Mesopore Modified Bagasse for Improving Patchouli Oil Quality

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Abstract

This study concerns with the development of natural bagasse. Synthesis of mesopore modified bagasse has been done using cetyltrimethyllammonium bromide as cationic surfactant for mesopore template. This material was used as an adsorbent for patchouli oil for improving its quality based on acidity value and the content of patchouli alcohol. The physicochemical characters of mesopore modified bagasse was investigated by using XRD, FTIR, nitrogen physisorption, and SEM-EDX. The XRD was used to show crystallinity structure of bagasse ash and mesopore modified bagasse. The FTIR spectra showed characteristic peaks for bagasse ash and synthesized material. The bands around 3400 cm^{-1} and 1600 cm^{-1} correspond to adsorbed water and bands around finger print area were characteristic for silica and alumina. Meanwhile physisorption nitrogen profiles gave information that modified material has larger specific surface area as well as pore diameter than raw material because of cationic surfactant involvement during synthesis. The morphologies of bagasse ash and synthesized sample as well as chemical composition of the particles were shown by SEM-EDX. There were changes particularly on SiO_2 and Al_2O_3 content after raw bagasse modified into mesopore material. Silica content rose meanwhile alumina content decreased significantly. Silica and alumina as primary component were reactive and reconstructed into nanomaterial during dissolution with base. In this study the potential application of mesopore modified bagasse as adsorbent for patchouli oil was investigated. The usage of modified material decrease acidity value into 48.80% than bagasse ash, which is 16.40%, with maximum mass 100 mg. The patchouli alcohol content was also gave significant result as well as acidity value after adsorption process. According to chromatogram, percentage of patchouli alcohol increases and new peaks were not identified indicated there was not any reaction appeared. Based on physicochemical data and the result of adsorption, it can be concluded that mesopore modified bagasse has been synthesized successfully and gave better result than raw bagasse for patchouli oil adsorption.

Keywords: raw bagasse, mesopore modified bagasse, patchouli oil, acidity value, patchouli alcohol

Introduction

Essential oil is now become one of the most potential export commodity from plantation sector and approximately 50% of these products are patchouli oil. This plant widely grown in Indonesia, Singapore, and some regions of India (Maiti *et al.*, 2006). In Indonesia we can find most of patchouli oil along Sumatra, Java, and Sulawesi islands. This essential oil is widely used in the perfume industry, pharmaceuticals, insecticides, aromatherapy, and cosmetics. It is also can be used as anti-inflammatory and antibacterial indicated by inhibiting the performance of Staphylococcus aureus and Bacillus subtilis (Kongkathip *et al.*, 2009).

Patchouli oil as a promising export product needs to maintain its quality which contains in SNI-06-2835-2006. The quality requirements are color, specific gravity, refractive index, solubility, acid number, Fe content and patchouli alcohol. The higher content of patchouli alcohol and low acid number are standard for international market. Refining process in Indonesia is still dealing with high iron contaminants and acid number of the products. Repetition of distillation process was able to overcome those problems but did not get time and cost efficiency. Therefore it needs an effective method to solve the problem without increasing production cost.

In this study, we developed an adsorption method because of easy application. The usage of bentonite was able to decrease Fe content and gave change on color from dark brown into light yellow (Sariadi, 2012). Chelating agent such as Na-EDTA could also increase the purity of patchouli alcohol. The improvement of patchouli oil quality using natural adsorbent was economically promising method. Sugarcane bagasse was chosen as natural adsorbent because of cheap, easy to get, and high abundant in Indonesia. Modification raw bagasse into mesopore material became important to enhance effectiveness and adsorption capacity. The prepared mesopore modified bagasse would have bigger surface area than parent material so the contact between adsorbent and adsorbate through binding site more possible. Hopefully this approach would resulted less contaminant in patchouli oil and provided high quality export product.

Method

Materials

Reagents used all were analytical grade. KOH (Merck), asam oksalat ($C_2H_2O_4 \cdot 2H_2O$) (Merck), etanol 96% (Merck), *cetyltrimetilammonium bromida* (CTABr; Applichem, 99%), NaOH (Merck), HCl 37% (Merck), phenolphthalein indicator, deionized water and filter paper Whatman. Patchouli oil was obtained from *Center of Essensial Oil Study* (CEOS) and raw bagasse from Sleman, Yogyakarta.

