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H-INDEX

10

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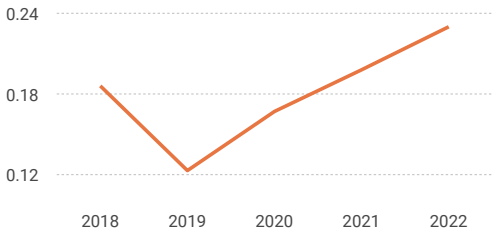

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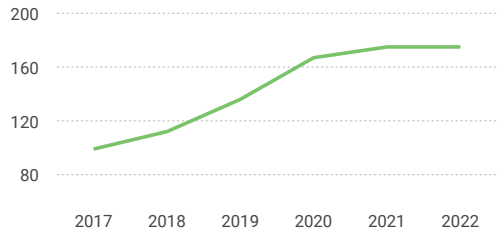

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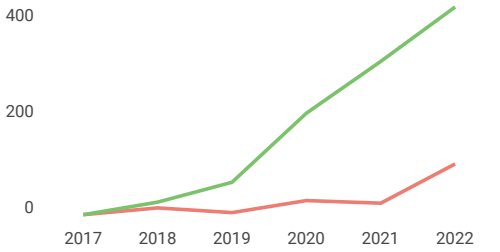

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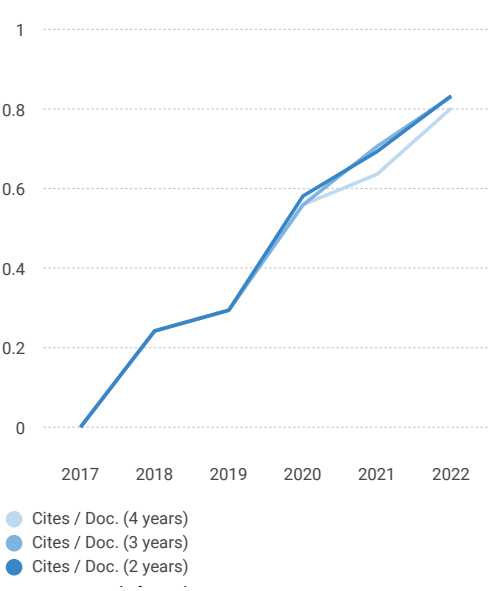

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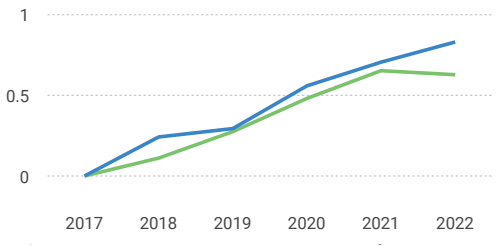

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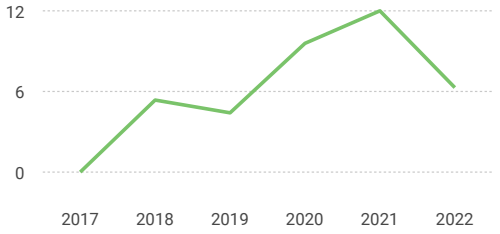

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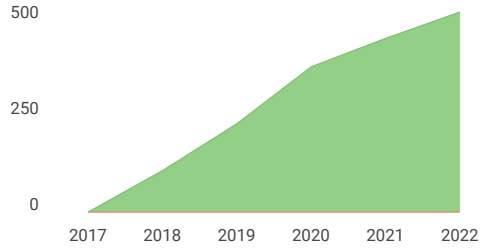

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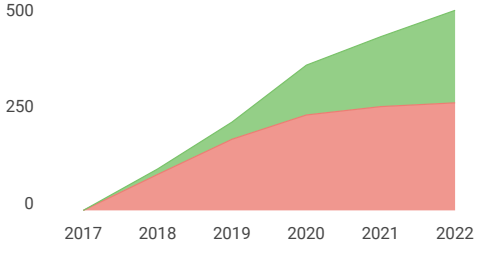

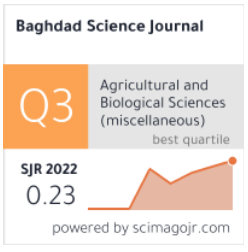

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Noncovalently D-arabinitol Molecularly Imprinted Polymers (MIPs) to Identify Different Sugar Alcohols

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Abstract:

Molecularly imprinted polymers (MIPs) are an effective method for separating enantiomeric compounds. The main objective of this research is to synthesize D-arabinitol MIPs, which can selectively separate D-arabinitol and its potential application to differentiate it from its enantiomer compound through a non-covalent approach. A macroporous polymer was synthesized using D-arabinitol as a template, acrylamide as a functional monomer, ethylene glycol dimethacrylate (EGDMA) being a cross-linker, dimethylsulfoxide (DMSO) being a porogen, as well as benzoyl peroxide being an initiator. After polymer synthesis, D-arabinitol was removed by a mixture of methanol and acetic acid (4:1, v/v). Fourier-Transform Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) distinguished the MIPs and NIPs. A selectivity test of MIPs against its enantiomers (L-arabinitol, xylitol, adonitol, and glucose) was carried out using the batch rebinding method. The binding site was quantitatively determined using the Langmuir equation. The results of the selectivity test showed that the MIPs produced was quite selective toward its enantiomer and could potentially be used to separate D-arabinitol from its enantiomer.

