

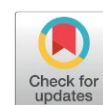
Phytochemical-Mediated Green Synthesis of ZnO/Hydroxyapatite Nanocomposite from Shallot Peel Extract and Seashell Waste for Visible-Light-Assisted Photocatalytic Degradation of Remazol Red RB Textile Dye

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Abstract

Textile wastewater containing persistent synthetic dyes poses significant environmental concerns due to the toxicity and low biodegradability of these dyes. This study developed a sustainable ZnO/hydroxyapatite (ZnO/HA) nanocomposite photocatalyst using shallot peel extract and seashell waste as renewable precursors for the visible-light-assisted degradation of Remazol Red RB (RRRB) dye. ZnO nanoparticles were synthesized through a phytochemical-mediated route using aqueous shallot peel extract, while hydroxyapatite was obtained from seashell waste. The resulting ZnO/HA nanocomposite, prepared at a mass ratio of 1:2.5, was characterized using XRD, FTIR, SEM-EDX, and point-of-zero-charge analysis. The effects of catalyst dosage, solution pH, initial dye concentration, and irradiation time on RRRB degradation were investigated under a 50 W visible-light source. XRD analysis confirmed the coexistence of crystalline ZnO and hydroxyapatite phases, with an average crystallite size of 24.80 nm and crystallinity of 80.20%. The highest degradation efficiency obtained in the investigated conditions was 95.85% for 10 mg/L RRRB in 250 mL solution at pH of 6 using 1.0 g of ZnO/HA after 150 min irradiation. Under identical conditions, pristine ZnO achieved 93.40% degradation. The modest improvement indicates that the contribution of hydroxyapatite was primarily associated with surface adsorption, dispersion of ZnO, and increased pollutant–catalyst interaction rather than a demonstrated modification of the ZnO band structure. Because UV–Vis diffuse reflectance and catalyst-reusability measurements were not performed, changes in optical bandgap and long-term catalyst stability could not be experimentally established. Nevertheless, the results demonstrate the feasibility of utilizing two locally available biowaste resources to prepare a ZnO/HA material for visible-light-assisted dye treatment.

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Keywords: Green synthesis; hydroxyapatite; remazol red RB; visible-light photocatalysis; ZnO/HA nanocomposite

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1. Introduction

Synthetic textile dyes are a major source of environmental contamination. Large quantities of these dyes are discharged from textile industries into aquatic environments, which serve as

essential resources for ecosystems and human communities. Among various synthetic dyes, azo dyes are the most widely used due to their strong color stability and cost-effectiveness. However, these compounds are highly persistent and pose significant risks to aquatic ecosystems and human health because many of them are toxic, carcinogenic, and mutagenic [1]. The discharge of

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untreated textile wastewater into water bodies also causes intense coloration and increased turbidity, which reducing light penetration into the water column. This condition disrupts photosynthetic processes and promotes anaerobic activity, leading to the formation of unpleasant and potentially harmful byproducts [2]. Therefore, the development of efficient, sustainable, and environmentally friendly technologies for the treatment of textile wastewater is urgently needed.

Various treatment technologies have been investigated, including physical methods such as adsorption using activated carbon and agricultural wastes [3-5], chemical oxidation processes such as electrochemical oxidation [6,7], biological degradation using bacteria [8,9] and fungi [10], as well as physicochemical approaches such as photocatalytic degradation [11,12]. Among these methods, photocatalytic degradation has attracted considerable attention due to its high efficiency and environmental compatibility.

Photocatalysis offers several advantages over conventional treatment methods. It can operate under mild environmental conditions, requires relatively low energy input, and is capable of completely mineralizing organic pollutants into harmless end products such as CO₂ and H₂O rather than merely transferring contaminants to another phase as occurs in adsorption or coagulation processes [13,14]. In addition, photocatalytic processes generally require minimal chemical additives and produce fewer secondary pollutants [15]. In this process, light irradiation activates a semiconductor photocatalyst generating highly reactive species, such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$), which play crucial roles in the degradation of organic pollutants [16].