Preparation of Bagasse Ash

Raw bagasse cleaned and washed repeatedly using deionized water then dried in oven for 24 hours at 70^oC. The dried bagasse was furnace at 750^oC for 4 hours.

Synthesis of Mesopore Modified Bagasse

Synthesis of mesopore material was conducted according to previous method by Lee *et al.* (2008). Bagasse was firstly dissolved on aqueous sodium hydroxide at certain molar ratio then added with 5 g demineralized water until formed clear solution with stirring. This solution became a source of mesopore material framework which is added into cationic surfactant (*cetyltrimethyllammonium bromide*) solution while stirring for 24 hours at room temperature. This mixture was heated for 24 hours and then filtrate was dried overnight at 373 K. The solid formed washed with HCl/ethanol and calcined at 823 K for 3 hours to remove the surfactant.

Characterization of raw bagasse and mesopore modified bagasse

Raw bagasse and mesopore modified bagasse were characterized by a number of methods including X-ray diffraction using Philips X-Pert Powder Diffractometer to identify structure identification, FTIR spectrophotometer Nicolet Avatar to analyze functional group, and SEM-EDX ZEISS EVO ® MA-10 to characterize morphology of material, Quantachrome Instruments for nitrogen adsorption-desorption, , Gas Chromatography Mass Spectrometer Shimadzu to identify patchouli alcohol.

Result

Synthesis of Mesopore Modified Bagasse

In this study, raw bagasse was used as silica source after being furnace into ash formed. The dissolution process of silica and alumina into nanoparticles was conducted using sodium hydroxide. Silica and alumina were then deconstructed with *cetyltrimethylammonium bromide* (CTAB) as mesostructure templating agent. Finally CTAB would be vanished after calcination process and resulted mesopore modified bagasse.

Powder X-Ray Diffraction Characterization

Figure 1 represents the diffractogram of raw bagasse and mesopore material. The XRD was used to show crystallinity structure of bagasse ash and mesopore modified bagasse. The diffraction spectrum with high instensity at 2θ values of 22° showed the existence of cellulose as previously reported by Utomo *et al.* (2015). The intense broad peak around 2θ values of 18° and 30° indicates a nature of amorphous silica as primary component of raw bagasse. The same results

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have also been reported by Govindarajan and Jayalakshmi (2011) and Worothanakul *et al.* (2009). Meanwhile the diffraction pattern of mesopore modified bagasse gave characteristic reflection at low angle region around 2θ values of 2°. The characteristic reflection of mesoporous material are correspond to (100), (110), (200) and (210) planes and only seen in low 2θ values around 2° - 5°. This result was confirmed by the study of Shaikh and Shaikh (2013). This reflection is typical of ordered hexagonal silica with uniform mesoporous structure.

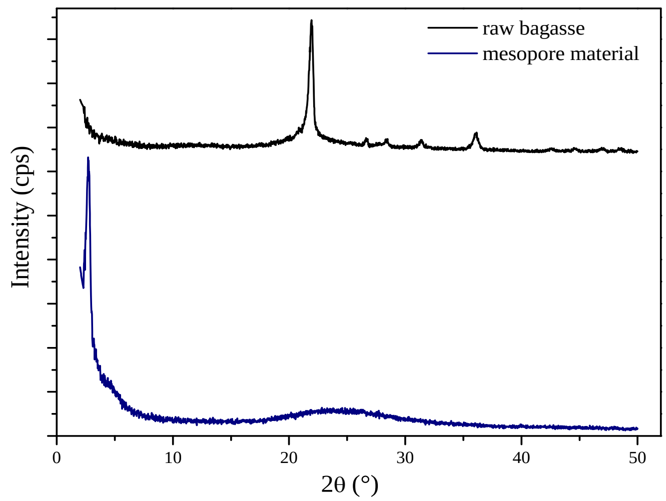

Figure 1. Diffractogram of raw bagasse and mesopore material

Infared Characterization

The infrared spectra of raw bagasse and mesopore material were shown in Figure 2. Infrared characterize the functional group and impurities of material. The FTIR spectra showed characteristic peaks for bagasse ash and mesopore material. The spectra showed similarities of functional group among two materials and slightly differences in peaks intensity.