Keywords: D-arabinitol, Enantiomer, MIPs, Non-covalent, Selective material.

Introduction:

D-arabinitol is a sugar alcohol with five carbon atoms which is a major metabolite of several *Candida sp*. Several studies have shown that patients with invasive candidiasis have higher D-arabinitol concentrations in their serum [1-6]. D-arabinitol has the potential to be used as a diagnostic tool for candidiasis patients[1,2,5-7]. However, D-arabinitol has low specificity as a diagnostic tool because of an increased level of D-arabinitol in the blood which has been found not only in candidiasis patients but also in patients suffering from kidney dysfunction. To avoid false-positive results due to kidney damage, D-arabinitol levels are usually expressed in the form of the ratio of D-arabinitol to creatinine or D-arabinitol to L-arabinitol [1].

D-arabinitol, L-arabinitol, xylitol, and adonitol are isomers present in urine in the form of enantiomers. They have the same molecular formula and weight, but they have different physical formulas, properties, and biological activity. A selectivity test was also carried out on glucose, which also has a similar structure to D-arabinitol but a different biological activity. Thus, to make D-arabinitol function as a diagnostic tool, a specific separation method that can separate D-arabinitol from its isomers and glucose is needed.

Molecularly imprinted polymers (MIPs) are a technique for producing a polymer that has cavities due to template disposal, where the cavity functions as a molecular identifier with the same size, structure, physical properties, and chemical properties. MIPs synthesis is carried out by self-assembly between functional monomers and template molecules in solution followed by copolymerization of functional monomers with a certain number of suitable cross-linked polymers. After the polymers are formed, the template molecule is delivered again using suitable solvents

or by heating so that cavities or empty spaces will be generated, like those in template molecules [8,9].
Molecular printing is based on copolymerization between the template and functional monomers (vinyl, acrylic, methacrylate) forming complexes that bind excess di- or tri-vinyl monomers, thus forming a network of porous organic material. The template is connected with functional monomers through covalent bonds of metal ions or non-covalent bonds. These two main approaches have been carried out with various modifications and combinations. The covalent approach was initiated by Wulff and Sarhan, and the non-covalent method was originally developed by Arshady and Mosbach. Compared to the covalent approach, the non-covalent method has several advantages, including its ability to function as a facilitator, its adaptability and rapid synthesis, its similarity to the mechanism of recognition of natural receptor molecules, and the amount of available literature related to functional monomers. The complexity and weak interactions in non-covalent printing, however, need to be carefully considered to control the nature of the introduction of non-covalent MIPs. Non-covalent MIPs applications have the advantage of separating the template from the polymer in terms of incubation time [10,11].
The synthesis of MIPs that has been carried out previously has used a covalent approach [12,13]. In this study, the synthesis of MIPs for the introduction of D-arabinitol used a non-covalent approach. Non-covalent imprinting is the most popular method due to the simplicity and rapidity of the method, besides non-covalent imprinting also has good characteristics such as more flexible interaction, binding, and release of template molecules is simpler and faster than covalent imprinting [14]. In this synthesis, D-arabinitol was utilized in the role of a template molecule, acrylamide as a functional monomer, EGDMA being a cross-linker and DMSO was used as a porogen. The specificity test of the MIPs produced was carried out using the MIPs selectivity test for other alcohol sugars that have the same molecular formula and molecular weight as D-arabinitol. The number of binding sites of D-arabinitol MIPs was examined by Langmuir equation.

Material and Methods:

Reagents

D-arabinitol, acrylamide, ethylene glycol dimethacrylate (EGDMA), dimethylsulfoxide (DMSO), L-Arabinitol, adonitol, xylitol, and glucose were purchased from Sigma-Aldrich Co., Ltd. (United States). Benzoyl peroxide (BP), methanol (MeOH), and chloroform were purchased from Merck (Germany). Acetic acid was obtained from Alpha Chemika (India), and other reagents of analytical grade were purchased from Sigma-Aldrich Co., Ltd. (United States).

