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Characterization of Chicken Eggshell-Derived Hydroxyapatite/Zeolite Composite as a Methylene Blue Absorbent

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ABSTRACT

Purebred chicken eggshell is a promising natural source because it contains high calcium carbonate ($CaCO_3$), which is used as a hydroxyapatite (HAp) precursor, with natural abundance and biodegradability, making it an eco-friendly alternative to synthetic materials. HAp is relevant for dye removal because of its high adsorption capacity, chemical stability, and ability to interact with dye molecules through ion exchange and surface interactions with the material. The composite adsorbent of Hap-zeolite is effective for wastewater treatment based on the result of HAp-zeolite composite's adsorption capacity against methylene blue. Methylene blue is one of the dyeing wastes originating from the textile industry. The method of synthesis of Hap used precipitation. The FTIR characterization results showed OH groups at wavenumber 3434 cm^{-1}, CO_3^{2-} group with wavenumber 1421 cm^{-1}, PO_4^{3-} *bending* group with wavenumber 565 cm^{-1}, and PO_4^{3-} *stretching* at wavenumber 1035 cm^{-1}. The highest peak XRD yield at an angle of 2θ=34.04º corresponds to a hexagonal crystal formed. The adsorption process is carried out with a HAp-zeolite mass ratio of 4:2 (w/w), with contact times for 180 minutes, resulting in the best adsorption efficiency around 99.99% measured via UV-Vis spectrophotometry. The results indicate that HAp-zeolite composites are highly effective for methylene blue removal and have potential application in wastewater treatment.

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INTRODUCTION

Eggs are one of the most common sources of animal protein. Indonesia's total and per capita production of eggs is still increasing, reflecting the growth in egg consumption. Based on BPS (2019), Indonesia produced 4,753,382.23 tons of eggs in 2019. Approximately 10% of this, around 475,338.223 tons per year, becomes eggshell waste. According to the data on egg consumption until 2025 in South Sulawesi from the National Food Agency (Bapanas), using the 2025 commodity balance, it was known that the average demand for broiler eggs per month in South Sulawesi would be 518,627 tons. Chicken eggshells are a solid waste abundantly generated in homes, restaurants, and industries, and have not been properly utilized [1]. The existence of waste is an inevitable by-product of human activities and can hardly be isolated from the environment [2]. It is an example of a positive

recycling of biomass for waste prevention, cleaner production, and a circular economy [3]. Eggshells are possibly a source of HAp (hydroxyapatite) [4].

Methylene blue (MB) is a synthetic dye commonly present in textile industry wastewater, an aromatic synthetic dye that is toxic and environmentally hazardous, adversely affecting human health [5]. MB is considered carcinogenic and non-biodegradable, posing a threat to human health and environmental safety. It is generally discharged into natural water bodies, thereby endangering biological life. Therefore, there is an increasing demand to design a green and feasible technology to eliminate MB from aqueous solutions [6]. At a concentration of 20 ppm, an absorption efficiency of 90.6% was achieved by chicken eggshells against dyes in methylene blue solution; hence, an eggshell-derived HAp-based material combined with zeolite can be exploited as a methylene blue adsorbent. From the background above, the study aimed to characterize hydroxyapatite obtained from chicken eggshells and evaluate hydroxyapatite-zeolite composites' absorption capability toward methylene blue [7].

Eggshells consist of 94–98% $CaCO_3$ (calcium carbonate), 3% phosphorus (P), magnesium (Mg), sodium (Na), potassium (K), zinc (Zn), manganese (Mn), iron (Fe), and copper (Cu) [7], [8]. Due to its polarity, calcium carbonate ($CaCO_3$) is the major constituent of eggshells. The calcination of $CaCO_3$ yields CaO. Hexagonal calcium oxide (CaO) possesses 10,000–20,000 mesopores, allowing solutes to be adsorbed onto CaO. Due to its high adsorptive performance, CaO is extensively employed as an adsorbent [9]. Calcium from eggshells can be used as a precursor for hydroxyapatite synthesis [10]. Preparing eggshell powder is one of the most attractive methods for utilizing eggshell waste [11].

