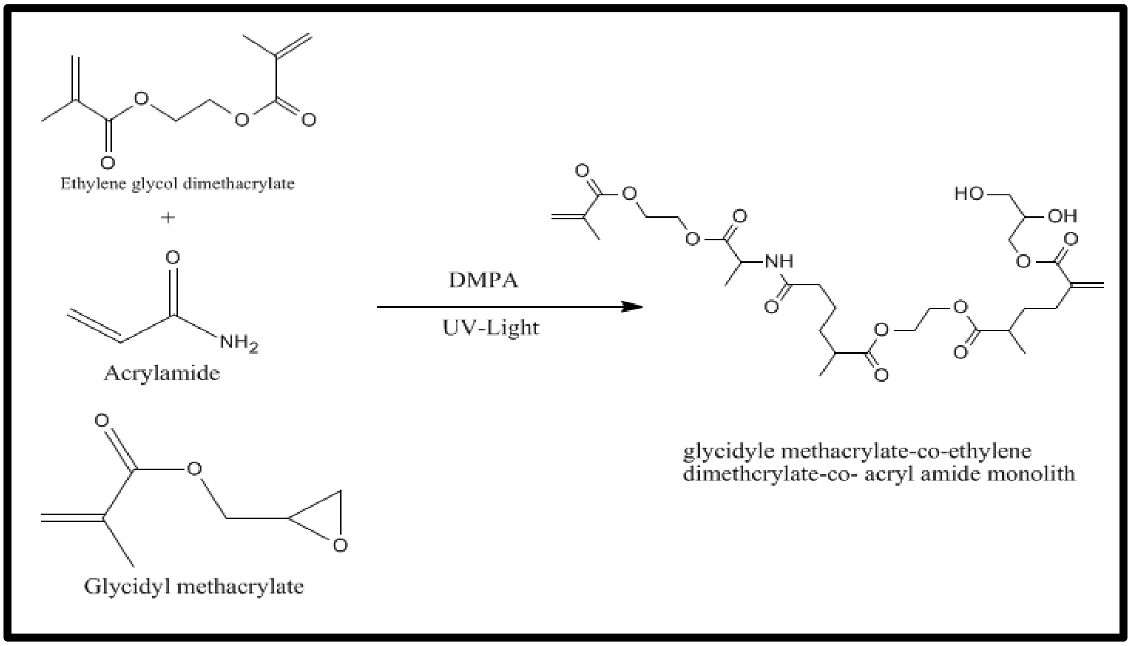


Figure 3-6 final formula of the polymer after the polymerization process is completed

Figure 3-7 shows the column without the polymer after silanization and the polymer inside the column.

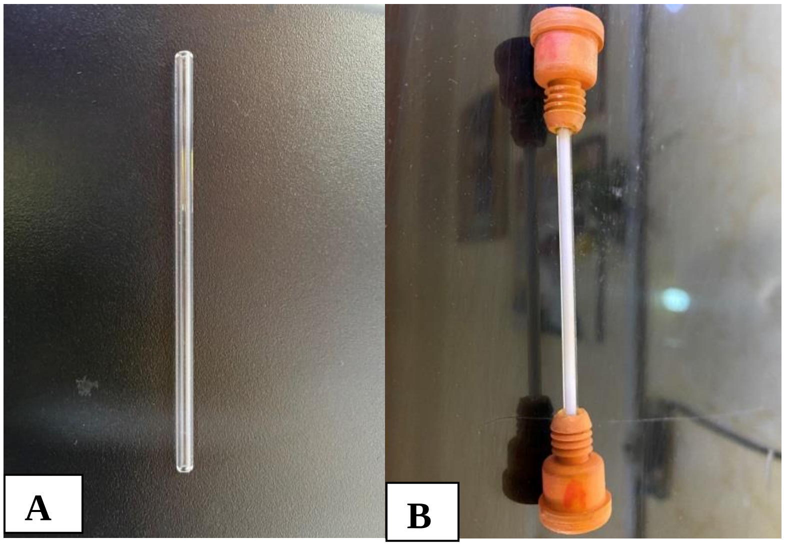


Figure 3-7 (A) column without the polymer after silanization

(B) Polymer inside the column.

3.4. Scanning electron microscope (FESEM) for glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolith

The morphlogical properties of a formed monolith was instivigated by using FESEM technique. The monolith's morphology exhibits significant cluster groups and macropores. The FESEM image of a prepared monolith is shown in Figure (3.6) Several necessary points for the prepared column can be deduced from Figure (3.6) Firstly, Monolithic media may be thought of as a network of enormous channels.24 Secondly, the mobile phase could be passed through these pores easily and this is useful in terms of reducing back pressure.24 On the other hand the surface area of the monolith can be increased due to the micropores and mesopores. These pores can contribute to increase the surface loading ability of the monolith. Moreover, they increase the interactions when using a high flow rate and low back pressure

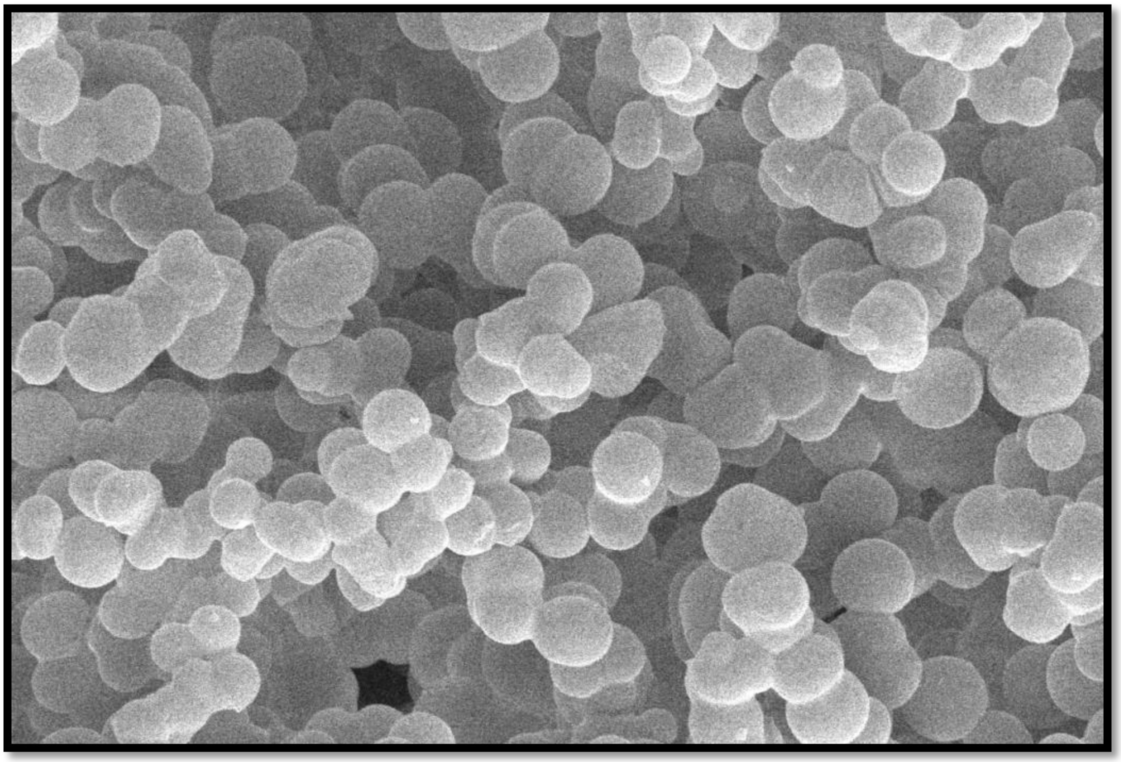


Figure 3.8 SEM image for the glycidyl methacrylate-co-acrylamide monolith

3.5. FT-IR spectroscopy for glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolith

One of the analysises that was used to detect the formation of the polymer is the FT-IR spectrum where the FT-IR spectrum gives a clear indication of the polymer formation by observing the main peaks in the monomers and the polymer formed. However, in the GMA monomer the main peaks 1716.40 cm-1 for (C=O), 1636.98 cm^{-1} for (C=C), 907.70 cm^{-1} for (epoxy ring), as shown in figure (3.7). These peaks refer to the vibrational stretching of these functional groups.

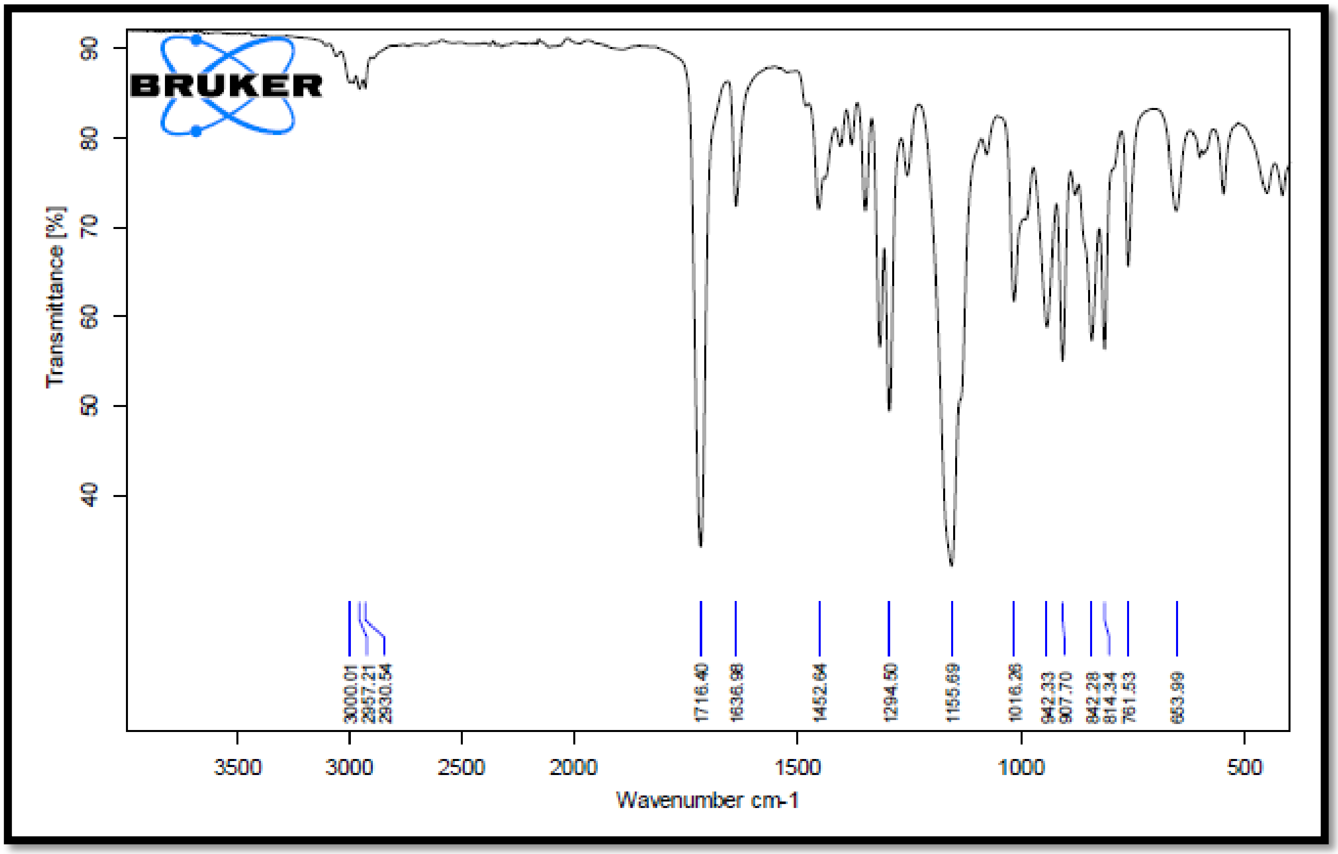


Figure 3.9 FTIR spectrum of GMA from 500 cm^{-1} to 4000 cm^{-1}

On the other hand the FT-IR spectra for A.Am figure (3.8) showed main peaks for (C=C) at 1609.83 cm^{-1}, (C=O) at 1666.02 cm^{-1}, and NH_2 at 3338.67 cm^{-1}.

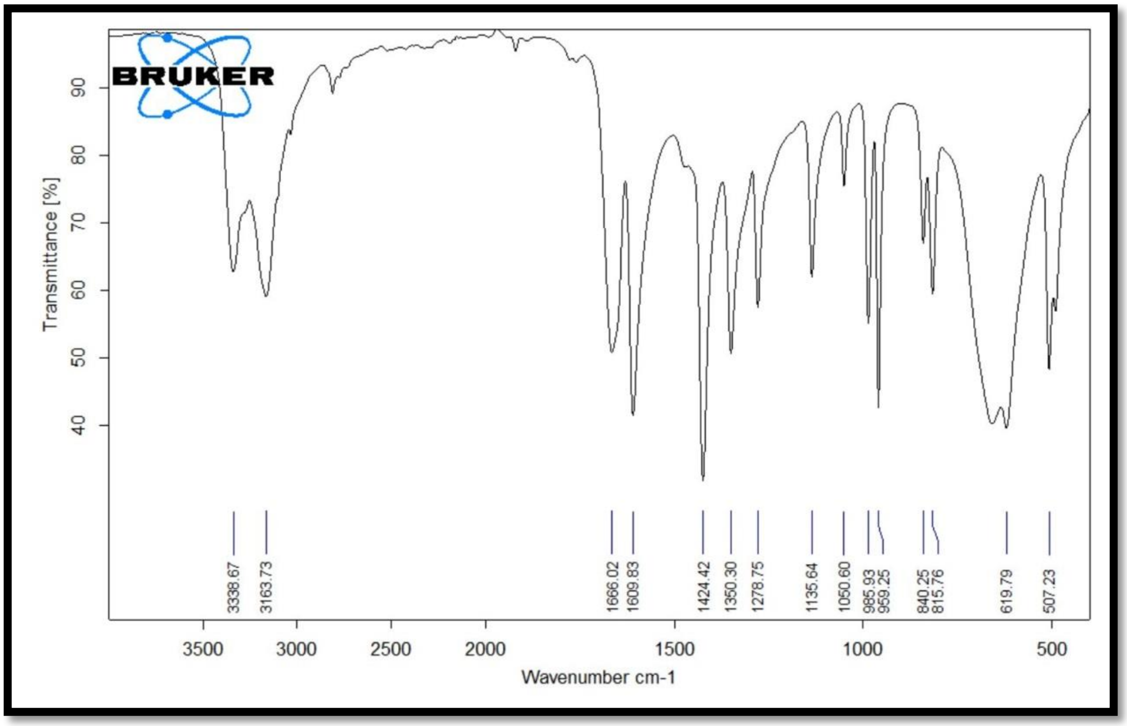


Figure 3.10 FTIR spectrum of A.Am from 500 cm^{-1} to 4000 cm^{-1}

On the other hand, the IR spectrum for EDMA is shown in figure 3-9. It gives important peaks at 1662 cm^{-1} and 1723 cm^{-1}, which refer to (C=C) and (C=O) groups respectively.

