Paper 5

Submission date: 17-Jun-2022 03:26PM (UTC-0500)
Submission ID: 1858692255
File name: 4_Characterization_of_Organic_polymer....pdf (6.39M)
Word count: 4003
Character count: 22831

CHARACTERIZATION OF ORGANIC POLYMER MONOLITH COLUMNS CONTAINING AMMONIUM QUARTERNARY AS INITIAL STUDY FOR CAPILLARY CHROMATOGRAPHY

Aster Rahayu[*], Siti Jamilatun[*], Joni Aldilla Fajri[**], Lee Wah Lim[***]
[*]*Departement of Chemical Engineering, Universitas Ahmad Dahlan, Yogyakarta, Indonesia, aster.rahayu@che.uac.ac.id, sitijamilatun@che.uad.ac.id*
[**]*Departement of Environmental Engineering, Universitas Islam Indonesia, Yogyakarta, Indonesia, joni.af@uii.ac.id*
[***] *Departement of Biomolecular Science, Gifu University, Gifu, Japan, lim@gifu-u.ac.jp*

Email Correspondence : aster.rahayu@che.uad.ac.id

10
Received : January 25, 2021 Accepted : May 12, 2021 Published : June 30, 2021

Abstract: The polymerization process with a simple step has become the centre of attention of several researchers. Various polymers have been developed, although in general, they use polymerization with a post-modification method. A quaternary ammonium monolith organic polymer has been prepared using a simple single thermal method in this research. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride was as the monomer, and ethylene dimethacrylate was as crosslinker. The polymerization proceeded in fused-silica capillary (100 mm, 0.32 mm i.d. x 0.45 mm o.d.) using a one-pot approach method. To achieve the perfect macropores, isopropyl alcohol, PEG 400, and ethanol were used as porogen. Characterization of the surface morphology was carried out using a Scanning Electron Microscope (SEM), and the existence of an amine group was characterized by Fourier Transform Infrared Spectroscopy (FTIR). The distribution size of pores in the polymer was in the range of 1.29 to 3.33 µm.
Keywords: *Monolith, Organic polymer, One-pot approach, Ammonium quarternary, Polymerization, Capillary*

Abstrak: Polimerisasi dengan proses yang sederhana dan simpel menjadi pusat perhatian beberapa peneliti. Berbagai macam polimer telah dikembangkan, akan tetapi pada umumnya menggunakan polimerisasi dengan metode *post-modification*. Pada penelitian ini, polimer organik yang mengandung amonium kuartener dalam bentuk monolit dengan polimerisasi yang menggunakan suhu tunggal dan sederhana telah dilakukan. *2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride* digunakan sebagai monomer dan *ethylene dimethacrylate* sebagai *crosslinker*. Polimerisasi dilakukan dengan metode *one-pot aaproach* di dalam kapiler silika (100 mm, 0,32 mm i.d. x 0,45 mm o.d.). Untuk mendapatkan makropori yang sempurna, isopropil alkohol, PEG 400 dan etanol digunakan sebagai porogen. Karakterisasi morfologi permukaan dilakukan dengan menggunakan *Scanning Electron Microscope* (SEM), dan *Fourier Transform Infrared Spectroscopy* (FTIR) untuk mengidentifikasi gugus fungsi gugus amina yang terdapat pada polimer. Ukuran distribusi pori pada polimer berkisar antara 1,29 sampai 3,33 µm.
Kata kunci: Monolitik, Polimer organik, *One-pot approach*, Amonium kuartener, Polimerisasi, kapiler

Recommended APA Citation :

Rahayu, A., Jamilatun, S., Fajri, J. A., & Lim, L. W. (2021). Characterization of Organic Polymer Monolith Columns Containing Ammonium Quarternary As Initial Study For Capillary Chromatography. *Elkawnie*, *7*(1), 119-130. https://doi.org/10.22373/ekw.v7i1.8764