Hydroxyapatite (HAp), with the molecular formula $Ca_{10}(PO_4)_6(OH)_2$, is the most stable form of polycrystalline calcium phosphate materials and is a subspecies of apatite [12]. The constituent ratios in hydroxyapatite compounds are calcium (Ca) 39.9%, phosphorus (P) 18.5%, hydrogen (H) 0.2%, and oxygen (O) 41.41% [13]. The percentage composition of hydroxyapatite after 5 hours of sintering was 74.74%. The hydroxyapatite product synthesized from eggshells occurred under a 0.5 M HNO_3 solvent concentration and a Ca/P reactant mole ratio of 1.77. In this state, the particle size is 40.38 nm, the BET surface area is 3.606 m^2/g, and the morphology of HAp is in the form of agglomerates [5]. The efficacy of HAp adsorption is due to its cost-effectiveness, environmental friendliness, thermal stability, and heavy metal removal capacity [9].

Hydroxyapatite has been synthesized using various methods such as precipitation, hydrothermal, sol-gel, and gamma radiolysis [14]. Among these, the precipitation method is preferred for producing hydroxyapatite [15]. This well-known wet chemistry method is the most preferred due to several advantages: inexpensive raw materials, simplicity of the chemical reactions, better control of particle size and homogeneity, minimization of

environmental pollution, and low contamination, thus limiting the need for purification during production [16]. According to the results, co-precipitation was the most effective method, yielding smaller particle sizes than other synthesis methods [17].

However, hydroxyapatite becomes brittle and its mechanical properties deteriorate, leading to structural instability when interacting with body fluids and blood. This weakness can be reduced by mixing it with zeolite to prepare a composite material [18]. Zeolite, as an ionic material, adsorbent, and catalyst, has been extensively applied, including in combination with materials like chitosan [19]. Zeolite's efficiency stems from its highly regular 3D framework structure composed of interconnected cavities, characteristic of aluminosilicate crystals. Zeolite has an extremely large surface area, making it highly efficient for biocomposite manufacturing [7]. Zeolite loading enhances tensile cracking control at a higher crack width and material strength stage [16].

A biocomposite is a composite material formed by a matrix (resin) and a reinforcement of natural fibers. Due to their renewability, low cost, and biodegradability, biocomposites are an alternative to conventional fibers for wood plastic composites (WPC). The potential of novel biocomposites as a sustainable replacement in the construction industry is evident, especially for adsorbent applications [21].

METHODS

1. Calcining of chicken eggshells

The mucous membrane and dirt were removed from the eggshells (up to 1 kg). The shells were then rinsed with fresh water and dried at 110°C for 2 hours in an oven. The eggshells were crushed into a powder and sieved through a 200-mesh screen. The powdered eggshells were subsequently calcined in a furnace at 900°C for 5 hours to produce calcium oxide (CaO) [22]. All CaO samples were then transformed into $Ca(OH)_2$ after being stored in an open room at room temperature for 7 days and placed in a desiccator. The chemical composition of calcined chicken eggshells was analyzed using X-Ray Diffraction (XRD) [13].

2. Hydroxyapatite Synthesis

The synthesis of hydroxyapatite (HAp) was conducted through a reaction between $Ca(OH)_2$ and $(NH_4)_2HPO_4$ using a working Ca/P mole ratio of 1.67. A $Ca(OH)_2$ suspension was prepared by weighing 14.7410 g of $Ca(OH)_2$, dissolved in 100 mL of aquadest. Separately, 15.7840 g of $(NH_4)_2HPO_4$ was dissolved in 100 mL of aquadest. The second solution was then added dropwise into the first solution at a rate of 5 mL/min for 100 minutes using a burette, and the mixture was stirred with a magnetic stirrer at 350 rpm until a uniform white-colored solution at pH 10 was obtained. The solution was then covered with aluminum foil and stored at room temperature for 24 hours. It was subsequently filtered using Whatman no. 42 filter paper, washed with aquadest, and dried for 3 hours at 110 °C. The dried precipitate was then ground into powder using a mortar and characterized by Fourier Transform Infrared (FTIR) spectroscopy [23].

3. Natural Zeolite Activation

Commercial natural zeolite was milled and sieved up to 250 g, using a 100 mesh sieve, shaken at 50 amplitude for 15 minutes. A 100 g portion of sieved zeolite was refluxed with 3 M HCl at 90°C for 30 minutes. The mixture was filtered using Whatman no. 42 paper and washed with distilled water until free of Cl^- ions. The activated zeolite was then dried at 120°C for 24 hours and ground into a fine powder [24].