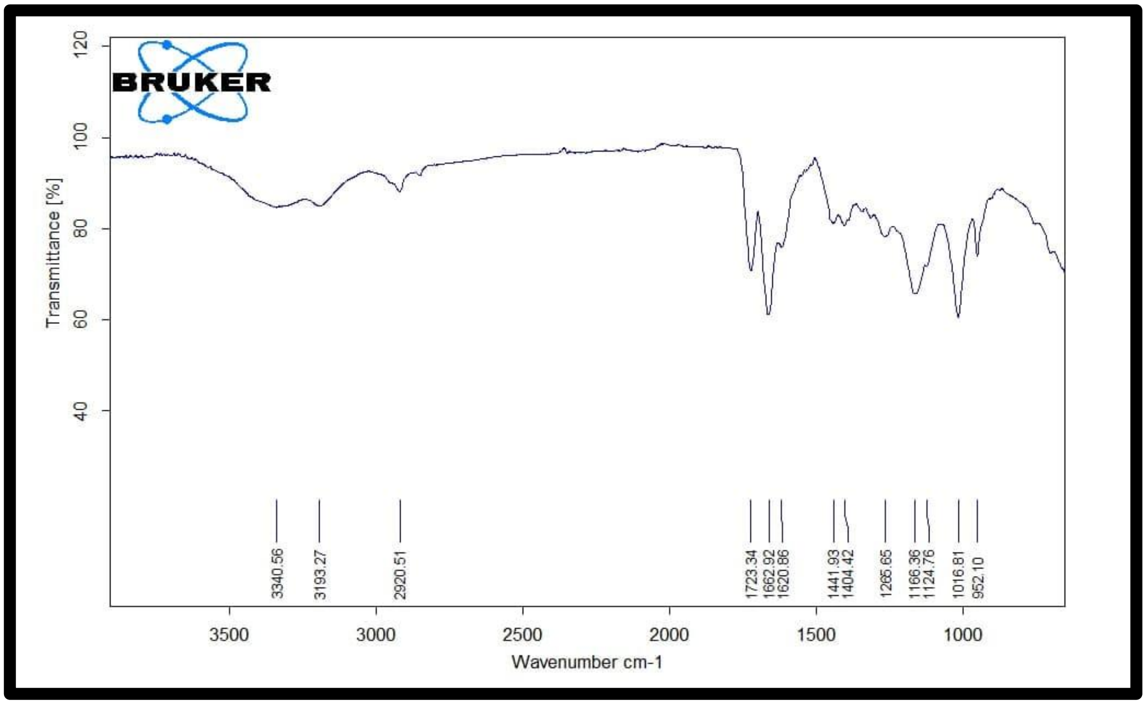


Figure 3.11 FTIR spectrum of EDMA from 500 cm^{-1} to 4000 cm^{-1}

The FT-IR spectra of GMA-co-EDMA-co-AAm figure (3.10) shows clear peaks for (C=O), (NH_2), and epoxy ring. In the same time, the (C=C) peaks in the monomers and cross-linker spectra disappears, this being a strong evidence of polymer formation.

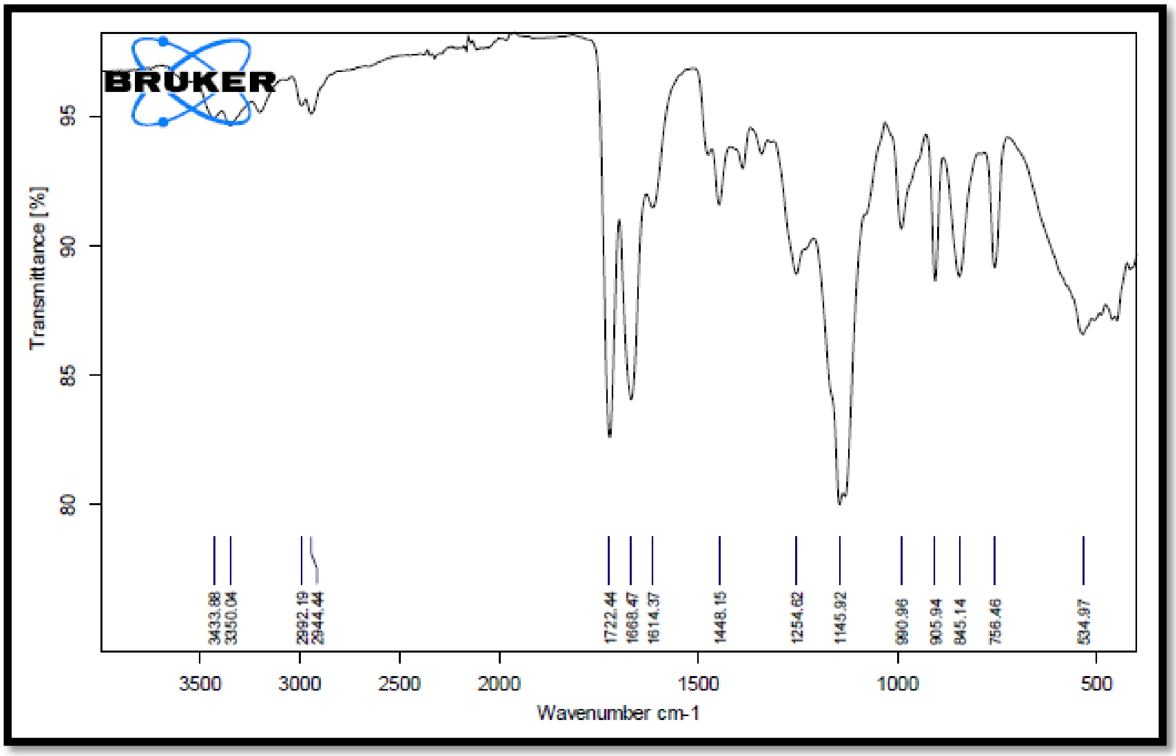


Figure 3.12 FT-IR spectra of GMA-co-EDMA-co-AAm from 500 cm^{-1} to 4000 cm^{-1}

3.6. Brunauer-Emmett-Teller (BET) analysis for glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolith

Brunauer-Emmett-Teller (BET) analyses demonstrate the surface area and the pore size of the gycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic column.

The results of Brunauer-Emmett-Teller (BET) analyses are (5.1859 nm), (16.021 m2/g) of pore size and surface area respectively, in this case pore size and surface area are interrelated as pore size is needed for the purpose of flow rate and surface area is required to provide a morphological environment for the purpose of creating reactions on the surface. The results are satisfactory, as high flow rates are obtained with moderate back pressures, and the reactions are carried out on the surface without hindrances.

3.7. ^{1}H NMR spectroscopy for glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolith

The prepared polymer (glycidyl methacrylate-co-ethylene dimethacrylate-co-acryl amide) is studied using nuclear magnetic resonance spectrometry (^{1}H NMR), with reference to the monomers it contains on CH_2, Alkene CH_2 and CH_3 the^{1}H NMR spectrum for the prepared polymer Figure 3.11 was showed a signal at 3.4 ppm that it belongs to the CH_2 group, it also gives a signal at 2.5 ppm which belongs to the CH_3 group noting that there is no indication of CH_2 alkene, which appears within 6.4 ppm in all monomers befor polymer formation, and this is a good evidence of the formation of the polymer.

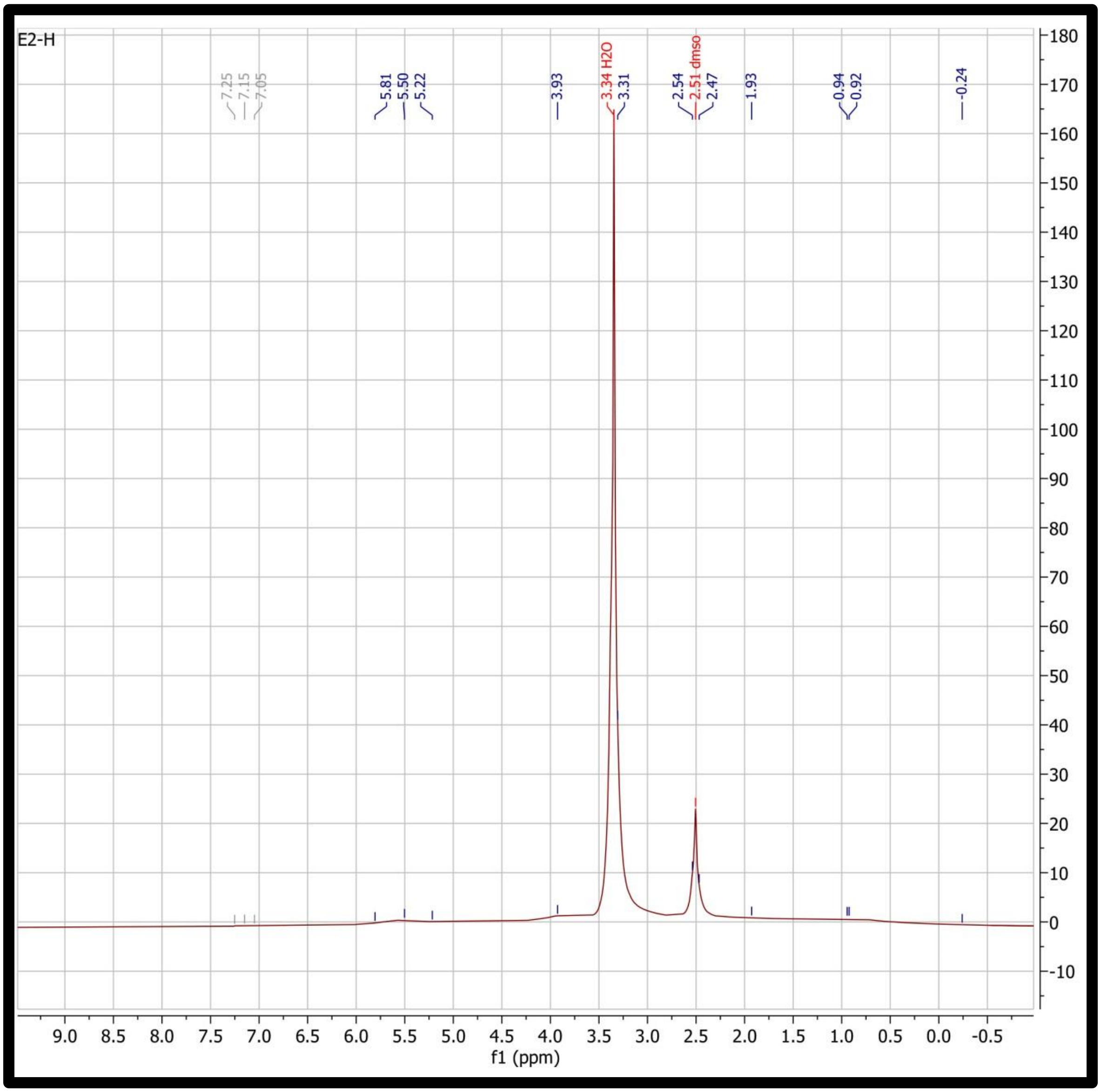


Figure 3.13. ^{1}HNMR spectroscopy for (glycidyl methacrylate-co-ethylene dimethacrylate-co-acryl amide)

3.8. Investigation of the irradiation time

The irradiation time is investigated for polymer formation to have an appropriate pore size and surface area was studied, different times are used to indicate the appropriate irradiation time as shown in the table 3.1

Table 3.1 Effect of irradiation time on polymer formation

Irradiation time/min	Result of the polymer formed
1	The polemer did not form
2	The polemer did not form
3	Polymer formed with low back pressure
4	Polymer formed with moderate back pressure
5	Polymer formaed with high back pressure
6	Polymer formaed but blocked

It can be seen from Table 3.1 that the irradiation time is the main factor in which the liquid polymer mixture is converted into a solid polymer. Therefore, when using an irradiation time of 5 minutes or more, the polymer chains grow rapidly and increase in the branching, and thus the resulting monolith has a very small porous structure and it is possible these pores become clogged when irradiation continues figuer 3.12C.

