

Fragrance Carrier Based on Zeolite-A Modified Bentonite as a Controlled Release System in Air Freshener Applications

(Pembawa Wangian Berdasarkan Zeolite-A Bentonit Terubah Suai sebagai Sistem Pelepasan Terkawal dalam Aplikasi Penyegar Udara)

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ABSTRACT

The quality of air fresheners with low cost production can be improved by using a carrier matrix such as synthetic zeolite to increase the long-lasting properties of fragrance product by encapsulation technique. The zeolite A is considered as a safe core fragrance carrier matrix to be able to release volatile fragrance from their pores when exposed to atmospheric humidity at room temperature. Zeolite A was synthesized from natural kaolin and was formed into tube pellets with bentonite (20 wt.%) as binder to produce zeolite A-bentonite (ZAB) cylindrical pellets composite and used as a fragrance carrier matrix with a rose essential oil (*Rose damascena* Mill.) as perfume model. The fresh bentonite can also adsorb the rose essential oil with adsorption capacity of 1.745 g/g bentonite (74.5%). Effects of chemical activation on zeolite-A using acid (HCl) of 0.1 M and base (NaOH) of 0.1 M were studied. The ZAB tube pellets were found to have high adsorption efficiencies of rose essential oil. ZAB4 has the highest efficiency and was used for regeneration test studies that was carried out over 10 cycles using HCl and NaOH, where the adsorption efficiency was 94.5 and 75.4%, respectively. The activated ZAB4 composite using HCl has a long life time until more than 5 weeks and more than 10 regeneration cycles. This fragrance carrier matrix based on ZAB has significant potential for extended carrier fragrance system.

Keywords: Air freshener; controlled release; essential oil; fragrance carrier; zeolite-A

ABSTRAK

Kualiti penyegar udara dengan pengeluaran kos rendah boleh dipertingkatkan menggunakan matriks pembawa seperti zeolit sintetik untuk meningkatkan sifat tahan lama produk wangian melalui teknik enkapsulasi. Zeolit A dianggap sebagai matriks pembawa wangian teras yang selamat untuk dapat mengeluarkan wangian yang tidak menentu dari liang-liangnya apabila terdedah kepada kelembapan atmosfera pada suhu bilik. Zeolit A telah disintesis daripada kaolin semula jadi dan telah dibentuk menjadi pelet tiub dengan bentonit (20 wt.%) sebagai pengikat untuk menghasilkan komposit pelet

silinder zeolit A-bentonit (ZAB) dan digunakan sebagai matriks pembawa wangian dengan minyak pati mawar (*Rose damascena* Mill.) sebagai model minyak wangi. Bentonit segar juga boleh menyerap minyak pati mawar dengan kapasitas penjerapan 1.745 g/g bentonit (74.5%). Kesan pengaktifan kimia ke atas zeolit-A menggunakan asid (HCl) 0.1 M dan bes (NaOH) 0.1 M telah dikaji. Pelet tiub ZAB didapati mempunyai kecekapan tinggi penjerapan minyak pati mawar. ZAB4 mempunyai kecekapan tertinggi dan digunakan untuk kajian ujian penjanaaan semula yang telah dijalankan selama 10 kitaran menggunakan HCl dan NaOH dengan kecekapan penjerapan adalah 94.5 dan 75.4%. Komposit ZAB4 yang diaktifkan menggunakan HCl mempunyai jangka hayat yang panjang sehingga lebih daripada 5 minggu dan lebih daripada 10 kitaran penjanaaan semula. Matriks pembawa wangian berasaskan ZAB ini mempunyai potensi besar untuk sistem wangian pembawa lanjutan.

Kata kunci: Minyak pati; pelepasan terkawal; pembawa wangian; penyegar udara; zeolit-A

INTRODUCTION

It has been reported that 20.4% of the population in United States displayed health problems because they were exposed to poor indoor air quality in terms of volatile contaminants, which could cause breathing disorders, mucosal symptoms, migraines, skin disorders, asthma, and nervous disorders (Steinemann 2016). To overcome these problems, essential oils have been considered as an alternative to replace the conventional chemical-based air fresheners. An improvement in the quality of air fresheners with low cost of production can be achieved by adding fixatives and/or using a carrier matrix to increase the long-lasting properties of fragrances (Edris & El-Galeel 2010). For example, rose essential oil is volatile at room temperature and can lose up to 50% of its total mass within 23.5 minutes (Rudolfi, Schedrina & Mindlin 1988). In this sense, natural and synthetic porous materials such as natural zeolite, natural zeolite Micro20, and zeolite X have been reported as fragrance carriers to control the release of the fragrance (Strzemiecka et al. 2012; Tekin & Bac 2016; Tekin et al. 2015).

Zeolites can control the release of volatile components of fragrance when exposed to atmospheric humidity at room temperature (Pan et al. 1997). It is also reported that zeolite types of X or Y can be used as a perfume delivery system in granular detergent. Encapsulation technique is one of effective methods to design controlled release system in order to extend the lifetime of fragrant product (Tekin et al. 2015). Practically, fragrance molecules are bound to the surfaces of fragrance carriers through their functional groups. For instances, and zeolite X (Tekin & Bac 2016; Tekin et al. 2015), natural zeolite Micro20 (Strzemiecka et al. 2012), polybutylcyanoacrylate (Hu et al. 2011), and polymer (Kaur et al. 2018) have been reported as adsorbent materials for the encapsulation of volatile fragrance components. More recently, the use of polysaccharide-based polymers were also shown to form stable complexes with several types of volatile trihalomethanes depending on the components of the biopolymer composites (Guo, Bharadwaj & Wilson 2021).

