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Characterization of Hydroxyapatite of Purebred Chicken Eggshells Composited with Gelatin as Methylene Blue Absorbent

Nurfadillah*, Kurnia Ramadani, Firnanelty, Sitti Chadijah, Aisyah, Asriani Ilyas, Arfiani Nur, Syarifah Rabiatul Adawiah, Titik Andriani

Department of Chemistry, Faculty of Science and Technology, Alauddin State Islamic University of Makassar, Jl. H.M. Yasin Limpo No. 36, Gowa, South Sulawesi

**Corresponding Author: nurfadillahpadelee@gmail.com*

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Abstract: *Chicken eggshells contain calcium carbonate ($CaCO_3$), which can serve as a source of calcium hydroxide ($Ca(OH)_2$). This calcium hydroxide can subsequently react with diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) to synthesize hydroxyapatite. This study aims to characterize hydroxyapatite derived from eggshells and to evaluate the adsorptive capacity of hydroxyapatite-gelatin composites for methylene blue. The hydroxyapatite was synthesized using the precipitation method. Calcination results indicated a calcium hydroxide ($Ca(OH)_2$) content of 68.3% in the eggshells. Fourier Transform Infrared (FT-IR) analysis of the hydroxyapatite revealed the presence of hydroxyl groups (-OH) at a wavenumber of 3434 cm^{-1}, carbonate groups ($-CO_3^{2-}$) at 1421 cm^{-1}, and phosphate groups ($-PO_4^{3-}$) at 1035 cm^{-1}, 604 cm^{-1}, and 471 cm^{-1}. X-ray diffraction (XRD) analysis confirmed the formation of pure hydroxyapatite crystals, showing peaks at an angle of $2\theta = 34.08°$ with a crystallinity of 100%. These peaks correspond to the Joint Committee on Powder Diffraction Standards (JCPDS) No. 09-0432. The synthesis of hydroxyapatite-gelatin composites revealed typical functional groups such as amine groups from gelatin and phosphate and carbonate groups from hydroxyapatite. The methylene blue absorption study demonstrated that the hydroxyapatite-gelatin composites reached optimal adsorption efficiency at a ratio of 2:4 after 240 minutes, achieving an efficiency of 63%. The data suggest that prolonged exposure time enhances the adsorption of methylene blue.*

Keywords*: Composite, Eggshell, Gelatin, Hydroxyapatite, Methylene blue*

INTRODUCTION

The rapid expansion of the textile industry has led to a significant increase in waste generation. Unchecked discharge of textile industry waste into water bodies poses a substantial threat to environmental integrity. To mitigate this, effective methods such as absorption have been advocated (Anggarayanti, 2017). Absorption, a liquid waste treatment process, has emerged as a viable solution due to its proven effectiveness, efficiency, and potential to address various water quality issues including odor, color, and organic pollutants, without generating harmful byproducts (Herawati et al., 2018). The efficacy of absorption hinges upon the selection of suitable absorbent media (Sausa et al., 2021). Optimal results are achieved when employing absorbents capable of effectively sequestering dyes such as methylene blue, with reported efficiencies reaching 99.9% in adsorption studies

Hydroxyapatite is utilized as an absorbent due to its porous, inert, wear-resistant structure and its capability as an ion exchanger, effectively reducing levels of metals and dyes. Furthermore, hydroxyapatite exhibits strong resistance to microbial growth, making it a robust inorganic material (Pandharipande & Sondawale, 2016). Hydroxyapatite can be synthesized from eggshell waste, which demonstrates a crystallinity of 97.436% as determined by X-ray Diffraction (XRD) analysis (Puspita & Sari, 2017).