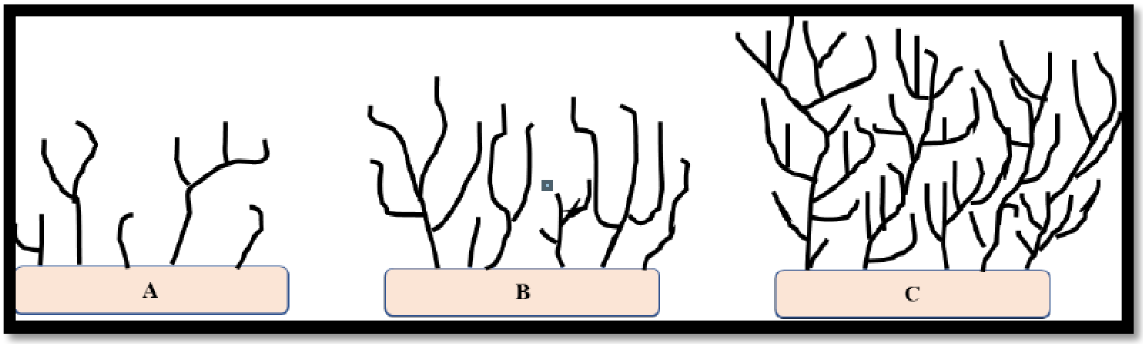


Figure 3.14 Effect of increasing the irradiation time on the growth of polymer chains

On the other hand, when using an irradiation time of less than 4 minutes, the polymer strands are few, and the polymer is not solid and has a gelatinous texture. Thus, we get an incompletely formed polymer with low efficiency (Figure. 3.12)(A), but when the time is 4 minutes, the polymer branches grow uniformly, and the resulting monolith has an ideal pore size and moderate return pressure (figure 3.12)(B)

3.9. Investigation of the distance between the irradiation source and the monolith column

The distance between monolith column and the irradiation source can affect by the formation of the polymer; different distances (table 3.2) between the irradiation source and the monolith column have been studied (2-14 cm). It can be seen from Table 3.2 during (2-6) cm that the polymer forms very quickly, but the polymer is difficult to wash due to the small pore size or that these pores are close, and during (8) cm the polymer is formed, but it is difficult to wash with high back pressure .When the time is reached (10) cm, the polymer is formed and can be washed easily with moderate back pressure that refer to the monolith with desird pore size and surfes eara.

Table 3.2 Effect of the distance between the irradiation source and the monolith column

Distance /cm	Result of the polymer formed
2	The polymer is formed, but it cannot be washed
4	The polymer is formed, but it cannot be washed
6	The polymer is formed, but it cannot be washed
8	The polymer is formed and can be washed, but with high back pressure
10	The polymer is formed and can be washed, and modrate back pressure
12	The polymer is formed,but with low back pressure
14	The polymer is not completely formed

But if the time is 12-14 minutes, the polymer is either formed, but by very low back pressure or the polymer is incompletely formed.

3.10. Permeability and the porosity of the Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic

The permeability of the prepared monolith Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic was calculated by evaluating the back pressure from a HPLC system pump by pumping distilled water at different rates. Figure 3.13 shows the results obtained from this process.

Figure 3.15 HPLC pump

It can be noticed from Figure(3.14) that the back pressure generated in the pump increases with the increase in the flow rate until it reaches a flow rate of 2000 µL.m^{-1}and the pressure is stable at this point by 540 PSI, when the flow rate increases more than 2000 µL.m^{-1}, the pump gives an error signal and the system shuts down or that the monolith column slips from the connections as a result of the pressure reaching a critical point, so the flow rate through the column was determined from(20 – 2000) µL.m^{-1} in other experiments.

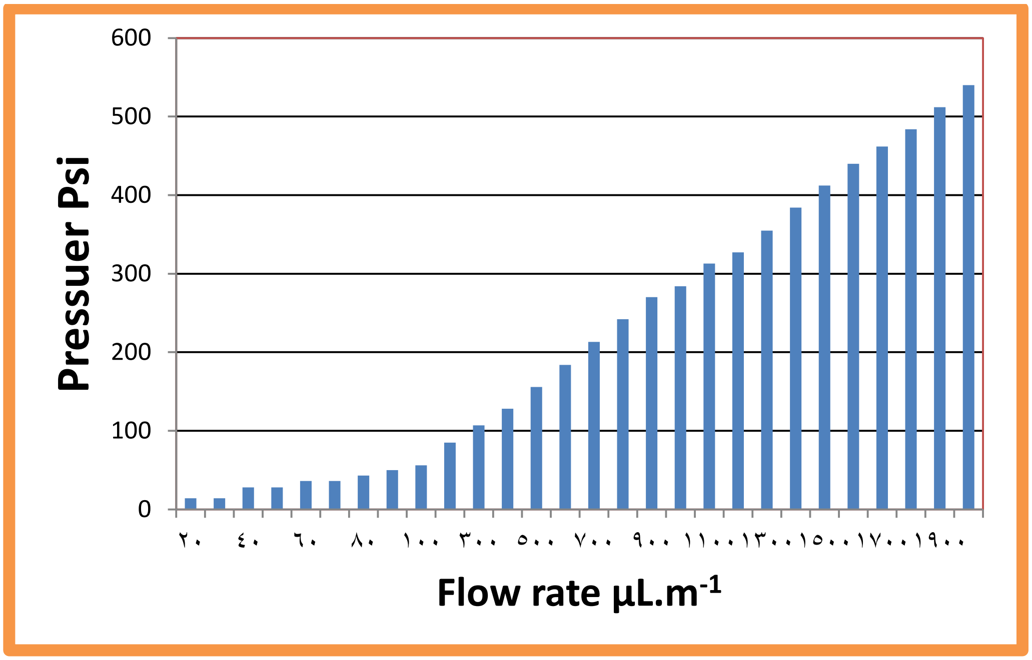


Figure 3.16The relationship between the back pressure and the flow rate for the Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic column

The porosity of the glycidyle methacrylate-co-ethylene dimethcrylate-co-acryl amide monolithic column is calculated by using the procedure that described in paragraph 2.15. The result shows the porosity of the column is 0.0360.

3.11. Swelling measurement of the Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic

The study of the percentage of polymer swelling is one of the important studies to choose the type of solvent to be used in the mobile phase, which carries samples, where crosslinked polymers with high molecular weights suffer swelling as a result of the diffusion of solvent molecules within the crystal lattice of polymers and leads to an increase in its size and this leads to the collapse of the polymer when exposed to mechanical stress or high pressure, there are two main factors that determine the degree of polymer swelling, which are the degree of crosslinking of the polymer and the nature of the solvent used.

Swelling percentage of prepared monolith glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide was calculated using the equation

$$swlling\% = \frac{mt - mo}{mo} \times 100 \qquad 3.1$$

Where

Mo: wihgt of polymer before swlling

Mt: wihgt of polymer after swlling

Alcohol solvents, different polar solvents and a mixture of solvents are used to test the degree of swelling of the polymer and when applying the equation the results appeared as in the tables (3.3), (3.4), and (3.5)

Table 3.3 shows the percentage swell of the polymer using different alcohol solvents

Time/hour	Swlling% metanol	Swlling% ethanol	Swlling% 1-propanol	Swlling% 2-butanol	Swlling% hexanol
1	4.6	6.1	4.1	10.1	12.4
6	4.6	6.1	4.1	10.1	12.4
24	4.6	6.1	4.13	10.1	12.5
120	4.66	6.14	4.16	10.3	12.6
240	4.7	6.15	4.16	10.5	12.6
360	4.7	6.15	4.19	10.5	12.9
480	4.7	6.15	4.19	10.5	12.9

It can be seen from table (3.3) the polymer swells significantly when using hexanol and1- butane, it could be the penetration of solvent molecules into the polymeric chain, causing the polymer to swell while the polymer remains insoluble. This penetration causes the monoliths to become small, causing a high back pressure on the pump, and on the other hand, the difficulty of loading samples due to the small pore size While the swelling of the polymer is less when using methanol, ethanol and 1-propanol so that the polymer maintains its porous structure as shown in Figure (3.17).

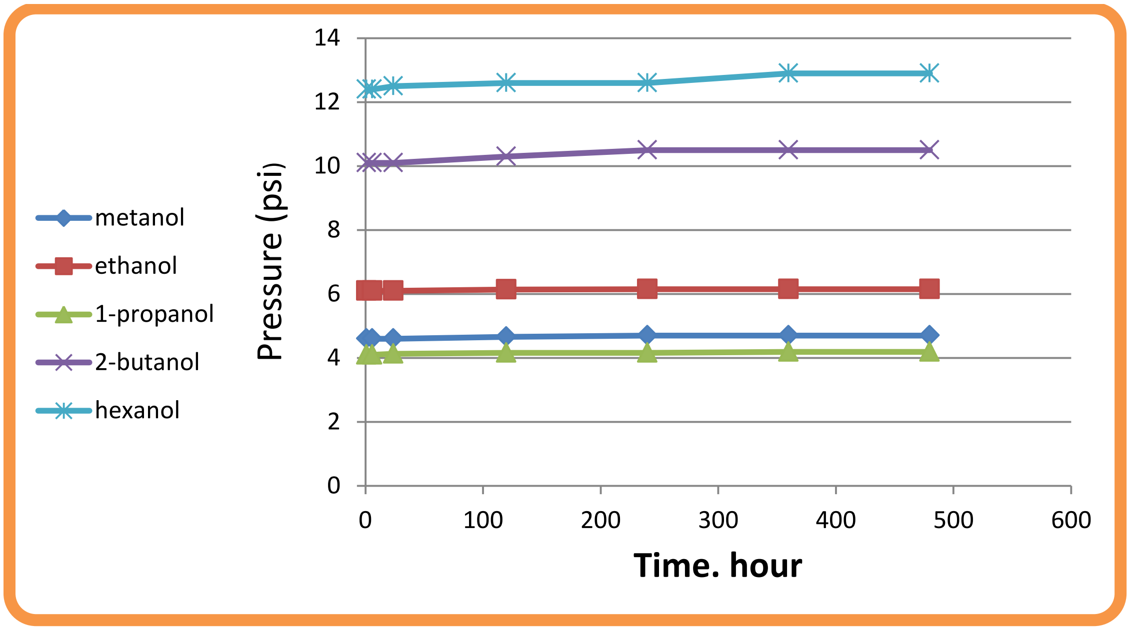


Figure 3.17 polymer sewlling by using different alcohol solvents

When using different polar solvents, it can be seen from Table 3.4 that when using acetonitrile and formic acid, the polymer begins to swell up to 240 hours, and then the polymer disintegrates as a result of the penetration of the solvent into the crystal lattice, which suffers either from chemical decomposition or as a result of swelling pressure, which led to the breakage of the polymer, and when used formic acid, the polymer suffers only swelling, while the polymer suffers a slight swelling that is almost imperceptible, as the polymer maintains its crystal lattice and pore size when using water, acetone and benzene figure 3.18

Table (3.4) shows the percentage swell of the polymer using different polar solvents

Time/hour	Swlling % water	Swlling% acetonitrile	Swlling% aceton	Swlling% formic acid	Swlling% benzen	Swlling% chloroform
1	**2.5**	**4.3**	**1.8**	**3**	**4.9**	**7**
6	**2.5**	**4.3**	**1.8**	**3**	**4.9**	**7**
24	**2.5**	**4.5**	**1.8**	**3.2**	**4.92**	**7.05**
120	**2.55**	**4.7**	**1.83**	**3.3**	**4.92**	**7.05**
240	**2.56**	**4.7**	**1.85**	**3.5**	**4.95**	**7.1**
360	**2.56**	**-**	**1.85**	**-**	**4.98**	**7.1**
480	**2.56**	**-**	**1.85**	**-**	**4.98**	**7.1**

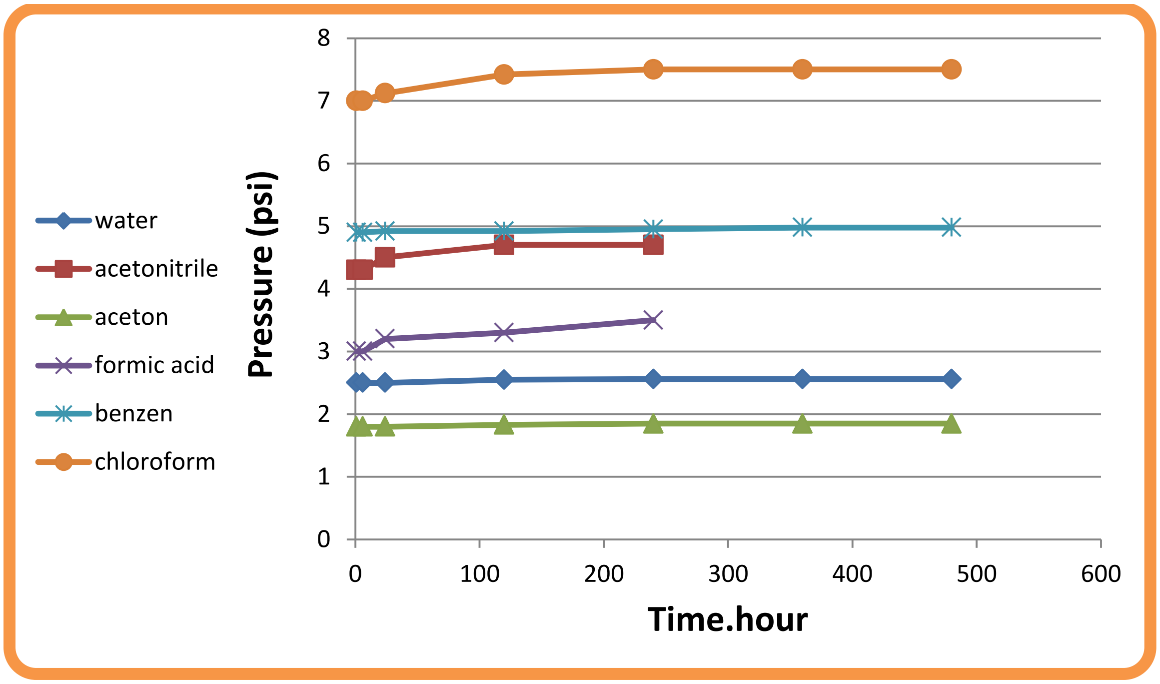


Figure 3.18 polymer sewlling by using different polar solvents

But when using a mixture of solvents, it can be seen from Table(3.5) that the mixture of water with acetonitrile exposes the polymer to swelling at first, and the reason may be attributed to the interaction between the particles of the mixture and the polymer, and in the end the polymer disintegrates as a result of the chemical decomposition of the polymer, but when a mixture of methanol-ethanol, ethanol-water, methanol-water is used, the polymer, as we can see from Table 3.5, suffers from a very slight swelling that does not affect the size of the pores while the polymer retains its general structure, and this indicates that there is no interaction between the polymer molecules and no decomposition chemiform figure(3.17).