Introduction

Polymers are large molecules composed of a series of monomers that are interconnected by the presence of crosslinkers. Monolith polymers can be broadly divided into two types, namely organic polymers and inorganic polymers (Rahayu *et al.,* 2015). Inorganic polymers are commonly based on silica and are widely used as a stationary phase. Several kinds of research have been reported in terms of application of inorganic polymers, such as separation and detection of cation levels in drinking water (Rahayu *et al.,* 2015), protein (Zhao *et al.,* 2012), tryptic digests of bovine serum albumin (BSA) (Zhang *et al.,* 2011), levodopa, carbidopa, benserazide, dopamine, and 3-O-methyldopa in plasma samples (Grecco *et al.,* 2020), polar compounds (Yang *et al.,* 2013) and other macromolecular compounds (Iwasaki *et al.,* 2012). However, time-consuming manufacturing and a limited variety of polymer-forming materials were obtained as disadvantages of inorganic polymer (Zhong *et al*., 2010, Lalli *et al*., 2020).

Organic polymers have been developed and applied as a stationary phase for separating compounds or ions in the chromatography system. The existence of pore in the monolith polymer can be served as an adsorbent. Some polymers have been widely used in the adsorption of several heavy metals and organic compounds. The Cr (VI) ion could be adsorbed using a magnetic polymer containing an amine group (Zhao *et al*., 2013, Zhao *et al*., 2010), removal of Pb^{2+}, $Cu^{2+,}$ and Zn^{2+} (Mokadem *et al*., 2020), trace Cd (II) in biological samples (Chen *et al.,* 2020), and removal of Pb(II) from water medium (Naushad *et al.,* 2020). Methacrylate-based polymers with the epoxy ring-opening method have been successfully prepared and applied for separation of organic compounds such as Bisphenol A (BPA) (Zhao *et al*., 2013), Bovine Serum Albumin (BSA) (Shamim *et al.*, 2007), alkylbenzene (Wang *et al.,* 2014), pentachlorophenol (Pan *et al.*, 2014), and enantioseparation (Angga *et al.,* 2019). Furthermore, it is also applied for the adsorption of some ions, such as Cu (II) (Shen *et al*., 2012) and Hg (II) ions (Pan *et al*., 2014, Pan *et al*., 2012). Overall, many of these polymers are applied as the stationary phase in the chromatography system.

Polymerization uses two-stage processes, namely the polymerization stage and the advanced modification stage. This advanced modification stage aims to add the desired active side group according to the intended purpose and application. However, a few organic polymers are synthesized using a one-pot approach method. This method was taking the attention of several researchers due to the simple step of the polymerization process.

The synthesizing of monolithic polymers with quaternary ammonium groups using a straightforward one-pot approach as a stationary phase in capillary system liquid chromatography will be the objective of this research. The monolithic polymers containing quaternary amine groups will be polymerized from 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride (META) and ethylene dimethacrylate (EDMA) with a short, simple and straightforward method, namely one-pot approach. The morphology surface of the polymer will be characterized before applying as the stationary phase in the capillary system liquid chromatography to separate organic compounds.

Material And Methods

Materials

The materials are purchased from a different source. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride (META), Ethylene dimethacrylate (EDMA), Isopropyl alcohol (IPA), ethanol were purchased from Wako 1st Grade, Japan, 2,2'-azobisisobutyronitrile (AIBN) was purchased from Trade TCI Mark, Japan, poly(ethylene oxide) Mn. 400 (PEG 400), 3-(trimethoxysilyl)-propyl methacrylate (γ-MAPS), uracil, toluene, 0.1 M NaOH, 0.1 M HCl were purchased from Nacalai Tesque, Kyoto, Japan, deionized water (water that has a known conductivity and is specifically used for ion chromatography) from GS-590 water distillation system (Advantec, Tokyo, Japan).

Apparatus

The surface morphology of quaternary ammonium organic polymer monoliths was characterized using Scanning Electron Microscope (SEM) S-4800 (Hitachi, Tokyo, Japan) mainly, the size of single unions macropores formed. Furthermore, identifying the functional group in the polymer was carried out using Fourier Transform Infrared (FTIR) Spectrum 400 Series (Perkin Elmer).