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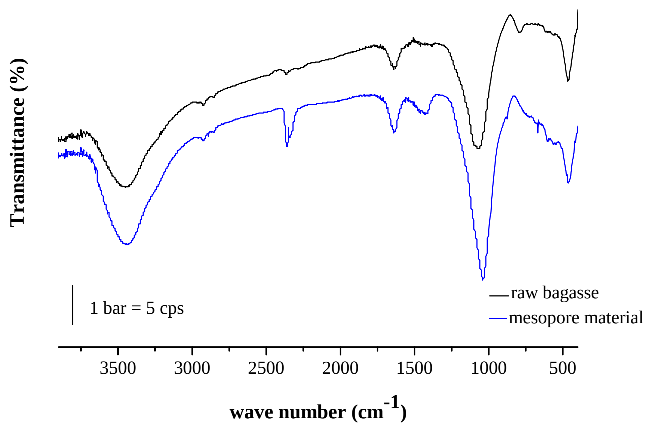

Figure 2. FTIR spectra of raw bagasse and mesopore material

The bands around 3400 cm^{-1} and 1600 cm^{-1} correspond to –OH stretching and bending of adsorbed water. The characteristic bands around 800 cm^{-1} and 400 cm^{-1} are respectively Si-OH stretching and Si-O bending. The resulted infrared spectra confirmed as previous research reported by Ibrahim *et al*. (1980), Mahamed *et al*. (2008), Suyanta and Kuncaka (2011), Govindarajan and Jayalakshmi (2011), and Moises *et al*. (2013).

Adsorption-Desorption Analysis

The nitrogen adsorption-desorption are physical adsorption to determine pore distribution and total surface area of solid material (Haber *et al*., 1995). The result analysis was shown in Figure 3.

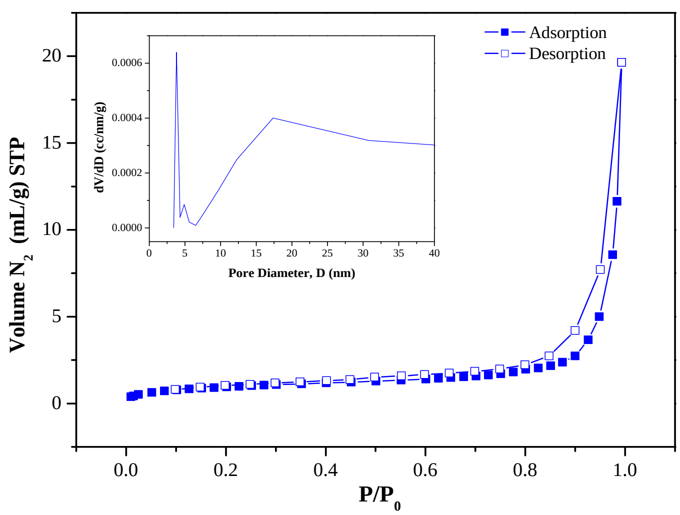

Figure 3. Nitrogen adsorption-desorption of mesopore modified bagasse

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The pattern of isotherm adsorption-desorption showed typical mesopore material from hysteresis loop in the middle area characteristic for pore size diameter between 2-50 nm (Gregg dan Sing, 1982). The existence of pore in the surface of solid material would cause capillary condensation and it creates hysteresis loop (Adamson, 1997).

The evidence of mesopore in the surface of prepared modified bagasse could also be seen from pore size distribution according to BJH analysis in inset picture. Based on Figure 3, pore distribution showed diverse peak at 3.82, 4.90, and 17.36 nm. The distribution pore were numerous around 3- 4 nm, therefore pore size of prepared modified bagasse was 3.82 nm. The surface area of modified bagasse according to BET analysis was 3,438 m^2/g.

SEM-EDX Analysis

The morphologies of bagasse ash and synthesized sample as well as chemical composition of the particles were shown by SEM-EDX. Figure 4 showed the SEM images of both types of material.