Table (3.5) shows the percentage swell of the polymer by using a mixture of two different solvents

Time hour	Swlling% ethanol + methanol	Swlling% Ethanol + water	Swlling% Methanol + water	Swlling% Acetonitrile + water
1	2.16	4.37	1.63	4
6	2.16	4.37	1.63	4.1
24	2.17	4.37	1.63	4.15
120	2.17	4.37	1.63	4.9
240	2.19	4.39	1.64	5.3
360	2.19	4.41	1.66	-
480	2.19	4.41	1.66	-

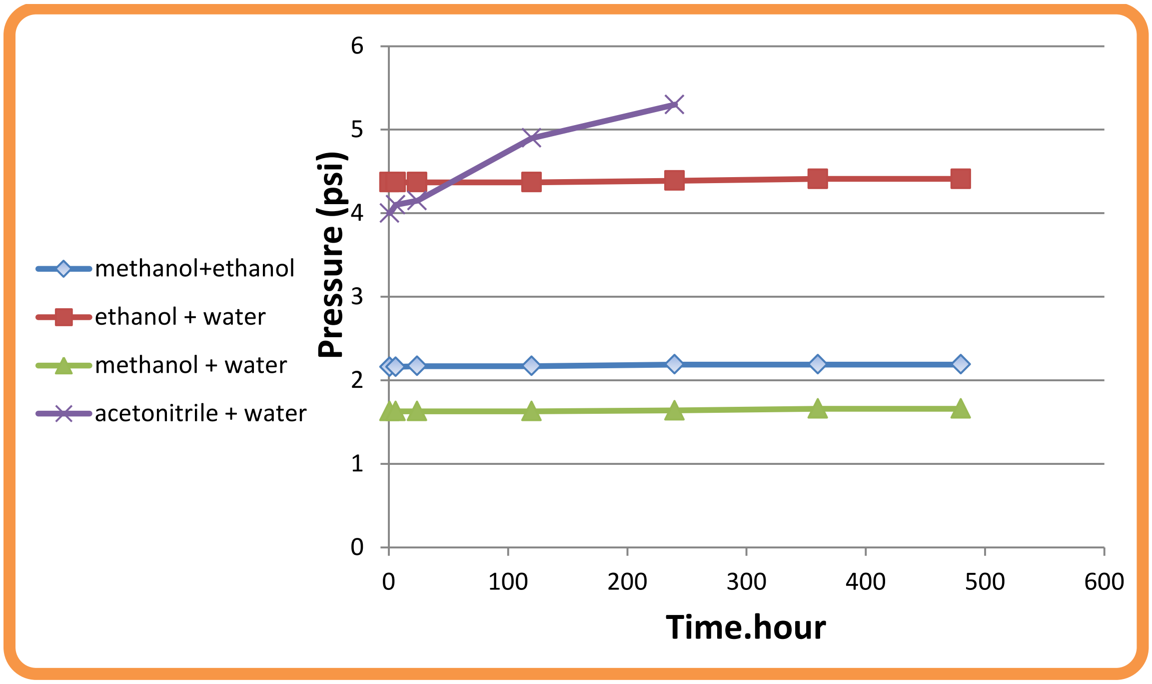


Figure 3.19 polymer sewlling by using a mixture of two different Solvents

Through the swelling experiments that were conducted on the polymer, we can see that its importance lies in giving indications about the mechanism of choosing the mobile phase and on the other hand knowing which solvent is best used as a preservation solution for the column, as it was found that water is the best solution used to keep the column, as the age of the column was when it was saved with water distilled up to 70 days.

3.12. Ring opening reaction of glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic by hydrolysis

The epoxy ring in methacrylate can modifying many post-polymerization reactions such as functionalisation with amines, functionalisation with thiols, functionalization with azide, functionalization with carboxylic acid and functionalisation with hydrolysis figure (1.8) Perhaps one of the easiest of these reactions is hydrolysis with the presence of acid as a catalyst, and due to the ease of this reaction, it achieves the goal, which is to convert the prepared monolith column into an inexpensive ion exchange column, so this reaction is used in this study.

The process of opening the ring is to convert the epoxy ring in the methacrylate monomer into a diol group this process was carried out by pumping a 0.2 M hydrochloric acid solution by the syringe pump Figure (3.18) at a speed of (20 µL.m^{-1})for a period of three hours. The presence of acid in the hydrolysis of the epoxy ring reduce the temperatures that must be provided during the opening process, as well as shortening the time lees than 24 hours, the opening process may be takes less than this time, but to ensure that the ring is fully opened, the time was considered as 3 hours as a limit to fully open the ring.

The FTIR technique was used to indicate the epoxy ring opening figure 3.18 A, B shown the FTIR for the polemer before and after epoxy ring opening.

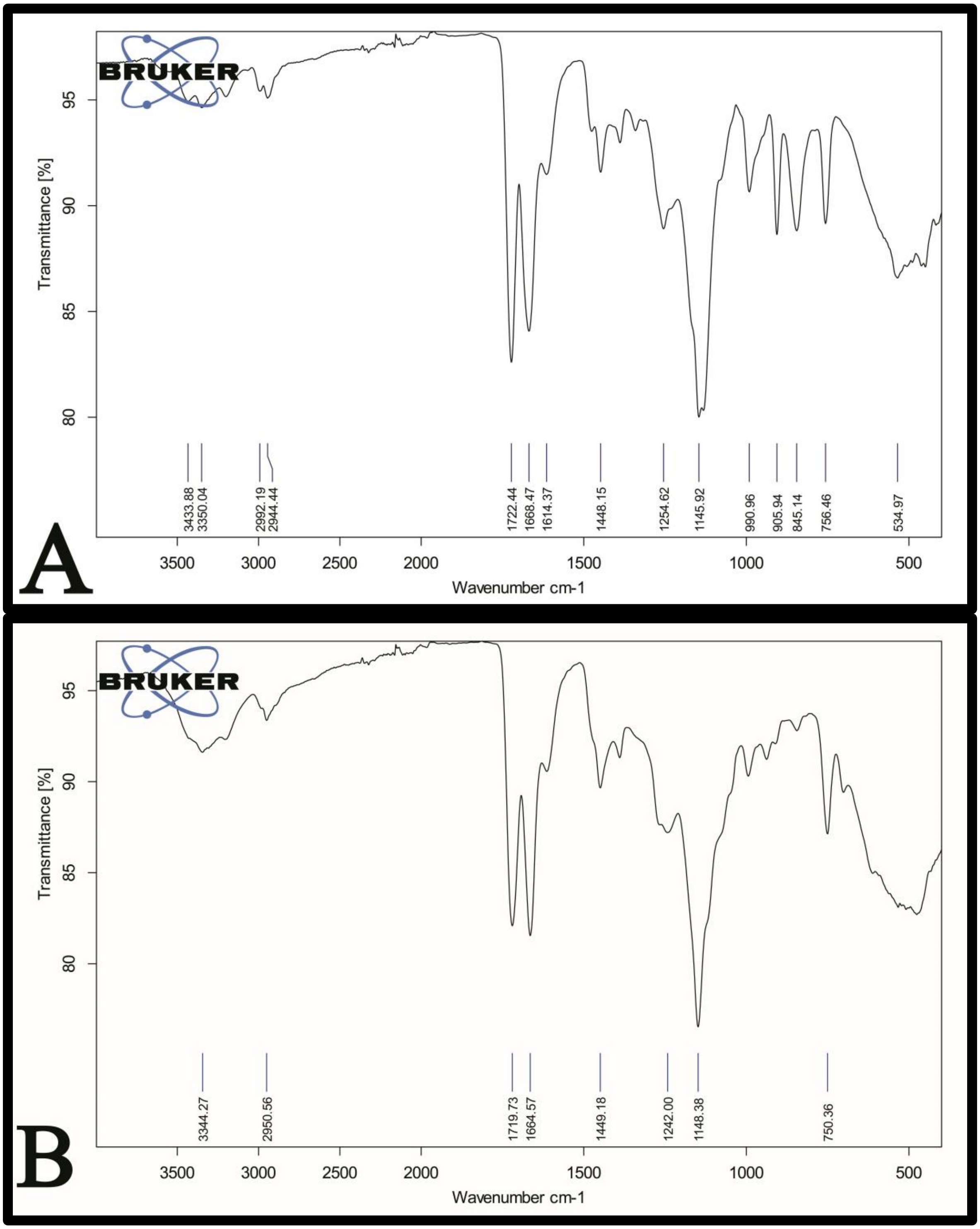


Figure 3.20 FTIR spectrium for glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic (A) before epoxy ring opening (B) after epoxy ring opening

It can be seen from Figure (3.19) A that epoxy ring which appears at 905 cm^{-1}which disappears after epoxy ring opening figure (3.19) B and the OH peak, which appears at 3344 cm^{-1}, after epoxy ring opening and this is the good evidence of opening the epoxy ring and transforming to diol groups.

3.13. Calculation chelating capacity for monolith column

A chelating capacity of the monolith was estimated from the amount of Cu^{2+} adsorbed on the prepared monolith Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide by using the following equation

$$\boldsymbol{Q = \frac{C \times V}{W}} \qquad \boldsymbol{(3-2)}$$

Where

Q is the adsorption capacity of the chelating monolith column, ($mmol.g^{-1}$),

V is the volume of the eluate (L).

C is the concentration of (M^{2+}) in the eluate ($mmol.L^{-1}$).

W is the dry weight of monolith inside the column (g).

The process is carried out by passing a 2.5mL solution of copper nitrate with a concentration of 10 ppm at a flow rate 10 $\mu L.min^{-1}$ the flow rate is reduced to give enough time for the exchange between ions for 3 hours. After that, the column is rinsed using deionized water to remove the remaining unexchanged copper ions that reside then; a strongly acidic solution with a concentration of 2 M of nitric acid is pumped into the pores of the column to displace copper ions from the column body. The displaced solution is collected and quantified. Then the column is washed with deionized water to displace the remaining acid particles in the column.

After applying the data in Equation 3.2, we find that the amplitude of the column is 2.3 PPm as follows:

$$\frac{1.68(mmol.L^{-1}) \times 0.0025(L)}{0.09569(g)} \qquad \textbf{(3 – 3)}$$

Q=0.04mmol.g^{-1}

Q=2.3PPM

3.14. Applications of Glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic as as strong cation exchange column

3.14.1. The process of loading samples into the column and their displacement

Initially, the column is connected to stainless steel union adapter attached to the peek-tube, then to the peek fitting, then it is connected to the syringe containing the sample solution, and then it is tightly connected to the syringe pump so that there is no leakage while pumping the sample as shown in Figure 3.19.

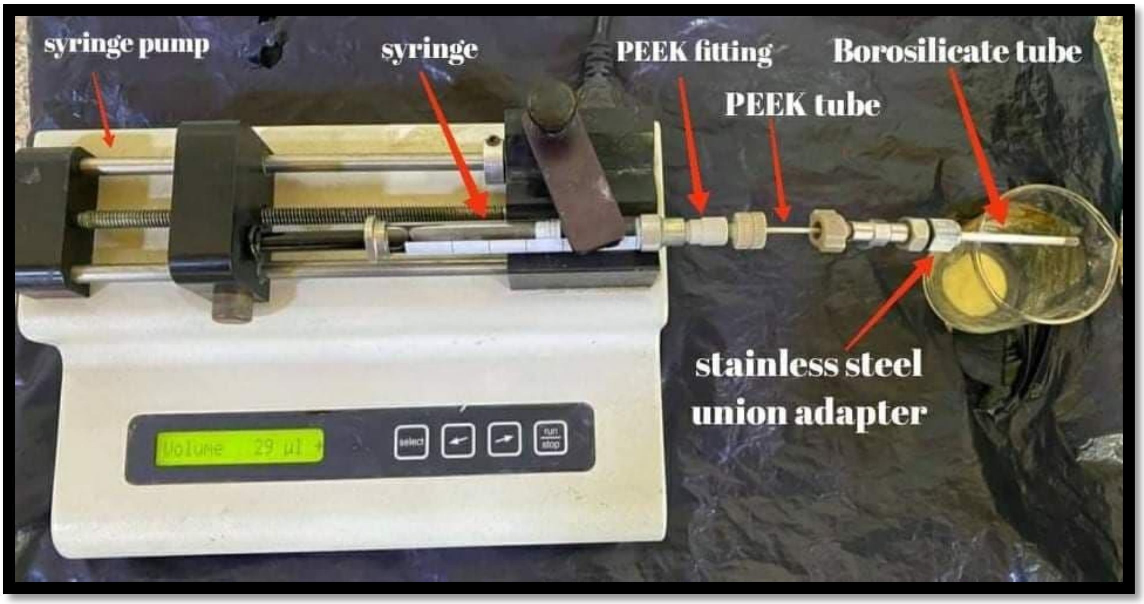


Figure 3.21 Loading samples into an ion exchange column

After that, the sample is injected at a flow rate of 20 microliters, and after the injection process is completed, the syringe is filled with deionized water to removing of the sample residue that fills the pores of the column. Then 0.2 M nitric acid solution is pumped to activate the column and displaces the sample that was separated in the column and collected for estimation.

