Selective Adsorption of Phenol and Vanillin Using Eugenol Based Molecularly Imprinted Polymer

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Abstract

Selective adsorption of phenolic compounds and vanillin by polyeugenol (derivative of eugenol) has been examined in this study. Eugenol was isolated from commercially available clove oil in order to increase the eugenol content from 77.86% to 97.47%. Isolated eugenol was polymerised by BF\textsubscript{3} diethyl ether to produce polyeugenol. Polyeugenol was used then as a monomer functional of MIP (Molecularly Imprinted Polymer). PEGDE (Polyethylene diglycidyl Ether) was used as a crosslinker. Phenol and vanillin MIP were prepared by up loading phenol to polyeugenol (phenol MIP) and vanillin to polyeugenol (for vanillin MIP) followed by crosslinking with PEGDE. The resin resulted was washed by solvent to release the phenol and vanillin bound in order to create holes that are specific hole to phenol or vanillin. Experimental results showed that polyeugenol based phenol MIP and vanillin MIP on have higher selectivity and adsorption capacity compared to NIP (Non Imprinted Polymer).

Keywords: MIP phenol, MIP vanillin, polyeugenol, eugenol, selective adsorption.

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Introduction

The removal of phenol from wastewater is very important to protect and preserve the environment; without proper treatment, it can lead to water pollution. One of the methods used to remove phenol from water is adsorption method. Bituminous coals (lignite coals), for example, had been used for the adsorption of phenol from wastewater with adsorption percentage of 43%-60% [1]. Rubber seed shell is also had been conducted for adsorption experiment of phenol from wastewater [2]. Meanwhile, a commercially available activated carbon had been successfully used for phenol adsorption using a semi-batch and continuous reflux [3]. Other methods that have also been used for the removal of phenol include biodegradation [4], UV/Fe\textsuperscript{3+}[5], extraction [6], oxidation [7]. However, the removal of phenol using the above mentioned methods is generally not beneficial because they require a great amount of energy and materials [8]. In addition, while these methods demand high operating costs, they offer low efficiency and may lead to the formation of harmful byproducts [9].

Proper waste treatment needed today should be able to utilize waste as a secondary source. Molecularly Imprinted polymer (MIP) with eugenol functional monomer and its derivatives are believed capable of performing such tasks. Using MIP as the adsorption agent, it is expected that after selectively adsorbed from the wastewater, phenol will be able to be recovered for use, while the waste can be safely discharged to the environment.

The adsorption method can also be used for vanillin adsorption. At the industrial level, natural vanilla extract was processed by conventional methods (maceration or percolation) for about 1 month using cured or dried vanillin because fresh vanilla beans have no aroma. Curing process begins 1 week after harvest, and consists of killing, sweating (fermenting), drying and conditioning. The whole process takes approximately 5 months produce the resulting dried vanilla (cured vanilla) [10]. The long fermentation process will change some glucosides into glucose, vanillin and other complex flavours.

Based on the issues mentioned above, this research was conducted as an effort to develop simpler extraction/isolation methods with the optimum results using molecular adsorption MIP (molecularly imprinted polymer).
Methodology

Materials
Clove oil market, technical methanol, ethanol technical, technical chloroform, phenol (SIGMA), vanillin (SIGMA), demineralized aqua from Bratachem, Chemicals all quality Merck's pure analysis is PEGDE (polyethylene diglycidil Ether), $\text{C}_4\text{H}_8\text{O}_2\text{C}_2\text{H}_4\text{O}$, $\text{BF}_3\text{O}[\text{C}_2\text{H}_4\text{O}]_2\text{C}_6\text{H}_5\text{OH}$, anhydrous Na$_2$SO$_4$, NaOH, HCl, CH$_3$OH, 4-aminooantipirin, K$_4$Fe(CN)$_6$, NH$_4$OH, K$_2$HPO$_4$, KH$_2$PO$_4$

Instrumentation.
UV-Vis shimadzu type 1601. Infrared spectrometer (FTIR, Shimadzu Prestige-21).

Procedure
Eugenol isolation from clove oil.
15 ml clove oil was stirred with 15 ml of 4N NaOH for 10 minutes. For the extraction, the bottom layer was separated and added with 20 ml Petroleum and shaken for 10 minutes. This step was repeated three times. The bottom layer containing sodium eugenolate was then neutralized using HCl 37%, after which two layers were formed: the bottom layer containing NaCl, and eugenol at the top layer. The top layer was then neutralized with demineralized water and dried with anhydrous Na$_2$SO$_4$.

