Original Article

Preparation and Application of (GMA-co-ACA co-AAM) as Cation-Exchange Monolithic Column for determination Nickel (II) ion

Salam M. Nasser[1,2], **Ahmeed A. Alkarimi**[1], **Dakhil N. Taha**[3]

[1]Department of Chemistry, College of Science, University of Babylon, Babel, Iraq
[2]Al-Mustaqbal University College, Babylon, Iraq
[3]Department of Chemistry, College of Science for Women, University of Babylon, Babel, Iraq

ABSTRACT

Ion exchange chromatography was created using a polymer-based monolithic column as a strong cation-exchange column with various function groups. Acrylic acid (A. acid), glycidyl methacrylate (GMA), and acryl amid were used to make monolithic columns via free radical polymerization (A. amid). The epoxy rings were then sulfonated at 70°C using Na_2SO_3. A model of common cation of Ni(II) spectrophotometry was used to assess the monolithic column, which was compared to atomic absorption approach. The LOD and LOQ were 0.001 g/mL and 0.002 g/mL, respectively, while the linearity (R2) was 0.9980. FTIR, Brunauer-Emmett-Teller (BET) analysis, and scanning electron microscopy were used to analyze the cation-exchange columns (SEM).

Keywords: GMA, Monolith, Ion exchange column, Nickel (II) .

INTRODUCTION

Nickel is a metallic element that occurs naturally in the earth's crust. In addition to being present in soil, nickel compounds exist in a variety of soluble and insoluble forms, including sulphides and silicates.[1] Significant quantities of nickel in various forms may be accumulated in the human body over the course of a lifetime due to occupational exposure and diet.[2] Therefore, it is not an essential trace element for humans. Its components are generally regarded as safe for consumption at levels found in foods and beverages, but those who have a contact allergy to nickel and are at risk of developing systemic responses through ingestion must limit their dietary exposure to nickel.[3] Increasingly, chemical precipitation, ion exchange, and functionalized polymers have been utilized to remove heavy metals from wastewater.[4,5]

In 1993, the name "monolith" was first applied to a single piece of functional cellulose sponge used to separate proteins.[6] Similarly, the term "monolithic" was coined to represent huge, porous polymers produced by bulk polymerization in a closed mold, and it became a standard very rapidly.[7] Microfluidics,[8] gas chromatography (GC),[9] catalysis[10] and supported organic processes (11) are among the several applications for monolith.[12] As a result of research in the late 1950s, large molecular polymers were developed for the fabrication of ion exchange resins with enhanced resistance to osmotic shocks and faster kinetics.[13,14] The individuals that found glycidyl methacrylate (GMA) polymers,[15] another form of reactive resins that has gained a great deal of interest, were the ones who discovered these polymers. The presence of epoxy groups permits a variety of changes. In numerous ways, the cross-linked GMA polymers have been changed. In addition to chromatographic separation media, ion exchange

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Address for correspondence: Ahmeed A. Alkarimi,
Al-Mustaqbal University College, Babylon, Iraq
E-mail address: sci.ahmed.alkarimi@gmail.com

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resins, catalyst supports, and enzyme immobilization, derivatized polymers have been used in chromatographic separation media, ion exchange resins, and catalyst supports.[16] In chiral chromatography, cross-linked polymers based on glycidyl methacrylate and hydroxyethyl methacrylate have been used efficiently as support materials.[17-19] There are numerous applications for polymeric monoliths, with this being only one. Ion exchange-based chromatography (17,20). Ion-exchange chromatography is one of the most prevalent techniques for purifying and separating charged biomolecule-containing materials.[21] This work describes how to fabricate monolithic columns that may be used to extract nickel ions from aqueous solutions and are imprinted with nickel ions.

EXPERIMENTAL

Apparatus

Infusion pump with dual syringes (kd Scientific Holliston,MAU.S.A.), Jasco pu-980 intelligent HPLC pump (Denver Instruments Germany TP-214 Analytical Balance), Nitrogen gas tank, (Irradiation device locally manufactured for high pressure mercury lamp with 220V-50Hz at 365 nm), (UV-Visible spectrophotometer, double-beam Shimadzu (UV-1700), Japan) (Sonicator ultra sonic bath India).