Eggshells, rich in calcium content (71.23%), present a valuable source for producing high-purity hydroxyapatite (Peungsamran et al., 2018). Hydroxyapatite derived from eggshells has shown superior sinterability compared to that synthesized from other sources (Suprianto et al., 2019). This superiority is evidenced by the work of Gago and Yulius (2021), who achieved a hydroxyapatite purity of 76.6%. Various methods exist for synthesizing hydroxyapatite, including sol-gel, hydrothermal, and precipitation methods. This study prefers the precipitation method due to its high reproducibility, rapid process, cost-effectiveness, simplicity, and superior yield without needing organic solvents (Khalid et al., 2022; Firnanelty et al., 2017).

According to Rahayu et al. (2021), synthesized hydroxyapatite crystals can absorb direct brown dye at an efficiency of 51.4%. However, this absorption efficiency is considered suboptimal due to hydroxyapatite's low mechanical properties, brittleness, and difficulty in resuspension after use. Therefore, hydroxyapatite must be modified or composited with other materials that possess complementary properties to enhance its absorption capacity (Negara & Nengah, 2018).

Research conducted by Asparma and Pepi (2020) demonstrated that a hydroxyapatite-gelatin composite adsorbent achieved a 79.90% absorption efficiency for methylene blue dye, indicating that compositing hydroxyapatite with other materials improves its mechanical properties and absorption capacity when measured using a UV-Vis spectrophotometer. This study thus explores hydroxyapatite-gelatin composites, as gelatin offers a large surface area, porosity, and good mechanical strength, making it a promising adsorbent material.

The objective of creating a hydroxyapatite-gelatin composite is to enhance the absorption capacity by combining the properties of both materials. A composite with a ratio of 90:10 (gelatin to hydroxyapatite) exhibits a 17-19 GPa hardness. In this composite, hydroxyapatite serves as an inorganic biomaterial, while gelatin functions as an organic biomaterial (Pandharipande & Sondawale, 2016). Thus, it is necessary to investigate the characterization of hydroxyapatite derived from chicken eggshells synthesized via the precipitation method and to determine the absorbability of hydroxyapatite-gelatin composites for methylene blue.

RESEARCH METHODS

Material and Tools

The materials used in this study were aluminum foil, distilled water (H_2O), chicken eggshell, diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), gelatin, Whatman 42 filter paper and methylene blue.

The tools used in this research are X-Ray Diffraction Shimadzu maxima XRD-7000, Fourier Transform Infra-Red (FT-IR) nicole iS10, Varian 50 Conc UV-Vis spectrophotometer, furnace, oven, analytical balance, sieve shaker, centrifugation, magnetic stirrer, shaker, Erlenmeyer, volumetric flask, stative and clamps, burettes, measuring cups, beakers, pestles and mortars, stirring rods and funnels.

Procedure

Calcining of Chicken Eggshells

One kilogram of eggshells was first cleaned to remove mucous membranes and any adhering dirt. They were then washed with clean water. Subsequently, the eggshells were dried in an oven at 110 °C for 2 hours. Following drying, the eggshells were ground into a powder and sieved using a 200-mesh sieve. The powdered eggshells were then calcined in a furnace at 900 °C for 5 hours to produce calcium oxide (CaO) (Mawadara et al., 2016). The CaO compounds were then converted to calcium hydroxide ($Ca(OH)_2$) by exposing them to air at room temperature for seven days (Pu'ad et al., 2020). The calcined chicken eggshells were subsequently analyzed for their crystal structure and chemical composition using X-ray diffraction (XRD) (Setiawan et al., 2020).

Hydroxyapatite Synthesis

Hydroxyapatite synthesis is carried out through a reaction between Ca(OH)2 with (NH 4) 2 HPO4 with a mole ratio of Ca / P 1.67. A suspension of Ca(OH)2 was prepared from Ca(OH)2 obtained from the calcination stage, weighed 14.7410 grams of Ca(OH)2 dissolved in 100 mL of aquades and for a solution of (NH4)2HPO4was prepared by weighing 15.7840 grams (NH4)2HPO4, dissolved in 100 mL of aquades. Next, drip the second solution into the first solution at a flow rate of 5 ml/minute for 100 minutes using a burette. Then, stir at 350 rpm using a magnetic stirrer until homogeneous. Once the solution is thoroughly mixed, cover the mixture with aluminium foil. The reaction mixture is then allowed to stand at room temperature for 24 hours, after which it is filtered using Whatman 42 filter paper. The precipitate obtained was rinsed with aqueduct at least three times. The precipitate is dried in the oven at 110 °C for 3 hours. After drying, the precipitate is crushed until smooth using a mortar. Then, it was characterized using *Fourier Transform Infra-Red (FT-IR*) (Suci & Yulius, 2020).

