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Comparison of bentonite and zeolite as adsorbent purification process of patchouli oil (*Pogostemon cablin*)

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Abstract

Many attempts to distill of patchouli oil from patchouli plants (Pogostemon cablin) are used the simple method, therefore the patchouli oil that produced does not have the best quality. The yield of patchouli oil is dark because it contains Fe metal. The content of patchouli alcohol compound is still low whereas patchouli alcohol is the main component of patchouli oil. Various ways can be done to purify patchouli oil, one of them is adsorption process. This study aimed to compare the advantages and disadvantages of bentonite and zeolite as adsorbent purification process of patchouli oil. Bentonite and Zeolite can be utilised as adsorbents because their properties and absorbency are influenced by the presence of pore spaces between the clay mineral bonds and the imbalance of electrical charges in their ions. After adsorption, there was a decrease in Fe content and increase in patchouli alcohol level. However, significant increases occur in bentonite adsorption, this is due to several influencing factors including activating acid type, cation type, Si/Al ratio, and pore geometry including inner surface area, pore size distribution, and pore shape. It can be concluded that in purification process of patchouli oil, bentonite has higher adsorption power than zeolite.

Keywords: Bentonite, Patchouli Oil, Zeolite.

INTRODUCTION

One type of essential oil is patchouli oil derived from patchouli plants (*Pogostemon cablin*). The advantage of patchouli oil that can not be replaced by artificial essential oil is high fixation power. This high fixation power is due to the patchouli alcohol compound which makes the aroma of patchouli oil more durable [1]. Patchouli oil in Indonesia has become an export commodity to many countries in the world. In fact, almost 90% of the world supply of patchouli oil comes from Indonesia [2]. The size of the world's patchouli oil needs can not be matched by the quality of patchouli oil produced by distillers so the selling price is still relatively low. Poor quality of patchouli oil is due to the distillation process that traditionally, one of them the use of iron drums. Iron drums become one of the causes of dissolved metal ions such as iron, magnesium, manganese, copper, and zinc that made the patchouli oil has dark brown color [3].

Determination of patchouli oil's prices is referred to a quality standard. The main of quality standard of patchouli oil including color, density, refractive index, optical round, patchouli alcohol level, iron content, acid number, and ester number[1]. One way to improve the quality of patchouli oil can be done by adsorption. The adsorption technique is the process of diffusion of components on a surface or between particles that the adsorbs surface binds to the adsorbate of atoms, ions, or molecules involving intramolecular bonds between them [4]. Adsorption of patchouli oil can be done with some adsorbents such as bentonite and zeolite. The use of bentonite and zeolite was chosen because of its properties and its absorption capacity is influenced by the presence of pore spaces between the clay mineral bonds as well as the imbalance of electrical charges within the ion.

The acid number on bentonite lower decrease but it is improving the quality of patchouli oil. Bentonite which has been activated by acid is able to absorb Cu metal by 99.16% [5] the amount of adsorption value on Cu metal can improve the quality of patchouli oil. This study aims to compare zeolite and bentonite adsorbents in improving the quality of patchouli oil. In practice as an adsorbent of patchouli oil, bentonite and zeolite have advantages and disadvantages of each.

DISCUSSION

Patchouli oil contains patchouli alcohol compounds which are the main components of patchouli oil and reach 50-60%. Patchouli alcohol is a water-insoluble compound, but soluble in alcohol, ether or other organic solvents, it has a boiling point of 280,37°C, and the crystals formed have a melting point of 56°C[6]. Patchouli oil quality analysis includes Fe content and Patchouli alcohol content. As a reference for quality standards of patchouli oil used SNI number 06-2386-2006 in 2006 shown Table 1.

