



Research Article

Enhanced Adsorption Capacity of Zeolite through Intercalation with Calcium Carbonate of *Batissa Violacea Celebensis* Shell Waste for Removing Detergent Waste

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Article info	Abstract
Received: June, 2024 Received in revised: July, 2024 Accepted: August, 2024 Available online: August, 2024	<p>Zeolites possess pores or layers that can be filled with other molecules, thereby enhancing their acidity, thermal capacity, and surface tension. This, in turn, improves their efficacy in adsorbing organic waste. The main objective of this study is to investigate the material characteristics of ZAA-CaCO₃ and its performance in adsorbing detergent waste. The research encompasses several stages, including the preparation of the shell of <i>Biavalvia violacea celebensis</i> waste, natural zeolite preparation, the intercalation process, material characterization, and measurement of adsorption capacity. XRD diffraction analysis revealed that the highest intensity of CaCO₃ was observed at angles of 2θ: 29.4°, 37.4°, and 51.9°. The results of infrared spectroscopy analysis indicated that the chemical activation spectra of ZAA and ZAA-CaCO₃ with a 300°C calcination were similar, except for absorptions at wave numbers 1386 cm⁻¹, 1417 cm⁻¹, 1635 cm⁻¹, 1997 cm⁻¹, and 2359 cm⁻¹, which indicated the presence of carbonate groups of calcium carbonate. Furthermore, morphological analysis using SEM revealed a significant difference between Zeolite Nature, Zeolite Natural Active, and ZAA-CaCO₃. The highest percentage of adsorption was observed with ZAA-CaCO₃ material at a ratio of 2:1 and a contact time of 120 minutes, resulting in an adsorption capacity of 89.67%.</p>

Copyright © 2024 *Int. J. Act. Mat.* **Keywords:** Zeolite, ZAA-CaCO₃, Adsorption, XRD, SEM

INTRODUCTION

The process of globalization continues to expand every year, but it also brings about negative consequences such as the generation of waste. This waste, particularly detergent waste from the laundry industry, is a cause for concern due to its harmful chemical compounds that are carcinogenic. If not properly treated, this waste poses a threat to ecological sustainability (Brough, Zhao, & Duong van Hoa, 2024; Saravanan et al., 2024). To overcome the problem, one possible solution is to use adsorption techniques. Adsorption is a physical phenomenon where gas or liquid molecules come into contact with a solid surface, causing some of the molecules to condense onto the surface of the solid (Vannier et al., 2024; Zhang et al., 2024).

Waste treatment can be improved through the use of the adsorption technique, which involves a variety of adsorbents. This method is considered advantageous due to its high effectiveness, large adsorption capacity, and lower operational cost (Han et al., 2025; Kusdarto, 2008; Wu et al., 2024). One particular adsorbent that shows promise is zeolite. Data from the Center of Mineral and Coal Technology Development (PPTNB) reveals that the mining of natural zeolite in Indonesia has been increasing, with 60 million tons produced in 2003. Furthermore, the Center for Geological Resources (PSDG) reported in 2015 that there are over 400 million tons of zeolite in Indonesia, spread across 20 potential zeolite sites (Kusdarto, 2008). Among these sites, the districts of Konawe and North Konawe in

Southeast Sulawesi are known for their zeolite potential.

Several studies have been conducted on the use of zeolite to degrade organic waste. However, most of these studies have focused on textile waste and have not explored the degradation of detergent waste. Fatimah & Wijaya, (2005) was investigated the application of zeolite/TiO₂ for degrading textile industrial waste. Another study by Qin et al. (2015) [4] examined the use of zeolites to remove water ions in water. Liu et al., (2013) used zeolite to prepare CNT/Ca-zeolite in order to increase its deionization capacity, as well as in several other studies.

Previous studies have not explored the connection between p-zeolites and calcium carbonate, specifically in their effectiveness for treating waste. Moreover, there is a lack of research on the use of zeolite to reduce detergent waste. Zeolite offers more advantages compared to other adsorbents. One particular zeolite has the ability to separate molecules based on their polarity, allowing only one type of molecule to escape while others are trapped. This selectivity factor is absent in other solid adsorbents. Additionally, zeolites have a layered structure, which can enhance their adsorption capacity when additional materials, such as calcium carbonate from shells, are added to the layers. The shells of *Bivalvia violacea celebensis*, a waste commonly found in river banks in Southeast Sulawesi, contain a high level of CaCO₃, ranging from 95-98% (Suarjowirayatno & Tamtama, 2018).

