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Adsorptive Distillation of Bioethanol from Cherry Fruit and Pineapple Peel Using Mg/Al-Hydrotalcite for Ethanol Enrichment

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Abstract. Bioethanol production from fruit biomass waste is a promising and sustainable approach to addressing both energy crises and environmental concerns. This study aims to evaluate the characterization of Mg/Al-hydrotalcite as an adsorbent, determine the optimum adsorption time and adsorbent mass for enhancing bioethanol concentration, and assess the physical properties of the resulting bioethanol. Mg/Al-hydrotalcite was synthesized using the coprecipitation method and characterized. The XRD analysis showed three major diffraction peaks at 2θ = 11.55°, 23.36°, and 34.89°, which are consistent with the standard diffractogram pattern of Mg/Al-hydrotalcite (JCPDS No. 89-0460). FTIR spectra confirmed the presence of M–O bonds, hydroxyl groups, and interlayer carbonate anions (CO_3^{2-}), indicating the successful formation of Mg/Al-hydrotalcite. The adsorption distillation process was carried out by varying the adsorption time (1, 3, and 4 hours) using 1 gram of adsorbent. In a separate experiment, adsorbent mass (1, 2, and 3 grams) was varied while maintaining a fixed adsorption time of 4 hours. Gas Chromatography analysis showed that the optimum adsorption time was 4 hours, yielding an ethanol concentration of 19.03%. The optimum adsorbent mass was found to be 3 grams, which increased the ethanol concentration to 33.71%.

Keywords : Bioethanol, adsorptive distillation, layer double hydroxide (LDH), cherry fruit, pineapple peel

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Introduction

Indonesia's natural resources have significant potential to be processed into high-value alternative fuels such as biodiesel and bioethanol, offering a viable solution to dwindling fossil fuel reserves. Unfortunately, these primary resources, such as agricultural products, generally compete with food crops, creating a dilemma. Fruit waste is more promising because it does not compete with food consumption. Various carbohydrate-rich agricultural products and organic waste—such as sweet potatoes, cassava, corn, banana peels, durian peels, cherries, and pineapple peels—can serve as raw materials for bioethanol production. Among these materials, cherries and pineapple peels [1] are particularly promising due to their high carbohydrate and glucose content. Pineapples have significant global importance and are among the most widely consumed fruits worldwide [2]. Pineapples rank third among tropical fruits in terms of global production [3]. Cherries contain 0.918 g/mL fructose, 0.661 g/mL glucose, and 0.351 g/mL sucrose, along with 7.55 g carbohydrates per 100 g of fruit [4]. In comparison, pineapple skin consists of 81.72% water, 20.87% crude fiber, 17.53% carbohydrates, 4.41% protein, and 13.65% reducing sugars [5]. This presents an opportunity not only to reduce waste but also to extract valuable resources for various applications [6].

Bioethanol, the fermented product, typically contains a mixture of alcohols with carbon chains ranging from C1 to C5 [7]. The fermentation process generally involves Saccharomyces cerevisiae, a microorganism capable of converting glucose into ethanol. A drawback of bioethanol produced from fruit waste is its relatively lower concentration compared to primary agricultural products. To obtain high-purity ethanol, conventional distillation is typically used. However, this method requires significant energy and is less economical. A more energy-efficient alternative is adsorption distillation—a combination of distillation and adsorption—where a porous medium is used to absorb water from the ethanol mixture. Adding an adsorbent can significantly improve ethanol purity in a more cost-effective manner. Several types of adsorbents are commonly used for ethanol purification, including natural zeolites, kaolin, and hydrotalcite. Hydrotalcite is known for its high adsorption capacity. Due to its layered structure and large surface area, hydrotalcite can effectively absorb impurities, making it a promising candidate for ethanol purification.

Various factors influence the adsorption process, including surface area, adsorbent type and molecular structure, adsorbent mass, temperature, pH, and contact time between the adsorbent and adsorbate. This study focuses on two key variables—adsorbent mass and adsorption time—to evaluate their impact on the purification of bioethanol produced from cherry fruit and pineapple peel fermentation.

Experimental

The Bioethanol Production. A total of 150 grams of cherry fruit and 150 grams of pineapple peel blended with 600 mL of distilled water. Subsequently, 3% sulfuric acid was added, and the mixture was stirred using a hot plate until the temperature reached 100°C. The solution was then cooled and adjusted to pH 4–5 using NaOH. The mixture was transferred into a sealed container, followed by the addition of yeast and sugar at 10% each. The glucose content was measured using a Brix refractometer, and the mixture was fermented for 3 days. The fermented solution was placed into a distillation flask and heated at a constant temperature of 78–80°C. The resulting distillate was collected and analyzed for ethanol content using Gas Chromatography (GC).