4. Hydroxyapatite-Zeolite Synthesis

Hydroxyapatite and zeolite were weighed in three ratios: 2:4, 2:2, and 4:2 (w/w). Each ratio was dissolved in 100 mL aquadest and stirred using a magnetic stirrer for 60 minutes. The mixture was then centrifuged at 3500 rpm for 15 minutes. The composite was dried for 1 hour and 30 minutes, and the resulting hydroxyapatite–zeolite powder was characterized using an FTIR spectrophotometer.

5. Methylene Blue Absorption Test [5]

The methylene blue (MB) adsorption test was carried out using hydroxyapatite–zeolite composites in three different ratios (2:4, 2:2, 4:2) with an MB solution concentration of 40 ppm. A reference curve was created by measuring the absorbance of methylene blue solutions at concentrations 0.5 ppm, 5.5 ppm, 10.5 ppm, 15.5 ppm, and 20.5 ppm, dissolved in HCl, using a UV-Vis spectrophotometer.

A 0.05 g of the hydroxyapatite–zeolite composite was weighed, and 15 mL of 40 ppm methylene blue solution was added to an Erlenmeyer flask. The solution was homogenized using a reciprocal shaker at 150 rpm for 120, 180, and 240 minutes. After agitation, the solution was centrifuged at 3500 rpm for 15 minutes. The absorbance of the filtrate was measured at a wavelength of 664.5 nm using a UV-Vis spectrophotometer..

RESULT AND DISCUSSION

1. Calcining of chicken eggshells

Calcination of the eggshell occurs to remove organic matter and to convert calcium carbonate ($CaCO_3$) to lime (CaO), with an initial mass of up to 0.9660 kg. The eggshell is predominantly composed of $CaCO_3$, which can be utilized to synthesize hydroxyapatite (HAp). However, a more refined synthesis process is needed to produce highly pure HAp. Most HAp synthesized via the calcination method exhibits high crystallinity [8].

Calcium carbonate ($CaCO_3$) is a white solid with up to 49% Ca content. The calcination temperature is set at 900 °C, during which a color change of the eggshell from light ash to white is observed [25]. The resulting adsorbent is odorless and in powdered form. Calcination at 900 °C promotes the formation of pure CaO crystals through the decomposition of $CaCO_3$, accompanied by the release of carbon-based organic residues, as per the reaction :

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Calcination reactions occur more rapidly at higher temperatures. The decomposition of $CaCO_3$ into CaO and CO_2 is accelerated as the temperature increases. The concentration of $CaCO_3$ and the calcination time also influence this process. As time increases, decomposition occurs at

the surface of the adsorbent and within its interior due to heat diffusion. Prolonged exposure to high temperatures (especially above 800–900°C) can lead to HAp decomposition or secondary phase formation [26]. The color change from yellowish-white to white is illustrated in Figure 1.

Figure 1. $Ca(OH)_2$ powder

2. Determination of Calcium (Ca) Levels

The calcium content of the eggshell derived after calcination was calculated using Atomic Absorption Spectroscopy (AAS), a commonly used method for quantitatively determining elements because of its high sensitivity and accuracy. In this research, the AAS was carried out on the broiler chicken eggshells-based sample in powder form 100% stoichiometric as-obtained calcined at 900°C for 5 h to guarantee the complete transformation of calcium carbonate ($CaCO_3$) into calcium oxide (CaO).

Before the AAS analysis, the calcium powder was dissolved in nitric acid (HNO_3) to bring the calcium into ionic form (Ca^{2+}). The sample solution was aspirated into, for example, a flame or graphite furnace and the absorbance was measured at the calcium resonance line (e.g., 422.7 nm). The absorbance was measured against standard Ca solutions of known concentrations by means of a calibration curve.

AAS showed that the calcium content of the calcined eggshell powder was 49%w/w, which agrees with the theoretical value of calcium in pure CaO and reflects a high degree of purity. The high content of Ca concludes that the chicken eggshell derived CaO is a good Ca precursor in hydroxyapatite (HAp) synthesis because hydroxyapatite requires a Ca/P molar ratio nearly equal 1.67. The high calcium content provides sufficient stoichiometric amount available for this synthesis, indicating that calcinated chicken eggshells would be appropriate to serve as a low-cost, green, and efficient calcium source for HAP preparation [27].