Hydroxyapatite-gelatin synthesis

Hydroxyapatite and gelatin were weighed in varying ratios of 2:4, 2:2, and 4:2 (w/w). Each ratio was dissolved in 100 mL of distilled water (Erdawati, 2012). The three different mixtures were stirred for 60 minutes using a magnetic stirrer. Following this, the mixtures were centrifuged for 15 minutes at a speed of 3500 rpm. The resulting composite was then dried for 1 hour and 30 minutes. The synthesized hydroxyapatite-gelatin composite powders were subsequently analyzed using a Fourier Transform Infrared (FT-IR) spectrophotometer (Monica, 2015).

Methylene Blue Absorption Test

A solution of methylene blue was prepared at a concentration of 40 ppm. The hydroxyapatite-gelatin composites (ratios of 2:4, 2:2, and 4:2) were each weighed to 0.05 grams and added to 15 mL of the methylene blue solution in Erlenmeyer flasks. The mixtures were homogenized using a shaker at a speed of 150 rpm, with contact times varied at 120 minutes, 180 minutes, and 240 minutes. After shaking, the mixtures were centrifuged for 15 minutes at 3500 rpm to separate the precipitates. The absorbance of the filtrates was then measured using a UV-Vis spectrophotometer at a wavelength of 664.5 nm (Trivana et al., 2015).

RESULTS AND DISCUSSION

Calcining of Chicken Eggshells

The calcination process of eggshell powder is carried out at a high temperature of 900 °C to eliminate organic compounds and decompose calcium carbonate compounds ($CaCO_3$) into calcium oxide (CaO). Calcination is the process of breaking down a compound through high-temperature heating which causes a decomposition reaction. The temperature in the furnace will make the chemical bond weak and the bonded atoms move freely so that the compound will escape according to its boiling point (Gago and Yulius, 2021: 31). The reaction equation in the calcination process is as follows:

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

The calcined eggshells exhibited an average mass reduction, resulting in a yield of 55.26%. This decrease in mass during calcination is attributed to the release of CO_2 gas and the decomposition of organic compounds. The organic components that are lost originate from proteins, specifically mucopolysaccharides, which include chondroitin sulfate A and B, glucosamine, galactosamine, galactose, mannose, and sialic acid (Gago and Yulius, 2021).

Conversion of Calcium Oxide (CaO) to Calcium Hydroxide $Ca(OH)_2$

Calcium Oxide (CaO) that has been formed from calcination is then left in an open space to react with water to form calcium hydroxide ($Ca(OH)_2$). The reaction of calcium hydroxide formation is as follows:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (2)$$

The conversion results need to be characterized using *X-Ray Diffraction* (XRD) to determine the type of mineral and crystallinity. The results obtained are as shown in figure 1.

