Development of fragrance carrier from Luffa acutangula using zeolite A

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Abstract. In order to study the effect of zeolite A (ZA) addition to adsorption efficiency of green tea oil (GTO) by Luffa fibre, an experiment has been carried out to prepare matrix zeolite A embedded in Luffa fibre composite (L-ZA) used as a fragrance carrier. LZA which retained the rate of release of GOT can be used as air freshener. This paper presents surface properties of ZA and influence of these properties on the ability to adsorb several fragrance compounds: cyclododecanol, heptanal,2-(phenylmethylene), isocitronellol, tonalid, and diethyl phthalate. The mass of ZA were varied 1; 2; 3 g and named as L-ZA1, L-ZA2 and L-ZA3 respectively. L-ZA composite was synthesized by mixing method using ZA and 1 g sodium alginate (SA). The function of SA is as a matrix binder, which it can also adsorb the GOT. The adsorption efficiency of perfume in L-ZA composite was observed by gravimetric analysis. Luffa, ZA and SA each have adsorption efficiency of 292.64%, 94.54% and 90.13%, respectively. Furthermore, the adsorption capacity were measured by gravimetric method, the structure of matrices was analyzed by SEM, and the bioactive compound of GTO were analyzed by FTIR and GC-MS.

1. Introduction

Studies conducted in the United States show that 20.4% of the population involved in health problems are exposed to outdoors, where breathing disorders, mucosal symptoms, migraines, skin disorders, asthma, nervous disorders, and others [1]. People have changed their lifestyle by replacing chemical air freshener with essential oils. In 2010, Indonesia essential oil exports reached up to 124 million US dollars. Essential oil-based perfume and air freshener industries are predicted to reach 10.4 billion US dollars in 2020. Essential oil is volatile at room temperature and can lose up to 50% of its total mass within 23.5 minutes [2]. Green tea oil (GTO) has pleasant aroma and therapeutic effect as it works as antioxidant, antimicrobe, anti-inflammation and anticancer. Encapsulation technique is an effective method to construct product with controlled release system in order to extend the function of fragrant product [3].

Luffa modified with porous material has successfully increase the oil adsorption capacity. Cellulose materials swell during adsorption of essential oil and works as carrier [4]. Luffa aegyptica mill fiber has been used as adsorbent due to the porous structure, high adsorption capacity as 6-12ml/g and inert [5]. It can adsorb various kind of oil up to 8-12 times its weight. The abundance of Luffa in Indonesia reach 8-12 ton/hectare as it is a promising utilization for large scale production.

Various materials such as zeolite, carbon, silica and polymer have been developed as fragrance carrier application. Zeolite is proven to have competence as fragrance carrier that can be regenerated.
Zeolite A has low Si/Al ratio which allows high cation exchange capacity (CEC) and has the ability to adsorb cations (H+ dan Na+) in alkali pH [6]. Cations in zeolite A will bind covalently with GOT molecular composition which will be released once exposed to atmospheric humidity [7].

2. Experimental

2.1. Materials
Natural kaolin was originated from Belitung Island, Indonesia. Sodium bentonite was purchased from PT. Maju Anugerah Mandiri (Indonesia). Sodium hydroxide (NaOH) (99% Analytical Reagent Grade) from Merck (Germany), aquadest, and hydrochloric acid (HCl) (Analytical Reagent Grade) were purchased from Merck (Germany). Green tea essential oil (Camellia sinensis) was purchased from Lansida Group (Indonesia). Dried bleached loofah fibre obtained commercially were boiled for 1 h in distilled water, followed by treating with hydrogen peroxide 30% for 3 h, then washed with distilled water until the smell of hydrogen peroxide disappeared.

2.2. Synthesis of zeolite A
Zeolite A was synthesized from natural kaolin using the hydrothermal method. Previous research has successfully synthesized zeolite A from Ethiopian kaolin using hydrothermal method with resulted pore size in the size 1.14, 0.6 and 0.4 nm [8]. The calcination operating conditions using the furnace were 750°C for 3 hours. The nucleation process of metakaolin conducted using NaOH 3M at a temperature of 60°C in stirring condition of 750 rpm for 3 hours for the nucleation process. After that, the temperature was raised to 90°C and under stirring for crystallization process during 7 hours. The pH of slurry zeolite A is about 12, thus it was washed again with distilled water to reach the pH 7.2 - 8.6. Zeolite A was dried using an oven by heating at a temperature of 90-100°C for 24 hours. Zeolite A obtained was grinded to obtain fine powder and kept in bottle and stored in a desiccator for further application.