The main objective of this study is to examine the properties and efficiency of zeolite material combined with calcium carbonate (CaCO₃) derived from the shell of *Biavalvia violacea celebensis* (ZAA-CaCO₃) for the adsorption of detergent waste.

MATERIALS AND METHODS

Materials

The materials utilized in this study include the shell of *B. violacea celebensis*, natural zeolite, 1M HCl, 0.1M blue methylene, chloroform, and aquadest. The research also employed various equipment such as glass tools, a jaw crusher, a disk mill, a pulverizer, an oven, a furnace, a UV-Vis spectrophotometer, X-ray Powder Diffraction (XRD), Fourier-Transform Infrared Spectroscopy

(FTIR), and a Scanning Electron Microscope (SEM).

Bivalvia Shell Preparation

There are several stages involved in preparing Bivalvia shells. The first stage is a preliminary treatment, which involves washing the shells and drying them at a temperature of 105°C. The next step is the smoothing process, which utilizes tools such as the Jaw Crusher, Disk Mill, and Pulverizer. The Jaw Crusher is used to achieve a smooth sample size of less than 5 mm. Afterwards, the sample is further refined to a size of less than 3 mm using the Disk Mill, and finally transformed into a 200 mesh powder using the Pulverizer.

Natural Zeolite Preparation

Natural zeolite (ZA) was processed into granules measuring approximately 1 cm in diameter. Two methods were used to activate the zeolite granules: chemical activation and thermal activation (through heating). For the chemical method, the zeolite was activated by immersing it in a 1 M HCl solution for 120 minutes. Afterwards, it was filtered and rinsed with distilled water. The ZA sample was then subjected to a 3-hour heating process at 100°C. In addition, thermal activation of ZA was performed by calcining the zeolite at 300°C for 3 hours. The Zeolite Natural Active (ZAA) sample was characterized using SEM, XRD, and FTIR techniques.

Intercalation Using Calcium Carbonate (CaCO₃)

The Zeolite Natural Active (ZAA) and shells of *B. violacea celebensis* were combined in ratios of 1:2, 1:1, and 2:1 in order to evaluate the effect of increasing calcium carbonate material from the shell *B. violacea celebensis* on the adsorption capacity of zeolite. Each sample of Zeolite Natural Active (ZAA) and shell *B. violacea celebensis* was placed in a 50 mL beaker and treated with 20 mL of 0.1 M HCl. The mixture was stirred for 4 hours and then filtered. The resulting filtrate precipitate was washed with distilled water until it reached a neutral pH, and then dried in an oven at 100°C for 2 hours. The samples were further characterized using SEM, XRD, and FTIR.

Adsorption Capacity

The adsorption capacity test was performed with two reviews, namely the effect of contact time and variation of concentration of Sodium dodecyl sulfate (SDS). The test to investigate the influence of contact time utilized 25 mL of SDS degradation solution with an initial concentration of 0.5 mg/L. The duration of the test ranged from 30 to 180 minutes in 30-minute intervals. Additionally, concentration variations ranging from 0.2 to 0.8 mg/L were tested during the optimal test duration. Prior to measurement using UV-Vis Spectrophotometers, the SDS degradation solutions underwent extraction with chloroform and methylene blue. Following extraction, the solutions were analyzed to determine the concentration of degraded waste (Ct) (Equation 1), the percentage of degradation (%), the adsorbate mass (mg) (Equation 2), and the adsorbate mass absorbed per unit of adsorbent mass (qe) (Equation 3). These parameters were determined using the calibration curve equation $y = ax + b$, where x represents Ct.

$$(Ct) = (y-b)/a \quad (1)$$

$$m_{adsorbat} = (Co - Ct) \times V_{compound} \quad (2)$$

$$(qe) = (Co-Ct)V/m \quad (3)$$

RESULTS AND DISCUSSION

Natural Active Zeolite Products (ZAA) Intercalated with CaCO_3 Shells *B.violacea celebensis* (ZAA- CaCO_3)

The ZAA- CaCO_3 product is obtained through the intercalation method, which involves inserting a guest species (ions, atoms, or molecules) into the interlayer space of a solid compound without causing any damage to its structure (Liu et al., 2013; Tauk et al., 2024).



(a)



(b)

Figure 1. (a) ZAA- CaCO_3 (b) Natural Zeolite (NZ).

In this case, calcium carbonate serves as the intercalant (the molecule being inserted), while zeolite acts as the intercalated (the molecule that has entered). The intercalation of CaCO_3 into ZAA leads to an increase in surface area and surface acidity, thereby enhancing its adsorption capacity for degrading detergent waste. The synthesis of the ZAA- CaCO_3 product is illustrated in Figures 1.