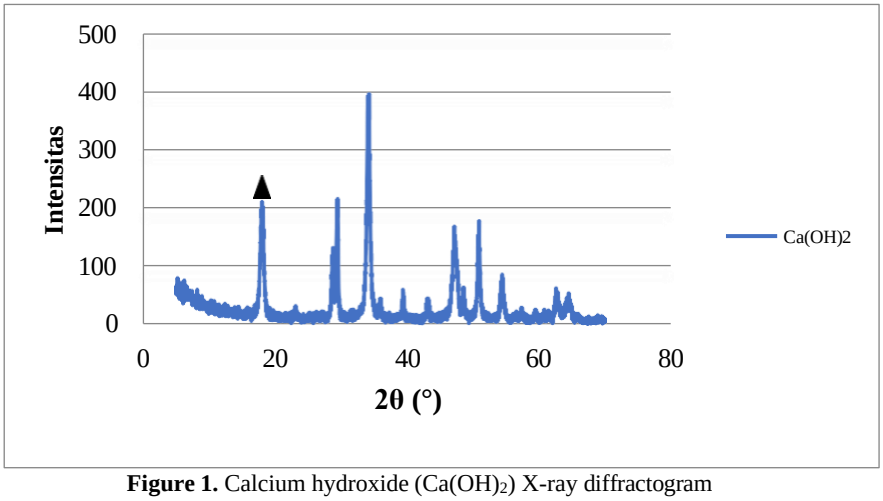

Figure 1. Calcium hydroxide ($Ca(OH)_2$) X-ray diffractogram

Based on the results of JCPDS data (reference number 84-1263), the compound formed is identified as calcium hydroxide ($Ca(OH)_2$) with a trigonal crystal structure, as evidenced by the three highest peaks at angles of 34.16°, 18.04°, and 47.20°, which correspond to $Ca(OH)_2$ (Figure 1). The chemical composition analysis reveals that calcium

hydroxide constitutes 68.3% of the sample, indicating the presence of other compounds. Specifically, calcium carbonate ($CaCO_3$) comprises 30.0%, and silicon dioxide (SiO_2) accounts for 1.7%. The presence of these additional compounds is attributed to the incomplete reaction of some samples with water (H_2O) when left in open air.

Determination of Calcium (Ca) Levels

Analysis of Ca levels in eggshells after calcination using XRD. The results of the analysis of purebred chicken eggshell powder showed a calcium (Ca) content of 49%.

Hydroxyapatite Synthesis

Hydroxyapatite synthesis is carried out using the precipitation method with calcium hydroxide ($Ca(OH)_2$) as a precursor of calcium and diamonium hydrogen phosphate $(NH\ 4)\ _2HPO_4$ as a phosphate precursor. The yield of hydroxyapatite obtained is 90.3081**.** The reaction of hydroxyapatite formation is like the following equation:

$$10Ca(OH)_2 + 6(NH_4)_2\,HPO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O + 12NH_4OH$$

X-ray Diffraction Characterization

Hydroxyapatite purity analysis is performed by looking at the diffractogram produced by *X-Ray Diffraction* of the sample. Figure 2 shows that these peaks are typical peaks from hydroxyapatite.