In this study, zeolite A was synthesized from natural kaolin by the hydrothermal method and was used as a core matrix for the controlled-release of perfume over an

extended releasing period. This strategy widens the field of application of zeolite A for the safe use as a fragrance carrier matrix. The naturally occurring kaolin was obtained from its deposit in Bangka, Belitung island, Indonesia (Samadhi et al. 2011). Thus, this kaolin resource is suitable for production of synthetic zeolite A in long term. Considering that its synthetic powder form is not very effective as a fragrance carrier, zeolite A can be blended with a binder such as bentonite to improve its performance. Bentonite is a montmorillonite-based clay mineral with high surface area, good colloidal characteristics, particle size of less than 1 μm , and high thermal stability, and is known as a good binder because it can aggregate with other mineral particles into a larger collection of aggregate particles.

Generally, bentonite appears as a mineral with the chemical formula being $\text{Al}_2\text{H}_2\text{Na}_2\text{O}_3\text{Si}_4$. Upon blended with zeolite A, SiO_2 and Al_2O_3 from bentonite could migrate to zeolite structure and maintain the crystallinity of the zeolite (Whiting et al. 2016). It is therefore reasonable to blend and form zeolite A into tube pellets with bentonite (20 wt.%) as binder. The use of 20 wt.% bentonite is able to increase matrix strength up to 232% and decrease surface area up to 66% (Charkhi et al. 2011). Usually, in the composite, the binder is considered as an inert compound, and zeolite and bentonite can interact with each other and enhance the interaction between the composite and rose essential oil as a model fragrance. Zeolite A-bentonite (ZAB) composites with different average particle diameter sizes from 4 mm to 10 mm were synthesized and characterized. Effects of chemical activation on zeolite-A using acid (0.1 M HCl) and base (0.1 M NaOH) on fragrance uptake were also studied. These acid or alkali treatment would modify and increase the active site on the surfaces of zeolite A, thus it can adsorb and accommodate higher amount of rose essential oil. In particular, the acid treatment will induce the dealumination process of the surfaces of zeolite A, making it more hydrophobic (Cakicioglu-Ozkan & Ulku 2005). The performance of both acid- and alkali-treated zeolite A as the matrix in ZAB composite and without bentonite were compared to obtain the best matrix to prepare the ZAB composite for fragrance carriers. With all these background, adsorption and desorption experiments for fragrance molecules from rose essential oil (*Rose damascena* Mill), as model fragrance, were also investigated.

EXPERIMENTAL DETAILS

MATERIALS

Natural kaolin was originated from Bangka, Belitung island, Indonesia. Sodium bentonite was purchased from Maju Anugerah Mandiri, Ltd. (Indonesia). Sodium hydroxide (NaOH) (99% analytical reagent grade) and hydrochloric acid (HCl; analytical reagent grade) were purchased from Merck (Germany), and rose essential oil (Rose damascena Mill) was purchased from Lansida Group (Indonesia).

PREPARATION OF ZEOLITE-A FROM NATURAL KAOLIN USING HYDROTHERMAL METHOD

Zeolite A from natural kaolin was prepared by hydrothermal method according to method that reported by Mualim (2019), Rahman et al. (2019), and Kusrini et al. (2020a, 2020b). This method was modified according to the time and temperature of the calcination and zeolite formation is well-known as a zeolitization steps, according to method reported by Kusrini et al. (2020a, 2020b). The calcination was done in a furnace at 750 °C for 3 h. The nucleation process of metakaolin conducted using 3 M NaOH at 60 °C with stirring at 750 rpm for 3 h. For the crystallization process, the temperature of the nucleation was raised to 90 °C whilst stirring over 7 h. The pH of zeolite A slurry is about pH 12, and it was then washed several times with distilled water to reach a final pH between 7.2 and 8.6. The synthetic zeolite A was finally dried at 90-100 °C for 24 h, then it was ground to obtain fine zeolite A powder and stored in a desiccator for further use.

ACTIVATION OF SYNTHETIC ZEOLITE-A WITH ACID (HCl) AND BASE (NaOH)

Zeolite-A was activated using HCl or NaOH solution. Firstly, 20 g of zeolite A was activated using HCl solution (0.1 M, 200 mL). The acidified zeolite A was heated at 60 °C for 2 h under magnetic stirring at 500 rpm. Acid activated zeolite A was oven dried at 90-100 °C for 24 h. The acid-treated zeolite A in ZAB composite was named as ZAB-HCl. The same process was conducted to activate zeolite A using alkaline solution (0.1 M, 200 mL NaOH) to obtain the alkali-treated zeolite A in ZAB composite, which was then called as ZAB-NaOH.