The deposition of calcium in eggshell after calcination was analyzed by Atomic Absorption Spectroscopy (AAS), which is an excellent tool for quantitative determination of metal ions due to the high sensitivity and accuracy for the most of elements. The AAS measurement of the eggshell powder sample that had been utilized for AAS measurement was carried out on the broiler chicken eggshells sample that undergoes calcination at 900°C for 5 hours representing 100% broiler chicken eggshells, to ensure that all-samples were fully converted from calcium carbonate ($CaCO_3$) to calcium oxide (CaO).

An AAS method (aqueous digest) was used, where digestion of the calcinated powder with nitric acid (HNO_3) was carried out to convert calcium to ionic form (Ca^{2+}). The sample solution was then immersed in a flame or graphite furnace, and the absorbance was read at a suitable calcium

resonance line (usually 422.7 nm). Absorbance was referred to the calibration curve obtained from standard calcium solutions with known concentrations.

The AAS data revealed that the Ca content of calcined eggshell powder was 49 weight percent. It is following the theoretical Ca content in pure CaO and the high purity of the sample. Thus, this high Ca content suggests that the chicken eggshell-derived CaO can be a potential precursor for hydroxyapatite (HAp) synthesis since the stoichiometric hydroxyapatite should have a Ca/P molar ratio of close to 1.67. The high calcium level provides more than enough stoichiometric availability for this synthesis, consequently, calcinated eggshell is shown to be a good, low-cost, sustainable, and effective source of calcium for HAp production [27]

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

This is due to the conversion of CaO to $Ca(OH)_2$, and this process is temperature-dependent, so that at high temperatures, $CaCO_3$ disappears more slowly, and the appearance of $Ca(OH)_2$ occurs since $CaCO_3$ decomposes to CaO. (B) CaO Conversion Purpose (i) CaO formed was left in the open air at room temperature for 1 week. This aimed to convert CaO to a reagent source of $Ca(OH)_2$ by contact with atmospheric moisture. The reaction associated with the hydration is

$$2CaO_{(s)} + H_2O_{(g)} \rightarrow Ca(OH)_{2(s)}$$

The calcination results of CaO transformed into $Ca(OH)_2$ due to contact with air were analyzed by XRD, as seen in Figure 2.

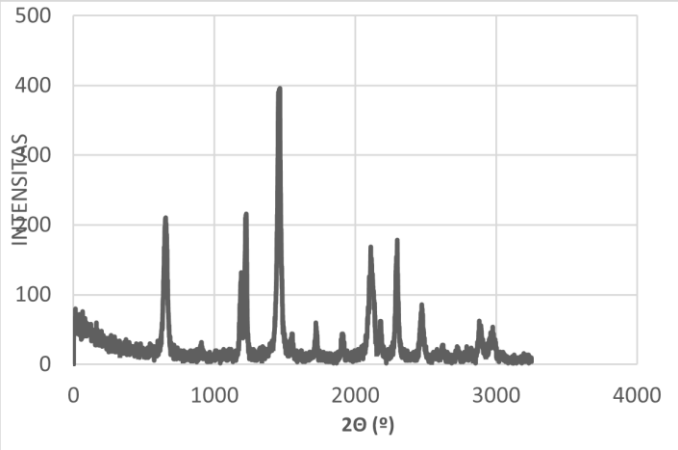

Figure 2 Diffractogram of CaO conversion to $Ca(OH)_2$

The phase purity from XRD peaks indicates the material's crystallinity. A well-crystallized HAp sample ideally exhibits only sharp, clear peaks coinciding with a pure hexagonal HAp pattern according to the JCPDS standard. Based on the XRD results, characteristic 2θ values of the calcined eggshell into $Ca(OH)_2$ were observed at 18.04°, 28.74°, 29.44°, 34.16°, 47.20°, 50.88°, and 54.42°, with the highest peak at 34.16°. These peaks correspond to $Ca(OH)_2$

compounds according to JCPDS card No. 41-1481.