The chromatographic system was performed to separate uracil and toluene using a capillary LC system constructed by an L.TEX-8301 Micro Feeder (L.TEX Corporation, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe 0.5 mL(Ito, Fuji, Japan) as a pump, a Model 7520 (Rheodyne, Cotati, CA, USA) injector with an injection volume of 0.2 µL, a 100 mm x 0.32 mm i.d. of microcolumn and a UV-1575 intelligent UV/Vis detector, (JASCO, Tokyo, Japan) that was operated at 254 nm. The data was acquired using a data processor CDS-Lite ver.5.0 (LA soft, Chiba, Japan).

Synthesis of quaternary ammonium organic polymer monoliths

Synthesize of organic polymer monoliths was started with pre-treatment of the inner wall of capillary silica. The capillary column was rinsed with 0.1 M NaOH, 0.1 M water, 0.1 HCL and flowed with acetone into the column flow rate of 2.5 µL/min for 60 minutes sequentially. The column was dried by flowing

nitrogen gas for 30 minutes. 30% (γ-MAPS) in acetone filled into the column, and then both column ends sealed. The anchor inner wall of the capillary column is allowed at 60 °C for 24 hours in the water bath. The capillary column was rinsed with acetone at a flow rate of 2.5 µL/min for 60 minutes and dried with nitrogen gas for 30 minutes.

Initially, the polymerization stage was carried out by preparing a mixture solution according to previous research with major modification (Rahayu *et al.,* 2015); 1.25 mL of META, 0.375 mL of EDMA, 1.75 mL of isopropyl alcohol, 0.35 mL of ethanol, 1.4 mL of PEG 400, and 2 mg 2,2'-azobisisobutyronitrile. The mixture solution was homogenized before filling into the pretreated capillary column. Subsequently, the polymerization was allowed at 60 ˚C for 24 hours in the water bath. The obtained polymer was rinsed with methanol to remove the residual reaction. Monolith polymers were applied in capillary system liquid chromatography for *the* separation of uracil and toluene.

Discussion

Synthesis of polymeric organic monoliths

The organic polymer monolith containing quaternary ammonium was synthesized directly in the capillary column (100 mm, 0.32 mm i.d. x 0.45 mm o.d.) with a single thermal polymerization one-pot approach method. The synthesis was carried out using a monomer containing a quaternary ammonium functional group. Quaternary ammonium groups in monomers act as strong anion exchangers and work well to separate either anion or organic compounds. The scheme of the expected reaction polymerization one-pot approach method is shown in Figure 1. The functional monomer introduced the quaternary ammonium in the organic polymer, which quaternary ammonium is the active group for the anion exchange.

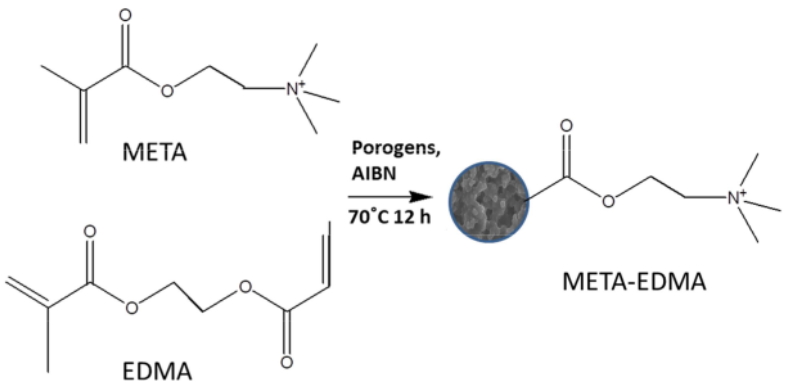


Figure 1. Scheme of the expected reaction of organic polymer

In the polymerization of organic polymer monolith, the ratio between monomer and porogen ratio was 20:80. Meanwhile, 20% was a mixture of monomer and crosslinker, and 80% was porogen. Interm of 20% for monomer and crosslinker, 50% of monomer, and 50% crosslinker were used. Three organic compounds acted as porogen, such as Isopropyl alcohol, polyethylene glycol 400, and ethanol. These three solutions worked to form macropores on the surface. Visually the polymer formed was solid white, as shown in Figure 2.

Figure 2. The visual organic polymer contained quaternary ammonium.