Characterization of ZAA- CaCO_3

Analysis of Diffraction Patterns Using XRD

The X-ray diffraction analysis result, represented as a diffractogram, is displayed in Figure 2. The diffractogram indicates that the highest intensity of CaCO_3 occurs at angles of 2θ : 29.4° , 37.4° , and 51.9° . These peaks align with the characteristic peaks of calcium carbonate, as previously reported by Qin, Wang, & Ma, (2010).

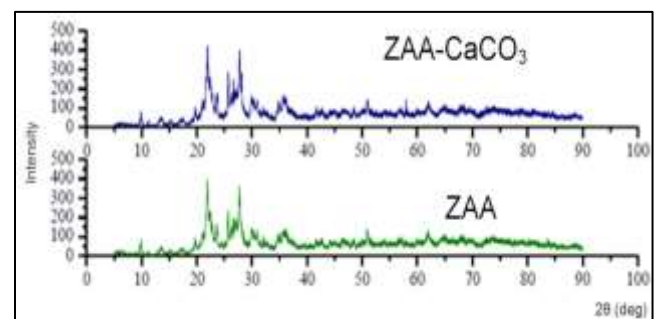


Figure 2. Diffractogram of ZAA- CaCO_3 and ZAA (Calcination 300°C)

Other peaks that indicate the presence of zeolite can be observed at the following diffraction angles: $2\theta = 6.44^\circ$, 9.82° , 13.42° , 22.32° , 23.57° , 25.65° , 26.27° , and 27.69° .

These peaks can be identified as characteristic zeolite peaks (Liu et al., 2013; Slavova, Slavov, Terziev, Mladenova, & Abrashev, 2024).

Functional Groups Analysis Using FTIR

The results of the analysis using infrared spectroscopy can only provide information about the absorption of functional groups. Therefore, in general, the spectra of ZAA-CaCO₃ chemical activation and ZAA-CaCO₃ with 300°C calcination are almost the same.