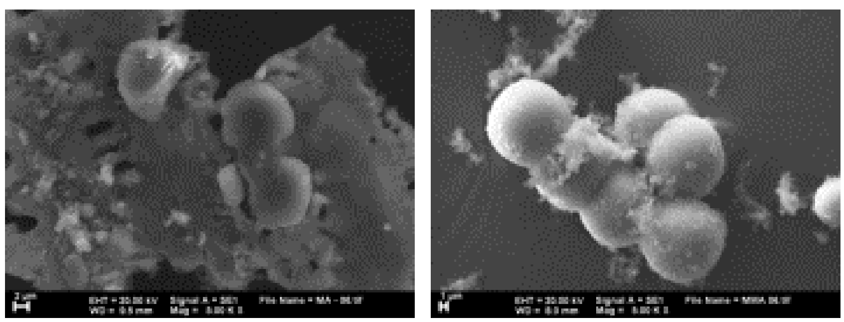

Figure 4. SEM images of bagasse unmodified CTAB (left side) and bagasse modified CTAB (right side)

The images gave the differences of the raw bagasse after being modified by CTAB surfactant. The modification process made the solid particles smaller and separated each other not formed lamellar anymore. The composition of the observed particles on the surface material was determined by EDX. . The result of elemental analysis of raw bagasse and and mesopore material are listed in Table 1.

Table 1. Result of elemental analysis by using EDX

Element (% Wt)	Raw bagasse	Mesopore material
O	80.06	55.65
Si	18.60	22.29
Al	0.15	10.73

There were changes particularly on SiO_2 and Al_2O_3 content after raw bagasse modified into mesopore material. Silica and alumina content rise significantly. Silica and alumina as primary component were reactive and reconstructed into nanomaterial during dissolution with base.

In this study the potential application of mesopore modified bagasse as adsorbent for patchouli oil was investigated. The purpose was to adsorbed impurities in order to increase the quality of patchouli oil. The adsorption process was conducted at varied adsorbent mass (25, 50, 75, and 100 mg) during 24 hours shaking. The acidity value was determined by KOH-ethanol volumetric method. The usage of modified material decrease acidity value into 48.80% than bagasse ash, which is 16.40%, with maximum mass 100 mg.

Table 2. Result of acidity value after adsorption

Mass of modified material (g)	Acidity value (mg/g)	Decreasing of acidity value (%)
0	11.7035	0
0.025	9.8709	12.16
0.050	7.3125	33.35
0.075	6.0322	44.00
0.100	5.4484	48.80

The patchouli alcohol content was also gave significant result as well as acidity value after adsorption process. Chromatogram of patchouli oil after adsorption treatment were shown in Figure 5.

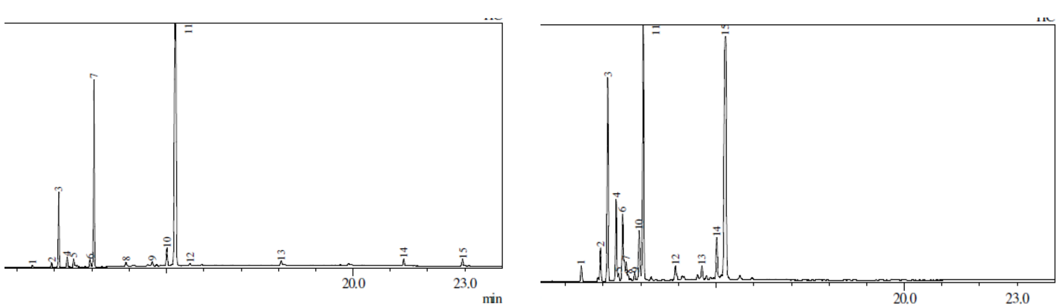

Figure 5. Chromatogram of intial patchouli oil (left side) and after adsorption process (right side)

According to chromatogram, new peaks were not identified indicated there was not any reaction appeared during adsorption process. Table 3 showed data of patchouli alcohol content after adsorption in adsorbent variation.