ZAB COMPOSITES

Zeolite A (100 g) was mixed with 20 g of bentonite (20 wt.%) in distilled water with a ratio of 5:1. The mixture of zeolite A and bentonite was stirred to obtain the gel zeolite A-bentonite, followed by pressing into pellets using a mold with a diameter of 4, 7, and 10 mm. The ZAB composites were dried at 90-100 °C for 24 h. The diameter sizes of ZAB tube pellets were either 4, 7, or 10 mm, and they are denoted as ZAB4, ZAB7, and ZAB10, respectively.

THE PERFORMANCE OF ZEOLITE A, BENTONITE, AND ZAB COMPOSITES AS FRAGRANCE CARRIER

Rose essential oil was imbibed in each sample by soaking 5 g for each adsorbent (zeolite A, bentonite, ZAB-HCl, ZAB-NaOH, or ZAB composites with diameter sized of 4, 7, and 10 mm) into 20 g of rose essential oil in liquid form at room temperature at various contact times (1, 5, 7, 9, and 11 h) to obtain the best time needed for the matrix to adsorb the rose essential oil as model fragrance system.

Equation (1) was used to estimate rose oil content in carrier matrix.

$$\text{Adsorption Capacity} = \frac{m_2 - m_1}{m_1} 100\% \quad (1)$$

where m_1 is the initial matrix mass before immersion; and m_2 is matrix mass after immersion.

THE RELEASE OF ROSE ESSENTIAL OIL FROM ZAB COMPOSITES

The release of rose essential oil from ZAB composites were expressed as weight of rose oil per unit time. The ZAB composites after uptake of the rose oil were exposed to the open ambient air at room temperature. After that, 30 mg of ZAB matrix which has released rose essential oil was dissolved in 3 mL *n*-hexane, then it was centrifuged for 30 minutes to obtain the remaining rose essential oil in the ZAB matrix. The release of rose essential oil was analyzed using Gas Chromatography-Mass spectrometry (GC-MS). The initial mass was measured shortly after the adsorption step of rose essential oil into ZAB was completed. The final mass was determined after the encapsulated matrix of rose essential oil was exposed to the air at room temperature for a certain time period (0 to 5 weeks).

The release of rose essential oil fragrance from the ZAB composites was extracted using *n*-hexane. The mixture was centrifuged for 30 min. The filtrate was injected into GC-MS to obtain qualitative results for the remaining components in the ZAB composite. The release rate of rose essential oil from carrier matrix was calculated by using Equation (2).

$$\text{Release rate} = \frac{m_3 - m_2}{i} \quad (2)$$

where m_3 is the mass of encapsulated rose essential oil matrix immediately after encapsulation; m_2 is a mass of encapsulated rose essential oil matrix; and i is the number of weeks that the pellet contacted with the air.

Measurements were conducted from 0 to 5 weeks to observe changes in the fragrance component of the matrix. The release of the essential oil was further analyzed by GC-MS.

REGENERATION OF ZAB4 COMPOSITES

ZAB4 has the highest efficiency and was used for regeneration test studies. For regeneration of ZAB4 composites after being used as a fragrance carrier, the composites were washed with distilled water three times and heated from 150 to 250 °C. The regenerated composite was reused to adsorb a rose essential oil. The adsorption capacity of regenerated ZAB4 composite was determined and calculated according to the Equation (1). A similar method was used for adsorption using the fresh ZAB4 composites as fragrance carriers. The desorption of fragrance oil from the spent ZAB4 composite was conducted by soaking 2 g of ZAB4 composite with 20 g of rose essential oil for 7 h at room temperature in the isolated condition system, which does not allow mass and energy transfer. The regeneration of the ZAB4 composite was carried out 10 times to observe the effect of the regeneration cycle on the adsorption capacity of rose essential oil over multiple cycles of re-use.

CHARACTERIZATIONS

The structure, surface area, functional groups, morphology, and composition of ZAB composites were characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analyses. The crystalline of samples were characterized using an X-ray diffractometer (Shimadzu XRD 700). The functional groups of the samples were evaluated using a FTIR spectrophotometer 8201PC Shimadzu. The morphology and composition of the samples were analyzed by SEM-EDX ZEISS EVO ® MA-10. The surface area was determined by using the Brunauer-Emmett-Teller (BET) model, based on a multipoint adsorption-desorption isotherm of N₂ at 77 K using an ASAP 2020 V4.02 gas sorption analyzer (Micromeritics, US).

Crystallinity of zeolite A was determined according to the Equation (3). The crystallite size of zeolite A was determined using the Scherrer Equation (4).

$$Crystallinity (\%C_{-XRD}) = \frac{\text{Intensity 5 Peaks Most Intense Product}}{\text{Intensity 5 Peaks most intense Standard}} \quad (3)$$

$$D = \frac{K\lambda}{\beta \cos \Theta} \quad (4)$$

where D is average crystal size; K is shape factor (0.92); λ is wavelength (0.154 nm); β is maximum half-peak line distance and FWHM; and Θ is the Bragg's angle (°).

RESULTS AND DISCUSSION

XRD STUDIES

XRD characterization was carried out to determine the crystallite size, composition, and type of crystal structure of ZAB composite. Materials with a crystal phase produce peaks in certain 2θ areas. These peak patterns can be read using Match software. The type of material can be compared with the catalog diffraction peaks and the characterized zeolite-A. The diffractogram of zeolite-A is shown in Figure 1, where the 2θ peaks correspond to the standard peaks of zeolite-A.