The ZnO is considered one of the most promising semiconductor photocatalysts due to its high electron mobility, chemical stability, low toxicity, low cost, and ease of synthesis [17,18]. However, ZnO suffers from several limitations, including the rapid recombination of photogenerated electron-hole pairs, which significantly reduces the formation of reactive radicals and consequently decreases photocatalytic efficiency [19]. However, the relatively wide band gap of ZnO (approximately 3.2–3.37 eV) intrinsically limits its strong optical absorption mainly to the ultraviolet region [20]. Therefore, the use of ZnO under visible-light irradiation requires careful interpretation because apparent visible-light-assisted activity does not necessarily demonstrate a reduction in the intrinsic band gap. Previous studies have explored the incorporation of ZnO with porous or mineral supports, including hydroxyapatite, to improve pollutant adsorption, ZnO dispersion,

surface accessibility, and interfacial interactions [21-23]. Such composite formation may facilitate the contact between pollutant molecules and photocatalytically active sites, although changes in the optical band structure should be verified experimentally using techniques such as UV-Vis diffuse reflectance spectroscopy (DRS). Despite the increasing number of studies on ZnO-based photocatalysts and ZnO-supported composites, several aspects remain insufficiently addressed. Previous studies have mainly focused on modifying ZnO using synthetic dopants, semiconductor heterojunctions, or conventional porous supports to improve photocatalytic performance [24-25]. Although hydroxyapatite has been investigated as a support for photocatalytic materials, the simultaneous utilization of shallot peel as a phytochemical-mediated precursor for ZnO synthesis and seashell waste as a precursor for hydroxyapatite provides an alternative biowaste-based material platform that has received comparatively limited attention for Remazol Red RB degradation. In addition, the integration of these two waste-derived components provides an opportunity to combine the photocatalytic function of ZnO with the surface and adsorption characteristics of hydroxyapatite.

Therefore, the scientific novelty of the present study lies in the integration of two locally available biowaste resources into a ZnO/HA nanocomposite, in which shallot peel phytochemicals are utilized during ZnO synthesis and seashell-derived hydroxyapatite serves as the mineral component. The novelty is further demonstrated through the systematic evaluation of the material characteristics and the effects of pH, initial dye concentration, catalyst dosage, and irradiation time on Remazol Red RB degradation under visible-light-assisted conditions. The present study does not claim a modification of the intrinsic ZnO bandgap or a specific charge-transfer mechanism, because such phenomena require additional optical and charge-carrier measurements. Instead, the study provides experimental evidence for the feasibility of a waste-derived ZnO/HA material and evaluates the contribution of hydroxyapatite as an adsorptive and supporting component in dye removal.

Based on this research gap, the objective of this study was to synthesize ZnO using phytochemical compounds from Balinese shallot peel extract, combine the synthesized ZnO with hydroxyapatite derived from seashell waste, characterize the resulting ZnO/HA nanocomposite, and evaluate its performance for the visible-light-assisted degradation of Remazol Red RB under different operating conditions.

2. Materials and Methods

2.1. Materials

The primary compounds utilized in this study, such as $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ Merck 108802, NaOH Merck 1.06498.1000, and HCl 37% Merck 1.00317.2500, are of analytical grade purity. The HA was obtained from previous synthesis [26], the Balinese local shallot peel was obtained from Buleleng traditional market, while RRRB dye was sourced from a textile dye manufacturer.

2.2. Preparation of Balinese local shallot peel aqueous extract

An aqueous extract of Balinese local shallot peel was prepared by placing 10 g of dried shallot peel powder into a 1000 mL beaker, then adding 350 mL of deionized water. The mixture was heated at 65 °C for 60 min. while stirring using a magnetic stirrer. Next, it was allowed to cool and filtered using Whatman filter paper size 42. Qualitative tests were carried out on flavonoids, alkaloids, and tannins contained in the shallot peel water extract.

2.3. Green synthesis of ZnO

The green synthesis of ZnO was conducted using phytochemical compounds present in the aqueous extract of Balinese local shallot peel as the biogenic component and zinc acetate dihydrate as the zinc precursor. Briefly, 10 g of dried shallot peel powder was dispersed in 350 mL of deionized water, corresponding to a solid-to-liquid ratio of 28.6 g/L. The suspension was heated at 65 °C for 60 min under continuous magnetic stirring and subsequently cooled to room temperature. The extract was filtered through Whatman No. 42 filter paper. For ZnO synthesis, 100 mL of the filtered shallot peel extract was transferred into a 500 mL beaker, followed by the addition of 4.5 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The resulting precursor mixture was stirred continuously and adjusted to pH 8 using NaOH solution 20 mol/L. The mixture was then maintained at 65 °C for 30 min until a yellowish paste was formed. The paste was collected and dried at 105 °C for 24 h. The dried material was subsequently calcined at 500 °C for 2 h to obtain ZnO powder.