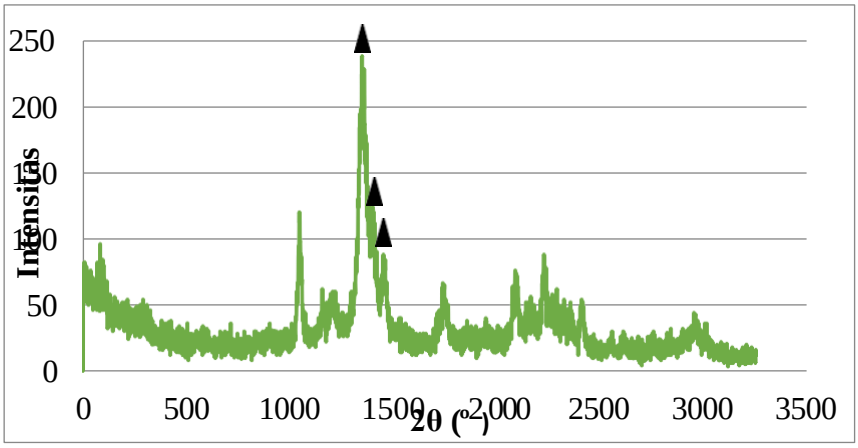

Figure 2. Hydroxyapatite X-ray Diffractogram

XRD characterization is performed to determine the crystal structure and size of the hydroxyapatite sample. The diffraction pattern of the hydroxyapatite sample is observed at angles ranging from 10° to 65°. Figure 2 highlights three prominent peaks at angles of 31.94°, 34.08°, and 35.64°. According to the Joint Committee on Powder Diffraction Standards (JCPDS) No. 09-0432, these peaks confirm that the compound formed is hydroxyapatite, characterized by a hexagonal crystal structure. The XRD analysis indicates that the sample consists of 100% hydroxyapatite, as all detected elements are constituents of hydroxyapatite. Additionally, the physical appearance of the white hydroxyapatite powder suggests that the calcination process was successful and that the stoichiometric Ca/P ratio of 1.67 was achieved. This observation aligns with the theory proposed by Haris (2016), which states that pure hydroxyapatite is predominant at a Ca/P ratio 1.67.

FT-IR Characterization

FT-IR analysis is conducted to identify the functional groups present in the hydroxyapatite crystals obtained. Based on the spectrum shown in Figure 4, hydroxyapatite samples derived from eggshells exhibit absorption bands characteristic of hydroxyl (-OH), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}) groups. The -OH group is detected at a wavenumber of 3434 cm^{-1}, indicating a broad and robust band, which suggests the presence of H_2O on the sample's surface. The CO_3^{2-} absorption band at 1421 cm^{-1} corresponds to asymmetric stretching vibrations. The presence of CO_3^{2-} in hydroxyapatite can inhibit crystal growth during synthesis.

Additionally, the PO_4^{3-} group is identified in several absorption bands: 1035 cm^{-1} (antisymmetric stretching vibrations, v_3), 604 cm^{-1} (bending antisymmetric vibrations, v_4), and 471 cm^{-1} (bending vibrations, v_2). The phosphate group also appears at wavenumbers 954 (v_1), 500-400 (v_2), 1100-1019 (v_3), and 605-530 (v_4) (Riano, 2022). According to Gago and Yulius (2021), the strongest PO_4^{3-} bond in hydroxyapatite is observed in the antisymmetric stretching vibration (v_3). Sharper peaks of the PO_4^{3-} and -OH groups indicate better crystal quality and superior hydroxyapatite (Lindawati & Sari, 2018). These three groups are characteristic of hydroxyapatite, confirming the formation of pure hydroxyapatite.

The successfully synthesized hydroxyapatite is then composited with gelatin as an adsorbent for methylene blue. The hydroxyapatite-gelatin composites are first characterized using FT-IR. The FT-IR spectrum of the sample is shown in Figure 3.

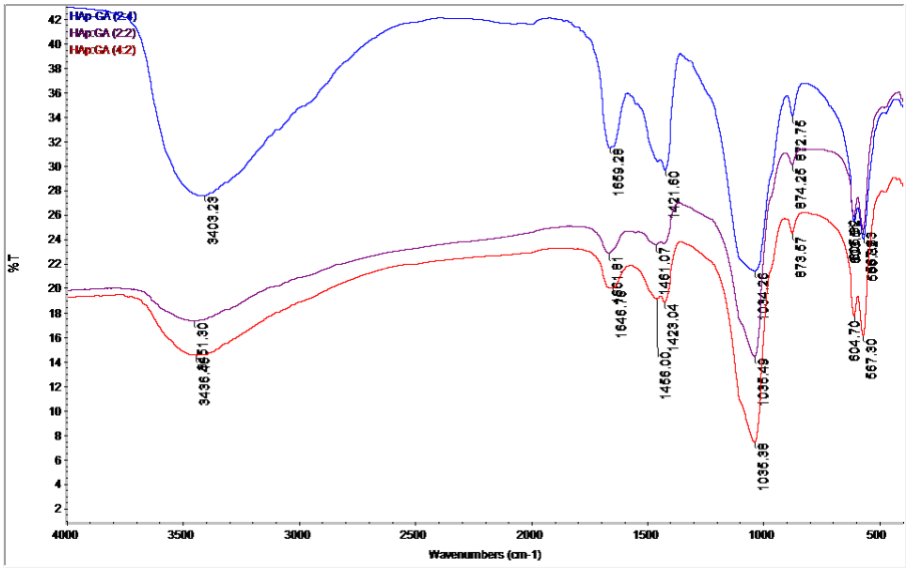

Figure 3. FT-IR HAp Spectrum : GA, 2:4 (——), 2:2 (——) and 4:2 (——)

