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# Temperature in the Extraction Process: The Number of Cavities Created in Polymer Based on Molecularly Imprinted Polymer (MIP) Caffeine

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**Abstract.** The extraction process is a crucial part of the synthesis of Molecularly Imprinted Polymers (MIP). The process will have a significant impact on the number of its cavities that affects the polymers' ability to recognize targets with the same physical and chemical properties as the analytes. Caffeine polymers have been prepared by the cooling-heating method using methacrylic acid (MAA) as a monomer, ethylene glycol dimethacrylate (EDMA) as a crosslinker, benzoyl peroxide (BPO) as an initiator, and chloroform as a solvent. The resulting caffeine polymer powder was extracted using chloroform, methanol / acetic acid (1:20), and methanol, respectively. Finally, the polymer powder is washed using the aquabidest, which is heated at 60°C. The results of FTIR, XRD, and SEM characterization showed that caffeine concentration was significantly reduced. The number of cavities obtained from caffeine MIP is 604 more than before extracted, which is 132 pieces.

## Introduction

Caffeine is a heterocyclic alkaloids chemical compound that belong to the methylxanthine class. Commonly it is found in coffee [1], the maximum level of caffeine consumption is 150 mg/serving or an average intake of 1.73 mg/kg body weight/day [2]. Excessive consumption of caffeine can cause adverse effects such as insomnia, nausea, anxiety, hypertension, convulsions, and a reduction in fine motor coordination. Thus, it is necessary to monitor caffeine content in various food and drinks.

Molecular Imprinting Polymers (MIPs) is a technique for synthesizing polymers that have specific molecular recognition properties of the target compound. Its high selectiveness and low cost are the primary reasons why MIP is very lucrative to be developed [3,4]. Extraction, which is the process of separating a mixture of several chemicals into separate components, is done by separating the polymer from its template molecule. When the template is separated, it will form a cavity that has the ability to recognize molecules with the same chemical-physical structure and structure as the analyte molecules [3,5,6]. The choice of solvent for the extraction process affects the number of cavities produced, temperature affects solubility (an increase in temperature will also increase solubility), and both temperature and stirring process will affect the bonds between molecules.

In general, MIP material synthesis requires a considerable amount of time [7,8] up to 48 hours [9]. However, by using the cooling-heating method in the polymerization process, it is possible to shorten the time required [4,10]. The process of extracting or removing the template from the polymer will produce a pore or cavity that will later recognize targets that are similar to the template molecule, both physically and chemically [6]. In this article, the process of making caffeine MIP will be described using a cooling-heating method that involves MAA as a functional monomer, EDMA as a cross-linker, BPO as an initiator, and chloroform as a solvent. The novelty of this article is that the extraction process is carried out at 60°C [10,11].

## Research Methods

Caffeine as an analyte (0.025 g), MAA as a functional monomer (0.3 mL), EDMA as a cross-linker (0.525 mL) and BPO (0.07 g) as an initiator were put into a tube containing chloroform (2.01 mL) and then stirred for 15 minutes. The homogeneous solution was cooled at -5°C for an hour and heated at 75°C-85°C for 6 hours. The solid polymer was then crushed and extracted to remove caffeine from the polymer. The extraction process was done in 16 hours using chloroform as solvent, methanol/acetate (1:20) solution for 1 hour three times, and using methanol for 1 hour three times. Finally, the polymer was cleaned using methanol/aquabidest solution (1:20) while being heated at 60°C for one hour. Another polymer without caffeine called Non-Imprinted Polymers (NIP) was also synthesized with the same procedure as a comparison to the MIP. Polymers were characterized using a Shimadzu Fourier Transform Infrared (FTIR) 8201PC spectrophotometer, PW3710 Type X-Ray Diffraction (XRD), and Hitachi Flexsem 1000 Scanning Electron Microscopy (SEM) Type.

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## Results and Discussion

The FTIR spectra of NIP and MIP caffeine are shown in Fig. 1. From the test, we could obtain transmittance values which are related to the concentration of substances contained in a sample. The FTIR spectrum in Fig. 2 shows a higher transmittance value from the caffeine MIP in several wavenumbers compared to NIP values. The C-N bond found in wave number 1250.05 $cm^{-1}$ has a transmittance value of 84% in MIP, which is greater than 82% found in NIP. Next, at wave number 1451.03 $cm^{-1}$ there is a C = C bond with 90% and 88% transmittance at MIP and NIP, respectively. At wave number 1721.33 $cm^{-1}$, the C = O bond has a transmittance value of 75% at MIP and 63% at NIP.