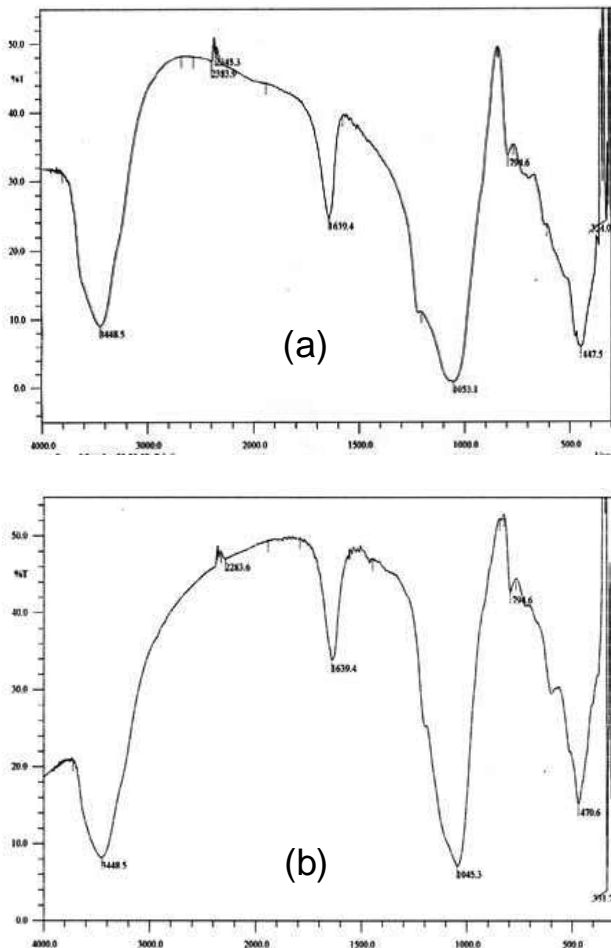


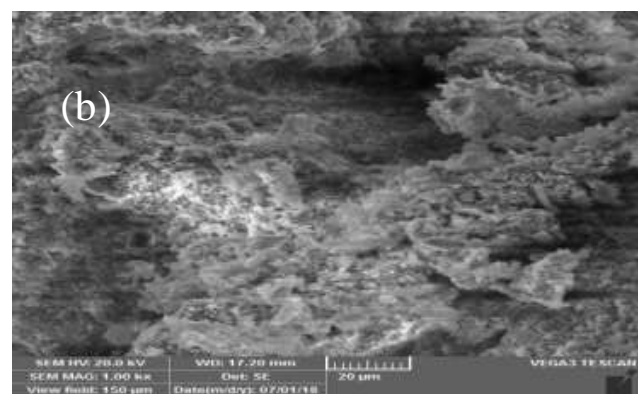
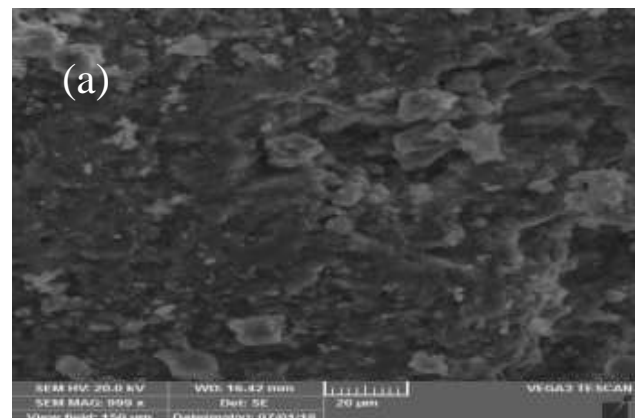
Figure 3. FTIR spectra of chemical activation ZAA-CaCO₃ and ZAA-CaCO₃ with 300°C calcination.

After calcination in natural zeolites, the absorption of functional groups occurs at 3436 cm⁻¹, indicating the presence of the H₂O-OH strain group and confirming that the zeolite has been dehydrated due to calcination. The absorption at wave number 1639.4 cm⁻¹ indicates the presence of buckling OH functional groups. At 1045.5 cm⁻¹, there are strains of O-Si-O and O-Al-O. In addition, there is absorption at wave numbers 1386 cm⁻¹, 1417 cm⁻¹, 1635 cm⁻¹,

1997 cm⁻¹, and 2359 cm⁻¹, which indicates the presence of carbonate groups (CO₃²⁻). The characterization of functional groups in ZAA-CaCO₃ chemical activation and ZAA-CaCO₃ with 300°C calcination can be seen in Figure 3.

Morphological analysis using SEM.

Figure 4 shows the SEM data for all four samples. Figure (a) displays the SEM result of natural zeolite (ZA) before activation. It is evident that the morphology of the zeolite is not clearly visible due to the presence of impurity substances attached to the surface of the zeolite. Additionally, there are dihydrated H₂O molecules present on the natural zeolite (ZA). In Figure (b), the activated zeolite (ZAA) is shown, revealing the presence of pores or layers. Activation opens up these pores and removes impurities, thereby increasing the specific surface area and the acidity and alkalinity of the adsorbent (Liu et al., 2013; Slavova et al., 2024). Figures (c) and (d) depict chemically activated ZAA-CaCO₃ and ZAA-CaCO₃ with 300°C calcination, respectively. Both images clearly show the porous surface of the zeolite, with the presence of white spheres suspected to be intercalated calcium carbonate.



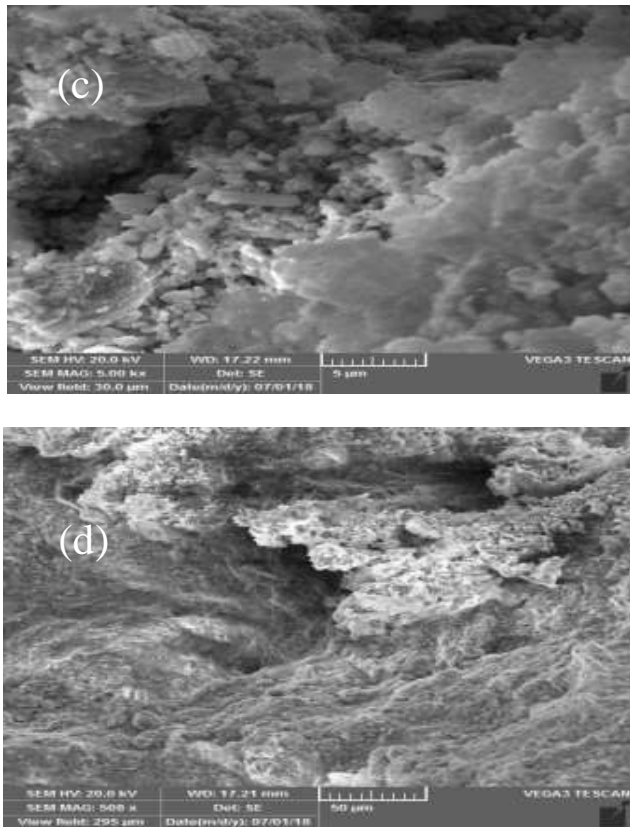


Figure 4. SEM (a) Natural Zeolite (ZA), (b) ZAA, (c) ZAA-CaCO₃ chemical activation (d) ZAA-CaCO₃ with 300°C calcination.