Characterization of organic polymer monoliths Using Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was carried out to determine the presence of amine compounds. The amine group itself was used as a strong anion-exchanger. The FTIR spectrum of organic polymer monolith was shown in Figure 3. In Figure 3, it can be seen that detected five peaks in the organic polymer monolith column. These five peaks were the first peak at wave number 1020.3 cm^{-1}, the second peak at wave number 1352.2 cm^{-1}, the third peak at wavenumber 1723.6 cm^{-1}, the fourth at wave number 2875.3 cm^{-1}, and the fifth peak at wavenumber 3433.6 cm^{-1}. The absorption area in the wavenumber between 1150-1085 cm^{-1} refers to the C-O (stretching) absorption area. The high intensity of the principal peak in organic polymer monolith describes many oxygen-containing groups after the polymerization process. The number of oxygen-containing groups came from either ethylene glycol dimetharyate or 2-[(methacryloyloxy) ethyl] trimethylammonium. The absorption area in the wavenumber between 1250-1020

cm-1 refers to C-N (amine) absorption area. Subsequently, the absorption area in the wavenumber around 1650-1580 cm^{-1} refers to N-H (amine) absorption area. These amine groups are contributed by functional monomers that are used. The absorption area in the wavenumber between 2853-2962 cm-1 refers to the C-H (stretching) absorption area. Then, in the wavenumber between 3000-3600 cm^{-1}, it relates to O-H functional group (Silverstein *et al.*, 2005). It can be concluded that existing bonds and functional groups are thought to come from the presence of a polymerization reaction involving an initiator, monomer, crosslinker, and porogen.

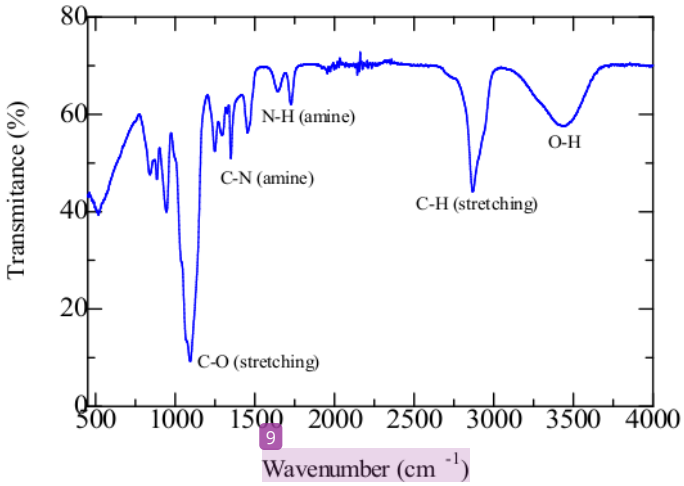
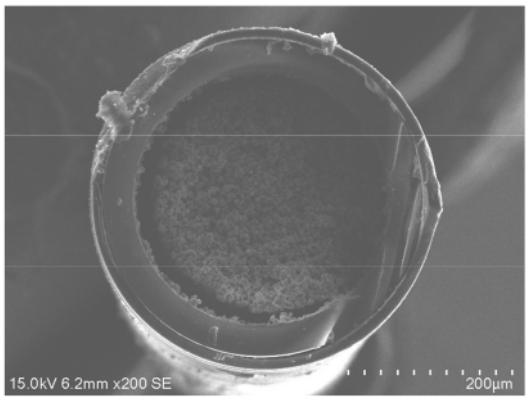


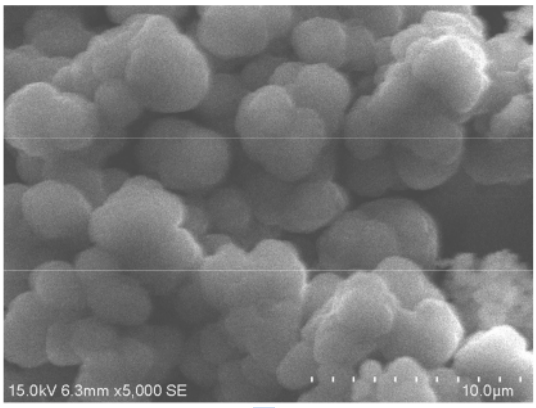
Figure 3. Fourier Transform Infrared (FTIR) spectrum of organic polymer monoliths.