FTIR analysis aims to identify the composite constituents that remain intact after mixing. This is evidenced in the spectrum of Figure 3, which shows that the hydroxyapatite-gelatin sample retains the typical functional groups of both hydroxyapatite and gelatin. The detected groups include the -N-H stretching vibration absorption from gelatin and the -CO_3^{2-} and -PO_4^{3-} groups, characteristic of hydroxyapatite. This indicates that the functional groups are not lost but rather exhibit a shift, confirming the formation of the composite. The formation of the composite is further indicated by a shiny appearance, suggesting that gelatin has attached to and filled the pores in hydroxyapatite (HAp). The best composite is achieved at a ratio of 2:4, as evidenced by the FT-IR spectrum

shift (Figure 4). The addition of gelatin is expected to reduce the brittle properties of porous HAp, resulting in both pressure-resistant and biodegradable composites.

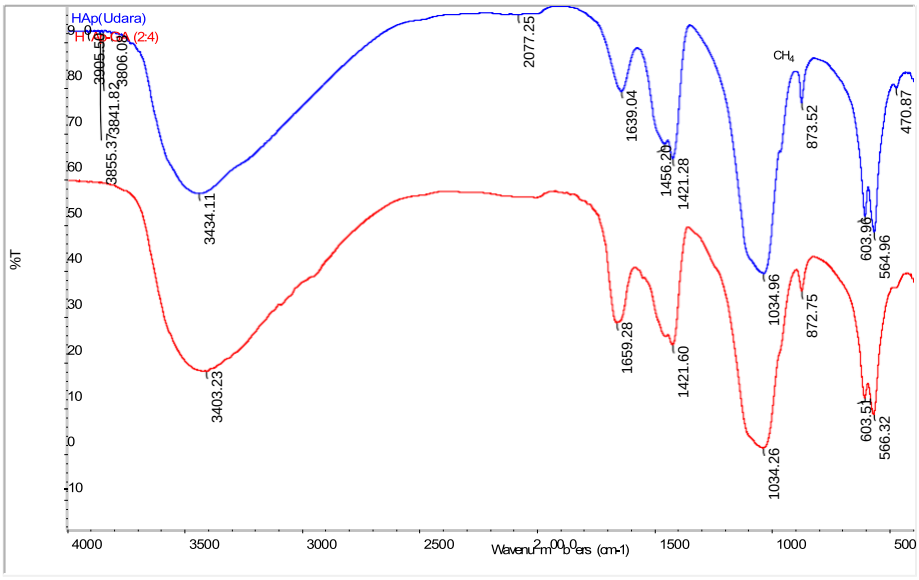

Figure 4. FT-IR HAp Spectrum and HAp:GA Composite (2:4)

Based on the spectrum shown in Figure 4, it is evident that some absorption regions produced by hydroxyapatite are similar to those in the composite spectrum. However, in the composite results, an amine group from gelatin is added at a wavenumber of 3403 cm^{-1}, replacing the hydroxyl group at 3434 cm^{-1}. This shift is attributed to the prolonged mixing time of the composite, resulting in hydrogen bonding between HAp and gelatin. The hydrogen bond forms between the hydroxyl group of HAp and the amine group of gelatin. The hydroxyl group shifts to the right (towards a smaller wavenumber), indicating that the bond between the groups has strengthened, requiring higher energy to vibrate. Consequently, the -OH group from HAp decreases or solubilizes, forming a more robust attachment with the amine group derived from gelatin (Milla & Decky, 2016). This interaction suggests that the hydroxyapatite-gelatin composite has bonded perfectly, as indicated by the formation of robust hydrogen bonds.