In the XRD diffractogram of metakaolin, the characteristic peak traces of natural kaolin at $2\theta = 12.465^\circ$ and $2\theta = 25.015^\circ$ disappeared. This indicates that natural kaolin has transformed into amorphous metakaolin (Mualim 2019). From the results, it can be seen that kaolin from Bangka can be used as a raw material for zeolite A. This is because a Si/Al ratio of natural kaolin is close to 1:1, thus in the activation process of kaolin into metakaolin, the metakaolin produced has transformed into an amorphous phase. According to Equations (3) and (4), the crystallinity of zeolite A is 99.73% with crystallite size of 49.222 nm.

BET CHARACTERIZATION

In this study, zeolite A was produced from natural kaolin by hydrothermal method. To optimize the dealumination process, zeolite A was activated using 0.1 M HCl, thus, it is more hydrophobic (Cakicioglu-Ozkan & Ulku 2005). Other purposes of this acid activation are to enlarge its pore size and to remove potential impurities. Based on the BET characterization, after activation with HCl 0.1 M solution zeolite A was found to have a pore size of 5.64 nm, particle size 2370.9 nm, pore volume 0.0038 cm³/g with surface of 2.531 m²/g. This indicates that temperature of the zeolite formation can be used to enlarge the pore size of zeolite A. Commercial zeolite A has a pore size that ranges from 0.2 to 0.4 nm in general (Chudasama, Sebastian & Jasra 2005). It is noted that the hydrothermal method can generate zeolite A with larger pore size so that it can adsorb volatile fragrance molecules such as rose essential oil. It is known that the molecules in rose essential oil have an average molecular size of 1 nm (Barbosa-Cánovas et al. 2005).

FTIR STUDIES

FTIR spectrum of zeolite A showed absorption bands at 3200 to 3600 cm⁻¹ as the result of stretching vibrations of hydroxyl groups (OH) (Figure 2). The absorption band at 967 cm⁻¹ shows stretching of the asymmetric Si–O–Si band. The absorption peak at 672 cm⁻¹ is assigned to the symmetrical stretching vibration of O–Si–O or O–Al–O. The bands at 466 cm⁻¹ and 651–1572 cm⁻¹ were attributed to the vibration and bending modes of Si–O–Si / Si–O–Al groups and the Si–OH or Al–OH groups, respectively.

The FTIR spectrum of bentonite shows an absorption band at 3624 cm^{-1} that indicates the stretching vibration of Al–OH–Al or Mg–OH–Al, while the broad bands at 3419 cm^{-1} indicates the OH stretching vibration. However, the peak at 1493 cm^{-1} shows the content of organic compounds in bentonite. The IR bands at 987 , 792 and $694\text{--}532\text{ cm}^{-1}$ were assigned to the stretching vibration of Si–O–Si, Si–O–Al and Si–O, and Al–O, respectively. The absorption band at 469 cm^{-1} shows the vibrational band related to Si–O–Si buckling.

SEM CHARACTERIZATION

Figure 3(a)-3(c) shows the SEM images of zeolite A, the fresh ZAB composite, and ZAB composite after adsorption with fragrance oil. The type of zeolites can be distinguished based on their morphology (Muriithi, Petrik & Doucetc 2020). In the present study, SEM image of Na-zeolite A indicated a crystalline morphology, which is characterized by cubic shaped crystal particles with sharp edges (Figure 3(a)), indicating that Na-zeolite A was formed. Meanwhile, the image of bentonite is characterized as a nest-like morphology, the formation of a composite with zeolite A results in the formation of ZAB composite with a hybrid morphology between zeolite A and bentonite (Figure 3(b)).

The effect of encapsulation on the particle surface is very clear where after the matrix was encapsulated with rose essential oil, particles of zeolite A and bentonite stick together and are coated with rose essential oil (Figure 3(c)). The side length of zeolite-A particle is $1.54\text{ }\mu\text{m}$. The diameter of the bentonite particle according to the SEM results varies from 0.6 to $2\text{ }\mu\text{m}$. The use of bentonite in the form of pellets is aimed to enhance the hardness of the ZAB composite and also to increase the surface area of composite. Thus, they have more active sites that are more readily available that can be bind to the fragrance oil.

The EDX data also showed the presences of other element including Fe as listed in Table 1. The Si/Al ratio of zeolite A has nearly unitary, and consists of a three-dimensional framework (Kusrini et al. 2024). The Si/Al ratio of zeolite A is 1.007 . This ratio is suitable with the ratio of Si/Al that reported for Na-zeolite A (1.097) (Kusrini et al. 2020a), and it is recommended range of $1.0 - 1.7$ for Na-zeolite A (Muriithi, Petrik & Doucetc 2020).

After the formation, ZAB composite showed the Si/Al ratio of 1.244 , and after encapsulation of rose essential oil fragrance the Si/Al ratio becomes 1.517 . The higher Si/Al ratio indicated that the ZAB composite after adsorption of fragrance model is more acidic than zeolite A.