2.4. Preparation and characterization of ZnO/HA nanocomposites

The ZnO/HA nanocomposite was synthesized by combining the prepared ZnO powder with HA at a weight ratio of 1:2.5. A certain amount of deionized water was added to the mixture until it formed a slurry and was then put into a milling machine for 24 hours to produce nano-sized particles. The ZnO/HA nanocomposites were

calcined at 600 °C for 3 hours, then characterized using an X-ray diffractometer (XRD; Bruker D8 Advance, Bruker, Germany) using Cu-K α radiation. Fourier-transform infrared (FTIR) spectra were recorded using an FTIR spectrometer (merk Shimadzu, type IR Prestige 21) over the wavenumber range of 400–4000 cm^{-1} . The morphology and elemental composition of the materials were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX; JEOL JSM-IT300 equipped with an Oxford XMax 20 EDX detector). The absorbance of RRRB solutions before and after photocatalytic treatment was measured using a UV–Vis spectrophotometer (Shimadzu UV-2600i, Shimadzu Corporation, Japan) at 518 nm.

2.5. Evaluation of the Point of Zero Charge (pH_{pzc}) of ZnO, HA, and the ZnO/HA Nanocomposite

The pH_{pzc} of ZnO, HA, and the ZnO/HA nanocomposite was evaluated to determine the surface charge characteristics of the materials. For this purpose, 0.1 g of each sample was individually dispersed in 25 mL of deionized water with predetermined pH values ranging from 2 to 12. The pH of the solutions was adjusted prior to the addition of the materials using dilute HCl or NaOH solutions. The suspensions were then allowed to equilibrate for 48 h to ensure sufficient interaction between the solid surface and the solution. After this period, the final pH of each suspension was recorded. The pH_{pzc} value was determined by plotting the final pH against the initial pH, where the pH at which no change in pH was observed was taken as the point of zero charge of the corresponding material.

2.6. Photodegradation test of textile dyes under visible light irradiation

Photocatalytic degradation tests were performed in a batch photoreactor under continuous illumination provided by a 50 W visible-light source. The RRRB, an anionic azo dye commonly used in textile applications, was selected as the model organic contaminant. The photocatalytic system consisted of a ZnO/HA nanocomposite serving as the active catalyst. A schematic diagram of the experimental setup for RRRB degradation under visible-light irradiation is presented in Figure 1.

A total of 1.0 g of ZnO/HA nanocomposite was added to 250 mL of 10 mg/L RRRB dye solution and continuously stirred using a magnetic stirrer. This effects of various operational parameters, including initial pH (4–8), dye concentration (5–20 mg/L), nanocomposite dosage (0.25–2.0 g), and irradiation time (30–180 min), on the photocatalytic degradation efficiency were

systematically investigated. The absorbance of dye solution before and after photocatalytic treatment was measured using a UV-Vis spectrophotometer at a wavelength of 518 nm. The photocatalytic degradation efficiency was calculated using the following equation:

$$\text{Degradation efficiency}(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where, A_0 and A_t represents the absorbance of the dye solution at the initial time and at the reaction time (t), respectively.

3. Results and Discussion

3.1. Phytochemical Screening of Balinese Local Shallot Peel Aqueous Extract

Phytochemical tests were conducted to identify the presence of flavonoids, alkaloids, and tannins in the aqueous extract of Balinese local shallot peel. These phytochemical compounds act as precursors in the formation of ZnO. The qualitative test results of the phytochemical compounds are summarized in Table 1.

3.2. Characteristic of ZnO, HA, and ZnO/HA Nanocomposite

3.2.1. XRD pattern

The crystalline structure and crystallite size of ZnO, HA, and the ZnO/HA composite were examined using XRD, and the corresponding diffraction patterns are presented in Figure 2. The average crystallite size was calculated from the most intense diffraction peak using the Debye-Scherrer equation [27]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where K represents the shape factor, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ corresponds to the Bragg diffraction angle.

The X-ray diffraction profile of the synthesized sample displayed a series of well-defined reflections at 2θ values of 25.96°, 29.49°, 31.93°, 33.09°, 34.22°, 36.34°, 39.99°, 46.85°, 49.60°, 56.97°, and 63.21°. These peaks were indexed to the (002), (210), (211), (300), (202), (302), (310), (222), (213), (004), and (304)

Table 1. Qualitative phytochemical analysis of the aqueous extract of locally sourced Balinese shallot peel.