2.3. Activation of zeolite A using acid (HCl) and base (NaOH) methods
Two methods to activate of zeolite A using acid (HCl) and base (NaOH) solutions. 20 g of zeolite A was activated using HCl solution (0.1 M, 200 mL) to optimize the dealumination process, thus zeolite obtained is more hydrophobic character [9]. The acid zeolite A was heated at 60°C for 2 hours under stirring conditions of 500 rpm using a magnetic stirrer. Activated acid zeolite A was dried at a temperature of 90-100°C for 24 h. using oven. Same process was also conducted to activate zeolite A using NaOH solution (0.1 M, 200 mL).

2.4. Preparation of L-ZA matrix
Zeolite A was mixed with sodium alginate (1 g) in 100 mL distilled water. 4 g Loofah was added to the mixture and dried using an oven at a temperature of 90-100°C for 24 hours. The L-ZA matrix was pressed using hydraulic press with a diameter of 5 cm. The mass of zeolite A were varied 2; 4; 6 g and then they were labelled by L-ZA2, L-ZA4 and L-ZA6, respectively.

2.5. Adsorption of GTO from matrix
Adsorption of green tea essential oil in the matrix is done by soaking 2 grams of each zeolite A, loofah, sodium alginate, and L-ZA, matrix into 20 g of green tea essential oil. Soaking at room temperature, carried out for 1, 5, 7, 9, and 11 hours to determine the time needed by the matrix to be able to adsorb green tea essential oil optimally. The following equation was used to determine green tea oil content (GTOC) in matrix.

\[
\text{GTOC} = \frac{m_{M} - m_{M}^{GTO}}{m_{M}^{GOT}} \times 100\%
\]

Where \( m_{M} \) = matrix mass before immersion, and \( m_{M}^{GTO} \) = matrix mass after green tea oil immersion.
2.6. Characterization

L-ZA composite was characterized using X-Ray Diffraction Shimazu XRD 700 to analyse the crystal. Brunauer–Emmett–Teller (BET) Micromeritics ASAP 2020 series to analyze surface area and pore size, FTIR spectrophotometer 8201PC Shimadzu to analyze functional group, and SEM-EDX ZEISS EVO® MA-10 to characterize morphology of material.

3. Results and discussion

3.1. Matrix BET characterization

BET characterization showed that zeolite A activated using 0.1 M HCl had a pore size of 5.64 nm. This shows that zeolitization temperature escalation was able to enlarge pore size of zeolite A. Commercial zeolite A generally has a pore size of 0.2-0.4 nm [10]. Hydrothermal synthesized zeolite A pore size in this study can adsorb volatile molecules in green tea essential oils which has an average molecular size of about 1 nm [11].

3.2. Matrix FTIR characterization

FT-IR characterization of hydrothermal synthesized zeolite A was identified with wave number peaks at 3200 to 3600 3235.17 cm\(^{-1}\) as the result of stretching vibrations of OH groups which indicate the presence of water in the sample. The peak at 966.75 cm\(^{-1}\) shows stretching of Si-O-Si asymmetry. The peak at 672.42 cm\(^{-1}\) is a symmetrical stretching vibration of O-Si-O or O-Al-O. Peak 465.64 cm\(^{-1}\) vibration bending Si-O-Si / Si-O Al group. The peak at 1650.94-1572.29 cm\(^{-1}\) arises due to the bending vibration of the Si-OH or Al-OH groups.

3.3. Matrix SEM characterization

SEM characterization showed mixture of zeolite A and alginate in figure 3. The effect of encapsulation on the particle surface is very clear where after zeolite A is encapsulated, particles of zeolite A stick together and are coated with green tea essential oil. The side length of zeolite-A particle according to SEM image is 1.54 µm.