Reagents

Glycidyl methacrylate(GMA98%), Acrylic acid ,acryl amid) Sigma-Aldrich Germany (and ethylene dimethacrylate (EDMA) as cross linker were used .Organic solvents (hexanol and ethanol)(BDH)and 2, 2-Dimethoxy-2-phenylacetophenone,(DAP99%))Sigma-Aldrich Germany (as an initiator, 1% based on the weight of the co –monomers and $Ni(NO_3)_2$ (99% ,BDH).

Fabrication of the Monolithic Materials

The monolith (GMA-co-ACA co-AAM) prepared inside borosilicate tube (6 x 0.15i.d x 0.3o.d) cm. Stainless steel union adapters were utilized to connect the polyether ether ketone (PEEK) to borosilicate. The PEEK tubing was connect to the glass syringe by microtight adapter. All solutions were injected using a syringe pump inside the borosilicate tube for polymerization process.

Preparation of Cation –Exchange Monolithic Column.

First, the inner wall of the borosilicate tube was silanized to ensure that the monolith would not push out the column when a high flow rate was applied (40). The monolith (GMA-co-ACA-co-AAM) was formed with (0.5 mL of GMA, 0.3 mL of ACA, and 0.4 mL of AAM, 0.06 mL of EDMA as a cross-linking agent, and 2, 2-Dimethoxy-2-phenylacetophenone as an initiator. All of these substances were dissolved in a porogenic solvent (1000 l ethanol and 650 l hexanol). Then, 5 minutes of N_2 purging to eliminate oxygen. Immediately after pumping the monomer solution into the borosilicate tube, the two ends of the tube were sealed using a stopper robber. The UV polymerization at 365 nm was let to continue for 3 minutes. Absolute ethanol and water were utilized to cleanse the monolith of any unreacted compounds after polymer synthesis.

Fabrication of the Monolith to form Strong Cation Exchanger

Epoxy groups on the surface of (GMA-co-ACA-co-AAM) monolithic columns interacted with a Na_2SO_3 solution to create $–SO_3Na$ groups (26). At 60-75°C, Na_2SO_3 (10 ppm) was pumped (30 l/min) over the monolithic column. The cation-exchange column was activated by pumping 0.2 M HCl and then rinsed for at least 2 hours with copious amounts of water.

Estimation of Cation-Exchange Capacity

Compared to the atomic absorption approach, the colorimetric method was employed to measure cation-exchange capacity. However, 100 ppm and 5 ppm of $Ni(NO_3)_2$ were pumped over a monolithic (GMA-co-ACA-co-AAM) column, the eluted solution was collected, and the capacity was determined to be 518 nm (41).

RESULTS AND DISCUSSIONS

Permeability

We were able to determine the permeability of the column by measuring the backpressure that was produced by pumping different flow rates with an HPLC pump. It was discovered that the pressure decreased from 55.103 psi to 150.923 psi at a normal flow rate of 50 microliters per minute (with varied flow rates ranging from 0.02-1.5 milliliters per minute). As can be seen in Table (1) and Figure 1, the predicted value for the monolithic column's net pressure is around 150.923 psi while operating at a flow rate of 1.5 mL/min (2).

Table 1: The Permeability of the (GMA-co-ACA co-AAM) monolith column

No.	*Flow rate (ml/min)*	*Pressure (Psi)*
1	0.02	55.103
2	0.03	57.289
3	0.05	60.124
4	0.08	62.445
5	0.1	64.599
6	0.3	76.179
7	0.5	87.245
8	0.6	93.779
9	0.8	105.489
10	1	117.734
11	1.3	134.281
12	1.5	150.923

Study the effects of irradiation time on (GMA-Co-ACA-Co-AAM) monolith column formation .

Figure (2) demonstrates that an irradiation duration of four minutes is required to create the surface area and pore size of a (GMA-co-ACA-co-AAM) monolith column. Due to the limited transmission of incident UV light close to the surface, a (5 min) of the monolith column leads to a high surface. The irradiation period ranged between 0.5 and 5 minutes. Irradiation times below 0.5 minutes were not used because they were insufficient for polymerization of monolithic beds, while irradiation times between 0.5 and 5 minutes did not increase surface photografting of monolith column. For the monolith synthesis, a photo polymerization time of 4 minutes was utilized.

SEM Analysis of Glycidyl Methacrylate -co -Acrylic acid- co- acryl Amid Monolith Column.