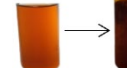
Phyto chemicals compound	Test/Reagents	Result
Flavonoid	Shinod test Mg + extract + HCl → orange 	Positive
	Ferric Chloride test FeCl ₃ + extract → Blackish green 	Positive
Alkaloid	Dragendorff's test Dragendorff's reagent + extract. → reddish-brown precipitate 	Positive
Tannin	Ferric chloride test Extract + FeCl ₃ → Blackish green 	Positive



Figure 1. Photoreactor setup for dye solution degradation.

crystallographic planes, respectively, which are recognized as the characteristic reflections of HA. The peak positions closely match the standard diffraction data for hexagonal HA (JCPDS/PDF No. 09-0432), confirming the successful formation of the apatite phase. In particular, the reflection at 25.96° corresponds to the (002) plane, while the prominent peaks at 29.49° , 31.93° , and 33.09° are associated with the (210), (211), and (300) planes. Additional reflections at 34.22° , 39.99° , 46.85° , and 49.60° were assigned to the (202), (310), (222), and (213) planes, whereas the peaks at 56.97° and 63.21° correspond to the (004) and (304) planes, respectively. Quantitative analysis yielded a degree of crystallinity of 78.20% and an average crystallite size of 25.81 nm, indicating a well-ordered crystal structure and the formation of nanocrystalline HA.

The XRD pattern of the ZnO synthesized using the aqueous extract of shallot peel exhibited distinct reflections at 2θ values of 31.797° , 34.470° , 36.280° , 47.589° , 56.637° , 62.914° , and 68.016° . These diffraction peaks are characteristic of crystalline ZnO with a hexagonal wurtzite structure. The reflection were indexed to the (100), (002), (101), (102), (110), (103), and (112) crystallographic planes, respectively, and were consistent with the standard reference data for ZnO (JCPDS No. 36-1451). The presence of sharp and well-defined peaks at these positions confirms the successful formation of crystalline ZnO. The sample exhibited a degree of crystallinity 79.90% and an average crystallite size of 20.26 nm. The relatively high crystallinity reflects effective crystal development during the green synthesis process and further supports the successful formation of ZnO.

The XRD pattern of the ZnO/HA nanocomposite displayed distinct reflections at 2θ positions of 25.944° , 29.497° , 31.991° , 32.279° , 33.062° , 34.237° , 36.336° , 39.472° , 46.821° , 47.385° , 49.566° , 56.708° , and 63.127° . The

presence of these reflections indicates the coexistence of HA and ZnO phases within the nanocomposite. The peaks at 25.944° , 31.991° , 32.279° , 33.062° , 34.237° , 39.472° , 46.821° , and 49.566° were indexed to the (002), (211), (112), (300), (202), (310), (222), and (213) planes of hexagonal HA, in good agreement with the standard data of JCPDS No. 09-0432. In addition, the reflections at 2θ values of 34.237° , 36.336° , 47.385° , 56.708° , and 63.127° corresponded to the (002), (101), (102), (110), and (103) planes of wurtzite ZnO, consistent with the reference pattern of JCPDS No. 36-1451. The simultaneous appearance of characteristic peaks from both HA and ZnO demonstrates the successful incorporation of the two crystalline phases into the ZnO/HA nanocomposite. The nanocomposite exhibited a degree of crystallinity of 80.20% and an average crystallite size of 24.80 nm, indicating the presence of well-developed crystalline domains and a relatively ordered structure.

3.2.2. FTIR spectrum

FTIR spectroscopy was employed to identify the functional groups presence in ZnO, HA, and the ZnO/HA nanocomposite, with the resulting spectra presented in Figure 3. The FTIR spectrum of the synthesized ZnO exhibited several prominent absorption bands at 3672.00 , 1650.15 , 1548.42 , 1434.04 , 838.71 , 591.35 , 554.65 , 509.55 , and 458.48 cm^{-1} . The absorption bands detected in the $458\text{--}591\text{ cm}^{-1}$ region were attributed to Zn–O stretching vibrations, which recognize the characteristic fingerprint region of ZnO and confirm its successful formation. The broad band at 3672 cm^{-1} , together with the band at 1650 cm^{-1} , was corresponded to O–H stretching and H–O–H bending vibrations, respectively. These bands indicate the presence of physically adsorbed water molecules and/or residual hydroxyl groups, which may be associated with incomplete dehydration of $\text{Zn}(\text{OH})_2$ intermediates during synthesis process.