The crystal shape observed is trigonal (space group R), with lattice parameters of a=3.5956a = 3.5956a=3.5956 Å and c=4.9280c = 4.9280c=4.9280 Å, dominated by the highest intensity peaks at 34.16°, 18.04°, and 47.20°. The elemental composition of the material consisted of O (44.8%), Ca (49.0%), C (3.6%), Si (0.8%), and H (1.9%)

4. Characterization of Hydroxyapatite

Hydroxyapatite was synthesized using the precipitation method, a wet chemical deposition method, and purebred chicken eggshells as the calcium source. The calcium (Ca) source was obtained from eggshells calcined into CaO and subsequently hydrated to $Ca(OH)_2$. The phosphate source was diammonium phosphate ($(NH_4)_2HPO_4$), yielding 91.30%. The reaction for hydroxyapatite formation is as follows:

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O + 12NH_4OH$$

In the chemical precipitation steps, adding distilled water to biphasic CaO and $Ca(OH)_2$ resulted in complete conversion of CaO to $Ca(OH)_2$. The $Ca(OH)_2$ precursor was then reacted with $(NH_4)_2HPO_4$ at a molar ratio of 1.67:1 to achieve complete formation of hydroxyapatite (HAp). The 1.67 Ca/P molar ratio is crucial for the formation of stoichiometric HAp, which theoretically has a Ca/P ratio of 1.67.

XRD characterization was used to identify the crystalline phases formed from the synthesis reaction between calcium oxide (CaO) and diammonium phosphate ($(NH_4)_2HPO_4$), as shown in Figure 3.

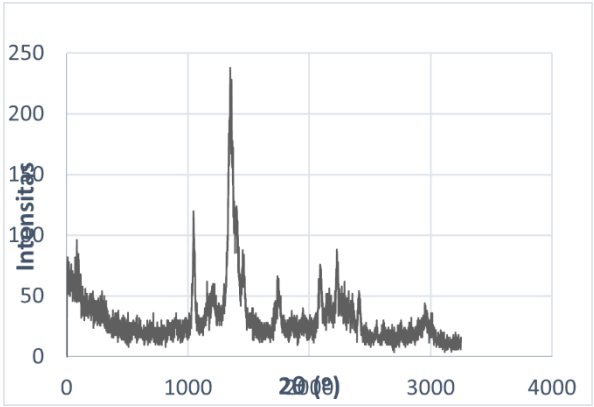

Figure 3. XRD results of synthesized hydroxyapatite

Hydroxyapatite peaks appeared at 2θ angles of 25.90°, 31.98°, 34.08°, 39.88°, 46.80°, and 49.56°. The analysis results confirmed that the sample was hydroxyapatite because the diffraction peaks matched the characteristic peaks of hydroxyapatite. The strongest peak appeared at 2θ = 31.98°, indicating high crystallinity. The XRD pattern matched the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ structure

according to JCPDS card No. 09-0432. The data indicated the crystal structure was hexagonal, with lattice parameters a = 9.4166 Å and c = 6.8745 Å. The elemental composition showed that the hydroxyapatite consisted of oxygen (O) at 41%, calcium (Ca) at 39.9%, phosphorus (P) at 18.5%, and hydrogen (H) at 0.2%, confirming the formation of pure hydroxyapatite. These results demonstrate that chicken eggshells are an excellent material for use as a calcium precursor in hydroxyapatite synthesis

5. Natural Zeolite Activation

The natural zeolites in Indonesia are abundant and inexpensive and have been widely sold in the market [28]. Natural zeolite activation in this study was achieved both physically and chemically. Physical activation included sample size reduction, sieving, and calcination, which increased the surface area and widened the zeolite pores, thereby enhancing the Si/Al ratio at the same volume of zeolite and increasing the specific surface area of the material [29].