Scanning Electron Microscope (SEM)

The morphology of the organic polymer monolith is one of the essential parameters to determine the adhesion condition of the polymer with an inner wall of the column. Furthermore, the range distribution of pores formed by using porogen in polymer solutions also can be observed. The porogen-created macropores as the distance between one polymer union and another. The morphology photo of the organic polymer monolith can be seen in Figure 4.



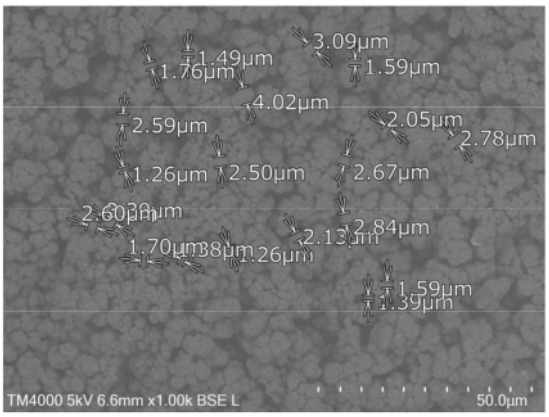
(a)



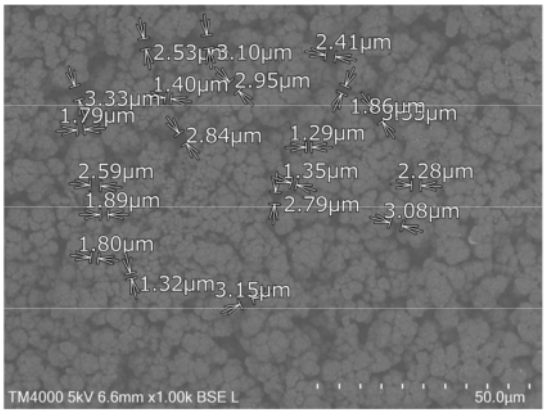
(b)

Figure 4. The morphology of the organic polymer monolith. (a). The magnification of 200x. (b). The magnification of 5000x

Figure 4 shows the performance of the organic polymer attaching into the inner wall of the capillary column by enlarging 200 and 5000 times. In Figure 4.(a). there is a sufficient optimal adhesion between the inner wall surface of the capillary and the organic polymer monoliths. The pre-treatment process in the capillary column using γ-MAPS dramatically affected the adhesion results for attaching the polymer to the inner wall of the capillary. The surface capillary column coated by the silanol group was perfectly laxative by γ-MAPS. Furthermore, Figure 4.(b). shows the distribution of unions and macropores in the organic polymer monolith. The macropores were significantly formed and evenly distributed. Subsequently, the size distribution of the union and macropores are shown in Figure 5. The range size for the union and macropore is 1.26-3.09 µm and 1.29-3.33µm, respectively.



(a)



(b)

Figure 5. The morphology of organic polymer monolith. (b). Distribution size of the union. (b). Distribution size of macropore

According to the distribution size union and macropore range, the organic polymer could be applied as a stationary phase for the capillary chromatography system. It is promoting good results with a reasonably good system pressure below 2 MPa.

Separation of Uracil and Toluene

The separation of organic compounds was conducted to observe the ability of organic polymer monolith as the stationary phase in the liquid chromatography capillary system. Uracil and toluene were used as analytes for the initial study. The separation of uracil and toluene by the liquid chromatography capillary system is shown in Figure 6. It can be seen that the toluene and uracil could be appropriately separated. The retention time of toluene and uracil are 1.9 minutes

and 2.4 minutes, respectively. Toluene was eluted first and then continued with uracil when 90% acetonitrile was used as eluent. These show that the organic polymer monolith column could work in non-polar compounds by reverse-phase mode. This result is promising for applying organic polymer monolith ammonium quaternary as a stationary phase in the liquid chromatography capillary system.