Finally, the C-H bond at wave number 2953.61 $cm^{-1}$ also has 96% transmittance value in MIP while it has 93% transmittance at NIP on the other hand. This data provides information that the MIP caffeine sample has a smaller concentration than the NIP. The greater the value of transmittance, the smaller the absorbance, which in turn means the solution contains a smaller concentration [12]. Table 1 shows different transmittance data (in %) between NIP and MIP.

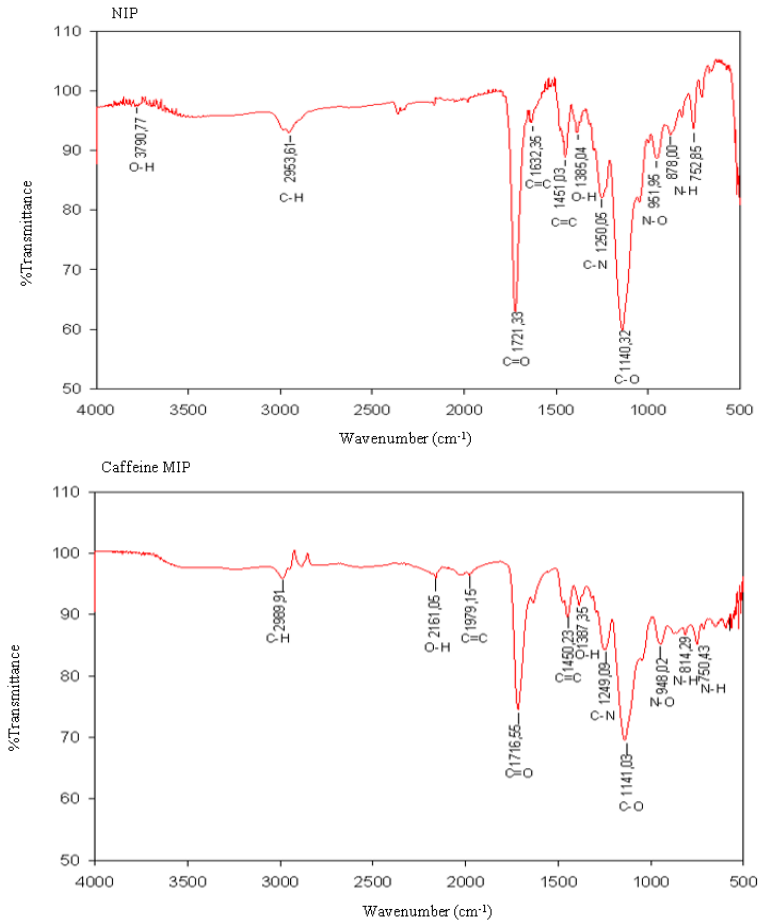



Fig. 1. FTIR spectra of NIP and MIP caffeine samples.

Table 1. Transmittance data from NIP and caffeine MIP.

| Wavenumber ($cm^{-1}$) | Functional group | % Transmittance | |
|---|---|---|---|
| | | NIP | MIP |
| 1140.32 | C–O | 60 | 70 |
| 1250.05 | C–N | 82 | 84 |
| 1451.03 | C=C | 88 | 90 |
| 1632.35 | C=C | 95 | 97 |
| 1721.33 | C=O | 63 | 75 |
| 2953.61 | C–H | 93 | 96 |

The XRD analysis results of the samples tested are shown in Fig. 2. Data obtained from this diffraction pattern can be used as a basis to explain crystal size using the Debye Scherrer equation [13].

$$L = \frac{k\lambda}{B\cos\theta} \tag{1}$$

The Scherrer constant ($k$) in the formula above takes into account the shape of the particle and is generally considered to have a value of 0.9. The graph of the XRD analysis results of caffeine NIP and MIP are presented in Fig. 2. The analysis of the obtained data can be seen in Table 2.