Synthesis of Mg/Al hydrotalcite Adsorbent. The synthesis of Mg/Al-hydrotalcite followed the method reported by[8]. A total of 32 grams of $MgCl_2·6H_2O$ and 22 grams of $AlCl_3·6H_2O$ were dissolved in 250 mL of distilled water and stirred until homogeneous, then transferred to a three-neck flask. A carbonate buffer solution was prepared by dissolving 6.7 grams of Na_2CO_3 and 8.8 grams of NaOH in 100 mL of distilled water. This solution was added dropwise to the three-neck flask until the pH reached 10. The mixture was then refluxed at 80°C for 1 hour. The resulting suspension was allowed to stand for 24 hours and washed repeatedly with distilled water until neutral pH was achieved. The precipitate was separated via centrifugation (4000 rpm, 5 minutes), dried, ground into powder, and characterized using XRD and FTIR.

Adsorption distillation

Effect of Adsorption Distillation Time on

Ethanol Content. A 30 mL bioethanol sample was mixed with 1 gram of Mg/Al-hydrotalcite and placed in a distillation column. Adsorptive distillation was carried out for varying durations: 1, 3, and 4 hours. The resulting distillate was analyzed for ethanol concentration using GC.

Effect of Adsorbent Mass on Ethanol Content. A 30 mL bioethanol sample was mixed with varying amounts of adsorbent (1, 2, and 3 grams), then subjected to adsorptive distillation for 4 hours for each treatment. The ethanol concentration in the resulting distillate was measured using GC.

Result and Discussion

Bioethanol Production. The mixture of cherry juice and pineapple peel has a glucose content of 5% based on measurement using a brix refractometer. This mixture is then hydrolyzed to break down the molecules by adding water (H2O), which aims to convert polysaccharides into simple monomers [9]. The hydrolysis process is a crucial step in bioethanol production, as it determines the amount of glucose that will be fermented into bioethanol. The hydrolysis process uses sulfuric acid as a catalyst to accelerate the reaction and induce hydrolysis, as water cannot induce hydrolysis in cherry and pineapple peel solutions [10]. Biomass that is hydrolyzed using H2SO4 sample changes to a blackish brown color, this is because H2SO4 as a dehydration agent can absorb water content (H and O) in a material containing carbohydrates, so the addition of concentrated H2SO4 will cause carbohydrates to dehydrate[11]. The chemical reaction during the hydrolysis process shown in Equation 1.

$$(C_6H_{10}O_5)_n + H_2O \xrightarrow{H_2SO_4} n(C_6H_{12}O_6) \quad (1)$$

The next stage is fermentation, which is the conversion of glucose into ethanol by releasing CO2 gas in an anaerobic or oxygen-free environment [12]. The solution of cherries and pineapple peel is added with NaOH solution to adjust the pH to 4–5. At this pH, the growth of the microorganism Saccharomyces cerevisiae occurs optimally[13], and the conversion of glucose into ethanol takes place. Then, the glucose content of the solution before fermentation was measured, and the glucose content was 6%. After that, sugar solution and yeast were added. The addition of yeast was intended to activate the Saccharomyces cerevisiae microorganisms. Chemical reactions in fermentation shown in Eq.2)

$$C_6H_{12}O_6 \xrightarrow{\textit{Saccharomyces cerevisiae}} 2C_2H_5OH + 2CO_2 \quad (2)$$

Bioethanol Distillation. The purpose of distillation is to separate ethanol from the cherry fruit and pineapple peel solution. Distillation is based on the principle of separating homogeneous liquids consisting of two or more components at different boiling points. The distillation process is carried out by heating at a temperature of 78-80 °C, which is the boiling point of ethanol. The water vapor that comes out is passed through a condenser and the distillate is ethanol. The distillate obtained is ethanol with a content of 5.07%.

Synthesis and Characterization of Mg/Al Hydrotalcite Adsorbents. Mg/Al hydrotalcite was synthesized using the coprecipitation method. This method is one of the most common methods for hydrotalcite synthesis. The synthesis was carried out by precipitating two or more metals and separating the precipitates under supersaturated conditions [14]. This synthesis was carried out by reacting a solution of inorganic salt $MgCl_2{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ then adding a carbonate buffer solution and an alkali solution (NaOH) until the pH reached 10. If the pH is significantly higher than the optimal pH, Al3+ ions will dissolve and cannot form a precipitate. In comparison, if the pH is lower than the optimal pH, compounds other than hydrotalcite will precipitate, resulting in a suboptimal product[15]. The alkali solution (NaOH) and carbonate buffer are added simultaneously drop by drop to the inorganic salt solution to facilitate precipitation. The resulting dry white solid is hydrotalcite with a physical form of fine white powder, as shown in Figure. 1.