Using scanning electron microscopy, the morphology of the monolithic (GMA-co-ACA-co-AAM) column was studied. The photos of a (GMA-co-ACA-co-AAM) monolith column are depicted in Figure 3. The monolith can be considered as an interconnected network of channels with high flow via pores. The advantages of these pores are that they boost the monolith's loading capacity and surface area.

Brunauer-Emmett-Teller (BET) Analysis for the (GMA-co-ACA- co-AAM) Monolith Column.

For a well-produced monolith, the nitrogen gas adsorption/desorption isotherm was studied to determine the average pore size and significant surface area. Surface area was found to be 29,725 m^2/g and pore size to be 13,5013 nm on average. In order to manage surface area and pore size, these data could be utilized to identify the ideal preparation conditions for an instantaneous porogenic solvent.

(FT-IR) spectroscopy for ring opening reaction and formation of cationic exchange (GMA-co-ACA-co-AAM) monolith column.

The FT-IR spectra of the monolithic (GMA-co-ACA-co-AAM) column are displayed in (Fig. 4). The primary peaks for the (C=O) group can be detected at 1720.90 cm^{-1}, with a small

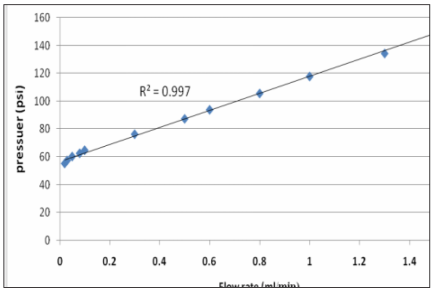

Fig. 1: The Permeability of the (GMA-co-ACA co-AAM) monolith column.

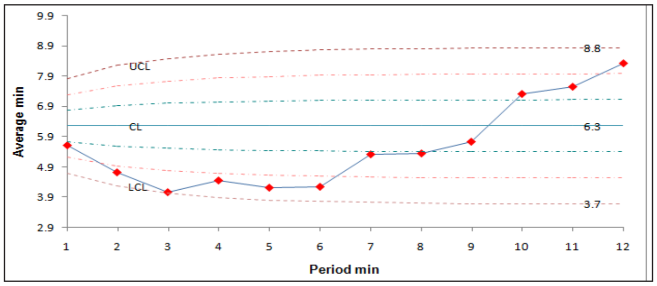

Fig. 2: Effect of increasing irradiation time on the monolith column.