Chemical activation was performed by immersing the zeolite in 3 M HCl solution. This chemical treatment aimed to remove and dissolve metal oxides covering the pores, allowing expansion of the cavity volume and facilitating adsorption between adsorbate and adsorbent. The use of 3 M HCl also positively promoted the decationization of the zeolite by leaching sodium (Na) and potassium (K), thus increasing the silicate modulus. Acid activation effectively removed most sodium and potassium impurities from the zeolite. The crystallinity of mordenite-type zeolite after activation was 23.8% [30]. The higher crystallinity after activation has been attributed to a reduction in impurities on the zeolite surface [24]

6. Hydroxyapatite-Zeolite Synthesis

The synthesis of the hydroxyapatite-zeolite composite involved combining reactants with both acidic and basic characteristics, such as hydroxyapatite and zeolite. The composites were prepared by mixing hydroxyapatite and zeolite powders at 2:4, 2:2, and 4:2 mass ratios to determine the optimal adsorbent composition. Characterization of the hydroxyapatite-zeolite composites was carried out using FTIR spectroscopy.

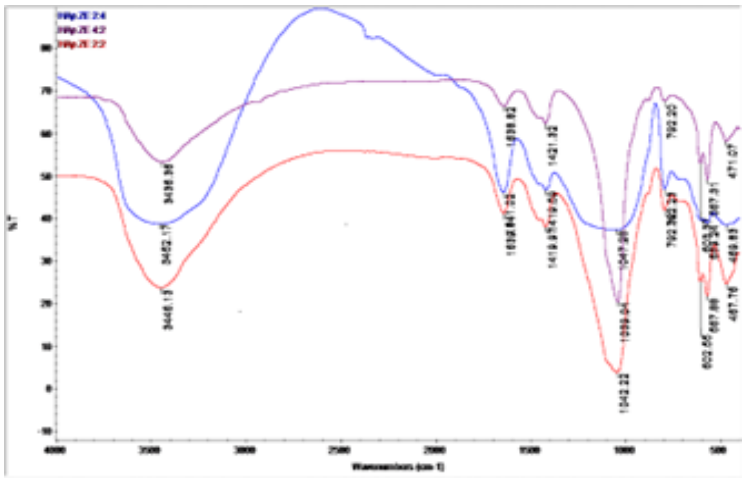

Figure 4. Composites of Hap-Zeolite 2:4; 2:2; and 4:2

The functional groups identified in the HAp-zeolite composites for the 2:4, 2:2, and 4:2 ratios included –OH, Si–O, and =C=C groups. In the 2:4 ratio, the –Si–O group appeared at a wave number of 1047 cm^{-1}, the =C=C group at 1420 cm^{-1}, and the –OH group at 3462 cm^{-1}. In the 2:2 ratio, the –Si–O group was observed at 1042 cm^{-1}, the =C=C group at 1420 cm^{-1}, and the –OH group at 3446 cm^{-1}. In the 4:2 ratio, the –Si–O group appeared at 1039 cm^{-1}, the =C=C group at 1421 cm^{-1}, and the –OH group at 3436 cm^{-1}. A common peak for all composites was also observed at 792 cm^{1} [7].

The hydroxyapatite and zeolite functional groups were consistently present across all mass ratios, with slight shifts in wave numbers. These small shifts are attributed to the absorption characteristics of the composites

7. Methylene Blue Absorption

The adsorption study was conducted by varying the contact times of 120, 180, and 240 minutes, and using different mass ratios of hydroxyapatite (HAp) to zeolite (2:4, 2:2, and 4:2). The concentration of unabsorbed methylene blue and the adsorption efficiency were measured and are presented in Table 1.

Table 1. Methylene Blue Adsorption Results Time Variation 120, 180, and 240 Minutes

Time (Minutes)	Hap-Zeolite	Unabsorbed Residual Methylene Blue Concentration (ppm)	Adsorbed Methylene Blue Concentration (ppm)	Uptake Efficiency (%)
120	2:4	0,3375	39,6625	99,1562
	2:2	0,3121	39,6879	99,2190
	4:2	0,2797	39,7203	99,3007
180	2:4	0,0994	39,9006	99,7515
	2:2	0,0751	39,9249	99,8120
	4:2	0,0034	39,9966	99,9915
240	2:4	0,3387	39,6613	91,1532
	2:2	0,0739	39,9261	99,8152
	4:2	0,5641	39,4359	98,5891

From the analysis of methylene blue adsorption at different contact times (120, 180 and 240 min) and different adsorbent mass ratios (2:4, 2:2 and 4:2 of HAp to zeolite), the best performances were obtained with 180 min of contact time when the mass ratio was 4:2. At this concentration, the adsorbed methylene blue concentration was 39.9966 ppm, translating into an adsorption efficiency up value of 99.9915%. This means the adsorption process was almost saturated, and the minimum amount of dye remained in the solution.