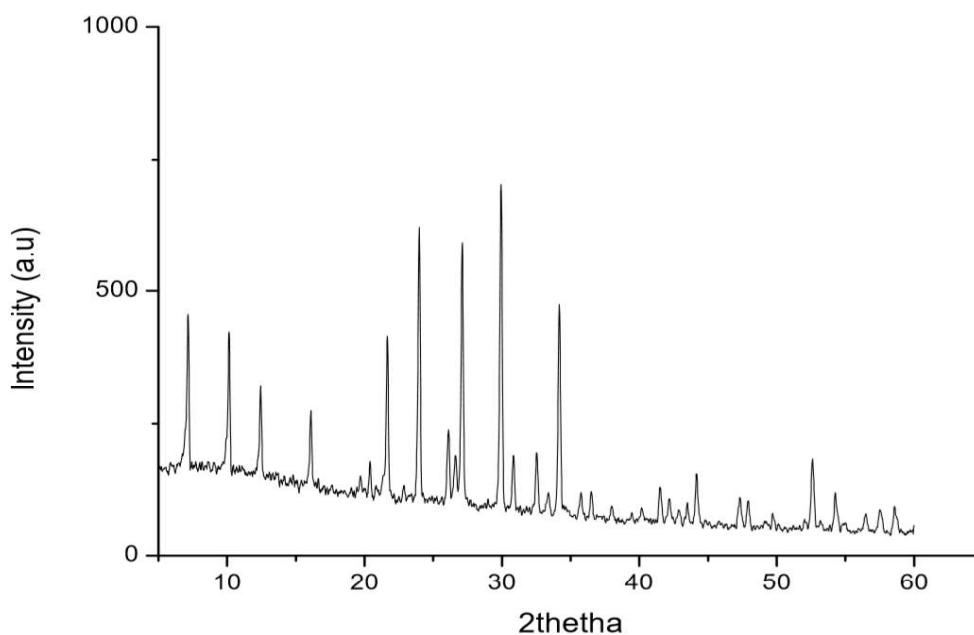


FIGURE 1. XRD pattern of synthetic zeolite A

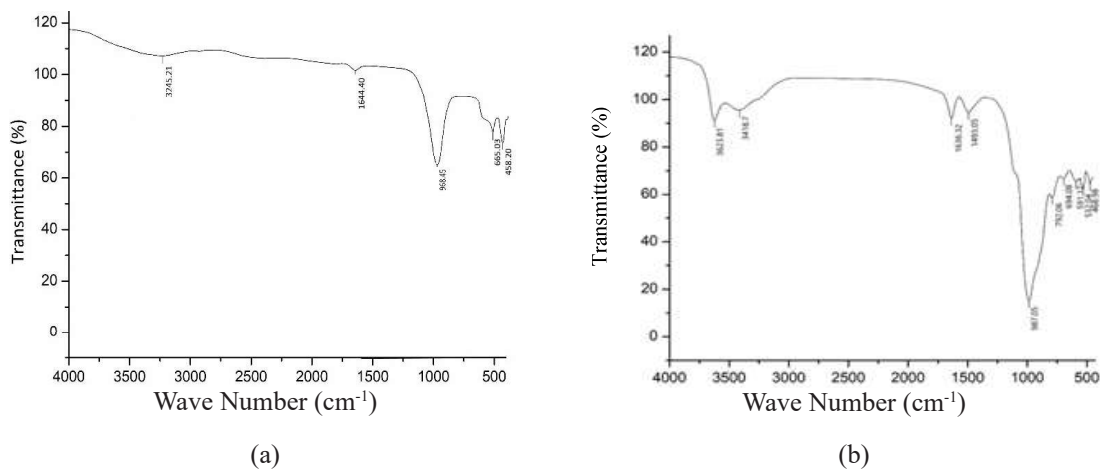


FIGURE 2. FTIR Spectrum of the Synthesized Zeolite A(a) (adapted from Kusrini et al. 2020a), and bentonite (b)