Apparatus

To scatter the mixtures and permit the polymer particles rebinding with the template, the Branson 2510 ultrasonic cleaner Marshall Scientific (USA) was used, and the Alpha eco Ge from Bruker (Billerica, MA. USA) was utilized to record the FT-IR spectra of polymer particles. W350T Water Bath-AAR 3060 from Memmert (Schwabach) was utilized to accomplish the polymerization. Centrifuging and dividing the polymer particles were done using the EBA20-Hettich. Scanning electron microscope (SEM) Inspect S-50; FEI Company, Hillsboro, OR (USA) was used to study the morphology of polymer particles. Shimadzu LC-MS 2020 from Shimadzu (Japan), a reversed-phase high-performance liquid chromatography (LC-MS), was utilized in the D-arabinitol, L-arabinitol, xylitol, adonitol, and glucose determination, and in the batch binding evaluation of polymer particles.

Procedures:

MIPs synthesis

MIPs were synthesized by mixing D- arabinitol (1.0 mmol) in the role of a template, acrylamide (5.0 mmol) in the role of a functional monomer, as well as EGDMA (25.0 mmol) dissolved in DMSO (20.0 mL) until it became a homogeneous solution, which was then added to a benzoyl peroxide solution (0.69 mmol) in chloroform (16.67mL). To release the oxygen, which performs as an anti-free radicals (antioxidant), this solution was then purified using nitrogen. The process of polymerization was carried out at a temperature of 60 °C for 12 h. Then, a mixture of methanol and acetic acid (90: 10, V/V) was used to wash the obtained MIPs for 30 minutes. This washing process was repeated until there was no D-arabinitol detected within the washing solution by LC-MS. After that, taking off the residual acetic acid was done by washing the particles using methanol and water. Non-imprinted polymers (NIPs) synthesis was carried out in the same way and under the same conditions as MIPs synthesis but without the addition of D-arabinitol. MIPs and NIPs were formed then filtered out with a vacuum pump and dried in the oven at 40 ℃ until dryness; they were then crushed and sieved through a 100 mess stainless-steel sieve.

Batch rebinding assay

The binding efficiency of polymers to D-arabinitol

was assessed by batch rebinding assay[15]. In this procedure, 50 mg of each dry polymers of MIPs and NIPs were placed in vials containing 10 mL D-arabinitol in water concentrations of 0.053 µmol/mL (defined as D-arabinitol initial) (C0) and then mechanically stirred at room temperature. Samples were taken at different time interludes 1, 2, 3, 4, 5, 6 and 7 hours after incubation. To separate the liquid from its solids, the polymer was centrifuged for 10 minutes at 5000 rpm. After incubation for a certain time, the remaining substrate concentration existed in the solution was filtered and analyzed with LC-MS to measure the amount of remaining D-arabinitol (which was not bound), which was expressed as Ct. NIPs were utilized as a control to decide the nonspecific bonds. The binding capacity (Q) was defined as the number of micromol molecules of D-arabinitol bound to each gram of polymers, calculated using Eq. 1 [16]:

$$Binding\ capacity(\mathrm{Q}) = \frac{v(C0 - Ct)}{w} \qquad 1$$

C0 (µmol/mL) represents the initial D-arabinitol concentration, Ct (µmol/mL) represents the free D-arabinitol concentration after incubation for a certain period, V (mL) represents the solution volume, and W, represents the polymers mass.

Isotherm adsorption study

An isotherm adsorption study was carried out by placing 50 mg of the polymers in an erlenmeyer tube containing 10 mL D-arabinitol (0.053 µmol/mL) which is dissolved in water. The solution was stirred mechanically at a speed of 150 rpm for 7 hours at room temperature. After reaching equilibrium, every single specimen was centrifuged for 10 minutes at a speed of 5000 rpm to separate the liquid from the solids. LC-MS was used to analyze the residual concentration of D-arabinitol. The total of D-arabinitol bound was determined from the dissimilarity between the initial D-arabinitol and also the D-arabinitol residue for each test solution[17]. The adsorption constant and maximum adsorption capacity in this study was determined using the Langmuir adsorption.Eq. 2:

$$\frac{Ce}{Qe} = \frac{1}{bQm} + \frac{Ce}{Qm} \qquad 2$$

in which Qm (µmol/ g) and Qe (µmol/ g) represents the adsorbent maximum and equilibrium capacity, respectively; b (mL/ µmol) represents the adsorption equilibrium constant; and Ce (µmol/ mL) represents the D-arabinitol equilibrium concentration [18]

The selectivity of the MIPs D-arabinitol

MIPs and NIPs selectivity were determined using a batch system. MIPs and NIPs D-arabinitol were each added to 10 mL of an enantiomer solution (L-arabinitol, xylitol, adonitol) and glucose in water, respectively, 0.053 µmol/ mL. Each mixture was then incubated for 7 h at pH 6 and room temperature with mechanical stirring. After incubation, this mixture was centrifuged for 10 minutes at 5000 rpm, and each remaining substrate concentration in the solution was analyzed by LC-MS[19]. The K value for each compound was determined against MIPs and NIPs. The K value was expressed in the following Eq. 3:

$$K = \frac{Cp}{Cs} \qquad 3$$

Where Cp (µmol/ g) represents the number of analytes adsorbed by MIPs, and Cs (µmol/ mL) represents the concentration of analytes left in the solution at saturation.