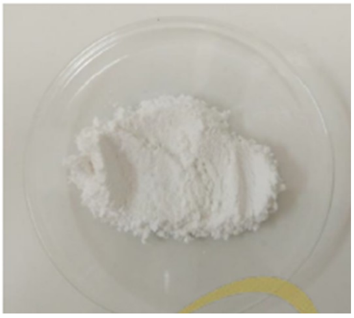

Figure 1. Mg/Al Hydrotalcite Powder Resulting from Synthesis

The results of XRD characterization (**Figure 2**) indicate that the three highest absorption peaks appear at 2θ = 11.55; 23.36 and 34.89. The positions of these peaks are similar to the data of the Mg/Al hydrotalcite reference diffractogram by [16], which shows absorption peaks at 2θ=11.59; 23.45 and 34.57, and with JCPDS number 89-0460, which shows three highest peaks at 2θ = 11.65; 23.42 and 34.19. Based on the similarity of the diffraction pattern data at the 2θ values of Mg/Al hydrotalcite from synthesis with the reference [16] and JCPDS number 89-0460, it is proven that the Mg/Al hydrotalcite from synthesis has been formed. According to [17], the d spacing value of 7.59 Å is characteristic of hydrotalcite with interlayer carbonate anions d spacing of 7.65 Å for the synthesized Mg/Al hydrotalcite, which appears at 2θ 11.55, shows that the interlayer anion of Mg/Al hydrotalcite is CO_3^{2}.

The sharp and broad absorption peak at 3432 cm^{-1} corresponds to the stretching vibration of hydroxyl (-OH) groups (see **Figure 3** and **Table 1**). This absorption indicates vibrations between hydroxyl groups originating from H_2O interacting with the metal in the hydrotalcite, as well as water molecules located in the interlayer [18]. The wavenumber 1631 cm^{-1} corresponds to hydroxyl groups (OH) that appear as reflections of H_2O bending in the interlayer region. Absorption also appears at a wavenumber of 1364 $cm-^{1}$, indicating the presence of carbonate groups (CO_3^{2-}) from the symmetric stretching vibration of C-O. Absorption at 688 $cm-^{1}$ corresponds to M-O. Based on FTIR, the presence of M-O, hydroxyl groups, and carbonate groups was identified, which are components of Mg/Al hydrotalcite with interlayer anions CO_3^{2-} and the general formula [M(II)1–xM(III)x(OH)2]x+(An–)x/n·mH2O [19].

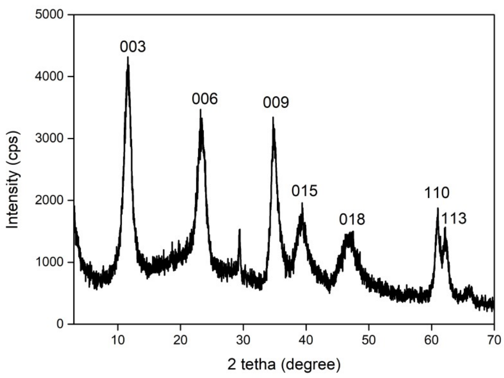

Figure 2. Difragtogram of Synthesized Mg/Al hydrotalcite

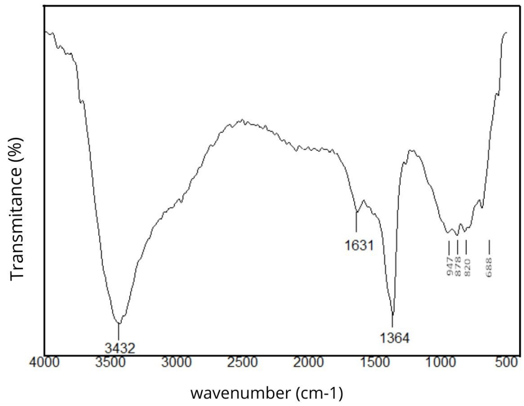

Figure 3. Spectra FTIR of Synthesized Mg/Al hydrotalcite

Table 1. Functional Groups of Synthesized Mg/Al Hydrotalcite

Functional group	Wavenumber (cm^{-1})	Refference
O-H Stretching (hydroxyl)	3432	3464 [14]
O-H Bending (H_2O)	1631	1627-1635 [14]
C-O Symmetric Stretching (carbonate)	1364	1350 [16]
M-O Stretching	688	555-671 [18]

The Effect of Distillation-Adsorption Time on Increasing Bioethanol Content. Increasing the adsorption distillation time resulted in an increase in ethanol concentration, which is consistent with previous research [20]. The longer the adsorption distillation time, the greater the transfer of water molecules or the amount of water absorbed onto the adsorbent surface. The highest ethanol concentration was obtained at a distillation-adsorption time of 4 hours, which was 19.03%, with an increase in ethanol concentration of 13.96% (see **Figure 4**). Meanwhile, the lowest concentration was obtained at a variation of 1 hour, which was 13.47%, with an increase in ethanol concentration of 8.40%.