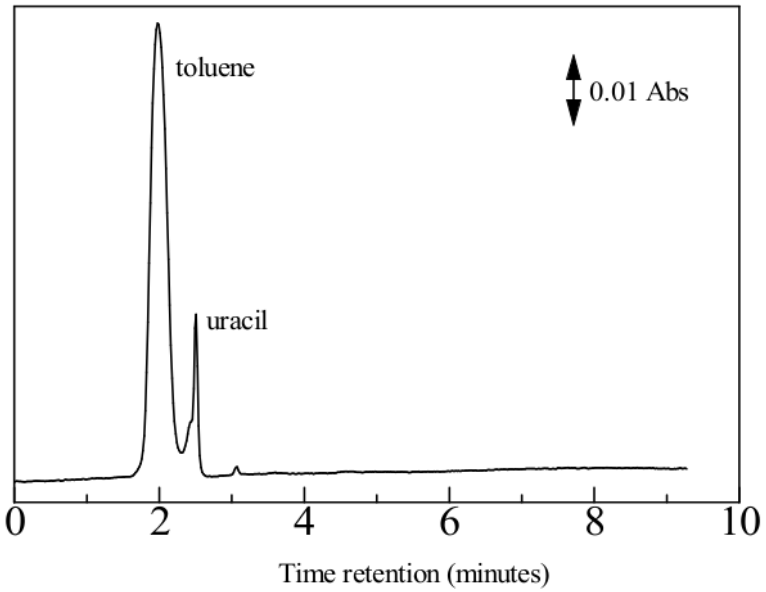


Figure 6. Separation of uracil and toluene by liquid chromatography capillary system. Experimental conditions: column: organic polymer containing ammonium quarternary monolithic (100 mm, 0.32 mm i.d. x 0.45 mm o.d.); mobile phase: 90% acetonitrile; flow rate: 3 µl/min; detection wavelength: 254 nm, injection volume: 0.02 µm.

Conclusions

An organic polymer monolith containing quaternary ammonium was successfully synthesized in the capillary column using a one-pot approach method. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride acted as a monomer, Ethylene dimethacrylate as a crosslinker, and three kinds of solution as porogen; isopropyl alcohol, PEG 400, and ethanol. The organic polymer monolith also contained an amine functional group (C-N) derived from the quaternary ammonium active group for separating uracil and toluene. The range distribution size of the union and macropore is 1.26-3.09 µm and 1.29-3.33µm, respectively.

Acknowledgements

The author would like to thank the research funding assistance through the Internal Grant with number PD-229/SP3/LPPM-UAD/2020 for the basic research

scheme through the Ahmad Dahlan University Research and Community Service Institute Yogyakarta. Thank you to Prof. Toyohisa Takeuchi, Prof. Lee Wah Lim, Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, and Prof. Fuseng Li, River Basin Research Center, Gifu University, Japan this research.

References

Angga, S. C., Septiana, D., Amalia, S., Warsito, Iltitaf, E. D., Sabarudin, A., (2019). Preparation of poly-(GMA-EDA-β-CD-co-TMPTMA) monolith as high-performance liquid chromatography chiral stationary phase column, Indones. J. Chem., 19 (4), 951 – 958.

Chen, B., Zhang, L., He. M., Hu, B. (2020). Cd (II) imprinted polymer modified silica monolithic capillary microextraction combined with inductively coupled plasma mass spectrometry for the determination of trace Cd (II) in biological samples, Spectrochimica Acta Part B: Atomic Spectroscopy, 164, 105751.

Grecco, C. F., Miranda, L. F. C., Queiroz, M. E. C. (2020). Aminopropyl hybrid silica monolithic capillary containing mesoporous SBA-15 particles for in-tube SPME-HILIC-MS/MS to determine levodopa, carbidopa, benserazide, dopamine, and 3-O-methyldopa in plasma samples, Microchemical Journal, 157, 105106.

Iwasaki, M., Sugiyama, N., Tanaka, N., Ishihama, Y. (2012). Human proteome analysis by using reversed phase monolithic silica capillary columns with enhanced sensitivity, Journal of Chrom. A., 1228, 292-297.

Lalli, E., Silva, J.S., Boi, C., Sarti, G.C. (2020). Affinity Membranes and Monoliths for Protein Purification, membranes, 10, 1-12.

