Zeolites as Adsorbent Materials for Decolorization of Crude Terpineol

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Abstract. Zeolites are microporous crystalline aluminosilicates extensively used as adsorbents, catalysts, and ion exchange beds. The adsorption property of zeolite is expected to be applied as a decolorization agent for terpineol. Terpineol is an alcohol compound derived from turpentine oil and widely used as an active ingredient for disinfectants, cleansers, perfumes, and pharmaceutical purposes. Industrial-scale of terpineol production used two stages of reaction: the first stage is hydration of turpentine into terpin hydrate and the second stage is dehydration of terpin hydrate to terpineol. However, as terpin hydrate is easily oxidized, the product color will change from clear into dark solution and make the price of product cheaper. This study aims to increase terpineol selling price by removing unreacted terpin hydrate (decolorization) from crude terpineol. Zeolite is the main absorbent used in this study along with other similar materials i.e. activated carbon and silica gel. Performances of the absorbent are indicated by its adsorption capacity and color clarity analysis. The results would be analyzed using GC-MS. Based on the experiment, it can be concluded that the best absorbent is zeolite activated by acetic acid with 8-15 mg/g adsorption capacity and producing a terpineol purity of 83.5%. This activated zeolite was able to remove terpin hydrate from 9.41% to 0% and other impurities from 14.06% to 6.78%.

1. Introduction
Zeolites are microporous crystalline aluminosilicates composed by silica, alumina, and oxygen atoms connecting and forming into a tetrahedral structure. These materials are extensively used as adsorbents, catalysts, and ion exchange beds. Zeolites can be found in nature but commonly produced in large scale industry to improve its substantial properties like surface area, selectivity, porosity, and thermal stability. Adsorbent applications of zeolites are highly implemented in purification and separation process of the chemical industry i.e. CO₂ removal of natural gas, sweetening of petroleum gas, and sulfur compound removal [1]. This adsorption property is expected to be applied as a decolorization agent for terpineol.

Terpineol (C₁₀H₁₈O) is an alcohol compound that can be processed from turpentine (α-pinene). Turpentine can be obtained from merkusii pine that contains 65 - 85% of α-pinene [2]. Terpineol is one of the most important derivative products of turpentine and commonly used as perfume, anti-fungal, disinfectant, and insect repellant [3]. The reaction of terpineol begins with the formation of terpin
hydrate and then followed by the formation of terpineol from terpin hydrate. Terpin hydrate can be formed by reacting dilute acids, such as hydrochloric acid, nitric acid, and phosphoric acid. The reaction of terpin hydrate formation is shown in Figure 1.

![Figure 1. The reaction of terpin hydrate formation.](image)

The process is then followed by the separation of dilute acid and purification of terpin hydrate by steam distillation and neutralization. Another method for separation of terpin hydrate is by washing terpin hydrate with water repeatedly. Terpin hydrate purification is very important to produce pure terpin hydrate product. Pure terpin hydrate is then processed into terpineol by dehydration. The dehydration process requires less mineral acids or organic acids such as sulfuric acid, oxalic acid, or phosphoric acid to take H atoms from terpin hydrate molecules and thus terpineol is formed [4].

This process produces terpineol with dark color which is due to the presence of terpin hydrate. Terpin hydrate has the properties of oxidizing easily which can cause the dark color of terpineol. In addition, terpin hydrate also has a stinging odor that can limit the uses of terpineol as a perfume. Therefore, the terpin hydrate component needs to be removed to increase the selling price of terpineol and increase the usefulness of the product itself [5].

Adsorption is chosen to decolorize crude terpineol because it is cheaper, simpler, and more energy saving. Adsorption has been applied in large scale of industry for years. Adsorption is usually affected by the type of adsorbent and adsorbate. Besides that, adsorption is also affected by adsorbent activation. Therefore, a suitable adsorbent and adsorbate selection is required in the adsorption process by varying the adsorbent composition. In addition, a suitable selection of chemical activation is also required by varying the chemical compound.

2. Research Method

2.1. Material
The materials used in this research were crude terpineol, zeolite, activated carbon, silica gel, nitric acid, acetic acid, hydrochloric acid, sodium hydroxide, and demineralized water. The crude terpineol was obtained from Perhutani Pine Chemical Industry (PPCI), Pemalang, Indonesia and used without further pretreatment.