The Effect of Adsorben Mass on the Increase in Bioethanol Content. An increase in adsorbent mass correlates with the total surface area that can absorb water compounds in bulk bioethanol. The adsorption distillation process was conducted at a temperature of 78–80°C. Heating affects the absorption of water by the adsorbent surface; the presence of heat causes an increase in adsorption capacity. Therefore, based on experimental data, the highest bioethanol concentration was obtained

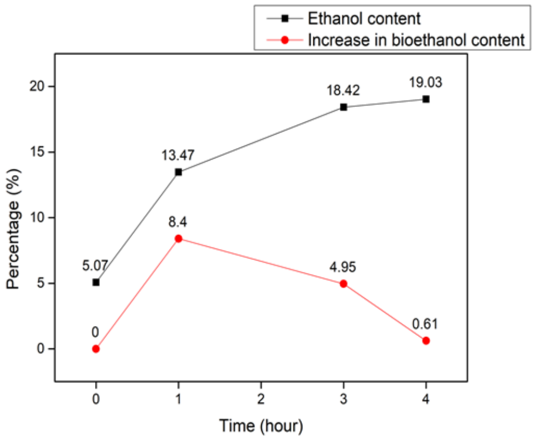

Figure 4. The Effect of Distillation- Adsorption Time on Increasing Ethanol Content

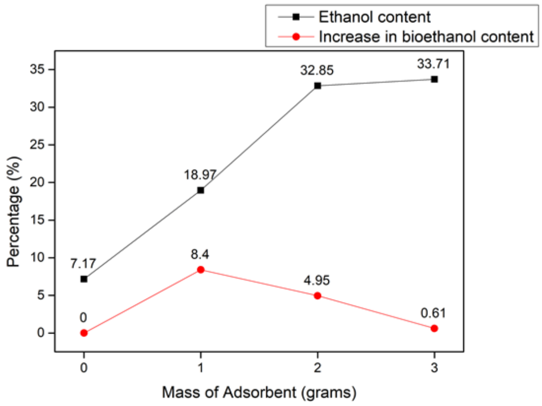

Figure 5. The effect of adsorbent mass on ethanol content increase in the adsorption distillation process.

at an adsorbent mass of 3 grams, which was 33.71%, with an increase of 26.53%. The lowest concentration was obtained at an adsorbent mass of 1 gram, which was 18.97%, with an increase of 11.79% (**Figure 5**).

Interaction between hydrotalcite adsorbent and water molecules from bioethanol. The interaction between hydrotalcite and water molecules in bioethanol occurs during the adsorption distillation process (**Figure 6**). In this process, there is direct contact between the adsorbent and water in the bioethanol mixture through the pores of the hydrotalcite. Absorption occurs because hydrotalcite has interlayers that can absorb anions and water. This interaction between hydrotalcite and water molecules is a physical water binding process, as physical adsorption is fully reversible, allowing desorption (the release of ions/molecules that have bonded with the active groups on the adsorbent). This is supported by the unique property of hydrotalcite known as the memory effect [21].

Conclusion

The characterization of synthesized Mg/Al-hydrotalcite using XRD and FTIR confirmed the successful formation of the hydrotalcite structure with CO_3^{2-} as the interlayer charge-balancing anion, consistent with JCPDS No. 89-0460. The application of Mg/Al hydrotalcite in the adsorption distillation of bioethanol produced from a mixture of pineapple peel and cherry fruit resulted in optimal ethanol purification at a distillation time of 4 hours, achieving an ethanol concentration of 19.03%—an increase of 13.96%. Additionally, the optimum adsorbent mass of 3 grams yielded a maximum ethanol concentration of 33.71%, corresponding to an enhancement of 26.54%.

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Author Contributions

F. I. P. S: conceptualization; investigation; visualization; formal analysis; writing-review and editing supervision. N. H: data curation, investigation; writing-original draft. BSW: conceptualization; investigation; writing-review and editing. All authors approved the final manuscript.

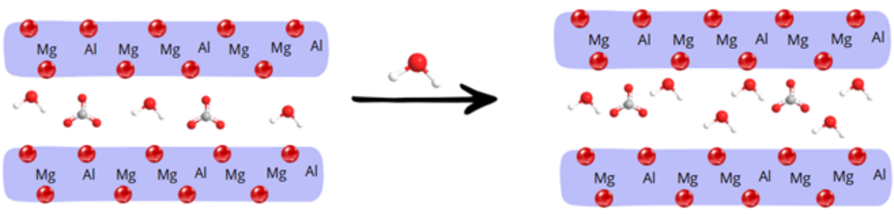

Figure 6. Mechanism of water molecule adsorption by Mg/Al hydrotalcite [22]

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