Synthesis of polyeugenol.
5.8 g eugenol obtained from Step 1 was put into a 3-neck flask and was added with 0.25 mL of boron trifluoride diethyl ether ($\text{BF}_3\text{O}[\text{C}_2\text{H}_4\text{O}]_2\text{C}_6\text{H}_5\text{OH}$) as catalyst for the polymerisation reaction. The addition of this catalyst was done 4 times every one hour while stirring with a magnetic stirrer at room temperature. The reaction is characterized by the colour change of the solution from colourless to red. After the last addition of the catalyst, the polymerisation reaction was allowed to continue for 12-16 hours, after which 1 mL of methanol was added into the flask to stop the reaction. The produced gel was dissolved in chloroform and transferred to a separating funnel and was then washed repeatedly with distilled water until neutral pH was obtained. The organic layer was transferred into a 50 mL Erlenmeyer flask and added with anhydrous Na$_2$SO$_4$ followed by decantation. The solvent was evaporated with a rotary evaporator at a 40 °C. The dried residue was then stored in a desiccator. The solid polymer produced was then weighed and characterized using FT-IR.

Synthesis of Phenol MIP
a. Phenol grafting with eugenol derivatives functional monomer eugenol. 0.5 g of polyeugenol is reacted with phenol with different concentration (25, 50, 100 dan 1000 ppm) for 24 h. The product was then filtered with filter paper and air dried at room temperature.
b. Crosslinking with Polyethylene glycol ether diglycidyl (PEGDE) as the crosslinker. 0.3 g polyeugenol-phenol obtained from step 3.A is crosslinked with PEGDE with a mole ratio of 1:1 by heating at of 80-90 °C for 15 minutes using 20 mLNaOH1M as catalyst. The product was then neutralized and dried in an oven at 115 °C for 6 h. The final material produced in this method is the MIP resin.
c. Eluting phenol from resin using an eluent. 0.2 gMIP resin synthesized in step B was eluted using an eluting solvent for 24 h. Phenol will be eluted during this process and phenol MIP will be produced.

Synthesis of Vanillin MIP
The synthesis was carried out in the same way as the synthesis of phenol MIP, except that here vanillin was used instead of phenol.

Synthesis of NIP (Non Imprinting Polymer).
NIP was synthesized the same way as the above method, except that here no phenol or vanillin grafting was done in the earliest stage.

Adsorption of phenol resin.
50 mg MIP phenol resin is contacted with ±50 ppm phenol at pH 6. Meanwhile, for vanillin adsorption, 10 mL of vanillin 100 ppm was adsorbed by 50 mg vanillin MIP also at pH 6.

The performance of phenol MIP and vanillin MIP were evaluated using different phenol and vanillin concentrations, different pH, different solvent and contact time.

Selectivity Test and adsorption capacity were compared to the NIP.
Phenol was characterized by UV-Vis using 4 AAP Phenol (amino antiphirin) as the complexing agent. Meanwhile, vanillin was analysed with UV at 348 nm

Results and Discussion
Isolation of Eugenol from clove oil in Market
The isolation of eugenol was carried out by adding NaOH followed by an extraction using Petroleum Ether. The concentration eugenol increased after the extraction from 77.86% to 97.47%. Afterwards, the isolated eugenol was then polymerised to produce polyeugenol using BF3 diethylether as catalyst. The infrared spectra of polyeugenol and eugenol isolated from clove oil can be seen in Figure 1.
Figure 1 shows that the absorption band of vinyl at 996.25 cm$^{-1}$ dan 914.83 cm$^{-1}$ initially present for the spectra of eugenol no longer exist at polyeugenol spectra, which should indicate the formation of polymerisation products has occurred.

Figure 1. IR spectra for polyeugenol, isolated eugenol dan clove oil.

**Synthesis of phenol MIP**

Polyeugenol was used to produce phenol MIP (molecularly imprinted polymer), and this was done by reacting 0.5 g of polyeugenol with phenol with concentrations of 25, 50, 500 and 1000 ppm for 24 hours. Afterwards, the material was crosslinked with PEDGE to form mold polymer. After the material is dried, phenol molecules that were bound the polyeugenol-crosslinked-PEDGE was eluted using ethanol, which is expected to form holes in the materials that are selective for phenol. Infrared spectrum that shows synthesise MIP Ph process is pointed at Figure 2. It can be seen that there are decreasing IR spectra at 3600 cm$^{-1}$ (OH functional group). It shows that any reactions involve OH functional groups.