Table 3. Result of patchouli alcohol content after adsorption

Adsorbent mass (g)	Retention time (minute)	*Patchouli alcohol content* [a] (%)	Increasing of *patchouli alcohol content* [b] (%)
0	12,114	7,56	0
0,025	12,121	13,86	83,33
0,050	12,122	13,71	81,34
0,075	12,119	13,68	80,95
0,100	12,122	14,00	85,18

The adsorbent mass variation increases the percentage of patchouli alcohol almost two times than before adsorption. The maximum mass of adsorbent yield the highest patchouli alcohol rising which is 85,18%.

Conclusion

Based on physicochemical data and the result of adsorption, it can be concluded that mesopore modified bagasse has been synthesized successfully and gave better result than raw bagasse for patchouli oil adsorption.

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References

Adamson, A. W., dan Gast, A. P., (1997), *Physical Chemistry of Surfaces,* John Wiley & Sons, Inc, New York.

Govindarajan, D., & Jayalakhsmi, G. (2011). XRD, FTIR and Microstructure Studies of Calcined Sugarcane Baggase Ash. *Advanced in Applied Science Research, 2(3),* 544-549.

Gregg, S.J. dan Sing, K.S.W. (1982), "*Adsorption, Surface Area and Porosity",* 2nd Edition, London: Academic Press.

Haber, J. Block, J.H. dan Delmon B. (1995), "Manual of Methods and Procedures for Catalyst Characterization", *Pure and Applied Chemistry,* Vol. 67, hal 1257-1306.

Ibrahim, D. M., El-Hemaly, S., & Abdel-Karem, F. (1980). Study of Rice Hush Ash Silica by Infrared Spectroscopy. *Thermochimica Acta, 37,* 307-314.

Kongkathip, N., Sam-ang, P., Kongkathip, B., Pankaew, Y., Tanasombat, M. Dan Udomkusonsri, P. 2009. Development of Patchouli Extraction with Quality Control and Isolation of Active Compounds with Antibacterial Activity. *Kasetsart J. (Nat. Sci.),* 43, 519-525.

Lee, H. I., Park, H. J., Park, Y., Hur, J. Y., Jeon, J., dan Kim, J. M., (2008), "Synthesis of highly stable mesoporous aluminosilicates from commercially available zeolites and their application to the pyrolysis of woody biomass", *Catalysis Today*, Vol. 132, hal. 68–74.

Mahamed, M. M., Zidan, F. I., & Thabet, M. (2008). Synthesis of ZSM-5 Zeolite from Rice Husk Ash: Characterization and Implications for Photocatalytic Degradation Catalysts. *Microporous and Mesoporous Materials, 108*, 193-203.

Maiti, S., Raju, S., Greta, K.A dan Mandal, K. 2006. *Good Agricultural Practices for Patchouli, Geranium and Lemongrass*. Gujarat, India : ICAR.

Moises, M. P., da Silva, C. T., Meneguin, J. G., Girotto, E. M., & Radovanovic, E. (2013). Synthesis of Zeolite NaA from Sugarcane Bagasse Ash. *Materials Letters, 108*, 243-246.

Sariadi. 2012. Pemurnian Minyak Nilam dengan Proses Adsorpsi Menggunakan Bentonit. *Jurnal Teknologi, 12(2)* , 100-104.

Shaik, I.R., and Shaik, A.A., 2013, Utilization of Wheat Husk Ash as Silica Source for The Synthesis of MCM-41 Type Mesoporous Silicates: A Sustainable Approach towards Valorization of the Agricultural Waste Stream, *Res. J. Chem. Sci*., 3(11), 66-72.

Suyanta, & Kuncaka, A. (2011). Utilization of Rice Husk as Raw Material in Synthesis of Mesoporous Silicates MCM-41. *Indo. J. Chem, 11(3)*, 279-284.

Utomo, D.H., Phoon, R.Y.N., Shen, Z., Ng, L.H., and Lim, Z.B., 2015, Removal of Methylene Blue Using Chemically Modified Sugarcane Bagasse, *Natural Resources,* 6, 209-220.

Worathanakul, P., Payubnop, W., & Muangpet, A. (2009). Characterization for Post-treatment Effect of Baggase Ash for Silica Extraction. *World Academy of Science, Enggineering and Technology, 56* , 360-362.