2.2. Experiment Variation
In this experiment, the decolorization was first performed by using zeolite, activated carbon, silica gel, a combination of zeolite-activated carbon, and zeolite-silica gel with a ratio of 1 to 1. These non-zeolite powders were used for screening material to find the best adsorbent. The best decolorization results will be used further in the variation of chemical activation. Chemical activation was performed to improve the adsorbent properties by acidic and base treatment. Nitric acid was used as the acid compound, while sodium hydroxide was used as the base compound. In the case that acid compound gave a better result, then the next experiment was continued by varying the acid compound and vice versa.
2.3. Adsorbent Preparation
First, the adsorbents were crushed with pestle and mortar, then filtered using mesh size of 100. The powder was then washed with aquadest and heated at 120°C for 24 hours then stored in the desiccator. The dried adsorbents were soaked with acid/base compound for 6 hours at 80°C. After that, the adsorbent was filtered and heated at 120°C for 24 hours then stored in the desiccator. Treated adsorbent will be used in the decolorization experiment.

During the experiment, 5 grams of adsorbent were fed into the adsorption column and crude terpineol was dropped slowly from the top of the column. The treated terpineol that came out from the column was collected on the watch glass. The mass per drop was weighed and the clarity was measured using a light lux meter. Data retrieval is done until the intensity was below 70%.

2.4. Sample Analysis
In order to measure the clarity of the product, 3 drops of demineralized water was put on the watch glass. Then, the intensity of demineralized water was measured with a lux meter as a reference intensity. A color clarity was done by using below equation. The data for the equation was obtained by measuring the light intensity of the sample every certain period. Color clarity analysis was performed to determine the level clarity of terpineol.

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\text{Sample clarity (\%)} = \frac{\text{sample intensity}}{\text{reference intensity}} \times 100\%
\]

Terpin hydrate removal analysis was carried out using Gas Chromatography-Mass Spectrophotometry (GC-MS) (Shimadzu GCMS-QP-2010 with Rtx-5MS capillary column). By evaluation of peak area, the concentration of the component could be calculated [6,7]. This analysis was performed to determine the adsorbent ability and efficiency in removing terpin hydrate as the impurities in crude terpineol.

3. Results and Discussion

3.1. Decolorization using Various Adsorbents
The result of decolorization process with the variation of adsorbent materials is shown in Figure 2 and Table 1. From these results, it shows that zeolite adsorbent produces the clearest color of terpineol product.

![Figure 2](figure2.png)

**Figure 2.** Results of crude terpineol decolorization with (a) activated carbon; (b) silica gel; (c) zeolite; (d) zeolite-activated carbon; (e) zeolite-silica gel.
Table 1. Results of crude terpineol decolorization using various adsorbents composition.

| Adsorbent                  | Clarity Percentage |
|----------------------------|-------------------|
| Activated carbon           | low               |
| Silica gel                 | 19                |
| Zeolite                    | 66.5              |
| Zeolite-activated carbon   | 45                |
| Zeolite-Silica gel         | 55                |

Decolorization results can be seen from the characteristic of adsorbent and its adsorbate. Terpin hydrate which acts as an adsorbate is a polar organic and hydrophilic compound because the synthesis reaction is done in acidic condition [2]. From these 3 adsorbents (activated carbon, silica gel, and zeolite), activated carbon is the only a hydrophobic adsorbent [8]. Thus, activated carbon could not adsorb terpin hydrate that has a hydrophilic characteristic and the color remained dark-colored terpineol. The clarity of dark colored-terpineol is unknown because its intensity could not be identified by lux meter because the value was too low.

Both silica gel and zeolite adsorbent were able to adsorb terpin hydrate in crude terpineol. But, from Figure 2 and Table 1, zeolite adsorbent produced clearer terpineol than silica gel adsorbent. These results are due to the fact that silica gel is an inorganic adsorbent, while zeolite is an organic adsorbent. Thus, zeolite will perform better because terpin hydrate is also an organic compound [9].

Zeolite adsorbent that has been combined, either with activated carbon or silica gel, produced less clear terpineol than single zeolite adsorbent. This was due to the amount of zeolite that was being reduced. When zeolite was not combined, the total mass of zeolite that was 5 grams, while after the combination, the mass was reduced to only 2.5 grams (the combination is done with a ratio of 1 to 1). By reducing zeolite mass, the performance of adsorption was also reducing.