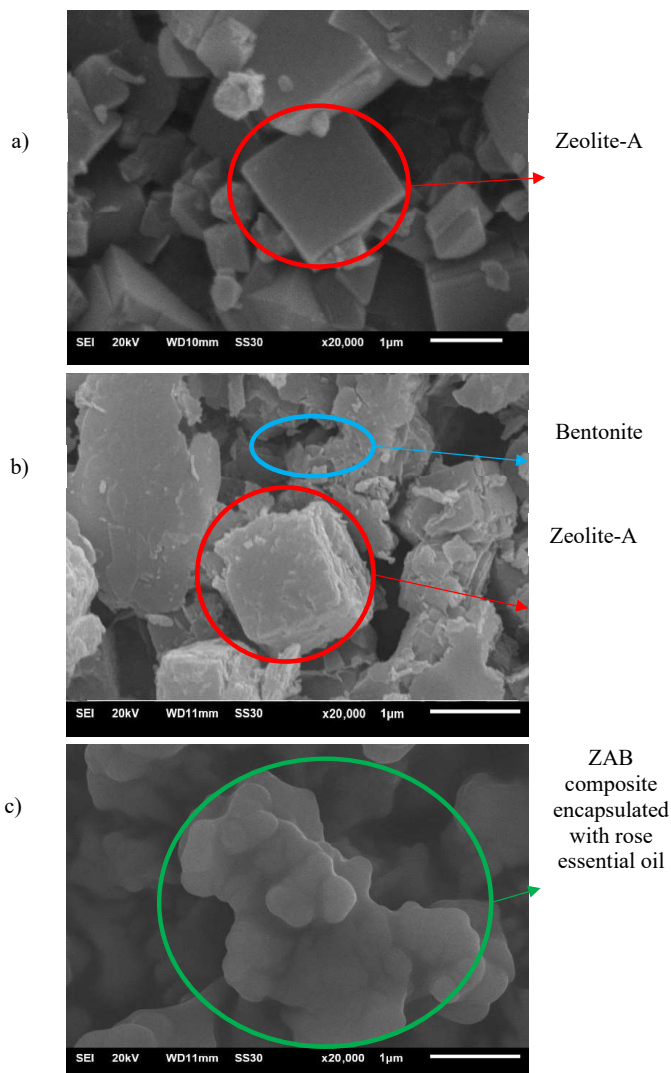


FIGURE 3. SEM images of adsorbent materials: a) zeolite-A, b) ZAB composite, c) ZAB composite after adsorption with rose essential oil

TABLE 1. Comparison the EDX elemental analysis of zeolite-A, fresh ZAB composite, and ZAB composite after use to adsorb of rose essential oil

Sample	wt%						
	C	O	Na	Si	Al	Fe	Si/Al Ratio
Zeolite-A	-	39.49	9.21	13.55	13.46	1.16	1.007
ZAB composite	9.14	33.5	6.02	17.36	13.95	1.07	1.244
ZAB encapsulated rose essential oil	64.50	19.47	1.44	3.14	2.07	-	1.517

ADSORPTION EFFICIENCY OF ZAB MATRIX

The performance of both acid- and alkali-treated zeolite A as the matrix in ZAB composite and without bentonite was compared to obtain the best matrix to prepare the ZAB composite. Zeolite-A without chemical activation has an adsorption capacity of rose essential oil of 86% with an optimum immersion time of 7 h. Whereas, a pristine bentonite has an adsorption capacity of 75% with an optimum immersion time of 5 h (Figure 4). Chemical activation changes the hydrophobic properties and the pore size of zeolite-A. The treatment with HCl increases the acidity of the matrix so that the matrix is hydrophobic and can interact more effectively with rose essential oil. The molecules that make up rose essential oil are non-polar and are more easily adsorbed by zeolite-A which is activated using acid. We assume that protonation would make the framework of zeolite A is more polar or in a charged state, unless the doping with HCl neutralized negatively charged aluminate centres. The amount of essential oil adsorbed along with the adsorption efficiency of the ZAB matrix is shown in Table 2. The highest efficiency (80.7%) for pellet with size of 4 mm. The adsorption capacity decreases with the increasing size of matrix pellets, as the surface area is reduced.

The ZAB matrix with a diameter of 0.4 cm was chosen as a matrix for further tests, especially its potential activation and ability to control the release of rose essential oil. Chemical activation changed the hydrophobic nature and change the pore size of zeolite A. Effect of acid and alkali activation of zeolite A on using alkaline and acid adsorption of rose essential oil is summarized in Table 3. Zeolite A was activated using HCl 0.1 M, and has a high efficiency for adsorption of rose essential oil (94.5%) after an immersion time of 7 h. Zeolite A activated by NaOH (0.1 M) has an efficiency of 75.4% at the same operating conditions. Activation using 0.1 M HCl increased the adsorption capacity of rose essential oil by zeolite A from 1.81 to 1.898 g/g matrix. While activation using 0.1 M NaOH decreased the adsorption capacity of rose essential oil from 1.81 to 1.52 g/g matrix.

The HCl treatment increases the acidity of the matrix so that the ZAB-HCl matrix was more hydrophobic and could interact with rose essential oil more effectively. Activation of the zeolite enlarged the pore size and minimized the effect of the addition of bentonite on the adsorption ability of rose essential oil by the ZAB matrix. The hydrophilic and polar nature of zeolite is an obstacle in the adsorption of polar organic molecules. Activation can affect the hydrophilic and hydrophobic nature of the zeolite. Geraniol, phenylethyl alcohol, linalool, citral, citronellol, and eugenol of the fragrance have hydroxyl groups. The OH groups will interact with the binding sites of the matrix structure, and can undergo dissociation, so that it may play an important role in the development of a negative surface charge depending on the pH of the medium. This surface charge or ionic charge can form electrostatic interactions with the site of the extra framework cation, namely ion Na^+ , which occur in the structure of zeolite A.

Zeolite A before activation can adsorb rose essential oil with an adsorption capacity of 1.86 g/g (efficiency of 86.4%) with an optimum immersion time of 7 h. Meanwhile, bentonite was able to adsorb rose essential oil 1.745 g/g (74.5%) with an optimum immersion time of 5 h. The addition of bentonite as a binder can increase the robustness of the matrix but reduce its adsorption ability. The ZAB matrix surface is formed due to the Si-O-Si bond on Si-tetrahedral sites. The charge on this surface is the result of isomorphic substitution of Si atoms by other cations. Other adsorption sites are on 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. ZAB4-HCl composite still contained the geraniol, phenylethyl alcohol, linalool, citral, citronellol and eugenol components in the fifth weeks with release rates (g/week) of 0.04, 0.07, 0.037, 0.021, 0.026, and 0.011, respectively. The constituent molecules of rose essential oil are non-polar so that they are more readily adsorbed by acid activated ZAB4-HCl composite.