Mokadem, Z., Besbes, S.S., Lebaz, N., Elaissari, A. (2020). Magnetic monolithic polymers prepared from high internal phase emulsions and Fe_3O_4 triazole-functionalized nanoparticles for Pb^{2+}, Cu^{2+} and Zn^{2+} removal, Reactive and Functional Polymers, 155, 104693.

Naushada, M., Ahamadab, T., Al-Sheetan, K. M. (2020). Development of a polymeric nanocomposite as a high performance adsorbent for Pb(II) removal from water medium: Equilibrium, kinetic and antimicrobial activity, Journal of Hazardous Materials, 407, 124816.

Pan, S. D., Shen, H. Y., Zhou, L. X., Chen, X. H., Zhao, Y. G., Cai, M. Q., Jin, M. C. (2014). Controlled synthesis of pentachlorophenol-imprinted polymers on the surface of magnetic graphene oxide for highly selective adsorption, J. Mater. Chem. A, 2, 15345–15356.

Pan, S., Zhang, Y., Shen, H., Hu, M. (2012). An intensive study on the magnetic effect of mercapto-functionalized nano-magnetic Fe3O4 polymers and their adsorption mechanism for the removal of Hg (II) from aqueous solution, Chem. Eng. J., 210, 564–574.

Rahayu, A., Lim, L., W., Takeuchi, T. (2015). Polymer monolithic methacrylate base modified with tosylate-polyethylene glycol monomethyl ether as a stationary phase for capillary liquid chromatography. Talanta. 134, 232-238.

Rahayu, A., Lim, L., W., Takeuchi, T. (2015). Preparation of a hybrid monolithic stationary phase with allylsulfonate for the rapid and simultaneous separation of cations in capillary ion chromatography. J. Sep. Sci. 38, 1109–1116.

Shamim, N., Hong, L., Hidajat, K., Uddin, M. (2007). Thermosensitive polymer (N-isopropyl acrylamide) coated nanomagnetic particles: preparation and characterization, Colloids Surf. B: Biointerfaces, 55, 51–58.

Shen, H., Pan, S., Zhang, Y., Huang, X., Gong, H. (2012). A new insight on the adsorption mechanism of amino-functionalized nano-Fe_3O_4 magnetic polymers in Cu (II), Cr (VI) co-existing water system, Chem. Eng. J., 183, 180–191.

Silverstein, R. M., Webster, F. X., Kiemle, D. J. (2005). Spectrometric identification of organic compounds, 7th edition. John Wiley & Sons, 512.

Wang, H., Ou, J., Lin. H., Liu, Z., Huang, G., Dong, J., Zou. H. (2014). Chromatographic assessment of two hybrid monoliths prepared via epoxy-amine ring-opening polymerization and methacrylate-based free radical polymerization using methacrylate epoxy cyclosiloxane as functional monomer, Journal of Chromatography A, 1367, 131-140

Yang, H., Chen, Y., Liu, Y., Nie, L., Yao, S. (2013). One-pot synthesis of (3-sulfopropyl methacrylate potassium)-silica hybrid monolith via thiol-ene click chemistry for CEC, Electrophoresis, 34, 510–517.

Zhao, Y. G., Chen, X. H., Pan, S. D., Zhu, H., Shen, H. Y., Jin, M. C. (2013). Self-assembly of a surface bisphenol A-imprinted core-shell nanoring amino-functionalized superparamagnetic polymer, J. Mater. Chem. A, 1, 11648–11658.

Zhao, Y. G., Shen, H. Y., Pan, S. D., Hu, M. Q., (2010). Synthesis, characterization, and properties of ethylenediamine-functionalized Fe_3O_4 magnetic polymers for removal of Cr (VI) in wastewater, J. Hazard. Mater., 182, 295–302.

Zhao, Y. G., Chen, X. H., Pan, S. D., Zhu, H., Shen, H. Y., Jin, M. C., (2013). Self-assembly of a surface bisphenol A-imprinted core-shell nanoring amino-functionalized superparamagnetic polymer, J. Mater. Chem. A, 1, 11648–11658.