Table 1: Indonesian standard quality of Patchouli oil

Test Parameter	Unit	Requirements
Colour	-	Yellow-brown reddish yellow
Specific Weight $25^0/25^0$	-	0.950-0.975
Refractive index nD^{20}	-	1.507-1.515
Solubility in Alcohol 90% at $20^0C \pm 3^0C$	-	Clear solution or light opalescence in volume comparison 1:10
Acid Number	-	Max. 8
Ester Number	-	Max. 20
Optic Radiant	-	$(-)48^0 - (-)65^0$
Patchouli alcohol ($C_{15}H_{26}O$)	%	Min. 30
Alpha copaene ($C_{15}H_{24}$)	%	Max. 0.5
Iron content (Fe)	mg/kg	Max. 25

Various porous materials can be used as adsorbents. These porous materials are chosen because they have a much larger internal surface area than the outer surface area [7].

Bentonite

The use of bentonite as an adsorbent material is possible because it has a large surface area. The nature of absorption capacity of bentonite occurs because of the pore space between the clay mineral bonds, and the imbalance between electrical charges in the ions. The absorbency is generally present at the end of the crystal surface, as well as the diameter of the clay mineral bond. Bentonite can be used as an absorbent material for a variety of purposes, both wet and dry [8]. High absorbency in bentonite is due to the bentonite properties which easily expand and soften like mush when exposed to water [9]. Several studies on the effectiveness of bentonite as an adsorbent on purification of patchouli oil have been done and shown Table 2.

The effectiveness of bentonite as a patchouli oil adsorbent has been proven [10]. The type of acid activating becomes the factor affecting the adsorption power of bentonite. Bentonite had been activated with 0,5M HCl which can decrease PA initial sample content by 29.64% to 36.11%. While the Fe^{2+} content of the initial sample was 24,960 ppm and after adsorbed to 23,001 ppm. The result shown in Figure 1 and Figure 2.

Table 2: The effectiveness of bentonite as adsorbent on purification of Patchouli oil

No	Analysis		Research sources
	Fe (ppm)	**PA (%)**	
1.	23,001	36,11	[10]Wibowo EAP. Comparative analysis of chemical components of purified essential oil from nilam plants using gas chromatography. J. Pure App. Chem. Res. 2017;6(1):1-6.
2.	0,00	32,818	[6]Sariadi. Pemurnian minyak nilam dengan proses adsorbsi menggunakan bentonit. Jurnal Teknologi. 2012;12(2):100-104.
3.	-	32,82	[11]Priambodo NA. Pemurnian minyak nilam menggunakan bentonit teraktivasi asam klorida. Universitas Islam Negeri Sunan Kalijaga: Yogyakarta, 2014.
4.	-	25,02	[12]Indeswari NS. Identification of Patchouli-chemical properties on oil purification by using acid-activated bentonite. International Journal on Advanced Science Engineering Information Technology. 2015;5(1):13-15.
5.	-	31	[13]Nurjanah S, Zain S, Rosalinda S, Fajri I. Kajian pengaruh dua metode pemurnian terhadap kerjernihan dan kadar patchouli alcohol minyak nilam (Patchouli oil) asal Sumedang. Jurnal Teknotan. 2016;10(1):24-29.

Bentonite content of 2.5% has a higher effectiveness than 5% bentonite content in patchouli oil purification [13]. On the addition of 2,5%, bentonite PA content on patchouli oil reached 31% whereas if patchouli oil is added bentonite with 2.5%, PA levels only 29%. This means that bentonite is more economical when used as an adsorbent.

Bentonite activated H_2SO_4 1,2 M has not been able to increase PA level significantly that is initial sample equal to 24,74% and after adsorbed to 25,01% [12]. This is alleged because, at the time of activation process, bentonite structure is damaged so that its adsorption ability is not maximal.

In addition, the type of acid that used to activate bentonite, the contact time between bentonite and patchouli oil can also affect the quality of patchouli oil. The circulation contact time greatly affects the improvement of quality patchouli oil[6]. The optimum contact time is at 90-minutes either on the increase in PA levels and on adsorption of Fe metals. Initial PA concentrations are 26.41% and increased after 30 minutes by 31.673% and continued to increase in 90 minutes by 32.818%, but fell back on contact time 120 minutes to 31.706%. Meanwhile, the Fe concentration analysis of the initial oil sample was 0.466 ppm, the 30-minute circulation decreased to 0.242 ppm, the circulation of 60 min to 0.325 ppm, and in the 90-minute circulation, the efficiency decreased the Fe 100% concentration to 0.00 ppm. However, Fe concentrations back again in the circulation of 120 minutes to 0.199 ppm.