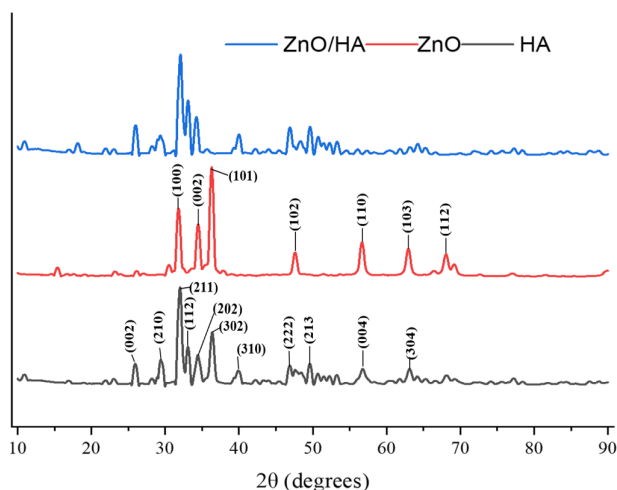


Figure 2. XRD pattern of ZnO, HA and ZnO/HA.

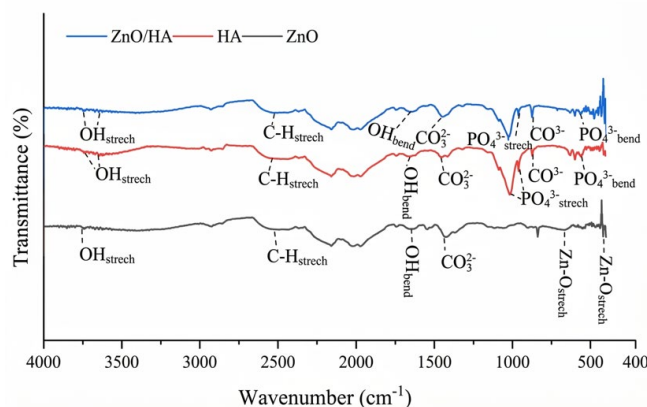


Figure 3. FTIR spectra of the prepared ZnO, HA, and ZnO/HA nanocomposite materials.

Moreover, the bands at 1434.04 and 1548.42 cm^{-1} may be attributed to carbonate species, possibly resulting from the adsorption of atmospheric CO_2 on the ZnO surface. The adsorption band 838.71 cm^{-1} may also be related to carbonate group species depending on the specific vibrational assignment used for the synthesized material.

The FTIR spectrum of HA displays several characteristic absorption bands at 3741.22, 3645.95, 1017.84, 962.14, 873.63, 630.82, and 561.63 cm^{-1} , corresponding to the characteristic vibrational modes of the HA framework. The bands observed at 3741.22 and 3645.95 cm^{-1} are assigned to the stretching vibrations of OH groups, which are characteristic of HA lattice. The prominent absorption band at 1017.84 cm^{-1} can be assigned to the asymmetric stretching vibration of the PO_4^{3-} groups, providing evidence for the presence of phosphate within the HA structure. In addition, the band at 962.14 cm^{-1} corresponds to the symmetric stretching vibration of PO_4^{3-} . The absorption feature at 561.63 cm^{-1} is associated with the bending vibration of the PO_4^{3-} groups and is commonly observed in crystalline HA. In addition, the bands detected at 1434.04 and 873.63 cm^{-1} are attributed to CO_3^{2-} groups, suggesting the incorporation of carbonate species, possibly through exposure to atmospheric CO_2 during the synthesis process.

The FTIR spectrum of ZnO/HA nanocomposite exhibits several characteristic absorption bands at 3672.00, 3646.57, 1650.29, 1454.06, 1025.04, 962.53, 875.34, 599.92, 563.78, 477.67, 450.53, and 431.40 cm^{-1} . The bands located at 3672.00 and 3646.57 cm^{-1} are assigned to the stretching vibrations of structural hydroxyl (OH) groups associated with the HA phase. The absorption feature at 1650.29 cm^{-1} is attributed to the bending vibration of molecular water adsorbed on the sample surface. Meanwhile, the bands at

1454.06 and 875.34 cm^{-1} indicate the presence of carbonate (CO_3^{2-}) groups, suggesting partial substitution of carbonate species within the HA lattice. The intense bands observed at 1025.04 and 962.53 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of PO_4^{3-} groups, respectively. The bands at 599.92 and 563.78 cm^{-1} are associated with the bending modes of PO_4^{3-} , further supporting the formation of the HA phase. In addition, the absorption bands at 477.67, 450.53, and 431.40 cm^{-1} can be assigned to Zn–O vibrational modes, providing evidence for the presence of ZnO in the nanocomposite. The coexistence of ZnO and HA phases in the nanocomposite was also confirmed by XRD data.