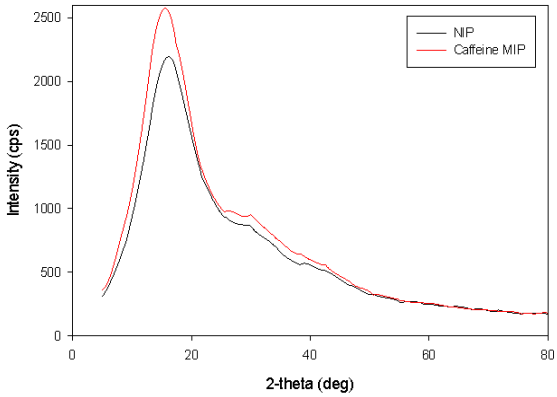


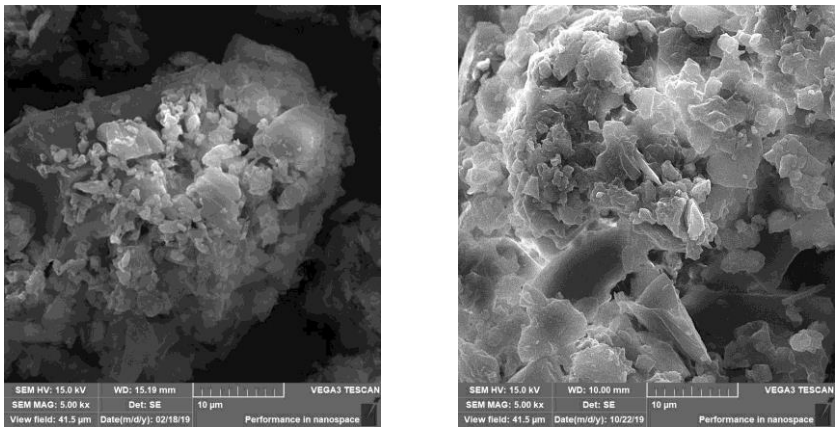

Fig. 2. The XRD pattern of the caffeine NIP (black line) and the caffeine MIP (red line).

Table 2. Analysis on XRD patterns of NIP and MIP caffeine.

| Sample | 2-Theta (°) | d-dist (Å) | FWHM (°) | Crystal Size (Å) |
|---|---|---|---|---|
| NIP | 16.14 | 5.49 | 9.07 | 0.88 |
| Caffeine MIP | 15.35 | 5.77 | 8.09 | 0.99 |

Table 2 shows that NIP has a FWHM that is greater than the MIP, which corresponds to its smaller crystal size when compared with the MIP. Smaller FWHM values show that the polymer has better mechanical properties [14]. The peak intensity of MIP caffeine, which is higher than NIP (the XRD results) shows that the number of atoms that cause diffraction in caffeine MIP is higher.

In a caffeine MIP, the number of cavities will determine its sensing ability when applied as a sensor material [15]. The number of these cavities is calculated from the SEM results, which can be seen in Fig. 3. The number of cavities of the unextracted polymer is also calculated as a comparison.




a b

Fig. 3. SEM images of unwashed polymer (a), and MIP Caffeine SEM (b).

The results of calculations on SEM images produced the number of cavities, as presented in Fig. 4. The number of cavities from caffeine MIP and unwashed polymer were calculated using software on SEM images [16].

MIP caffeine has 604 cavities, which are far more than the polymers before being extracted (132 cavities). This shows that the extraction process by heating has a very significant effect. Cavities created from the extraction results have shown that the material produced has the potential to be applied as a sensor membrane.

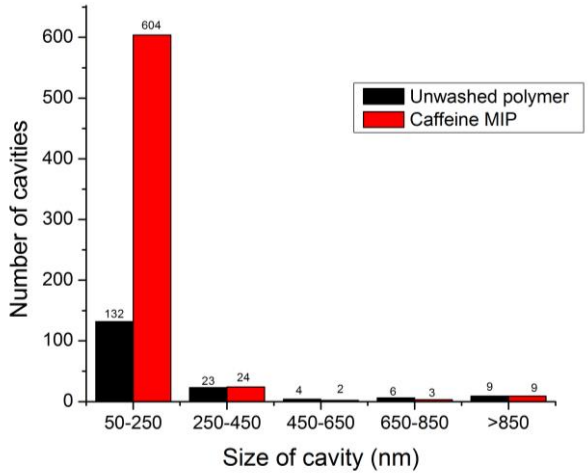



Fig. 4. Number of cavity size distributions of unwashed polymer and caffeine MIP.

## Summary

FTIR data reveals that the concentration of caffeine decreases after the extraction process. The comparatively smaller FWHM value of caffeine MIP in the XRD graph plot indicates that the caffeine MIP has better mechanical properties than the NIP. Calculation of SEM reveals that the caffeine MIP has 604 cavities. It can be concluded that heating in the extraction process during the separation of caffeine from the polymer can reduce the concentration of caffeine significantly so that the resulting material has the potential to be applied as a sensor membrane.

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