3.14.2. Copper separation and determination

Two types of copper samples were used, the first type is a standard solution of copper nitrate with a concentration of 2 ppm, and the second type is a wastewater sample that was fetched from the wastewater treatment plant in Al-Maamera, the samples were injected into the column for separation as in paragraph (3.15.1), after collecting samples, samples were estimated by two methods spectrophotometric method and atomic absorption spectrophotometer method.

In spectrophotometric method neocuproine reagent was used to determine the eluted copper from the column after its reduction from Cu^{+2} to Cu^{+1} by using uric acid and modifying the pH of the solution in the range (7.5-8) a yellow complex formed when Neocuproine react with copper and the maximum absorbs of the complex was 455 nm, Beers' Lambert law was applied to constrict the calibration curve in the range (0.5-28 ppm) A calibration curve is shown in Figure (3.20) and all calculated parameters are shown in Table (3.6).

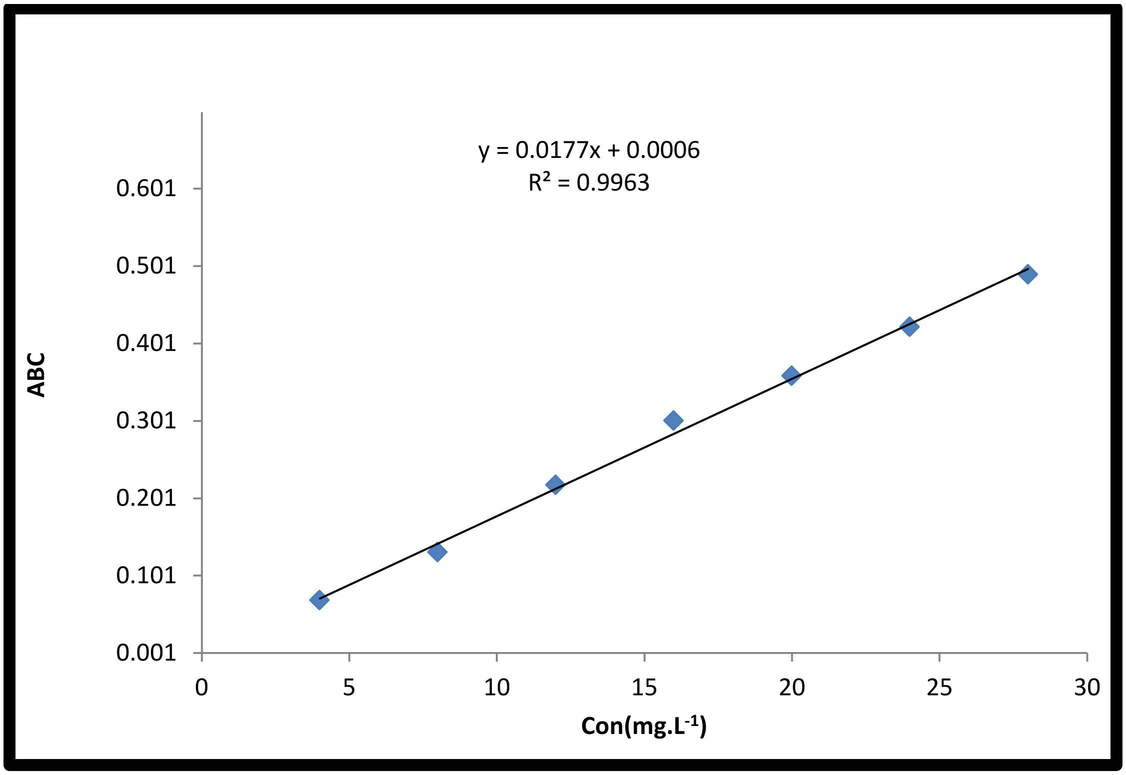


Figure 3.22 Calibration curve for spectrophotometric method

Table (3.6) all the parameters that could be obtained from the calibration curve.

parameters	Values
Range	(0.5-28)mg.L^{-1}
slop	0.0178
ɤmax	455nm
Intercept	0.0006
R^2	0.9963
LOD	0.129
LOQ	0.353
Sandle Index µg/cm^2	0.0561
ε(L/mol.cm)	1129

The same samples have been measured in an atomic absorption spectrometer. Table 3.7 shows the results obtained for copper ions by both methods.

Table (3.7) the comparison between the calculated concentration of copper using spectrophotometric and atomic absorption method

Type of sample	Spectrophotometric determination n=3 In $mg.L^{-1}$			Atomic absorption determintion n=3 In $mg.L^{-1}$		
	Befor using column	After using column	RSD	Befor using column	After using column	RSD
$2mg.L^{-1}$ (Standard solution)	2.0	1.9331	0.38%	1.9887	1.9676	0.05%
Wastewater(in flow)	0.1213	0.3404	3.79%	0.1521	0.0420	1.12%
Wastewater (out flow)	0.0871	0.0652	0.54%	0.0956	0.0260	0.77%

It can be seen from Table(3.7) that when pumping (2 $mg.L^{-1}$) of copper, the results are close between the spectroscopic method and the absorption method, which is a clear indication of the efficiency of the ion exchange column with a small difference that may be due to laboratory errors. In the case of wastewater samples, the concentration of copper ions is in the entering water mor than out water, the reason is that the principle of the station work is absolute biological treatment so that bacteria can be fed on organic compounds, on the other hand, the wastewater contains many elements in addition to the copper element, which was separated by column with copper.

3.14.3. lead separation and determination

A standard solution of lead (2mg.L^{-1}) is used and injected into the monolith column as in paragraph (3.15.1) the collected sample was measured by atomic absorption spectroscopy; the samples collected from the wastewater treatment station in Al-Maamera were also examined using atomic absorption spectrometry the results are shown in Table (3.7).

Table (3.8) the results of the atomic absorption test for lead ions for concentrated solution and waste water

Type of sample	**Atomic absorption determintion n=3 In mg.L^{-1}**		
	Befor usingcolumn	After using column	RSD
2mg.L^{-1} (Standard solution)	1.9808	1.9611	0.09%
Wastewater(in flow)	0.1521	0.0425	0.71%
Wastewater (out flow)	0.0901	0.0263	2.52%

From Table (3.7) it can be seen that the difference is slight between the concentration of the standard solution before and after using the separation column, and this indicates the high separation efficiency that characterizes the column, as for the wastewater samples, it can be seen that the column separated(0.042) mg.L^{-1} from(0.15) mg.L^{-1} lead ions present in the water entering the station, and (0.026) mg.L^{-1} from(0.09) mg.L^{-1} lead ions were separated from the water leaving the station, and this is due to the presence of a lot of other ions that It contains waste water that was separated using the column in addition to lead ions.

3.14.4. Nickel separation and determination

A standard solution of lead (2mg.L^{-1}) was used and injected into the monolith column as in paragraph (3.15.1) the collected sample was measured by atomic absorption spectroscopy; the samples collected from the wastewater treatment station in Al-Maamera were also examined using atomic absorption spectrometry the results are shown in Table (3.8).

From Table (3.8) it can be seen that the difference is slight between the concentration of the standard solution before and after using the separation column, and this indicates the high separation efficiency that characterizes the column, as for the wastewater samples, it can be seen that the column separated (0.7224) mg.L^{-1} from(1.5954) mg.L^{-1} lead ions present in the water entering the station, and (0.4235) mg.L^{-1} from(1.2361) mg.L^{-1} lead ions were separated from the water leaving the station, and this is due to the presence of a lot of other ions that It contains waste water that was separated using the column in addition to lead ions.

Table (3.9) the results of the atomic absorption test for Nickel ions for concentrated solution and waste water

Type of sample	**Atomic absorption determintion n=3 In mg.L^{-1}**		
	Befor usingcolumn	After using column	RSD
2mg.L^{-1} (Standard solution)	1.9921	1.9591	0.38%
Wastewater(in flow)	1.5954	0.7224	1.49%
Wastewater (out flow)	1.2361	0.4235	2.68%

3.14.5. Separation and determination of a mixture of copper lead and nickel

2 mg.L^{-1} of each of copper, lead and nickel was mixed in a Becker and injected into the monolith column as in paragraph (3.15.1) the displacement solution was collected and tested in atomic absorption spectrometry. Table 3 shows the results obtained from this test.

Table (3.10) the results of the atomic absorption test for a mixture of copper lead and nickel

Type of sample			Atomic absorption determintion n=3 In mg.L^{-1}	
	Befor using column		After using column	RSD
2mg.L^{-1} (Standard solution) Cu^{2+},Pb^{2+},Ni^{2+}	Cu^{2+}	1.9851	0.8223	0.94%
	Pb^{2+}	1.9420	0.8010	2.12%
	Ni^{2+}	1.9903	0.6742	0.37%

It can be seen from Table 3 that the results indicate that the column separates the three ions, but in varying proportions. This is due to the competition between the ions. The size of the ion may play an important role in the competition. It is known that copper and nickel fall into the same cycle. The difference in size is very simple, so it came the results are similar, but the lead ion is larger than copper and nickel, so the amount of lead separated by the column is less compared to copper and lead.

3.15. Column efficiency study

The efficiency of the prepared column was studied in the separation process by taking several different concentrations of copper solution (0.5, 1, 1.5, 2, and 3) mg.L^{-1} and injecting it into the column and then removing it as in paragraph 3.14. 1 In addition, the remainder of the injection process was collected for each of the concentrations mentioned above; the copper displaced from the column and the residual from the injection process was estimated using the neocuproine reagent as shown in paragraph (1.14.3) and as shown in Table (3.10).

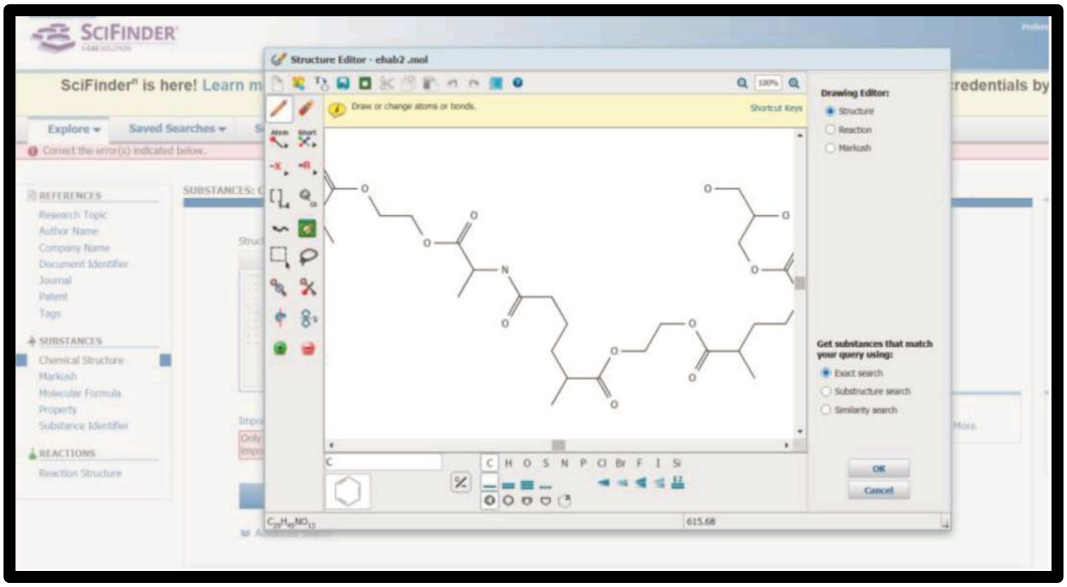
Table 3.11 Results of the spectrophotometric mothed of copper concentrations displaced from the column and the remainder of the injection process

Appliyed concentration mg.L^{-1}	Copper concentration displacement from column mg.L^{-1}	RSD%	Residual copper concentration from the injection process mg.L^{-1}	RSD%
0.5	0.4989	0.48%	0.0008	0.39%
1	0.9985	0.42%	0.0012	0.33%
1.5	1.4968	0.29%	0.0029	0.11%
2	1.9885	0.36%	0.0097	0.21%
3	2.2951	0.28%	0.6981	0.46%

We can see from Table (3.10) the high efficiency of the column in the separation process, as the concentrations (0.5, 1, 1.5, 2) mg.L^{-1} were separated almost completely, with a small amount of copper concentration in the remainder of the injection process, but in the case of concentration 3mg.L^{-1} the column did not separate it completely This is because the column capacity is 2.3mg.L^{-1}.

3.16. Proof that the polymer was not prepared previously

Through the foregoing and by reviewing previous studies in the course of the research and based on the Sci- Finder program, it is found that the polymer is prepared for the first time, and this in turn enhances the accuracy and modernity of the prepared polymer, as shown in the figures



● Structure
○ Reaction
○ Markush

● Exact search
○ Substructure search
○ Similarity search

$C_{29}H_{45}NO_{13}$ 615.68

Figure 3.23 the structural formula of the structural unit of the polymer under study

SciFinder^n is here! Learn more about the power of n. Participating customers can access using their existing SciFinder credentials b
https://scifinder-n.cas.org

Click image to change structure or view detail.