3.4. Adsorption efficiency of matrix L-ZA

Activation of zeolite first to enlarge the pore size to minimize the effect of the addition of alginate to the ability of adsorption of GOT by the L-ZA matrix. The hydrophilic and polar nature of zeolite is an obstacle in the ability to adsorb it to organic molecules. Activation can affect the hydrophilic and hydrophobic nature of zeolite, cyclododecanol, heptanal,2-(phenylmethylene), isocitronellol, tonalid, and diethyl phthalate have hydroxyl groups in its chemical structure. The -OH group will interact with the cation site in the matrix structure. Hydrogen from hydroxyl group dissociated so that it plays an important role in the development of a negative charge depending on pH. This negative charge then bonded to the site of the extra framework cation which is in the structure of zeolite A, namely Na\(^+\). The interactions that occur between the constituent compounds of GOT and the zeolite A are illustrated in figure 1.

The L-ZA matrix surface is formed due to the Si-O-Si bond on Si-tetrahedral. The charge on this surface is the result of isomorphous substitution of Si atoms by other cations. The surface of oxyhydroxide, formed by O-Al-OH bonds on Al-octahedral. In addition to the hydroxyl group bond with the site of the extra cation (Na\(^+\)) framework, the hydroxyl (-OH) group can also bind to Si and Al on the surface of zeolite A as shown in figure 1b.
The 5th Annual Applied Science and Engineering Conference (AASEC 2020)
IOP Conf. Series: Materials Science and Engineering 1098 (2021) 022005
doi:10.1088/1757-899X/1098/2/022005

Figure 1. Molecular interaction between cyclododecanol and isocitronellol to zeolite A active site (Na⁺).

ZA can adsorb GTO 1.864 g/g zeolite A (efficiency of 86.40%) with optimum immersion time for 7 hours. Luffa can adsorb GTO 1.847 g/g Luffa (efficiency of 92.03%). Meanwhile, alginate was able to adsorb GTO 0.725 g/g (72.26%) alginate with an optimum immersion time of 5 hours as shown in figure 4.

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Figure 2. FT-IR characterization of zeolite A.

Figure 3. SEM characterization of zeolite A.

Figure 4. Adsorption Efficiency of Luffa (L), Zeolite A (ZA) and Sodium Alginate (SA).

The addition of alginate as a binder can increase the robustness of the matrix but reduce its adsorption ability as shown in figure 3. The adsorption capacity increases with the increasing mass of zeolite A with the surface area of matrix is getting higher. The amount of GTO adsorbed along with the adsorption efficiency of the L-ZA matrix is shown in Table 1.
Table 1. The effect of ZA mass in matrix on adsorption of green tea essential oil.

| Matrix | Green Tea oil adsorbed (g/g matrix) | Efficiency (%) |
|--------|------------------------------------|----------------|
| LZA1   | 1.411                              | 41.10          |
| LZA2   | 1.6245                             | 62.45          |
| LZA3   | 1.807                              | 80.70          |

Chemical activation changed the hydrophilic and hydrophobic nature and change the zeolite A pore size. Activation using 0.1 M HCl increased the ability of adsorption of GTO by zeolite A from 1.807 g/g matrix to 1.8975 g/g matrix. While activation using 0.1 M NaOH causes the ability of adsorption of GTO decrease from 1.807 g/g matrix to 1.516 g/g matrix. Addition of HCl increases the acidity of the matrix so that the matrix is more hydrophobic and can interact with green tea essential oil better. The constituent molecules of green tea essential oil are non-polar so that they are more easily adsorbed by acid Activated L-ZA matrix.

4. Conclusion
Hydrothermal synthesis of zeolite A formed cubical particle with the size of ~ 1.7 µm and a pore size of 5.64 nm which allows the green tea essential oil molecules to be adsorbed into the pore of the particles. The higher the mass of the zeolite A, the better the ability to adsorb green tea essential oil. The amount of green tea essential oil adsorbed by a matrix measuring 5 cm in diameter is 1.807 g/g matrix (80.70%). Activation of zeolite A with 0.1 M HCl can increase the ability of adsorption of green tea essential oil by the matrix to 1.8975 g/g matrix (94.54%).

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