The higher performance at such a ratio is because of the synergistic effect of hydroxyapatite and zeolite, at a certain percentage of zeolite addition which is responsible in increasing the surface area of the composites and increasing the active site of the composites. The incorporation of zeolite is associated with decreased coloration of the solution, demonstrating efficient dye adsorption. It is widely recognized that color removal depends on adsorption; the deeper, the better, and the more apparent the solution, the higher the adsorption.

Moreover, the improved efficiency could be due to the mechanisms such as electrostatic interaction, ion exchange, surface complexation, etc, between the dye molecules and the functional groups present in the composite surface. The decreased efficiency at contact times longer than 240 minutes (i.e., for 2:4 and 4:2) is probably related to desorption processes or to the saturation of binding sites. These findings support the principle that a longer duration is not automatically associated with a better adsorption result, but can also lead to negative diffusion of adsorbed molecules. This result agrees with the findings of previous works [14], [31], which indicated that the optimal values for contact time and material ratio are necessary to reach the maximum adsorption capacity and process efficiency.

8. Characterization of HAp and HAp-Zeolite

a. FTIR spectrum of HAp synthesis

FTIR analysis is a standard method used to identify functional groups in a material and examine interactions among its constituents. In the synthesized hydroxyapatite (HAp), a broad absorption band corresponding to hydroxyl groups (–OH) was observed at 3434 cm¹. The carbonate group (CO_3^{2-}) was detected at 1421 cm^{-1}, while the stretching vibration of the phosphate group ($–PO_4^{3-}$) was found at 1035 cm^{-1}. Bending vibrations of the phosphate group ($–PO_4^{3-}$) appeared at 565 cm¹. The FTIR data confirm the formation of HAp in the samples, with phosphate groups being the dominant component and minor signals attributed to residual calcium carbonate ($CaCO_3$).

b. HAp-Zeolite Synthesis Spectrum

In the FTIR spectra of the HAp–Zeolite composite, characteristic peaks for hydroxyl (–OH), carbonate (CO_3^{2-}), and phosphate ($–PO_4^{3-}$) groups remained evident at 3446 cm^{-1}, 1421 cm^{-1}, and 1035 cm^{-1}, respectively. New functional groups were also observed, including a strong Si–O stretching vibration at 1042 cm^{-1} and a C=C stretching band at 1420 cm^{-1}. These peaks suggest successful incorporation of zeolite into the composite material.

The broadening of the composite's Si–O absorption band further supports the formation of a HAp–Zeolite hybrid. This indicates that zeolite was successfully integrated into the HAp matrix via precipitation. The addition of zeolite improved the physicochemical stability of hydroxyapatite and mitigated its known mechanical limitations. The optimized composite (HAp: Zeolite ratio of 4:2, contact time of 180 minutes) demonstrated excellent adsorption efficiency of 99.9915% for methylene blue dye, highlighting its potential as an effective adsorbent

CONCLUSION

FTIR characterization of hydroxyapatite revealed functional groups including carbonate (CO_3^{2-}) at 1421 cm^{-1}, hydroxyl (–OH) at 3434 cm^{-1}, and phosphate (PO_4^{3-}) stretching bands at 1035 cm^{-1}, with antisymmetric bending vibrations at 604 cm^{-1} (v_4) and 471 cm^{-1} (v_2). XRD analysis confirmed the formation of HAp, showing a

main peak at 2θ = 34.04°, in agreement with the JCPDS standard No. 09-432.

The synthesis of the hydroxyapatite–zeolite composite was also successful. The FTIR spectra showed new functional group signals at 3446 cm^{-1} (–OH), 1042 cm^{-1} (Si–O), and 1420 cm^{-1} (C=C), indicating the incorporation of zeolite. The enhanced Si–O absorption band further validated the presence of zeolite in the composite matrix. Performance evaluation revealed that the hydroxyapatite–zeolite composite achieved a maximum methylene blue adsorption efficiency of 99.9915% at a 4:2 mass ratio and 180-minute contact time. These results suggest the composite material has strong potential for dye removal applications in wastewater treatment.

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