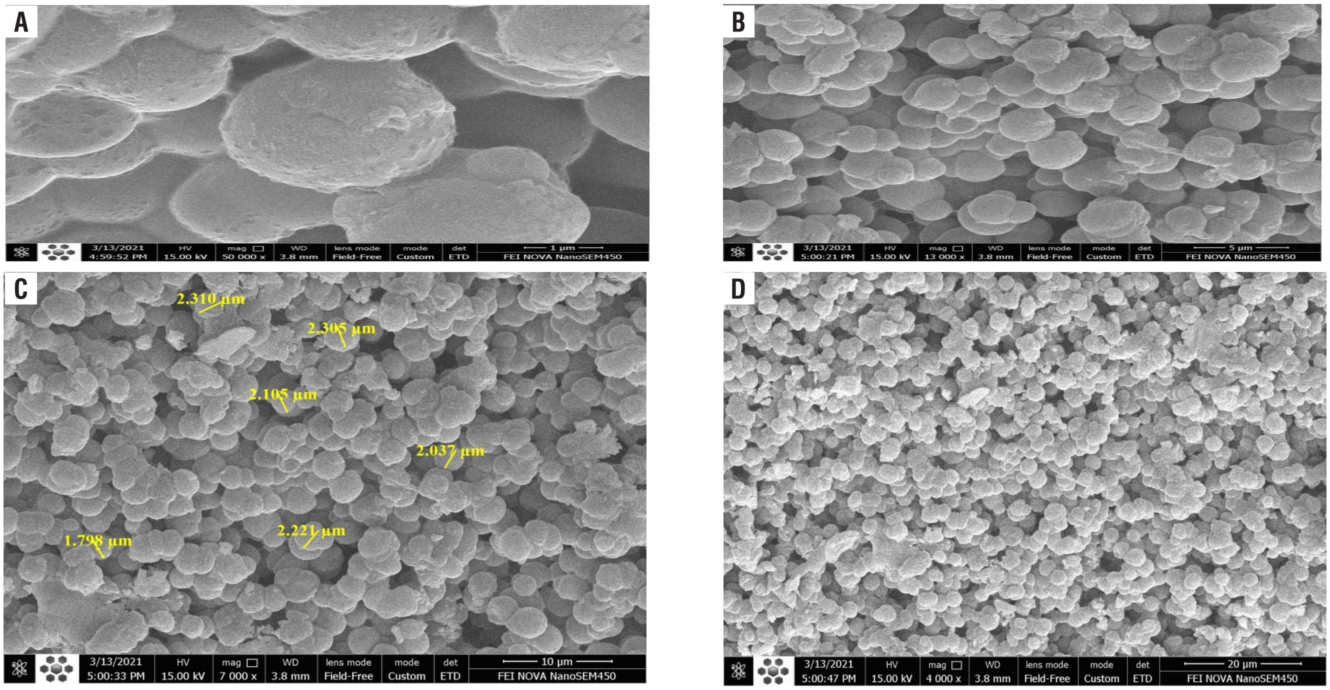

Fig. 3: Scanning electron micrographs of monoliths((A) 1 μm ,(B) 5 μm,(C) 10 μm,(D) 20 μm) at magnification.

shift in the epoxy group to 906.14 cm^{-1}, while the (C=C) peak disappeared and a cationic exchange monolithic column formed at 1637 cm^{-1}.

Strong cation exchange monolithic column was demonstrated by changing the epoxy groups to SO_3Na and OH groups as shown in Fig (5). It is clearly seen that the peak at 906.14 cm^{-1} for epoxy groups were vanished, and two new peaks clearly formed, at 951.62 cm^{-1}, and 1016.06 cm^{-1} and for S-O and R-SO3 groups. In addition, a medium N-H stretching of secondary amine at 3342.49 -3199.65 cm^{-1} was observed, the peaks at 1721.60 cm^{-1}back to C=O, while at 1160.89 cm^{-1} back to C-O ester groups, these peaks are unchanged due to non-subscribe of these groups in sulfonation process.[42,43]

The Measurement of Total Porosity for the GMA-co-ACA-co-AAM Monolith.

The total porosity $\boldsymbol{\Phi_T}$ of the monolith can be calculated using equation

$$\boldsymbol{\Phi_T = W_M - W_T / \ dLR^2\pi}$$

$\mathbf{W_M}$ and $\mathbf{W_T}$ are the weights of water filled monolith and dry filled monolith. **L** is the length of the column, while, **d** is the density of water. **R** is the radius of the cylindrical monolith.[44,45]

After three times measurements and the average has taken, it was found that the total porosity of the monolith is 0.8127.

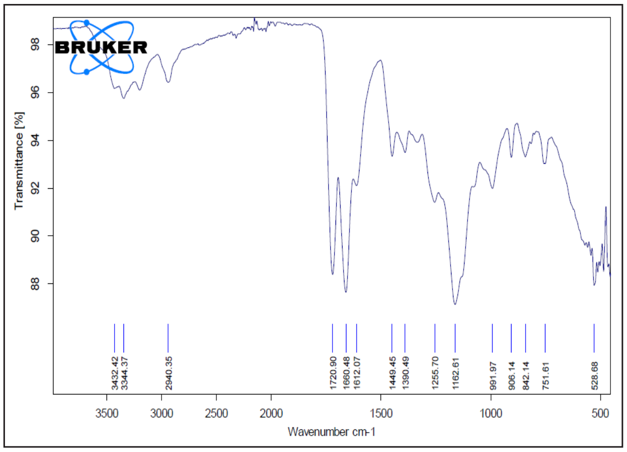

Fig. 4: FT-IR spectrum of GMA-co-ACA-co-AAM monolithic column

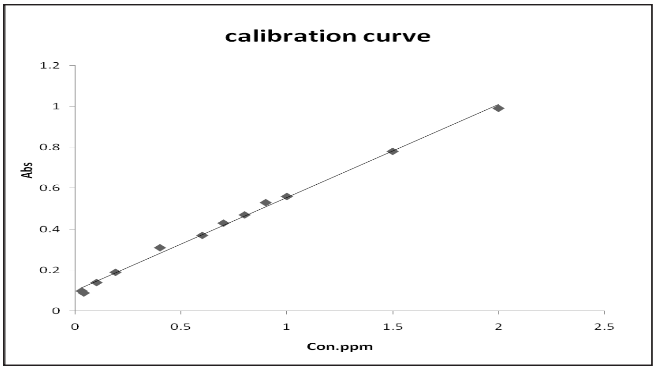

Fig.6: Calibration curve for Ni^{+2}

Incorporation of Ni^{2+} ion with the GMA-co-ACA-co-AAM Monolith Column.