Zhong. Y., Zhou. W., Zhang. P., Zhu. Y. (2010). Preparation, Characterization, and Analytical Applications of a Novel Polymer Stationary Phase with Embedded or Grafted Carbon Fibers, Talanta, 82, 1439- 1447.

Zhao, K., Yang, L., Wang, X., Bai, Q., Yang, F., Wang, F. (2012). Preparation of a novel dual-function strong cation exchange/hydrophobic interaction chromatography stationary phase for protein separation, Talanta, 98, 86-94.

Zhang, Z., Lin, H., Ou, J., Qin, H., Wu, R., Dong, J., Zou, H. (2011). Preparation of phenyl-silica hybrid monolithic column with "one-pot" process for capillary liquid chromatography, Journal of Chromatography A, 1228, 263-269.

Paper 4

ORIGINALITY REPORT

14%	12%	9%	2%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	repository.lib.gifu-u.ac.jp Internet Source	5%
2	api.crossref.org Internet Source	1%
3	link.springer.com Internet Source	1%
4	www.google.com Internet Source	1%
5	worldwidescience.org Internet Source	1%
6	pdfs.semanticscholar.org Internet Source	<1%
7	www.jstage.jst.go.jp Internet Source	<1%
8	www.researchgate.net Internet Source	<1%
9	downloads.hindawi.com Internet Source	<1%

10	escholarship.org Internet Source	<1 %
11	docplayer.net Internet Source	<1 %
12	repositorio.uam.es Internet Source	<1 %
13	Lianqin Zhao, Sheng-Tao Yang, Ailimire Yilihamu, Deyi Wu. "Advances in the applications of graphene adsorbents: from water treatment to soil remediation", Reviews in Inorganic Chemistry, 2019 Publication	<1 %
14	Qingguo Song, Kailou Zhao, Hongjun Xia, Jiawei Liu, Quan Bai. "A novel reversed-phase and weak anion-exchange mixed-mode stationary phase based on horizontal polar-copolymerized approach for separation of small organic molecules and inorganic anions", Talanta, 2019 Publication	<1 %
15	espace.curtin.edu.au Internet Source	<1 %
16	www.mdpi.com Internet Source	<1 %
17	Anang Sedyohutomo, Lee Wah Lim, Toyohide Takeuchi. "Development of packed-column	<1 %

suppressor system for capillary ion chromatography and its application to environmental waters", Journal of Chromatography A, 2008
Publication

18	Tao Zhu, Kyung Ho Row. "Preparation and applications of hybrid organic-inorganic monoliths: A review", Journal of Separation Science, 2012 Publication	<1 %
19	Thomas L. Chester. "Recent Developments in High-Performance Liquid Chromatography Stationary Phases", Analytical Chemistry, 2012 Publication	<1 %
20	Yoshihiro Saito, Masatoshi Nojiri, Yoshiaki Shimizu, Kiyokatsu Jinno. "Liquid Chromatographic Retention Behavior of Polycyclic Aromatic Hydrocarbons on a Novel Chitosan - Based Stationary Phase Synthesized with a Trifunctional Cross - Linker", Journal of Liquid Chromatography & Related Technologies, 2007 Publication	<1 %
21	business.gwu.edu Internet Source	<1 %
22	file.scirp.org Internet Source	<1 %

23	"Nanomaterials in the Environment", American Society of Civil Engineers (ASCE), 2015 Publication	<1 %
24	Haiyang Zhang, Junjie Ou, Yinmao Wei, Hongwei Wang, Zhongshan Liu, Lianfang Chen, Hanfa Zou. "A novel polymeric monolith prepared with multi-acrylate crosslinker for retention-independent efficient separation of small molecules in capillary liquid chromatography", Analytica Chimica Acta, 2015 Publication	<1 %
25	Petar Žuvela, Magdalena Skoczylas, J. Jay Liu, Tomasz Ba□czek, Roman Kaliszan, Ming Wah Wong, Bogusław Buszewski. "Column Characterization and Selection Systems in Reversed-Phase High-Performance Liquid Chromatography", Chemical Reviews, 2019 Publication	<1 %

Exclude quotes	On	Exclude matches	Off
Exclude bibliography	On		