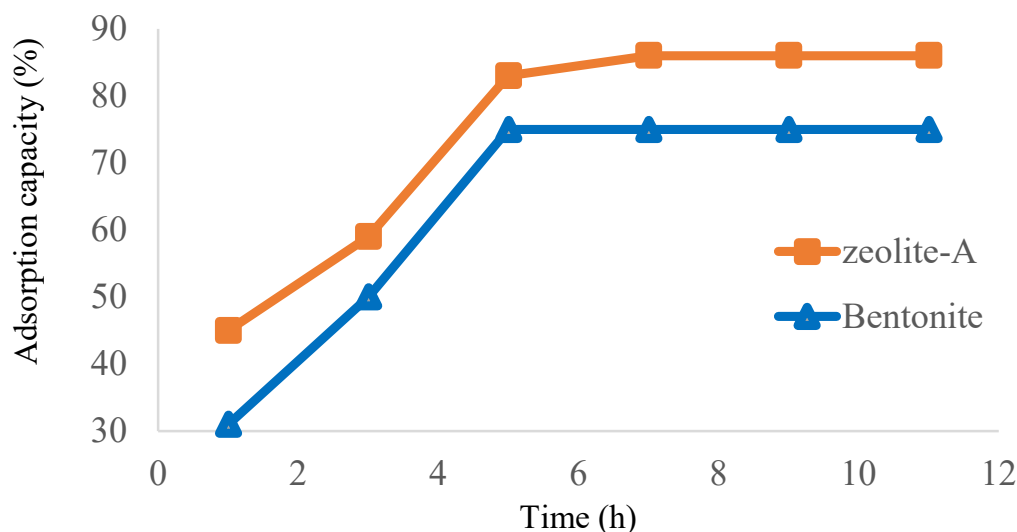


FIGURE 4. Comparison of the performance of bentonite and zeolite-A as fragrance carrier systems

TABLE 2. The effect of matrix size of ZAB for zeolite-A without chemical activation on adsorption of rose essential oil

Pellet size (mm)	Immersion time (h)	Rose oil adsorbed (g/g matrix)	Efficiency (%)
4	7	1.807	80.70
7	7	1.6245	75.20
10	7	1.411	41.10

TABLE 3. Effect of activation zeolite-A using alkaline and acid solution on adsorption of rose essential oil by ZAB4 composite

Solution	Immersion time (h)	Mass (g)		Rose essential oil adsorbed (g/g matrix)	Efficiency (%)
		Before immersion	After immersion		
HCl 0.1 M	7	2	3.903	1.8975	94.54
NaOH 0.1 M	7	2	3.502	1.516	75.38
-	7	2	3.614	1.807	80.70

SLOW RELEASE OF ROSE ESSENTIAL OIL FROM ZAB4 TUBE PELLET COMPOSITE

Water vapor can be adsorbed and replace the position of the perfume that is absorbed in the pore matrix effectively as much as 95-98%. The slow release measurement was carried out by gravimetric analysis and GC-MS characterization. The results of controlled release of aroma of rose essential oil using GC-MS resulted in a decrease in the levels of geraniol compounds, phenylethyl alcohol, linalool, citral, citronellol and eugenol from 0-5 weeks. Decreased levels of the constituent compounds of rose essential oils in the matrix are shown in Figure

5. The results indicated that all compounds evaporate at room temperature and still have a small portion that remains in the matrix after 5 weeks. This shows that ZAB4-HCl matrix was able to hold the release of rose essential oil for more than 5 weeks, equivalent to most types of commercial air freshener. Each compound has an evaporation rate as shown in Table 4.

REGENERATION OF ZAB4 MATRIX

Matrix regeneration at 150, 200, and 250 °C is completed in 4.5, 2, and 2 h, respectively. The adsorption of rose

essential oil by a regenerated matrix ZAB4-150 and ZAB4-200 is 1.95 g/g matrix (94.7%) and 1.94 g/g matrix (94.4%), respectively. Both have very similar adsorption capabilities, but the regeneration rate of 200 °C is much faster. The adsorption ability of rose essential oil by a regenerated matrix at 250 °C is 1.83 g/g matrix (82.8%). This decrease is caused by the damage of matrix structure during heating at 250 °C. It is assumed that a chemical reaction happens at the elevated temperature since one would expect that the evaporation rate would increase with time.

The adsorption ability decreased along with the number of the regeneration cycles. However, this decrease is not significant so the matrix still has a good adsorption ability of up to 10 cycles of regeneration. The effect of the matrix regeneration cycle on the adsorption of rose essential oil is shown in Figure 6. The results show that zeolite A and bentonite can be used to produce a sustainable fragrance matrix carrier.

FT-IR characterization results of regenerated ZAB4 tube pellet composite show that composite has functional groups similar to the initial matrix (before adsorption of rose essential oil). The FTIR band at 3238 cm^{-1} is the result of stretching vibrations of the OH group. The band at 984 cm^{-1} shows stretching of the symmetric Si–O–Si group. The band at 672 cm^{-1} is a symmetric stretching vibration of O–Si–O or O–Al–O bond. The vibrational band at 462 cm^{-1} relates to bending of the Si–O–Si / Si–O–Al groups. The peak at 1641 cm^{-1} arises due to bending vibration of the Si–OH or the Al–OH groups from zeolite A.