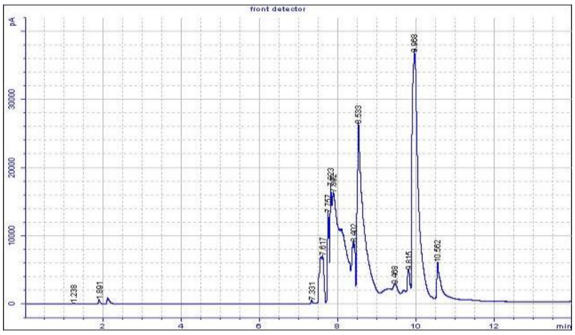

Figure 1: Chromatogram of patchouli oil before purification with bentonite [10]

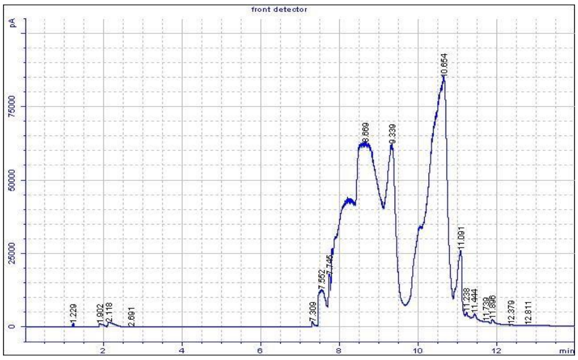

Figure 2: Chromatogram of patchouli oil after purification with bentonite [13]

Besides being able to decrease the concentration of Fe, bentonite has a good ability in terms of adsorption because the size of the colloidal particles is very small and has a large ionised surface capacity. Bentonite is able to absorb various kinds of dyes contained in the oil. Bentonite is also able to adsorp the dye of carotene, ß-carotene, xanthophyll, chlorophyll, and anthocyanin contained in palm kernel oil [14].

Bentonite may increase its surface area due to isomorphous displacement in the octahedral layer (Mg by Al) in retaining an excess charge at the end of the lattice. The presence of an electrostatic force bonding the crystals at a distance of 4.50 from the surface which causes to be strong enough to retain the ions on the surface of the units and to keep them from being close together. In the chemical adsorption process, the adsorbate and adsorbent interactions through the formation of chemical bonds. Kemisorpsi begins with physical adsorption of Fe ions and particles approaching the surface of bentonite adsorbents through Van der Waals forces or through hydrogen bonds [15].

Zeolite

In addition to bentonite, the adsorbent that can use to absorb the impurities is the zeolite. Zeolite is a mineral in the form of alumina silica crystals consisting of three components ie interchangeable cations, alumina-silicate framework, and water [16]. Zeolites could absorb the liquid impurities on patchouli oil and could serve as a gas or liquid absorber [17].

Zeolite is better at lowering acid number in patchouli oil. The decrease in acid number by 4.71% using zeolite while at bentonite adsorbent is only 1,45%[1]. Patchouli alcohol content after absorption using activated zeolite increased and could be observed using Gas Chromatography[18]. The result is shown in Figure 3.

The result of patchouli alcohol fraction analysis was found at retention time 27,806 with patchouli alcohol level of 22,98869%. The peak of patchouli alcohol in patchouli oil chromatogram is located at the end of chromatogram which proved that patchouli oil has a high boiling point so it has a durable aroma. Although the results of chromatogram have been able to prove that the high boiling point of patchouli oil, but the results of observation patchouli alcohol level have not been meet the SNI standards.