The investigation of copper ion was carried out for the prepared monolith. Firstly, it was washed with 2.5 mL distill water, after that 2.5 mL Ni (II) as($Ni(NO_3)_2$.Two solutions 5 mg/L and 10 mg/L was pumped separately through the monolith column for 2 hrs. at room temperature, then, 2.5 mL pumped into monolithic column with distilled water to be washed again and then the column was activated with hydrochloric acid (0.2 M). The Ni^{2+} ions concentration in the eluent were calculated spectrophotometrically, using a specialize reagent (MPDADPI) for the nikel ion (Ni^{+2}).The obtained results were compatible with that obtained by atomic absorption as the concentration result was (3.066 ppm) and (6.55 ppm) respectively. After the Ni^{2+} ion concentration was determined (eluent) by using atomic absorption spectroscopy for comparison.

The Calibration Curve for Ni^{+2}

To examine the calibration curve, a series of nickel concentrations were constructed using the optimal parameters. The calibration curve reveals that the unknown concentration of the standard sample (5.5 ppm) fed through the monolith is equivalent to 5.48 ppm, as shown in Fig (6).

A stander method was applied to determine concentration of copper ion **Ni^{+2}** in two samples and the result is show in Table 2.

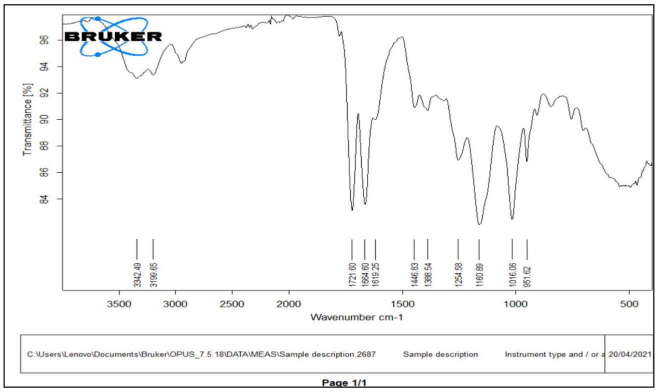

Fig. 5: FT-IR spectrum of the GMA-co-ACA-co-AAM monolith after ring opening

Table 2: Parameter of the calibration curve

Parameter	*Value*
Accuracy	99.825 ± 5.9511
Regression Equation	y = 0.455x + 0.099
Slope	0.4550
Y-intercept	0.0990
Linearity Range	0.003—2 µg/mL
Correlation Coefficient	0.9980
SE Intercept	0.0032
SD Intercept	0.0096
LOD	0.001 µg/mL
LOQ	0.002µg/mL
Average SD	0.0001
Average RSD%	0.2583

CONCLUSIONS

The Ter-polymeric monolithic column (GMA-co-ACA-co-AAM) is a novel preparation according to the Sci-finder certificate and was created as a white block after 4 minutes of irradiation. Using a sulfonation reaction, the epoxy rings in the monolithic column were transformed to the (-SO$_3$Na) group. According to the FT-IR data, the peak at 906.14cm^{-1} for the epoxy groups in the produced monolithic column has disappeared, and two new peaks at 1016.06 cm-1 and 951.62 cm^{-1} correspond to the R-SO$_3$ and S-O groups. A medium N-H stretching secondary amine was discovered at 3342.49 -3199.65 cm^{-1}, and the epoxy ring was broken. The findings of the BET study indicated that the monolithic column had a low average surface area of 29.725 m^2/g and an average pore size of 13.5013nm. The research of nickel ion to determine (eluent) for the GMA-co-ACA-co-AAM monolith column by spectrophotometric analysis gave results that were in good agreement with those obtained by atomic absorption, which were used as a comparison.

Ethical Clearance

The Research Ethical Committee at scientific research by ethical approval of both MOH and MOHSER in Iraq

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