Results and Discussion:

Synthesis of MIPs can be carried out through two approaches, namely, covalent and noncovalent approaches. MIPs, which has been successfully synthesized and previously reported, are carried out through a covalent approach involving the formation of a reversible weak covalent bond between the vicinal arabinitol hydroxyl group and using boron acid substituents from bithiophene functional monomers[12]. MIPs synthesis through the covalent approach has several disadvantages: It requires complex chemical synthesis, more chemical reagents, and it requires optimization in the polymerization and rebinding process. Furthermore, this approach produces a strong bond between the template and the polymer, which renders it difficult to remove the template from the polymer. The illustration of the formation of MIPs D-arabinitol is shown in scheme 1

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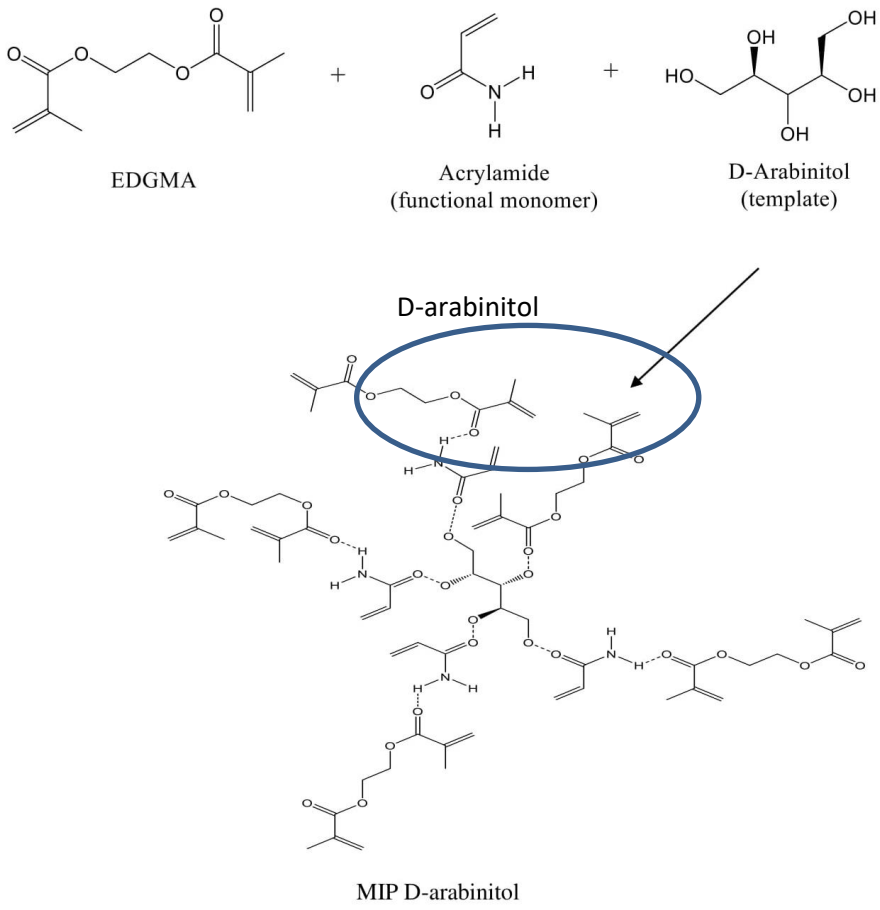