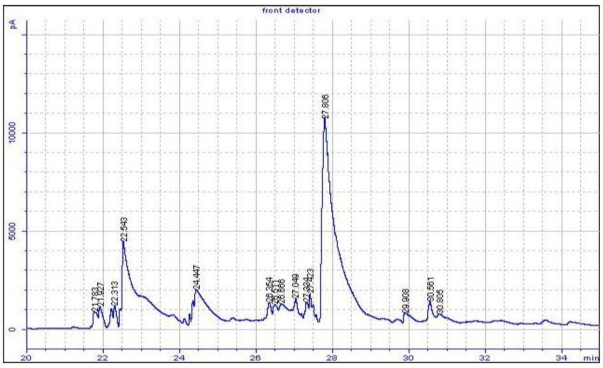

Figure 3: Chromatogram of patchouli oil after purification with zeolite [18]

Although zeolites also have surfaces with H^+ active sites their adsorption power against impurities on patchouli oil is lower than bentonite. The low zeolite adsorption power may be due to the activating acid used to activate too dense. Concentrated acids could cause damage to environmental structures [19]. This is also in line with research that the adsorption capacity of bentonite is higher when compared to the zeolite adsorption power [20]. The surface acidity (Bronsted acid) of bentonite is relatively high, so it is able to adsorb more than zeolite. In surface chemistry, acid-base properties could impact role in the formation of the interface [21]. As with natural bentonite, natural zeolites have very regular crystal shapes with interconnected cavities in all directions. However, because these zeolites are in nature, their cavities have been filled with metal ions, water molecules, and other impurities. Good zeolite activation using HCl 6N, activation of zeolite with acid will dissolve some alkali metals such as Ca^{2+}, K^+, Na^+, and Mg^{2+} which cover part of the cavity so that the zeolite is more porous and the surface is more active [22].

Other factors that cause the low adsorption efficiency of patchouli oil by zeolite are cation type, Si/Al ratio and geometry of zeolite pores, including inner surface area, pore size and pore size distribution [23]. In the zeolite framework, each Al atom is negative and will be neutralised by bonds with interchangeable cations. The interchangeable cations present in this zeolite framework will have an effect on the adsorption process and the thermal properties of zeolites [7]. The change of Si/Al ratio of a material will affect the properties of the material. The higher Si/Al ratio of a material the more material is hydrophobic. An increase in Si/Al ratio will have an effect on the properties of zeolites such as the occurrence of changes in the electrostatic magnetic field in zeolites.

Thus affecting the interaction of zeolite adsorption. Low-silicon zeolites will be hydrophilic while high-silicon zeolites are hydrophobic [24]. Polar molecules will interact more strongly with an intracristal electronic field gradient, than non-polar molecules. Zeolites with substantial isomorphic framework tend to choose polar molecules to adsorb. In contrast, non-polar molecules will be absorbed by zeolites with high Si/Al ratios. In addition, treatment on zeolite activation also affects the adsorption power. This is in line with research that on activation by heat (physiology) the size of zeolite crystals is relatively less uniform when compared with zeolites that are activated with NaOH, thus causing the zeolite adsorption capacity to be lower. The Si/Al ratio was initially 7.74 and decreased to 5.87 on the activation process with NaOH and 7.06 on the activation process with heat [25]. The possibility of zeolite used as an adsorbent on purification of patchouli oil was conducted is a zeolite with high Si/Al ratio, so that the zeolite surface is more likely to absorb non-polar molecules on patchouli oil. As a result, the observed patchouli alcohol level has not been in accordance with the Indonesian Standard Quality [18].

The inner structures of zeolites that form holes and joints could be filled with other molecules, including water molecules. Molecules that could enter into zeolite structures are only molecules that have a size equal to or smaller than the size of a zeolite hole therefore that molecules larger than the size of the zeolite hole could not enter. The temperature is not optimal at activation of zeolite could affect the adsorption of impurities on patchouli oil. The best temperature for the activation of natural zeolite which is 300^0C [25]. At below temperatures, not all water and organic impurities are evaporated. However, if the temperature is more than 300^0C then it is possible to damage the zeolite frame.

CONCLUSION

Bentonite and zeolite can be used as the adsorbent in the purifications process of patchouli oil. The adsorption ability is determined by the surface acidity. Bentonite has a better adsorption capacity than zeolite that indicated by an increase in patchouli alcohol content over Indonesian Standard Quality of patchouli oil.

No conflict of interest: Nil

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