3.2.3. SEM-EDX of ZnO/HA nanocomposite

The morphology and elemental content of HA and ZnO/HA composite were assessed using SEM-EDX, in which the surface morphology and distribution of ZnO on HA surface are exhibited in Figure 4. SEM analysis of the ZnO/HA nanocomposite reveals a highly porous morphology, with ZnO particles distributed across the HA matrix. The corresponding EDX spectrum confirms the presence of Zn, Ca, P, and O, consistent with the elemental composition of the ZnO and HA phases. These findings further support the successful formation of the ZnO/HA nanocomposite.

3.2.4. Surface charge of ZnO, HA, and ZnO/HA nanocomposite

The point of zero charge (pH_{pzc}) is an important physicochemical parameter that influences the catalytic behavior of a material. It describes the pH at which the net surface charge becomes zero and, consequently, plays a

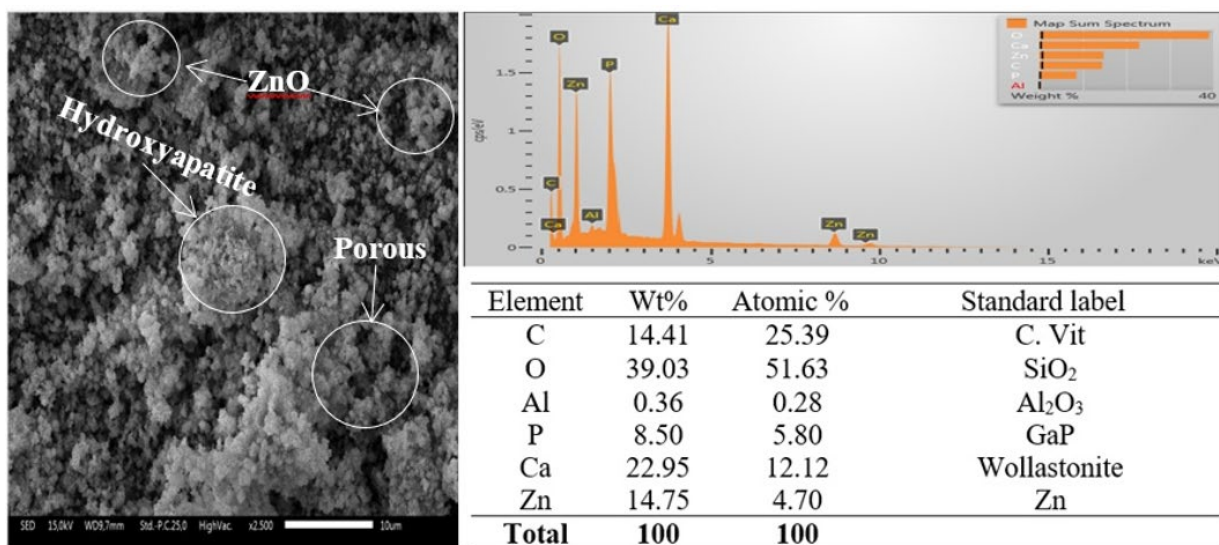


Figure 4. SEM-EDX images of ZnO/HA nanocomposite.

significant role in governing the electrostatic interactions between the catalyst surface and pollutant species. The pH_{pzc} values of ZnO synthesized using a local Balinese shallot aqueous extract, HA derived from seashells, and the ZnO/HA nanocomposite were determined by suspending 0.1 g of each material in 25 mL of water adjusted to different initial pH values ranging from 2 to 12. The suspensions were allowed to equilibrate for 48 h, after which the final pH (pH_f) was measured. The initial pH (pH_i) and final pH values were recorded using a portable pH meter (pH 850 Portable pH Meter). The pH_{pzc} was determined by plotting the initial pH (pH_i) against the change in pH ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i$). The resulting plots and pH_{pzc} values are presented in Figure 5.