Scheme 1. Synthetic design of MIPs D-arabinitol

In this research, the synthesis of MIPs was carried out through a non-covalent approach using the free radical solution polymerization method. Preparing the molecular imprinted polymers for D-arabinitol was done by mixing D-arabinitol, acrylamide, and EDGMA. In this MIPs synthesis, D-arabinitol was used as a template due to the requirement to use a template that has functional groups, can be polymerized, and has no potential to inhibit or slow down free radical polymerization[15]. A monomer utilized was acrylamide since the acrylamide amide group is a stronger functional group of hydrogen bonds; it also acts as an acid monomer so that the polymer can be created in the absence of the charged groups presence, hence it can reduce the non-specific ionic interactions[19]. EDGMA was used as a cross-linker in this study. EGDMA is one of the cross-linkers that is currently used in the synthesis of MIPs because EGDMA is diester with no free hydrophilic groups, which offers low viscosity, flexibility, high crosslink density various polymer applications and safety[20]. Optimizing the proportion of the molecules of functional monomers, template, and the cross-linker agent was achieved in this study. The proper molar ratio of the template to the functional monomers and the cross-linker in polymerization was selected as 1:5:25 and also the three ordinary organic solvents (MeOH, Acetonitrile, as well as DMSO) were used in the optimization of porogenic solvents. The polymers synthesis could not be done successfully when MeOH and acetonitrile were utilized as the porogen for polymerization for 12 hours. DMSO was used as a porogen due to its ability to dissolve all the components used in MIPs synthesis, thus improving the interaction. The polymers prepared in DMSO was successfully obtained. Therefore, the best polymerization solvent chosen was DMSO. The obtained polymers have high IF to D-arabinitol that of the corresponding NIP were obtained.

Physical and morphological characterization

FT-IR analysis of imprinted polymers.

To verify the successful synthesis of MIPs and NIPs, FT-IR spectra were studied for D-arabinitol, acrylamide, MIPs, and NIPs [17,20]. The FT-IR spectra results are shown in Fig. 1. The FT-IR spectra were carried out to confirm that the imprinted polymers were produced by distinguishing the functional groups in the polymers.

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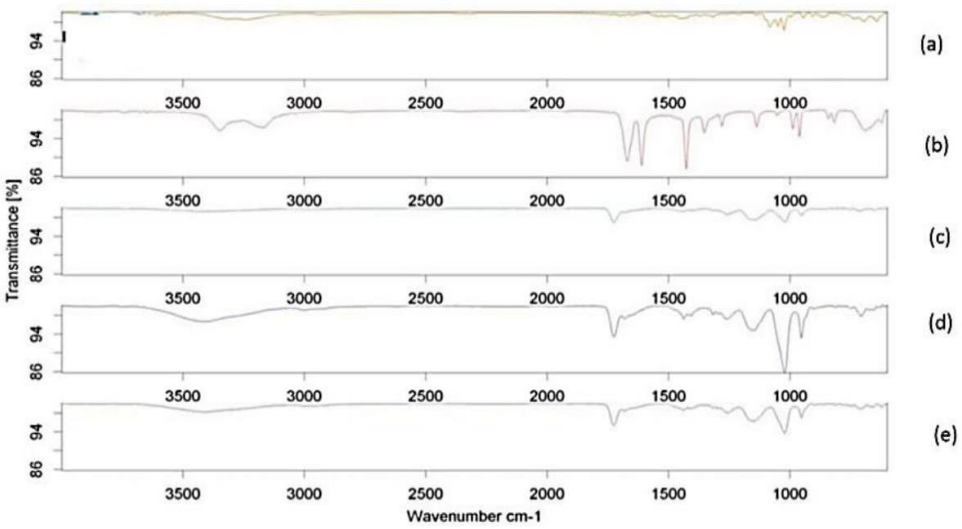
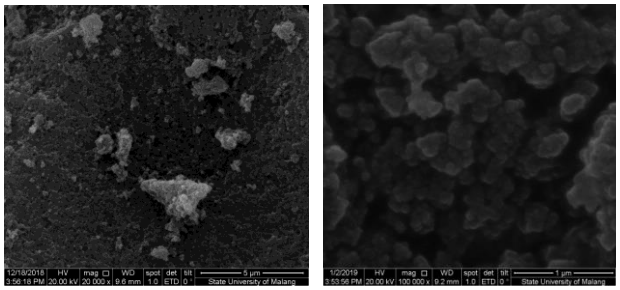


Figure 1. FT-IR spectra of (a) D-arabinitol, (b) acrylamide, (c) MIPs before the template was removed, (d) NIPs and (e) NIPs MIPs after the removal template