Search Type:
● Exact Structure
○ Substructure
○ Similarity

☐ Show precision analysis

Launch a SciFinder/SciFinder^n substance or reaction search directly from the latest version of ChemDraw. Learn More

Figure 3.24 adding the polymer composition to complete the series of the program sed

SciFinder^n is here! Learn more about the power of n. Participating customers can access using their existing SciFinder credentials b
https://scifinder-n.cas.org

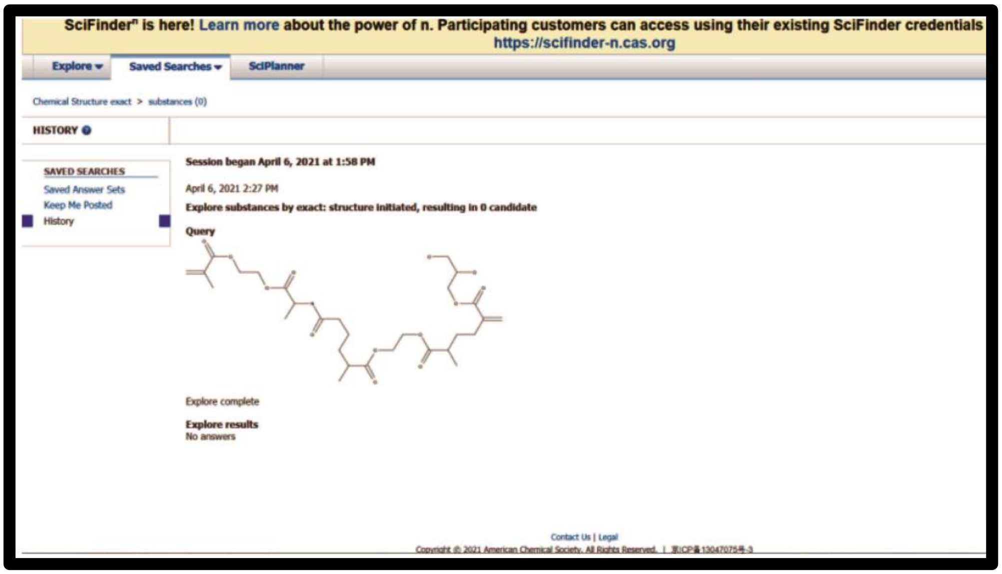
Searching...

Did you know for any known molecule, SciFinder-n will perform a full retrosynthetic analysis utilizing the renowned CAS collection of reactions, presenting results in a highly intuitive retrosynthesis plan? See more at https://www.cas.org/products/scifinder-n/retrosynthesis-planning

Click image to change structure or view detail.

Launch a SciFinder/SciFinder^n substance or reaction search directly from the latest version of ChemDraw. Learn More

Figure 3.25 supplement the search series for the program used



SciFinder^n is here! Learn more about the power of n. Participating customers can access using their existing SciFinder credentials https://scifinder-n.cas.org

Session began April 6, 2021 at 1:58 PM

April 6, 2021 2:27 PM

Explore substances by exact: structure initiated, resulting in 0 candidate

Query

Explore complete

Explore results
No answers

Figure 3.26 Accuracy, quality and novelty of the compound under study

3.17. Conclusions

Glycidyl methacrylate copolymer monolithic column have been investigated using acryl amide alongside to glycidyl methacrylate (GMA). Ethylene glycol dimethacrylate (EDMA) is used as cross-linker, while, 2,2-dimethoxy-2- phenylacetophenone is used as initiator. This monolith was prepared inside the borosilicate tube by in-situ polymerization to produce non expensive ion exchange monolithic columns. It is found that the (GMA-co- EDMA-co-A.Am) monolithic column is formed using (50:50) % of GMA: A.AM after 4 minutes of irradiation time. The BET analysis results demonstrate that the monolithic column has high average surface area (16.021 m2 g-1), with average pore size of (5.1859 nm).

The GMA-co-EDMA-co-A.Am as polymer monolithic column is demonstrated using FTIR and 1HNMR analysis. The results show that the polymer has three peaks indicating the presence of (C=O) and epoxy group and NH2 group. While (C=C) peak in the monomers, and crosslinker is disappeared, this is good evidence for the formation of the polymer by incorporation of both monomers and cross-linker using (C=C) bonds, moreover the peak of epoxy group disappears after pumping 0.2 M HCl and this is good evidence for the formation of ring opening . The 1HNMR analysis shows that the (C=CH2) bonds around (6.4) ppm in the monomers and cross linker have disappeared in the polymer 1HNMR spectrum.

The irradiation time is investigated to form the monolith. It was found that the monolith is formed after 4 minute, moreover the distance between the monolith column is investigated and it is found that the ideal distance is 10cm in addition the the porosity of the of glycidyle methacrylate-co-ethylene dimethcrylate-co- acryl amide monolithic column is calculated the result shows that the porosity of the column was is 0.0360.The chelating capacity of the monolith is estimated. It found that 2.3 ppm and the swelling of polymer are tested by using different solvents and the result shows the water conceder a good solution for keeping the column and water, methanol, ethanol and 1-propanol, acetone, benzene, methanol-ethanol, ethanol-waterand methanol-water a good solvents to use as astatinary phase.The GMA-co-EDMA-co-A.Am monolith column is used as an ion exchange column after opening the epoxy ring to rmove cataions.

3.18. Future work

1- Developing the ion exchange monolithic column by investigating other monomers that have different properties to separate different ranges of the samples in a single run.

2- Developing more ways to modify the epoxy ring to expand the separation range of different particles and ions.

3- Prepared monolithic columns with wider pore sizes for large molecules by tuning the polymerization mixture to give monolithic columns significantly enhanced chromatographic performance for large molecules.

4- Using the amine group in the GMA-co- EDMA -co- A.Am monolithic column to separate the anions and thus prepare a zwitterion separation column.

5- Investigate the length of the GMA-co- EDMA -co- A.Am monolithic columns, and the effect on the separation performance.

6- Using other porogenic solvents and studying their relationship to pore size and surface area.

7-Preparation of other types of monoliths such as the inorganic monoliths and Hybrid monolith.

Refrence

1. Mould D, Synge RJA. 1952. Electrokinetic ultrafiltration analysis of polysaccharides. A new approach to the chromatography of large molecules. 77:964-9
2. Mould D, Synge RJBj. 1954. Separations of polysaccharides related to starch by electrokinetic ultrafiltration in collodion membranes. 58:571
3. Kubin M, Špaček P, Chromeček RJCoCCC. 1967. Gel permeation chromatography on porous poly (ethylene glycol methacrylate). 32:3881-7
4. Ross WD, Jefferson RTJJoCS. 1970. In situ—formed open-pore polyurethane as chromatography supports. 8:386-9
5. Hileman FD, Sievers RE, Hess GG, Ross WDJAC. 1973. In situ preparation and evaluation of open pore polyurethane chromatographic columns. 45:1126-30
6. Schnecko H, Bieber OJC. 1971. Foam filled columns in gas chromatography. 4:109-12
7. Belenkii B, Podkladenko A, Kurenbin O, Mal'tsev V, Nasledov D, Trushin SJJoCA. 1993. Peculiarities of zone migration and band broadening in gradient reversed-phase high-performance liquid chromatography of proteins with respect to membrane chromatography. 645:1-15
8. Tennikova T, Svec F, Belenkii BJJoLc. 1990. High-performance membrane chromatography. A novel method of protein separation. 13:63-70
9. Peters EC, Petro M, Svec F, Fréchet JMJAC. 1997. Molded rigid polymer monoliths as separation media for capillary electrochromatography. 69:3646-9
10. Hjerten S, Liao J-L, Zhang RJJoCA. 1989. High-performance liquid chromatography on continuous polymer beds. 473:273-5
11. Minakuchi H, Nakanishi K, Soga N, Ishizuka N, Tanaka NJAc. 1996. Octadecylsilylated porous silica rods as separation media for reversed-phase liquid chromatography. 68:3498-501
12. Nakanishi K, Soga NJJotACS. 1991. Phase separation in gelling silica–organic polymer solution: systems containing poly (sodium styrenesulfonate). 74:2518-30
13. Wang QC, Svec F, Frechet JMJAC. 1993. Macroporous polymeric stationary-phase rod as continuous separation medium for reversed-phase chromatography. 65:2243-8

14. Petro M, Svec F, Gitsov I, Fréchet JMJAc. 1996. Molded monolithic rod of macroporous poly (styrene-co-divinylbenzene) as a separation medium for HPLC of synthetic polymers:“On-Column” precipitation−redissolution chromatography as an alternative to size exclusion chromatography of styrene oligomers and polymers. 68:315-21
15. Guiochon GJJoCA. 2007. Monolithic columns in high-performance liquid chromatography. 1168:101-68
16. Tanaka N, Nagayama H, Kobayashi H, Ikegami T, Hosoya K. 2000. Monolithic silica columns for HPLC, Micro-HPLC, and CEC. 23:111-6
17. Ishizuka N, Kobayashi H, Minakuchi H, Nakanishi K, Hirao K. 2002. Monolithic silica columns for high-efficiency separations by high-performance liquid chromatography. 960:85-96
18. Arrua RD, Strumia MC, Alvarez Igarzabal CIJM. 2009. Macroporous monolithic polymers: preparation and applications. 2:2429-66
19. Odero-Marah VA, Khalkhali-Ellis Z, Chunthapong J, Amir S, Seftor RE. 2003. Maspin regulates different signaling pathways for motility and adhesion in aggressive breast cancer cells. 2:398-403
20. Vervoort N, Gzil P, Baron GV, Desmet GJAc. 2003. A correlation for the pressure drop in monolithic silica columns. 75:843-50
21. Tanaka N, Kobayashi H, Ishizuka N, Minakuchi H, Nakanishi K. 2002. Monolithic silica columns for high-efficiency chromatographic separations. 965:35-49
22. Svec F, Huber CG. 2006. Monolithic materials: promises, challenges, achievements. ACS Publications
23. Xie S, Allington RW, Fréchet JM, Svec FJMAiC. 2002. Porous polymer monoliths: an alternative to classical beads.87-125
24. Müllner T, Zankel A, Höltzel A, Svec F, Tallarek UJL. 2017. Morphological properties of methacrylate-based polymer monoliths: from gel porosity to macroscopic inhomogeneities. 33:2205-14
25. Zhang Y-P, Li W, Wang X-J, Qu L-B, Zhao G-L. 2009. Fast preparation of polystyrene-based monolith using microwave irradiation for micro-column separation. 394:617-23
26. Hoegger D, Freitag RJJoCA. 2001. Acrylamide-based monoliths as robust stationary phases for capillary electrochromatography. 914:211-22
27. Nema T, Chan EC, Ho PCJJoP, Analysis B. 2014. Applications of monolithic materials for sample preparation. 87:130-41
28. Hjerten SJI, research ec. 1999. Standard and capillary chromatography, including electrochromatography, on continuous

polymer beds (monoliths), based on water-soluble monomers. 38:1205-14

29. Tanaka N, Kobayashi H, Nakanishi K, Minakuchi H, Ishizuka NJAC. 2001. A new type of chromatographic support could lead to higher separation efficiencies. 73:420A-9A
30. Svec FJJoss. 2009. My favorite materials: porous polymer monoliths. 32:3-9
31. Premstaller A, Oberacher H, Huber CGJAc. 2000. High-performance liquid chromatography− electrospray ionization mass spectrometry of single-and double-stranded nucleic acids using monolithic capillary columns. 72:4386-93
32. Xie S, Allington RW, Svec F, Fréchet JMJJoCA. 1999. Rapid reversed-phase separation of proteins and peptides using optimized 'moulded'monolithic poly (styrene–co-divinylbenzene) columns. 865:169-74
33. Peters EC, Petro M, Svec F, Frechet JMJAc. 1998. Molded rigid polymer monoliths as separation media for capillary electrochromatography. 2. Effect of chromatographic conditions on the separation. 70:2296-302
34. Seto H, Shibuya M, Matsumoto H, Hoshino Y, Miura YJJoMCB. 2017. Glycopolymer monoliths for affinity bioseparation of proteins in a continuous-flow system: glycomonoliths. 5:1148-54
35. Noppe W, Plieva FM, Vanhoorelbeke K, Deckmyn H, Tuncel M. 2007. Macroporous monolithic gels, cryogels, with immobilized phages from phage-display library as a new platform for fast development of affinity adsorbent capable of target capture from crude feeds. 131:293-9
36. Du K, Yang M, Zhang Q, Dan SJI, Research EC. 2016. Highly porous polymer monolith immobilized with aptamer (RNA) anchored grafted tentacles and its potential for the purification of lysozyme. 55:499-504
37. Dong S, Chen L, Dai B, Johnson W, Ye J. 2013. Isolation of immunoglobulin G from bovine milk whey by poly (hydroxyethyl methacrylate)-based anion-exchange cryogel. 36:2387-93
38. Zhou D, Zou H, Ni J, Yang L, Jia L. 1999. Membrane supports as the stationary phase in high-performance immunoaffinity chromatography. 71:115-8
39. Yu R, Hu W, Lin G, Xiao Q, Zheng J, Lin ZJRa. 2015. One-pot synthesis of polymer monolithic column by combination of free radical polymerization and azide–alkyne cycloaddition "click"

reaction and its application in capillary liquid chromatography. 5:9828-36

40. Qin J, Bai L, Wang J, Ma Y, Liu H. 2015. A novel ionic liquid-based monolithic column and its application in the efficient separation of proteins and small molecules by high-performance liquid chromatography. 7:218-25
41. Guo R, Zhang D, Zhu X, Tang L, Zhang X. 2017. Preparation of a polymer monolithic column using ionic liquid as porogen and its application in separations of proteins and small molecules. 80:23-30
42. Eeltink S, Wouters B, Desmet G, Ursem M, Blinco D, et al. 2011. High-resolution separations of protein isoforms with liquid chromatography time-of-flight mass spectrometry using polymer monolithic capillary columns. 1218:5504-11
43. Walsh Z, Paull B, Macka MJAca. 2012. Inorganic monoliths in separation science: a review. 750:28-47
44. Jandera PJJocA. 2013. Advances in the development of organic polymer monolithic columns and their applications in food analysis—a review. 1313:37-53
45. Lin Z, Huang H, Li S, Wang J, Tan X. 2013. Preparation of phenylboronic acid-silica hybrid monolithic column with one-pot approach for capillary liquid chromatography of biomolecules. 1271:115-23
46. Cabrera KJLGM-NA-SfS. 2012. A new generation of silica-based monolithic HPLC columns with improved performance. 69:56
47. Ou J, Lin H, Liu Z, Zhang Z, Dong J, Zou HJSpCJoC. 2013. Preparation and modification of polyhedral oligomeric silsesquioxane-containing hybrid monolithic capillary columns. 31:322-8
48. Dulay MT, Kulkarni RP, Zare RNJAC. 1998. Preparation and characterization of monolithic porous capillary columns loaded with chromatographic particles. 70:5103-7
49. Martínez-Ortega A, Herrera A, Salmerón-García A, Cabeza J, Cuadros-Rodríguez L, Navas NJIjobm. 2018. Validated reverse phase HPLC diode array method for the quantification of intact bevacizumab, infliximab and trastuzumab for long-term stability study. 116:993-1003
50. Jakschitz TA, Huck CW, Lubbad S, Bonn GKJJoCA. 2007. Monolithic poly [(trimethylsilyl-4-methylstyrene)-co-bis (4-vinylbenzyl) dimethylsilane] stationary phases for the fast separation of proteins and oligonucleotides. 1147:53-8