Characterization using GC-MS was also carried out to observe the rose essential oil compounds remaining in the regenerated ZAB4 tube pellet composite. Based on GC-MS characterization, peaks which show geraniol levels, phenylethyl alcohol, linalool, citral, citronellol, and eugenol have not reappeared because almost all the compounds have evaporated in the regeneration process at 200 °C.

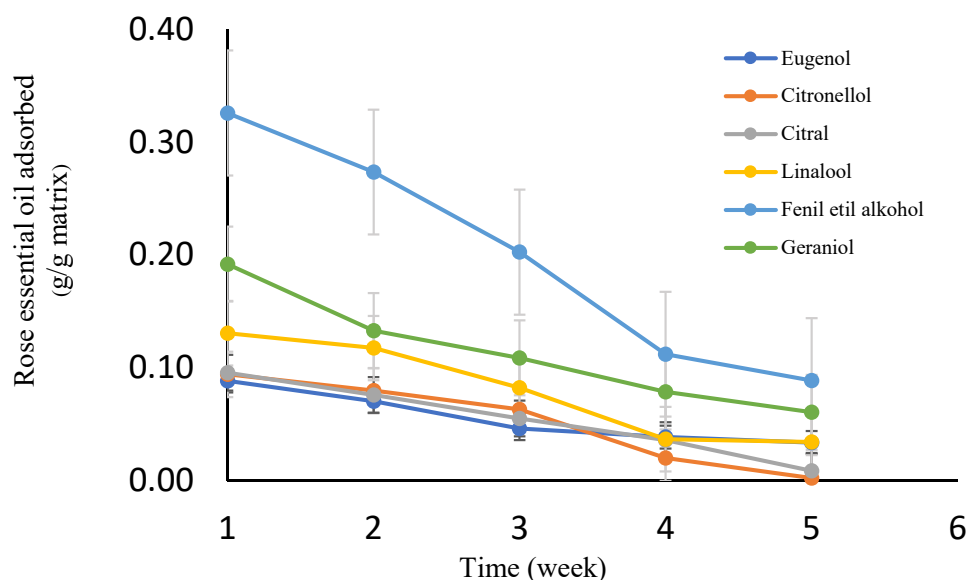


FIGURE 5. Decreased levels of the component compounds of rose essential oils in the ZAB4-HCl tube pellet composite is more than 5 weeks

TABLE 4. Evaporation rate of rose essential oil from the ZAB4-HCl tube pellet composite

Component in rose essential oil	Molecular weight (g/mol)	Evaporation rate (g/week)
Phenyl ethyl alcohol	122.16	0.071597
Citral	152.24	0.021045
Geraniol	154.25	0.043717
Linalool	154.25	0.037353
Citronellol	156.27	0.026903
Eugenol	164.2	0.011065

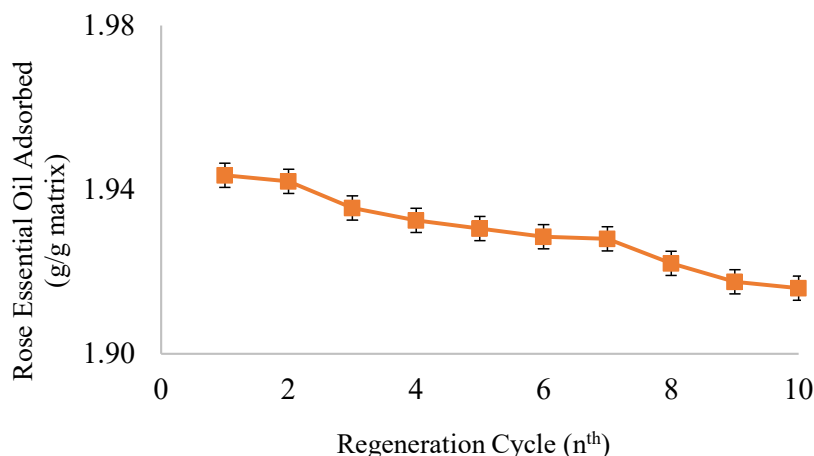


FIGURE 6. Effect of regeneration cycle (nth) of ZAB4 composite on adsorption of rose essential oil

CONCLUSION

Hydrothermal synthesis of zeolite A formed cubic shaped particles with a size of $\sim 1.7 \mu\text{m}$ and a pore size of 5.6 nm which allow adsorption of essential oil of rose. The smaller the size of the ZAB4 tube pellets matrix, the better the ability to adsorb rose essential oil. The amount of rose essential oil adsorbed by a ZAB tube pellet matrix with 0.4 cm in diameter is 1.81 g/g matrix (80.7%). Activation of zeolite A with 0.1 M HCl can increase the ability of adsorption of rose essential oil by the matrix to 1.898 g/g matrix (94.5%). The encapsulation of rose essential oil molecules in the ZAB4 pellet matrix is able to maintain the release profile of the volatile compounds into the air for more than 5 weeks. The optimum regeneration conditions of the ZAB4 pellet matrix were obtained at 200 °C for 2 h and the tube pellet matrix can be reused up to 10-cycles of regeneration.

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