Fig.1a, shows the FT-IR spectrum of D-arabinitol, where the C–H stretching vibration in methyl or methylene showed the peaks at 2938.75 cm^{-1}, and the O-H stretching vibration absorption was represented by the multiple peaks nearby 1600-1300, 1200-1000, 800-600 cm^{-1}. The FT-IR spectrum of Acrylamide is shown in Fig.1b, where the primary absorption reaches at 3348.6 and 3172.37, 1669.5, 1610.54, and 1427.01 cm^{-1}were attributed to the stretching vibrations of N–H, C-O, C-C and C–N, respectively. Fig.1c, illustrates the MIPs spectrum before the template molecule was removed, where a broad peak at 3413.69 cm^{-1} was assigned to N–H, and the peaks at 2990.21 cm^{-1} should be attributed to the stretching vibrations of methyl or methylene, meanwhile, a strong absorbance peak at 1725.58 cm^{-1} and the stretching vibrations of C=O and C–O–C for the ester group in cross-linker EDMA should cause two peaks at 1257.78 and 1143.96 cm^{-1}, respectively. Additionally, the stretching vibrations of >CH should cause a strong peak at 1020.63 cm^{-1} for the methyne group in cross-linker EDMA. All of the above information proposed that acrylamide and the cross-linking EGDMA was polymerized in the MIPs. The multiple peaks within the 700 to 600 cm^{-1} wavenumber region are shown in Fig.1d, indicated the presence of stretching vibrations O-H bending from D-arabinitol. These end results indicated that D-arabinitol was efficiently imprinted within the polymers all likelihood through hydrogen bonds between C-O within the template molecule D-arabinitol and N–H of acrylamide within the polymers. The MIPs spectrum after the template molecule was removed is illustrated in Fig.1e wherein the feature signals were almost identical to the ones of MIPs before removing the template, except there was not a D-arabinitol template because the spectra in the fingerprint region did not have absorption in the wavenumber region of 600 cm^{-1}. Fig.1d, is a consultant for the FTIR spectrum of NIPs, wherein the feature signals were almost similar to the ones of MIPs after casting off the template D-arabinitol.

The Morphology of the Imprinted Polymers

The surface functions of the MIPs and NIPs were analyzed by making use of scanning electron micrographs (SEM) as proven in Fig.2.



(a) (b)

Figure 2. SEM pictures of (a) MIPs and (b) NIPs

Based on Fig.2, it can be known that MIPs in Fig.2a and NIPs in Fig.2b showed considerable porous structures in morphology, indicating that the received MIPs should be accessible for the adsorption and dissociation of template molecules, and there is no apparent distinction between MIPs and NIPs in morphology.

Batch rebinding assay

The capacity of the adsorption is a crucial factor because it shows how much adsorbent is needed to

Baghdad Science Journal
P-ISSN: 2078-8665
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quantitatively concentrate the analyte from a given solution. This research is intended for determining the binding efficiency of MIPs and NIPs to D-arabinitol. The test of the efficiency of MIPs binding to the template in this study was carried out under optimum conditions, in accordance with the results of the optimization carried out previously, and the results were analyzed by LC-MS in order to measure D-arabinitol remaining in the solution. The results of the measurement of binding efficiency at different time intervals for MIPs and NIPs for D-arabinitol are depicted in Fig.3.

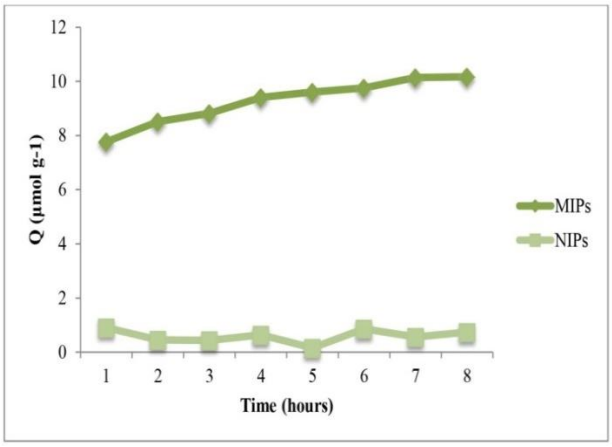

Figure 3. Batch rebinding test results of the MIPs and NIPs

Fig.3 suggests that the capacity of the binding of the MIPs multiplied with the incubation time until it reached an equilibrium situation after 7 hours. After the equilibrium condition was reached, the binding capacity value of MIPs was relatively constant. This shows that there were initially many pores in MIPs that could bind to the template specifically, but after equilibrium conditions were reached, all the binding sides of the MIPs were filled by the template so that the MIPs could no longer bind to the template. In NIPs, the binding capacity was relatively constant with increasing incubation time because this did not have a specific binding side to the template, therefore it could not bind the template. The resulting MIPs had a much greater binding capacity of 7.17 µmol/g when compared to the NIPs, which only had a binding capacity of 0.56 µmol/g. This corresponds to precise interactions between the template and the residual of functional monomer within the MIPs. Non-particular rebinding within the NIP is because of hydrogen bonds, electrostatic interactions, and van der Waals forces among the template and the residual functional agencies in the polymer. These results prove that the MIPs produced have some binding site for D-arabinitol, whereas the NIPs do not have any binding site complimentary with D-arabinitol.