51. El-Safty SA, Shenashen M, Khairy MJC, Biointerfaces SB. 2013. Bioadsorption of proteins on large mesocage-shaped mesoporous alumina monoliths. 103:288-97
52. Hong T, Chi C, Ji YJJoss. 2014. Pepsin-modified chiral monolithic column for affinity capillary electrochromatography. 37:3377-83
53. Wu M, Zhang H, Wang Z, Shen S, Le XC, Li X-FJCC. 2013. "One-pot" fabrication of clickable monoliths for enzyme reactors. 49:1407-9
54. Rivera JG, Messersmith PBJJoss. 2012. Polydopamine-assisted immobilization of trypsin onto monolithic structures for protein digestion. 35:1514-20
55. Kupfer GJKCT, Peters PKB. 2014. Application of Silica Monoliths for Bioanalysis.
56. Zhu T, Row KHJJoss. 2012. Preparation and applications of hybrid organic–inorganic monoliths: a review. 35:1294-302
57. Xu L, Lee HKJJoCA. 2008. Preparation, characterization and analytical application of a hybrid organic–inorganic silica-based monolith. 1195:78-84
58. Chen J, Du Y, Que W, Xing Y, Chen X. 2015. Crack-free polydimethylsiloxane–bioactive glass–poly (ethylene glycol) hybrid monoliths with controlled biomineralization activity and mechanical property for bone tissue regeneration. 136:126-33
59. Ou J, Liu Z, Wang H, Lin H, Dong J, Zou HJE. 2015. Recent development of hybrid organic-silica monolithic columns in CEC and capillary LC. 36:62-75
60. Oki A, Qiu X, Alawode O, Foley BJML. 2006. Synthesis of organic–inorganic hybrid composite and its thermal conversion to porous bioactive glass monolith. 60:2751-5
61. Barner-Kowollik C, Davis TP, Stenzel MHJP. 2004. Probing mechanistic features of conventional, catalytic and living free radical polymerizations using soft ionization mass spectrometric techniques. 45:7791-805
62. Nakanishi K, Shikata H, Ishizuka N, Koheiya N, Soga NJJoHRC. 2000. Tailoring mesopores in monolithic macroporous silica for HPLC. 23:106-10
63. Buchmeiser MRJP. 2007. Polymeric monolithic materials: Syntheses, properties, functionalization and applications. 48:2187-98
64. Hawker CJ, Bosman AW, Harth EJCr. 2001. New polymer synthesis by nitroxide mediated living radical polymerizations. 101:3661-88

65. Mihelič I, Koloini T, Podgornik AJJoaps. 2003. Temperature distribution effects during polymerization of methacrylate-based monoliths. 87:2326-34
66. Aoki H, Kubo T, Ikegami T, Tanaka N, Hosoya K. 2006. Preparation of glycerol dimethacrylate-based polymer monolith with unusual porous properties achieved via viscoelastic phase separation induced by monodisperse ultra high molecular weight poly (styrene) as a porogen. 1119:66-79
67. Yu C, Svec F, Fréchet JMJEAIJ. 2000. Towards stationary phases for chromatography on a microchip: Molded porous polymer monoliths prepared in capillaries by photoinitiated in situ polymerization as separation media for electrochromatography. 21:120-7
68. Kaur M, Srivastava AJJoMS, Part C: Polymer Reviews. 2002. Photopolymerization: A review. 42:481-512
69. Khimich G, Rakhmatullina E, Slabospitskaya MY, Tennikova TJRjoac. 2005. Synthesis and pore structure of monolithic polymeric sorbents. 78:617-22
70. Moad G, Chiefari J, Mayadunne RT, Moad CL, Postma A, et al. Initiating free radical polymerization. *Proc. Macromolecular Symposia*, *2002*, 182:65-80: Wiley Online Library
71. Mishra V, Kumar RJJSR. 2012. Living radical polymerization: A review. 56:141-76
72. Srivastava A, Mishra V, Singh SK, Kumar RJJoaps. 2010. Vanadium (V)/mandelic acid initiated graft copolymerization of acrylamide onto guar gum in an aqueous medium. 115:2375-85
73. Tennikova T, Bleha M, Švec F, Almazova T, Belenkii BJJoCA. 1991. High-performance membrane chromatography of proteins, a novel method of protein separation. 555:97-107
74. Courtois J, Byström E, Irgum KJP. 2006. Novel monolithic materials using poly (ethylene glycol) as porogen for protein separation. 47:2603-11
75. Ponten E, Viklund C, Irgum K, Bogen ST, Lindgren ÅNJAC. 1996. Solid phase chemiluminescence detection reactors based on in situ polymerized methacrylate materials. 68:4389-96
76. Xie S, Svec F, Fréchet JMJCom. 1998. Porous polymer monoliths: preparation of sorbent materials with high-surface areas and controlled surface chemistry for high-throughput, online, solid-phase extraction of polar organic compounds. 10:4072-8
77. Girma K, Lorenz V, Blaurock S, Edelmann FTJCCR. 2005. Coordination chemistry of acrylamide. 249:1283-93

78. Sennakesavan G, Mostakhdemin M, Dkhar L, Seyfoddin A, Fatihhi SJPD, Stability. 2020. Acrylic acid/acrylamide based hydrogels and its properties-A review. 180:109308
79. Seabrook SA, Gilbert RGJP. 2007. Photo-initiated polymerization of acrylamide in water. 48:4733-41
80. Vlakh E, Korzhikov V, Tennikova TJRCB. 2012. Solid-state systems of biological recognition based on macroporous polymer monoliths. 61:937-61
81. Hradil J, Azanova A, Ilavsky M, Svec FJAMC, 141. 1992. Synthesis and properties of poly (glycidyl methacrylate-co-N-vinyl-2-pyrrolidone-co-ethylene dimethacrylate) membranes. 149
82. Hahn R, Podgornik A, Merhar M, Schallaun E, Jungbauer AJAc. 2001. Affinity monoliths generated by in situ polymerization of the ligand. 73:5126-32
83. Yu C, Xu M, Svec F, Fréchet JMJJoPSPAPC. 2002. Preparation of monolithic polymers with controlled porous properties for microfluidic chip applications using photoinitiated free-radical polymerization. 40:755-69
84. Nordborg A, Svec F, Fréchet JM, Irgum KJJoss. 2005. Extending the array of crosslinkers suitable for the preparation of polymethacrylate-based monoliths. 28:2401-6
85. Hemström P, Nordborg A, Irgum K, Svec F, Fréchet JMJJoss. 2006. Polymer-based monolithic microcolumns for hydrophobic interaction chromatography of proteins. 29:25-32
86. Courtois J, Szumski M, Georgsson F, Irgum KJAc. 2007. Assessing the macroporous structure of monolithic columns by transmission electron microscopy. 79:335-44
87. Gu B, Armenta JM, Lee MLJJoCA. 2005. Preparation and evaluation of poly (polyethylene glycol methyl ether acrylate-co-polyethylene glycol diacrylate) monolith for protein analysis. 1079:382-91
88. Viklund C, Svec F, Frechet JM, Irgum KJCom. 1996. Monolithic,“molded”, porous materials with high flow characteristics for separations, catalysis, or solid-phase chemistry: control of porous properties during polymerization. 8:744-50
89. Steinke J, Dunkin I, Sherrington DJM. 1996. Transparent macroporous polymer monoliths. 29:5826-34
90. Svec FJJoss. 2004. Preparation and HPLC applications of rigid macroporous organic polymer monoliths. 27:747-66

91. Bakry R, Bonn GK, Mair D, Svec FJAc. 2007. Monolithic porous polymer layer for the separation of peptides and proteins using thin-layer chromatography coupled with MALDI-TOF-MS. 79:486-93
92. Safrany A, Beiler B, László K, Svec FJP. 2005. Control of pore formation in macroporous polymers synthesized by single-step γ-radiation-initiated polymerization and cross-linking. 46:2862-71
93. Matyjaszewski K, Xia JJCr. 2001. Atom transfer radical polymerization. 101:2921-90
94. Canamero PF, de la Fuente JL, Madruga EL, Fernández-García MJMC, Physics. 2004. Atom transfer radical polymerization of glycidyl methacrylate: a functional monomer. 205:2221-8
95. Yin H, Zheng H, Lu L, Liu P, Cai YJJoPSPAPC. 2007. Highly efficient and well-controlled ambient temperature RAFT polymerization of glycidyl methacrylate under visible light radiation. 45:5091-102
96. Sha K, Li D, Li Y, Liu X, Wang S,. 2007. Synthesis, characterization, and micellization of an epoxy-based amphiphilic diblock copolymer of ϵ-caprolactone and glycidyl methacrylate by enzymatic ring-opening polymerization and atom transfer radical polymerization. 45:5037-49
97. Hayek A, Xu Y, Okada T, Barlow S, Zhu X. 2008. Poly (glycidyl methacrylate) s with controlled molecular weights as low-shrinkage resins for 3D multibeam interference lithography. 18:3316-8
98. Yang Q, Balverde S, Dumur F, Lalevée J, Poly JJPC. 2016. Synergetic effect of the epoxide functional groups in the photocatalyzed atom transfer radical copolymerization of glycidyl methacrylate. 7:6084-93
99. Gao H, Elsabahy M, Giger EV, Li D, Prud’homme RE, Leroux J-CJB. 2010. Aminated linear and star-shape poly (glycerol methacrylate) s: synthesis and self-assembling properties. 11:889-95
100. Edmondson S, Huck WTJJoMC. 2004. Controlled growth and subsequent chemical modification of poly (glycidyl methacrylate) brushes on silicon wafers. 14:730-4
101. Stuparu MC, Khan A. 2016. Thiol-epoxy “click” chemistry: Application in preparation and postpolymerization modification of polymers Part A Polymer chemistry.
102. Brändle A, Khan AJPC. 2012. Thiol–epoxy ‘click’polymerization: efficient construction of reactive and functional polymers. 3:3224-7

103. Tsarevsky NV, Bencherif SA, Matyjaszewski KJM. 2007. Graft copolymers by a combination of ATRP and two different consecutive click reactions. 40:4439-45
104. Tsyalkovsky V, Klep V, Ramaratnam K, Lupitskyy R, Minko S, Luzinov IJCoM. 2008. Fluorescent reactive core–shell composite nanoparticles with a high surface concentration of epoxy functionalities. 20:317-25
105. Chang S-C, Chiu S-J, Hsu C-Y, Chang Y, Liu Y-LJP. 2012. White-light fluorescent nanoparticles from self-assembly of rhodamine B-anchored amphiphilic poly (poly (ethylene glycol) methacrylate)-b-poly (glycidyl methacrylate) block copolymer. 53:4399-406
106. Chuo TW, Wei TC, Liu YLJJoPSPAPC. 2013. Electrically driven self-healing polymers based on reversible guest–host complexation of β-cyclodextrin and ferrocene. 51:3395-403
107. Gudipati CS, Tan MB, Hussain H, Liu Y, He C, Davis TPJMrc. 2008. Synthesis of Poly (glycidyl methacrylate)-block-Poly (pentafluorostyrene) by RAFT: Precursor to Novel Amphiphilic Poly (glyceryl methacrylate)-block-Poly (pentafluorostyrene). 29:1902-7
108. Gu W, Ma Y, Zhu C, Chen B, Ma J, Gao HJEjops. 2012. Synthesis of cross-linked carboxyl poly (glycerol methacrylate) and its application for the controlled release of doxorubicin. 47:556-63
109. Cuatrecasas P, Wilchek M, Anfinsen CBJPotNAoSotUSoA. 1968. Selective enzyme purification by affinity chromatography. 61:636
110. Harwood L. 1989. CJ Moody in Experimental Organic Chemistry. Blackwell Scientific Publ., Oxford
111. Karlsson E, Rydén L, Brewer J. 1998. Ion exchange chromatography. In *Protein purification*:145-205: Wiley-VCH, New York. Number of 145-205 pp.
112. Biosciences AJBS. 2002. Ion Exchange chromatohgraphy, Principles and methods, Amercham Pharmacia. 751
113. Majors REJLGM-NA-SfSS. 2006. Developments in HPLC column packing design. 29:8-15
114. Haddad PR, Nesterenko PN, Buchberger WJJoCA. 2008. Recent developments and emerging directions in ion chromatography. 1184:456-73
115. Nordborg A, Hilder EFJA, chemistry b. 2009. Recent advances in polymer monoliths for ion-exchange chromatography. 394:71-84
116. Paull B, Nesterenko PNJA. 2005. Novel ion chromatographic stationary phases for the analysis of complex matrices. 130:134-46