The materials were then used for adsorption experiments using 10 mL phenol 50 ppm. The adsorption percentage of the phenol MIP synthesized using different phenol concentrations can be seen in Figure 3.

It can be seen from Figure 3 that the percent adsorption is reaches maximum for phenol MIP synthesized using 50 ppm of phenol. It would seem that the higher the phenol concentration being used for the synthesis, the lower the adsorption percentage of phenol by the MIP. This might due to the fact that for high phenol concentration, there are still phenol molecules that were not eluted by ethanol, so that the pores was blocked by the adsorbed.

**Variation of Eluting solvent**

The following experiment was conducted to study the most effective solvent to elute phenol so that phenol selective holes are formed in the MIP. The solvents used in this study were water, methanol, ethanol land chloroform. Figure 4 shows the results of this study.

Figure 4 clearly shows that the more polar the solvent, the lower the adsorption. This might be because the relatively polar properties of phenol. The study also shows that the most optimum solvent to be used was methanol.

**Variation of pH of the adsorbate**

Figure 3. The adsorption percentage of phenol MIP synthesized using different phenol concentration. 10 mL of phenol 50 ppm was used as the initial concentration.
pH of the adsorbate, or in this case phenol, is very important as phenol can be easily ionized by salt, which might make it difficult to be adsorbed. The performance of phenol MIP in adsorbing phenol at different pH is illustrated in Figure 5. It can clearly be seen from Figure 5 that the more basic the pH, the lower the adsorption capacity, which means that in basic condition, phenol was easier to be ionized to form salt.

pH 2 to be the optimum pH for phenol transport using SLM techniques using vegetable oil as carrier membrane [11], while pH 4.6 to be the optimum pH for phenol transport using ELM technique [12].

Contact time variation
To study the effects of contact time on the adsorption effectiveness, the adsorption study was carried out using different contact time of 1, 6, 12, 24 and 48 h. The results obtained in this study was compared to that of NIP (Non Imprinting Polymer) which was made without any imprinting process. The results can be seen in the following figure (Figure 6): It can be seen from Figure 6 that compared to NIP, MIP is far more superior especially at short contact time. The optimum contact time was obtained at 24 h.

![Figure 5. Performance of phenol MIP for different pH](image)

![Figure 6. The effects of contact time on the adsorption of phenol by NIP and phenol MIP](image)

Adsorption capacity
To study the adsorption capacity of the MIP, the following experiments were carried out to which the result were compared to that of NIP. The experimental results can be seen in Figure 7.

From Figure 7, it can be seen that MIP has a higher adsorption capacity than NIP, so that it can be concluded that MIP is better than NIP.

Selectivity test of phenol MIP
To study the selectivity of MIP as an adsorbent, a series of experiments were carried out in which phenol MIP was used to adsorb a mixture of phenol and vanillin using the mole ratios of 1:0.25, 1:0.5 dan 1:1. Vanillin was used in this experiment due to its structural similarity to phenol (figure 8). The experimental results can be seen in Table 1.

From Table 1, it can be seen that the selectivity of phenol MIP was tested good in that the adsorption capacity of phenol MIP in adsorbing phenol was not influenced by the presence of vanillin up to the mole ratio of 1:0.5. However, at the mole ratio of 1:1, the presence of vanillin greatly influenced the adsorption capacity for phenol.

Surface Area Analysis using BET Method.
MIP phenol = 2.328 m²/g.
NIP = 3.859 m²/g.

It can be seen that the specific surface area of phenol MIP according to BET method was far smaller that of NIP. This indicates that MIP has exhibited structural organization when compared to NIP.

Vanillin MIP
Preparation of Vanillin MIP
Polyeugenol was used to prepare vanillin MIP (Molecularly Imprinted Polymer). This was carried out by adding 0.3 g polyeugenol with vanillin at 25, 50, 500 dan 1000 ppm for 24 h. Afterwards, the material was crosslinked with PEDGE to form polymer mold. After dried, vanillin that was crosslinked to the polyeugenol-PEGDE was eluted using ethanol. It was expected that vanillin selective holes will be formed in the material as a result. Vanillin MIP compared to NIP and polyeugenol can be seen at Figure 9.

It can be seen at figure 9 that there are decreasing IR spectra at 3600 cm⁻¹ (OH functional group). It shows that, that any reactions involve OH functional groups.