The adsorption isotherm

The adsorption isotherms are beneficial in knowing the adsorption interaction mechanism of D-arabinitol with the surface of MIPs. The D-arabinitol binding isotherms to MIPs and NIPs indicated that as the concentration of the template solution added increased, the amount of the bound template also increased until it reached a stable value that indicated that the adsorption had reached saturation conditions, as illustrated in Fig. 4.

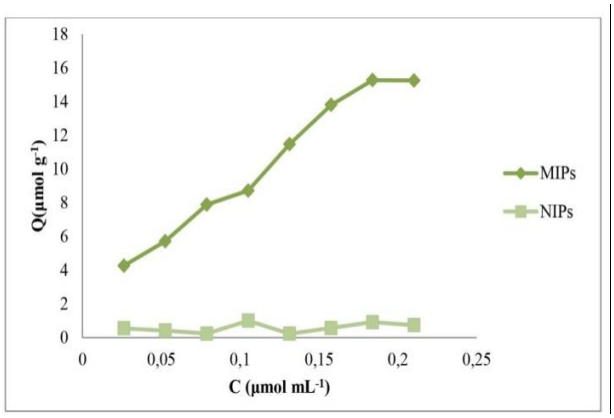

Figure 4. Adsorption isotherm of MIPs and NIPs

The capacity of the binding of MIPs became much greater than that of NIPs. The difference within the binding potential of MIPs and NIPs rose with the increasing concentration for the template solution. This demonstrates that the two polymers had the same composition but had significant structural differences. MIPs could bind to the template much more than NIPs; this shows that the MIPs produced had a cavity recognizing template molecules and this cavity was not possessed by the NIPs, thus the resulting NIPs was unable to recognize and bind to the template molecule. The results of this study indicate that polymer particles from MIPs and NIPs contain almost the same elements but have significantly different space structures. The resulting MIPs have the ability to bind the much more template compared to the NIPs because the resulting MIPs contain imprinted cavities that generated specific recognition for the template .

The correlation between the ability of the adsorption of sorbent and the concentration of template remaining in solution in a certain model is illustrated by an adsorption isotherm. The model of Langmuir isotherm outlines monolayer adsorption based totally at the speculation that each and every adsorption sites have identical template affinity and that adsorption at one site does no longer have an effect on adsorption at an adjacent site. MIPs adsorption of D-arabinitol using the Langmuir equation was shown by the value of $R \geq 0.9$, which was 0.99, as shown in Fig. 5.

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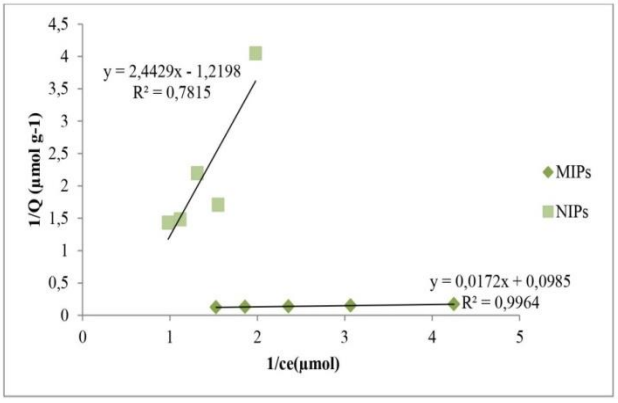

Figure 5. Langmuir plot of MIPs and NIPs to the D-arabinitol

This result indicated the presence of one surface layer with homogeneous sides. Based on the slope and intercept of the regression line equation, it was determined that the Qm value of MIPs and NIPs were 10.15 µmol/g; 0.819 µmol/g respectively. The Langmuir constants (KL) was adequate for the Qe/Ce (C→0) value. The values of KL of the MIPs and NIPs had been 5.73; 0.50, respectively. The values of KL of MIPs were larger than the ones of NIPs and were the end result of the particular recognition by using MIPs for D-arabinitol.

MIPs D-arabinitol selectivity to other sugar alcohol and glucose

In this study, selectivity was determined using a batch rebinding method [18,19], namely, by adding D-arabinitol, L-arabinitol, xylitol, adonitol, and glucose to MIPs and NIPs in the same number of moles and incubating the compounds for 7 hours. The results regarding the selectivity of each compound are presented in the following Tab. 1and Fig. 6.

Table 1. K values of sugar alcohol and glucose on MIPs and NIPs D-arabinitol

Sugar and Alcohol Sugar	MIPs	NIPs
Glucose	0.008	0.026
D-arabinitol	6.397	0.045
L-arabinitol	0.038	0.019
Xylitol	0.053	0.051
Adonitol	0.060	0.034

[a] polymer mass 50 mg, incubation time 7 hours, analytes concentration 8 mg/L, volume of solution 10 ml, water solvent.