3.2. Decolorization with the Variation of Physical and Chemical Activation Method

From the previous results, it can be concluded that adsorption with zeolite produced the clearest terpineol. Thus, only zeolite adsorbent was used for the decolorization with the variation of activation type. The yield of decolorization is shown in Figure 3 and Table 2.

![Figure 3. Results of crude terpineol decolorization using treated zeolite (a) physically activated; (b) Physically-chemically activated.](image)

| Zeolite Adsorbent      | Clarity Percentage |
|------------------------|--------------------|
| Physically activated   | 66.5               |
| Physically-chemically activated | 81.5               |

From Figure 3 and Table 2, physically-chemically activated zeolite produced clearer terpineol than physically activated zeolite. Physical activation was used to evaporate water that is trapped in the pores of zeolite crystal. Thus, the number of zeolite pores and the surface area will significantly
increase. Chemical activation was used to clean the pore surface and to arrange the position of the atom that can be exchanged to enhance zeolite ion exchange-ability. By combining physical and chemical activation, zeolite’s surface area will increase, and its adsorption ability will also increase.

3.3. Decolorization with the Variation of Acid-Base Chemical Activation

From the previous results, it can be concluded that adsorption with physically-chemically activated zeolite produced the clearest terpineol. Thus, variation is only done by a variating compound that is used in chemical activation. The yield of decolorization is shown in Figure 4 and Table 3.

![Figure 4](image)

**Figure 4.** Results of crude terpineol decolorization with chemically treated zeolite (a) Nitric acid activated; (b) Sodium hydroxide base.

| Zeolite Adsorbent                  | Clarity Percentage |
|-----------------------------------|--------------------|
| Nitric acid activated             | 81.5               |
| Sodium hydroxide base activated   | 59                 |

From Figure 4 and Table 3, the adsorption process using nitric acid activated zeolite produced clearer terpineol than sodium hydroxide base activated zeolite. Zeolite is an adsorbent that is composed of tetrahedral’s units of AlO$_4$ and SiO$_4$ which is connected by O atom. Acid-activated zeolite will cause zeolite’s surface to be surrounded by H$^+$ ion because zeolite functional groups are protonated. In the acidic condition, the zeolite surface becomes positive [10]. Thus, resulting in an exchange between H$^+$ ion and Si element that has positive charges in zeolite [11]. The ratio of Si/Al in zeolite will decrease and zeolite will have hydrophobic characteristic [12]. This causes zeolite to adsorb terpin hydrate better because both zeolite and terpin hydrate has the same hydrophilic characteristic.

On the contrary, base activated zeolite will cause zeolite’s surface to be surrounded by OH$^-$ ion. Zeolite surface will become negative resulting in an exchange between OH$^-$ ion and Al element [10,11]. Thus, the ratio of Si/Al in zeolite will increase. Base-activated zeolite produced zeolite with a hydrophobic characteristic that caused zeolite to have the worse ability in adsorbing terpin hydrate that has hydrophilic characteristic.

3.4. Type Decolorization with the Variation of Acid Chemical Activation

From the previous results, it can be concluded that adsorption with acid-activated zeolite produced the clearest terpineol. Thus, variation is only done by variating acid compound. The yield of decolorization is shown in Figure 5 dan Table 4.
Figure 5. Results of crude terpineol decolorization with acid-treated zeolite (a) Nitric acid activated; (b) Acetic acid activated; (c) Hydrochloric acid activated.

Table 4. Results of crude terpineol decolorization with the variation of acid chemical activation.

| Zeolite adsorbent            | Clarity Percentage |
|------------------------------|--------------------|
| Nitric acid activated        | 81.5               |
| Acetic acid activated        | 83.5               |
| Hydrochloric acid activated  | 71.5               |

From Figure 5 and Table 4, acetic acid activated zeolite produced the clearest terpineol. These results are due to acetic acid that has the characteristic of polar organic acid, while nitric acid and hydrochloric acid has the characteristic of an inorganic acid. Impurities in terpineol was a polar organic compound because terpineol is synthesized from $\alpha$-pinene in an acidic condition that form carbocation [13]. A carbocation is a carbon atom that has three bonds, positive charges and more favorable in polar organic condition [14]. Thus, terpineol impurities were easier to be adsorbed using organic material. In this case, acetic acid will give the best result since acetic acid is the only organic acid.