Adsorption Capacity

a. Effect of contact time.

The optimum period for degrading SDS was determined based on the relationship between the degradation period and the residual SDS adsorbency.

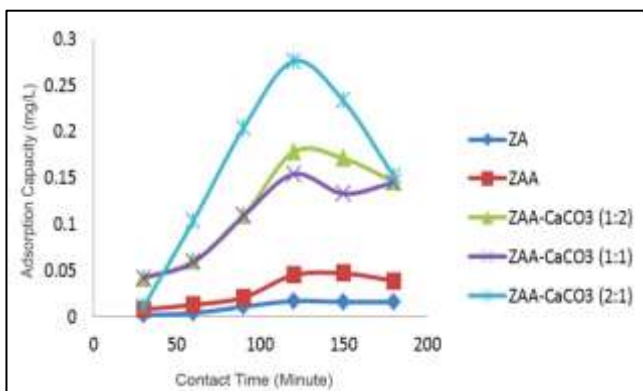


Figure 6. Graph of effect of contact period on adsorption capacity of SDS solution (mg/L)

The optimum period is defined as the period that results in the lowest residual SDS concentration, or can be determined by

identifying the highest percentage of degraded SDS. The analysis of the results indicates that the degradation time of 120 minutes is the optimum period for degrading SDS (Figure 6).

The optimum period for optimal and efficient degradation of the detergent is determined to be 120 minutes, based on the study's result. However, at 150 and 180 minutes, there is a decrease in the adsorption percentage. This decrease is likely because the surface of the adsorbent becomes saturated or reaches equilibrium. While a longer contact period between the adsorbent and the adsorbate will result in more adsorbate being adsorbed, there is a maximum amount that can be achieved within a certain period. This is because the adsorbent becomes unable to adsorb more adsorbate once the surface is saturated, leading to a reduction in the adsorption rate (Ruíz-Baltazar, 2024; Slavova et al., 2024; Zhang et al., 2024).

b. Effect of Detergent Concentration.

The data showed (Figure 7) that there was an increase of adsorption capacity up to concentration of 0.7 mg/L. However, there was a decrease in adsorption capacity at a concentration of 0.8 mg/L. This shows that at concentrations of 0.8 mg/L the active adsorbent sites have been saturated.

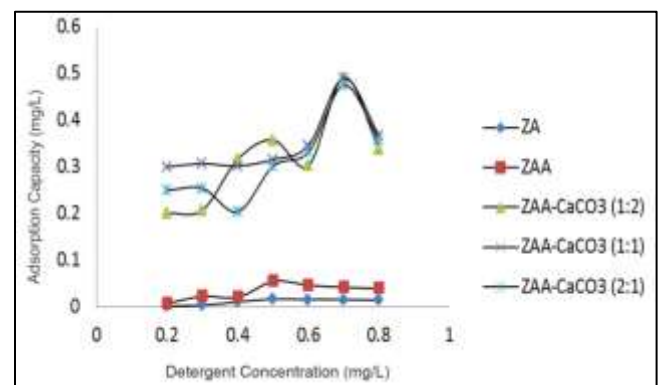


Figure 7. Graph of detergent concentration effect (mg/L) on the adsorption capacity of SDS solution (mg/L)

Langmuir adsorption theory states that on the surface of the adsorbent (ZAA: CaCO₃) there is an active site which is proportional to the area of the adsorbent surface. In the case of active sites not saturated yet, then the increase in adsorbance will increase linearly with the amount of adsorbed adsorbant. If the site is actively saturated, then the concentration of adsorbant will not increase (Ezzati, Ezzati, & Azizi, 2024; Lv

et al., 2024; Singh, Hakimabadi, Van Geel, Carey, & Pham, 2024; Yu, Zhou, Guo, Cheng, & Hu, 2008).

CONCLUSION

The characterization of ZAA-CaCO₃ material by employing SEM, FTIR and XRD shows the difference of zeolite before and after activation and after intercalation with calcium carbonate of Pokea shell (*Bivilia*). The enclosure of CaCO₃ into ZAA resulted in increased surface area and surface acidity which influence towards increase its adsorption capacity in degradation waste detergent. The ZAA-CaCO₃ material exhibits a sufficiently good adsorption performance in degrading the detergent. The highest degradation percentage was shown at optimum contact period of 120 minutes on ZAA-CaCO₃ material within 2: 1 ratio of 89.67%.

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