As presented in Figure 5, the pH_{pzc} values of the synthesized ZnO, HA, and ZnO/HA nanocomposite were determined to be 9.41, 7.60, and 8.47, respectively. The relatively high pH_{pzc} value of the ZnO nanoparticles (9.41) may be associated with their high crystallinity (79.9%), which reflects a well-ordered crystal structure. This result is comparable to the findings of Zubair *et al.* who reported a pH_{pzc} of 9.30 for ZnO nanoparticles synthesized using hexamethylenetetramine [28]. Previous studies have reported pH_{pzc} values for ZnO nanoparticles within the range of approximately 7–10. For example, ZnO prepared from *Nauclea latifolia* fruit exhibited a pH_{pzc} of 7.61 [29], whereas ZnO synthesized using *Saccharomyces cerevisiae* showed a pH_{pzc} of approximately 8.7 [30]. The HA sample exhibited a pH_{pzc} of 7.60. At solution pH values below this point, the HA surface is expected to possess a net positive charge, which can promote electrostatic attraction toward anionic RRRB species and facilitate their interaction with the ZnO active sites. Such interactions may contribute to enhanced photocatalytic degradation of the dye. Reported pH_{pzc} values for

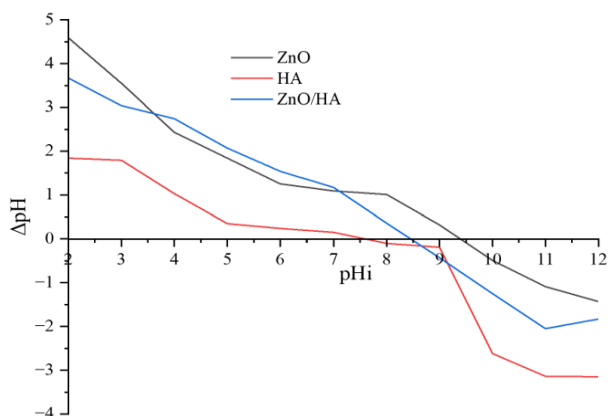


Figure 5. Determination of the point of zero charge (pH_{pzc}) of ZnO, hydroxyapatite, and ZnO/HA nanocomposite based on the relationship between initial pH (pH_i) and ΔpH .

HA generally fall within the range of 7–9, depending on the precursor and synthesis conditions [31,32]. For the ZnO/HA nanocomposite, a pH_{pzc} of 8.47 was obtained. Therefore, at pH values below 8.47, the nanocomposite surface is expected to exhibit a predominantly positive charge, favoring electrostatic attraction of the anionic RRRB dye. This surface-charge behavior can enhance dye adsorption and facilitate its interaction with photocatalytically active sites, thereby potentially improving the degradation process. Consequently, the photocatalytic degradation of RRRB is expected to be more favorable under acidic to near-neutral conditions, particularly at pH values below the pH_{pzc} of the ZnO/HA nanocomposite.

3.3. Photocatalytic Degradation Studies of Textile Dye

3.3.1. Effect of pH on photocatalytic degradation efficiency

Solution pH is an important factor governing photocatalytic performance because it influences the surface charge of the photocatalyst and the interaction between the catalyst and dye molecules. At a pH below the pH_{pzc} , protonation of surface hydroxyl groups generally results in a predominantly positive surface charge. In contrast, when the solution pH exceeds the pH_{pzc} , deprotonation of these surface groups leads to a more negatively charged surface. Changes in surface charge can consequently affect dye adsorption and the overall photocatalytic degradation process. To evaluate the influence of pH on the photocatalytic performance of the ZnO/HA nanocomposite, 250 mL of RRRB textile dye solution with an initial concentration of 10 mg/L was treated with 1.0 g of ZnO/HA nanocomposite. The experiments were conducted using a batch method under 50 W visible-light irradiation for 120 min. During the treatment, aliquots were collected at 30 min intervals, and the dye concentration was monitored using a UV–Vis spectrophotometer at a wavelength of 518 nm. The effect of solution pH on the RRRB degradation efficiency is presented in Figure 6.

Figure 6 illustrates that the absorbance of RRRB textile dye dropped when the pH medium of the photocatalytic process rose from 4 to 6, followed by a decline in absorbance when the pH was further raised to 8. The photocatalytic degradation efficiency of RRRB dye increased from 74.84% to 91.05% as the photodegradation pH was raised from 4 to 6; however, a subsequent decrease to 72.46% was observed at pH of 8. The photocatalytic degradation of RRRB, an anionic dye, over the ZnO/HA nanocomposite exhibited optimal performance at pH of 6. This behavior is strongly associated with the pH_{pzc} of the ZnO/HA