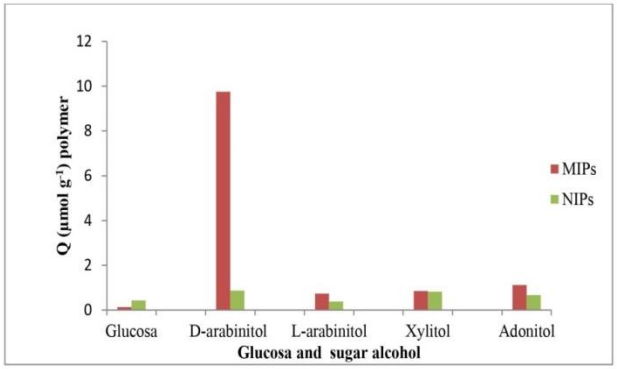

Figure 6. The selectivity of MIPs and NIPs against glucose and sugar alcohol

The binding ability of MIPs might be correlated to the level of similarity to the initial print molecule and this end result relied on its chemical structure. As a result of earlier than the excessive selectivity observed is convinced to be chiefly because of the shape of the cavity and the sites of the binding in the cavity that are mainly accountable for the driving force to carry the substrates into the cavity. Table and Fig. 6 show that the MIPs produced were selective against D-arabinitol with a K value of 6.397, while the MIPs selectivity for glucose and other sugar alcohol was very low when compared to the MIPs selectivity for D-arabinitol. These results demonstrated that the ability of MIPs introduction to recognize sugar and sugar alcohol was mainly determined by the degree of similarity in chemical structure between the template and the analyte, the shape of the cavity and the binding sites within the cavity and the location of the functional group in the MIPs.

Conclusion:

In this study, the MIPs D-arabinitol is synthesized through a simple non-covalent approach, in which the acrylamide is used in the role of the functional monomer, EGDMA as the cross-linker, and D-arabinitol as the template. The Langmuir equation is utilized to evaluate the MIPs binding affinity. The MIPs polymer produced has much better absorption capacity than the NIPs polymer; the MIPs polymer produced also has high selectivity that could distinguish between D-arabinitol and its sugar alcohol enantiomers. The resulting MIPs have a binding site with a high affinity for D-arabinitol. The results of this study indicate the potential for noncovalent printing technique development for D-arabinitol molecules in various complex samples, such as biological samples.

Authors' declaration:

- Conflicts of Interest: None.

- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- The author has signed an animal welfare statement.
- Ethical Clearance: The project was approved by the local ethical committee in University of Jember.

Authors' contributions:

Y.R.,G.S.,R.I. contributed the conception and design. Y.R.,G.S,S.S. contributed to acquisition, analysis and interpretation of data. Y.R. contributed to drafting the manuscript and revision.G.S. contributed to proofreading.

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بوليمرات الطبعة الجزيئية(MIPs) ل دي -ارابينيتول D-arabinitol غير التساهمية لتحديد كحول السكر المختلف

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الخلاصة:
تعد البوليمرات التي تطبع جزيئيًا (MIPs) طريقة فعالة لفصل المركبات الطيفية. الهدف الرئيسي من هذا البحث هو تجميع D-arabinitol MIPs ، والتي يمكن أن تفصل بشكل انتقائي بين D-arabinitol وتطبيقه المحتمل لتمييزه عن مركب enantiomer الخاص به من خلال نهج غير تساهمي. تم تصنيع بوليمر ضخم باستخدام D-arabinitol كقالب ، الأكريلاميد كمونومر وظيفي ، إيثيلين جليكول dimethacrylate (EGDMA) كونه رابطًا متقاطعًا ، ثنائي ميثيل سلفوكسيد (DMSO) كان بوروجان ، وكذلك بنزويل بيروكسيد كونه بادئًا. بعد تصنيع البوليمر ، تمت إزالة D-arabinitol بمزيج من الميثانول وحمض الخليك (4: 1 ، v / v). يقوم التحليل الطيفي بالأشعة تحت الحمراء (FT-IR) والفحص المجهري الإلكتروني (SEM) بتمييز MIPs و NIPs. تم إجراء اختبار انتقائي لـ MIPs ضد enantiomers (L-arabinitol و xylitol و adonitol و glucose) باستخدام طريقة إعادة الدفعة. تم تحديد موقع الارتباط كمياً باستخدام معادلة لانجمير. أظهرت نتائج اختبار الانتقائية أن MIPs التي تم إنتاجها كانت انتقائية تمامًا تجاه enantiomer ويمكن استخدامها لفصل D-arabinitol عن enantiomer.

الكلمات المفتاحية: دي –ارابينيتول ، أيزومرات بصرية ، بوليمرات الطبعة البوليمرية ، مواد غير تساهمية ،مواد انتقائية.