The experimental result for different vanillin concentration uploaded used can be seen in Figure 10.
Figure 7. Adsorption capacity (mg/g) of phenol MIP as compared to NIP

Figure 8. Chemical Structure of Phenol and Vanillin

Table 1. Selectivity test of phenol MIP in adsorbing phenol in the presence of vanillin.

<table>
<thead>
<tr>
<th>Mole ratio of Ph : van</th>
<th>% phenol adsorbed</th>
<th>% vanillin adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIP</td>
<td>NIP</td>
</tr>
<tr>
<td>1:0.25</td>
<td>99.7</td>
<td>36.6</td>
</tr>
<tr>
<td>1:0.5</td>
<td>99.6</td>
<td>8.9</td>
</tr>
<tr>
<td>1:1</td>
<td>1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Figure 9. Infrared spectroscopy of vanillin MIP

Figure 10. Adsorption percentage of MIP for different vanillin concentration

From Figure 10, it can be seen that the adsorption percentage is highest at vanillin concentration of 100 ppm. In addition, the higher the concentration, the lower the adsorption percentage, which can be caused by pore blockage due to incomplete elution of vanillin molecules in the MIP.

The Effects Eluent variation on the adsorption percentage

The following are a series of experiments to examine which solvent is most effective to be used to elute vanillin from the MIP, so that vanillin selective holes are formed in the MIP. Different solvents were used for the experiment, namely water, methanol, ethanol, and chloroform. The result of this study can be seen in Figure 11.

From Figure 11, it can be seen that the adsorption percentages are lower the more polar the solvents are. This is because vanillin is relatively polar, and results indicate that the most effective eluent is methanol.

The effects of pH of adsorbate on the adsorption percentage.

pH of the adsorbate, or in this case vanillin, is very important due to the easiness of vanillin to be ionized by salts, which may hinder the adsorption process. The following results were obtained from the experiment (figure 12)

It can be seen from Figure 12 that the more basic the pH, the lower the adsorption percentage. It can also be seen that the optimum condition was at pH 5, so that pH 5 was used for the subsequent experiments.
The effects of contact time on adsorption percentage

To examine the performance of vanillin MIP at different contact time, a series of experiments was carried out by contacting vanillin MIP with vanillin using different contact time. The results for this experiment can be seen in Figure 13.

From Figure 13, it can be seen that the longer the contact time, the lower the adsorption percentage. This might be due to desorption for some of the adsorbed vanillin.

Selectivity test of vanillin MIP

To study the selectivity of vanillin MIP as an adsorbent, a series of experiment were carried out using vanillin MIP to adsorb vanillin in the presence of phenol, using mole ratios of 1:0.25,1:0.5 and 1:1. Phenol was used in this experiment due to its structural similarity to vanillin. The experimental results can be seen in Figure 14.

From Figure 14, it can be seen that the selectivity of vanillin MIP was not influenced by the presence of phenol up to the mole ratio of vanillin:phenol 1:0.5. However, at mole ratio of 1:1, the presence of phenol affected the adsorption selectivity. The adsorption percentage of phenol from this experiment can be seen in Figure 15.

Figure 14 and 15 also demonstrate that vanillin MIP is more selective than the NIP although not as selective as phenol MIP.

Conclusion

From this research, it was obtained that the adsorption capacity of both phenol and vanillin MIP is better than that of the non-MIP (NIP). Meanwhile, the performance of both MIPs are influenced by a number of factors, such as the concentration of phenol and vanillin being used, eluting solvent (eluent), pH as well as the concentration of the adsorbate. This research also indicates that phenol MIP is selective in adsorbing phenol despite the presence of another compound with structural similarity to phenol, or in this case...
vanillin. Similarly, vanillin MIP also exhibited similar selectivity for the adsorption of vanillin in the presence of phenol. Finally, it would seem that the interaction between phenol and vanillin with the MIPs involves not only the –OH groups but also molecular bonds.

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References


Presentation Discussion

Q: Combine FeO*4* + HA give synergic phenome, give me explaination about advatages if we combine FeO*4* + HA.

A: advantages if coating (combine) FeO*4* + HA

* Stability of acidity range pH 3-9 (if using HA only → just pH lower)

* Preventing aggregation in FeO*4* (FeO*4* easily aggregated and oxidation)

If to use degradation of organic material (phenol, …) using FeO*4* /HA give higher of adsorption capacity