117. Tian K, Dasgupta PK, Anderson TAJAC. 2003. Determination of trace perchlorate in high-salinity water samples by ion chromatography with on-line preconcentration and preelution. 75:701-6
118. Hutchinson JP, Hilder EF, Shellie RA, Smith JA, Haddad PRJA. 2006. Towards high capacity latex-coated porous polymer monoliths as ion-exchange stationary phases. 131:215-21
119. Zakaria P, Hutchinson JP, Avdalovic N, Liu Y, Haddad PRJAc. 2005. Latex-coated polymeric monolithic ion-exchange stationary phases. 2. Micro-ion chromatography. 77:417-23
120. Pelzbauer Z, Lukáš J, Švec F, Kálal JJJoCA. 1979. Reactive polymers: XXV. Morphology of polymeric sorbents based on glycidyl methacrylate copolymers. 171:101-7
121. Rais S, Islam A, Ahmad I, Kumar S, Chauhan A, Javed HJFC. 2021. Preparation of a new magnetic ion-imprinted polymer and optimization using Box-Behnken design for selective removal and determination of Cu (II) in food and wastewater samples. 334:127563
122. Vareda JP, Valente AJ, Durães LJJoem. 2019. Assessment of heavy metal pollution from anthropogenic activities and remediation strategies: A review. 246:101-18
123. He J, Yang Y, Christakos G, Liu Y, Yang XJG. 2019. Assessment of soil heavy metal pollution using stochastic site indicators. 337:359-67
124. Kumar A, Ramanathan A, Prasad M, Datta D, Kumar M. 2016. Distribution, enrichment, and potential toxicity of trace metals in the surface sediments of Sundarban mangrove ecosystem, Bangladesh: a baseline study before Sundarban oil spill of December, 2014. 23:8985-99
125. Christensen JMJSotte. 1995. Human exposure to toxic metals: factors influencing interpretation of biomonitoring results. 166:89-135
126. Arredondo M, Núñez MTJMaom. 2005. Iron and copper metabolism. 26:313-27
127. Aksu Z, Dönmez GJJoES, Health PA. 2001. Comparison of copper (II) biosorptive properties of live and treated Candida sp. 36:367-81
128. Chen J, Xiao S, Wu X, Fang K, Liu WJT. 2005. Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction. 67:992-6
129. Comitre ALD, Reis BFJT. 2005. Automatic flow procedure based on multicommutation exploiting liquid–liquid extraction for spectrophotometric lead determination in plant material. 65:846-52

130. Di Nezio MaS, Palomeque ME, Band BSFJT. 2004. A sensitive spectrophotometric method for lead determination by flow injection analysis with on-line preconcentration. 63:405-9
131. Grabow WJWS. 1996. Waterborne diseases: Update on water quality assessment and control. 22:193-202
132. Harasim P, Filipek TJJoE. 2015. Nickel in the environment. 20
133. Shahzad B, Tanveer M, Rehman A, Cheema SA, Fahad S, et al. 2018. Nickel; whether toxic or essential for plants and environment-A review. 132:641-51
134. Huš S, Kolar M, Krajnc PJJoCA. 2016. Separation of heavy metals from water by functionalized glycidyl methacrylate poly (high internal phase emulsions). 1437:168-75
135. Liu D, Pan J, Tang J, Lian NJRa. 2018. Preparation of polymethacrylate monolith modified with cysteine for the determination of Cr (iii) ions. 8:24906-12
136. Svec F, Frechet JMJJoCA. 1995. Modified poly (glycidyl metharylate-co-ethylene dimethacrylate) continuous rod columns for preparative-scale ion-exchange chromatography of proteins. 702:89-95
137. Viklund C, Svec F, Frechet JM, Irgum KJBp. 1997. Fast Ion-Exchange HPLC of Proteins Using Porous Poly (glycidyl methacrylate-co-ethylene dimethacrylate) Monoliths Grafted with Poly (2-acrylamido-2-methyl-1-propanesulfonic acid). 13:597-600
138. Kramberger P, Petrovič N, Štrancar A, Ravnikar MJJovm. 2004. Concentration of plant viruses using monolithic chromatographic supports. 120:51-7
139. Bisjak C, Bakry R, Huck CW, Bonn GJC. 2005. Amino-functionalized monolithic poly (glycidyl methacrylate-co-divinylbenzene) ion-exchange stationary phases for the separation of oligonucleotides. 62:s31-s6
140. Wieder W, Bisjak CP, Huck CW, Bakry R, Bonn GKJJoss. 2006. Monolithic poly (glycidyl methacrylate-co-divinylbenzene) capillary columns functionalized to strong anion exchangers for nucleotide and oligonucleotide separation. 29:2478-84
141. Hanora A, Savina I, Plieva FM, Izumrudov VA, Mattiasson B, Galaev IYJJob. 2006. Direct capture of plasmid DNA from non-clarified bacterial lysate using polycation-grafted monoliths. 123:343-55
142. Bobalova J, Chmelik JJJoCa. 2007. Proteomic identification of technologically modified proteins in malt by combination of protein fractionation using convective interaction media and matrix-assisted

laser desorption/ionization time-of-flight mass spectrometry. 1163:80-5
143. Petrič TČ, Brne P, Gabor B, Govednik L, Barut M. 2007. Anion-exchange chromatography using short monolithic columns as a complementary technique for human serum albumin depletion prior to human plasma proteome analysis. 43:243-9
144. Brne P, Podgornik A, Benčina K, Gabor B, Štrancar A, Peterka MJJoCA. 2007. Fast and efficient separation of immunoglobulin M from immunoglobulin G using short monolithic columns. 1144:120-5
145. Danquah MK, Ho J, Forde GMJJoss. 2007. Performance of R-N (R′)-R″ functionalised poly (glycidyl methacrylate-co-ethylene glycol dimethacrylate) monolithic sorbent for plasmid DNA adsorption. 30:2843-50
146. Danquah MK, Forde GMJJoCT, Biotechnology: International Research in Process E, Technology C. 2007. Towards the design of a scalable and commercially viable technique for plasmid purification using a methacrylate monolithic stationary phase. 82:752-7
147. Eder K, Huber CG, Buchmeiser MRJMrc. 2007. Surface-Functionalized, Ring-Opening Metathesis Polymerization-Derived Monoliths for Anion-Exchange Chromatography. 28:2029-32
148. Ma J, Dai Q, Li X, Zhu X, Ma T, et al. 2017. Dipentaerythritol penta-/hexa-acrylate based-highly cross-linked hybrid monolithic column: Preparation and its applications for ultrahigh efficiency separation of proteins. 963:143-52
149. Smrekar F, Ciringer M, Peterka M, Podgornik A, Štrancar AJJoCB. 2008. Purification and concentration of bacteriophage T4 using monolithic chromatographic supports. 861:177-80
150. Shrestha P, Oh T-J, Liou K, Sohng JKJAm, biotechnology. 2008. Cytochrome P450 (CYP105F2) from Streptomyces peucetius and its activity with oleandomycin. 79:555-62
151. Evenhuis CJ, Buchberger W, Hilder EF, Flook KJ, Pohl CA 2008. Separation of inorganic anions on a high capacity porous polymeric monolithic column and application to direct determination of anions in seawater. 31:2598-604
152. Frankovič V, Podgornik A, Krajnc NL, Smrekar F, Krajnc P, Štrancar AJJoCA. 2008. Characterisation of grafted weak anion-exchange methacrylate monoliths. 1207:84-93

153. Chen X, Tolley HD, Lee MLJJoss. 2009. Polymeric strong cation-exchange monolithic column for capillary liquid chromatography of peptides and proteins. 32:2565-73
154. Bruchet A, Dugas V, Mariet C, Goutelard F, Randon JJJoss. 2011. Improved chromatographic performances of glycidyl methacrylate anion-exchange monolith for fast nano-ion exchange chromatography. 34:2079-87
155. Chen X, Tolley HD, Lee MLJJoss. 2011. Weak cation-exchange monolithic column for capillary liquid chromatography of peptides and proteins. 34:2063-71
156. Sabarudin A, Huang J, Shu S, Sakagawa S, Umemura TJAca. 2012. Preparation of methacrylate-based anion-exchange monolithic microbore column for chromatographic separation of DNA fragments and oligonucleotides. 736:108-14
157. Liu J, Ren L, Liu Y, Li H, Liu ZJJoCA. 2012. Weak anion exchange chromatographic profiling of glycoprotein isoforms on a polymer monolithic capillary. 1228:276-82
158. Talebi M, Arrua RD, Gaspar A, Lacher NA, Wang Q. 2013. Epoxy-based monoliths for capillary liquid chromatography of small and large molecules. 405:2233-44
159. Bibi NS, Fernández-Lahore MJBP. 2013. Grafted megaporous materials as ion-exchangers for bioproduct adsorption. 29:386-93
160. Singh NK, Dsouza RN, Grasselli M, Fernández-Lahore MJJoCA. 2014. High capacity cryogel-type adsorbents for protein purification. 1355:143-8
161. Perçin I, Khalaf R, Brand B, Morbidelli M, Gezici OJJoCA. 2015. Strong cation-exchange chromatography of proteins on a sulfoalkylated monolithic cryogel. 1386:13-21
162. Vonk RJ, Wouters S, Barcaru A, Vivó-Truyols G, Eeltink S. 2015. Post-polymerization photografting on methacrylate-based monoliths for separation of intact proteins and protein digests with comprehensive two-dimensional liquid chromatography hyphenated with high-resolution mass spectrometry. 407:3817-29
163. Gu H, Yin D, Ren J, Zhang B, Zhang QJJoCB. 2016. Preparation of quaternary amine monolithic column for strong anion-exchange chromatography and its application to the separation of Enterovirus 71. 1033:399-405
164. Du K, Zhang Q, Dan S, Yang M, Zhang Y, Chai DJJoCA. 2016. Fabrication and characterization of aligned macroporous monolith for high-performance protein chromatography. 1443:111-7

165. Ren J, Beckner MA, Lynch KB, Chen H, Zhu Z. 2018. Two-dimensional liquid chromatography consisting of twelve second-dimension columns for comprehensive analysis of intact proteins. 182:225-9
166. Liu D, Zhang T, Cheng Y, Jia QJJoss. 2014. Poly (glycidyl methacrylate-co-N-methylolacrylamide-co-ethylene dimethacrylate) monolith coupled to high-performance liquid chromatography for the determination of adenosine phosphates in royal jelly. 37:1826-33
167. Peterson DS, Rohr T, Svec F, Fréchet JMJAC. 2003. Dual-function microanalytical device by in situ photolithographic grafting of porous polymer monolith: integrating solid-phase extraction and enzymatic digestion for peptide mass mapping. 75:5328-35
168. Huo Y, Schoenmakers PJ, Kok WTJJoCA. 2007. Efficiency of methacrylate monolithic columns in reversed-phase liquid chromatographic separations. 1175:81-8
169. Armenta JM, Gu B, Thulin CD, Lee MLJJoCA. 2007. Coupled affinity-hydrophobic monolithic column for on-line removal of immunoglobulin G, preconcentration of low abundance proteins and separation by capillary zone electrophoresis. 1148:115-22
170. Unger KK, Skudas R, Schulte MMJJoCA. 2008. Particle packed columns and monolithic columns in high-performance liquid chromatography-comparison and critical appraisal. 1184:393-415
171. Hebb AK, Senoo K, Bhat R, Cooper AIJCom. 2003. Structural control in porous cross-linked poly (methacrylate) monoliths using supercritical carbon dioxide as a “pressure-adjustable” porogenic solvent. 15:2061-9
172. Safa KD, Nasirtabrizi MHJPB. 2006. Ring opening reactions of glycidyl methacrylate copolymers to introduce bulky organosilicon side chain substituents. 57:293-304
173. Samanta S, Chatterjee DP, Layek RK, Nandi AKJJoMC. 2012. Nano-structured poly (3-hexyl thiophene) grafted on poly (vinylidene fluoride) via poly (glycidyl methacrylate). 22:10542-51
174. Labbé A, Brocas A-L, Ibarboure E, Ishizone T, Hirao A. 2011. Selective ring-opening polymerization of glycidyl methacrylate: toward the synthesis of cross-linked (co) polyethers with thermoresponsive properties. 44:6356-64
175. Wang J, Lü H, Lin X, Xie ZJE. 2008. Monolithic column with double mixed-modes of hydrophilic interaction/cation-exchange and reverse-phase/cation-exchange stationary phase for pressurized capillary electrochromatography. 29:928-35

176. Rahmi D, Takasaki Y, Zhu Y, Kobayashi H, Konagaya S. 2010. Preparation of monolithic chelating adsorbent inside a syringe filter tip for solid phase microextraction of trace elements in natural water prior to their determination by ICP-MS. 81:1438-45
177. Courtois J, Szumski M, Byström E, Iwasiewicz A, Shchukarev A, Irgum KJJoss. 2006. A study of surface modification and anchoring techniques used in the preparation of monolithic microcolumns in fused silica capillaries. 29:14-24
178. Nischang I, Brueggemann O, Svec FJA, chemistry b. 2010. Advances in the preparation of porous polymer monoliths in capillaries and microfluidic chips with focus on morphological aspects. 397:953-60
179. Sun J, Akdogan EK, Klein LC, Safari AJJon-cs. 2007. Characterization and optical properties of sol–gel processed PMMA/SiO2 hybrid monoliths. 353:2807-12