Even though both nitric acid and hydrochloric acid are inorganic acids, but nitric acid activated zeolite produces better terpineol than hydrochloric acid activated zeolite. This result is due to nitric acid that is more polar compared to hydrochloric acid. The level of polarity is determined by dipole moment value. The dipole moment is a quantity to describe two different charges that are separated by distance. The greater the dipole moment value of a compound, the greater its polarity. Nitric acid has 2.17 D, while hydrochloric acid has 1.07 D [15]. Thus, nitric acid is more polar than hydrochloric acid and nitric acid will adsorb terpin hydrate better.

3.5. Removal of Terpin Hydrate
From the previous results, it can be concluded that adsorption with acetic acid and nitric acid produce clearer terpineol. The results of GC-MS analysis are shown in Table 5.

Table 5. Results of GC-MS analysis.

| Compound          | Composition (%) |
|-------------------|-----------------|
|                   | Crude | Acetic Acid Activated | Nitric Acid Activated |
| Terpineol         | 58.18 | 81.42                  | 78.98               |
| Terpin hydrate    | 9.41  | 0                      | 0.19                |
| $\alpha$-pinene   | 1.29  | 0.58                   | 1.05                |
| Limonene          | 8.24  | 9.85                   | 13.46               |
| Camphene          | 8.82  | 1.39                   | 0.81                |
| Undefined residue | 14.06 | 6.78                   | 5.52                |

From this analysis result, it can be concluded that both adsorbents can remove terpin hydrate. Terpin hydrate is a by-product that is produced from terpineol’s synthesis reaction. Terpin hydrate is
wished to be removed from terpineol because terpin hydrate is easily oxidized that causes terpineol to have a dark color. This dark-colored terpineol will cause terpineol selling price to decrease.

Even though both adsorbents can remove terpin hydrate, but acetic acid activated zeolite perform better by removing terpin hydrate perfectly. This is due to terpin hydrate is an organic compound [13]. Thus, terpin hydrate can be adsorbed easier by acetic acid activated zeolite because acetic acid is also an organic compound. On the contrary, nitric acid is an inorganic compound. Thus, nitric acid activated zeolite performs worse than nitric acid zeolite.

3.6. Adsorption Capacity

The adsorption capacity was determined by comparing the percentage clarity of the solution product. The adsorption capacity was calculated at the clarity limit of 70%. This was because 70% of clarity is the minimum standard from the industry. The trend of terpineol clarity by acid activated zeolite is shown in Figure 6. Adsorption capacity calculation result is shown in Table 6.

![Figure 6. The trend of product clarity as a function of liquid mass for 5 grams of adsorbent.](image)

| Zeolite Adsorbent                | Capacity (mg/g) |
|---------------------------------|-----------------|
| Nitric acid activated           | 6.6-9           |
| Acetic acid activated           | 8-15            |
| Hydrochloric acid activated     | 2.6             |

It shows that acetic acid zeolite has the greatest adsorption capacity. This is due to terpin hydrate is a polar organic compound and since acetic acid is the only organic compound, acetic acid activated zeolite was able to adsorb terpin hydrate better [14].

Even though both nitric acid and hydrochloric acid were inorganic acid, nitric acid activated zeolite has greater adsorption capacity than hydrochloric acid activated zeolite. This is due to nitric acid’s polarity is greater than hydrochloric acid’s polarity. The level of polarity can be determined by each compound’s dipole moment. Nitric acid has 2.17 D, while hydrochloric acid has only 1.07 D [15]. Thus, since terpin hydrate is a polar organic compound, nitric acid that has more polar characteristic will also have a greater adsorption capacity.

4. Conclusions

A decolorization process of crude terpineol has been conducted by using zeolites and other non-zeolites powder, such as activated carbon and silica gel. Adsorption with acetic acid activated zeolite
produced the clearest terpineol product. Adsorption process using acetic acid activated zeolite was able to remove terpin hydrate perfectly from crude terpineol. Among other acid compounds, acetic acid activated zeolite has the best performance that has the greatest adsorption capacity of 8-15 mg/g.

5. References

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