Methylene Blue Absorption

Based on the absorbance of the standard series, the absorption ability of hydroxyapatite-gelatin composites with an initial concentration of 40 ppm and several variations in composite comparisons using a UV-Vis spectrophotometer can be analyzed

Table 1. Contact Time Relationship with Absorbance

Contact Time (Minutes)	HAp: GA	MB residual concentration (ppm)	MB Absorbed Concentration (ppm)	Uptake Efficiency (%)
120	2:4	15,0104	24,9896	62,4740
	2:2	16,9456	23,0544	57,6360
	4:2	15,6728	24,3272	60,8180
180	2:4	16,2739	23,7239	59,3152
	2:2	19,2312	20,7688	51,9220

	4:2	18,4786	21,5214	53,8035
240	2:4	14,4381	25,5619	63,9047
	2:2	14,8265	25,1736	62,9337
	4:2	15,1872	24,8128	62,0320

The synthesized hydroxyapatite-gelatin composite was further evaluated for its dye absorption capacity, specifically using methylene blue. Methylene blue is chosen for this study due to its propensity to form positively charged ions upon interaction. Prior to the absorption tests, the maximum wavelength for standard methylene blue solutions (0.5, 5.5, 10.5, 15.5, and 20.5 ppm) was determined using a UV-Vis spectrophotometer.

Based on the results obtained in table 1 and figure 4 It is known that the optimum contact time best obtained from the absorbent of the HAp:GA composite occurs at a time of 240 minutes in all variations of the HAp:GA composite (2:4, 2:2 and 4:2). Based on these data, it shows that the longer the time given, the greater methylene blue is absorbed. This can be because at first many of the active sides of the adsorbent are empty, so the tendency of the solution to be absorbed into the absorbent is higher because the active groups in the absorbent have not interacted optimally. The longer the interaction time, the more absorbent is absorbed because the more opportunities the absorbent particles have to come into contact with the absorbat. This causes more absorbat to be absorbed

This study also investigated the effect of adsorbent composite mass variation on the adsorption process. Table 4.4 shows that among the three Hap composite variations, the 2:4 ratio exhibits the highest absorption capacity, indicating that less hydroxyapatite and more gelatin improve the adsorption performance. This finding aligns with the theory proposed by Asparma and Pepi (2020), which states that increasing the amount of gelatin enhances methylene blue absorption. Gelatin improves cell attachment and growth due to its numerous arginine-glycine-aspartic acid (RGD) protein chains and sequences. Additionally, gelatin coats hydroxyapatite particles, reducing their brittleness. Including gelatin densifies hydroxyapatite by filling its pores, thereby increasing its structural integrity and preventing easy degradation (Fatma et al., 2021).

CONCLUSION

The conclusions of this study are as follows:

1. FT-IR characterization of hydroxyapatite compounds identified the presence of functional groups: -OH- at 3434 cm^{-1}, -CO_3^{2-} at 1421 cm^{-1}, and -PO_4^{3-} at absorption bands 1035 cm^{-1} (antisymmetric stretching vibrations, v_3), 604 cm^{-1} (bending antisymmetric vibration, v_4), and 471 cm^{-1} (bending vibration, v_2). XRD characterization revealed the highest peak at an angle of $2\theta = 34.04^o$, confirming the formation of hydroxyapatite in accordance with JCPDS standard No. 09-432.

2. The hydroxyapatite-gelatin composite demonstrated the ability to absorb methylene blue dye, achieving an absorption efficiency of 63% at a ratio of 2:4 with a contact time of 240 minutes. The hydroxyapatite-gelatin composite shows significant potential for absorbing methylene blue based on the absorption efficiency values obtained.

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