nanocomposite, which was determined to be 8.47 (Figure 5). The charge of catalyst's surface in aqueous medium might have a positive or negative depending on the pH level. At pH values below the pH_{pzc} , the catalyst's surface is predominantly positively charged, thereby enhancing electrostatic attraction toward anionic dye species. This favorable interaction promotes dye adsorption on the catalyst surface and subsequently facilitates the photocatalytic degradation process. In contrast, at pH value higher than pH_{pzc} , surface deprotonation induced by hydroxyl ions results in negatively charged sites, leading to weakened dye-catalyst interactions and reduced photocatalytic efficiency [33,34]. These findings are consistent with previous studies reporting that the photocatalytic degradation of the anionic dye Methyl Orange is more effective under acidic conditions than under alkaline conditions. Hamid *et al.* (2024) reported that a MoS_2/CdS composite ($pH_{pzc} \approx 6.2$) exhibited the highest photocatalytic degradation efficiency at pH of 3, while its performance decreased under alkaline conditions [35]. Similarly, Parsafard and Shabani found that a $MnCeO_x-TiO_2$ composite ($pH_{pzc} \approx 6.5$) achieved its optimum photocatalytic performance for Methyl Orange degradation under acidic conditions [36].

3.3.2. Effect of dye concentration on photocatalytic degradation efficiency

Evaluating the impact of dye concentration on photocatalytic degradation efficiency is important for the effective design of photocatalytic wastewater treatment systems. In this experiment, 250 mL of RRRB textile dye solution at concentrations ranging from 5–20 mg/L was treated with 1.0 g of ZnO/HA nanocomposite. The photocatalytic process was performed at pH of 6 under 50 W visible light irradiation for 120 min, and dye decolorization was monitored at 30 min

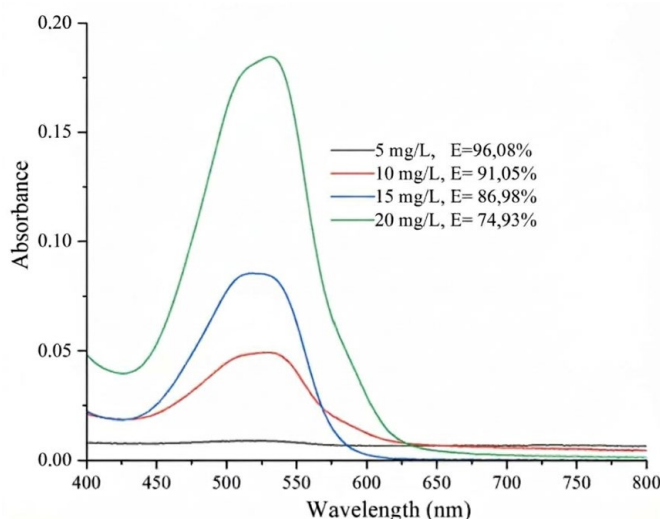


Figure 6. The effect of pH on photocatalytic degradation efficiency.

intervals. The degradation performance is presented in Figure 7.

Figure 7 illustrates that the visible-light-driven photocatalytic performance of the ZnO/HA composite toward RRRB is markedly influenced by the initial dye concentration. Noticeably, at 5 ppm, the degradation efficiency reached 96.08%, whereas it declined to 91.05%, 80.98%, and 74.93% when the RRRB concentration was increased to 10 mg/L, 15 mg/L, and 20 mg/L, respectively. This decrease in photocatalytic activity with increasing dye concentration is likely related to the reduced formation of hydroxyl ($\cdot OH$) and superoxide ($\cdot O_2^-$) radicals, which play a crucial role in the degradation process [37,38]. At lower dye concentrations, the adsorption of RRRB molecules onto the catalyst surface occurs more effectively, facilitating interfacial charge transfer and improving photodegradation efficiency. Conversely, with increasing initial dye concentration, most photons are absorbed by the dye molecules in solution before reaching the catalyst surface, thus limiting the formation of $\cdot OH$ and ($\cdot O_2^-$ radicals. In addition, higher dye concentrations promote saturation of the photocatalyst surface, thus limiting the interaction between adsorbed species and radicals.

3.3.3. Effect of ZnO/HA nanocomposite weight on photocatalytic degradation efficiency

The photocatalyst dosage employed in a heterogeneous photocatalytic reaction system represents a critical operational parameter. At low catalyst loadings, the generation of $\cdot OH$ and $\cdot O_2^-$ radicals are insufficient, thereby limiting the effectiveness of the photocatalytic degradation of pollutants. Increasing the use of photocatalysts to a certain extent leads to an increase in the efficiency of dye degradation due to the presence of additional surface-active sites

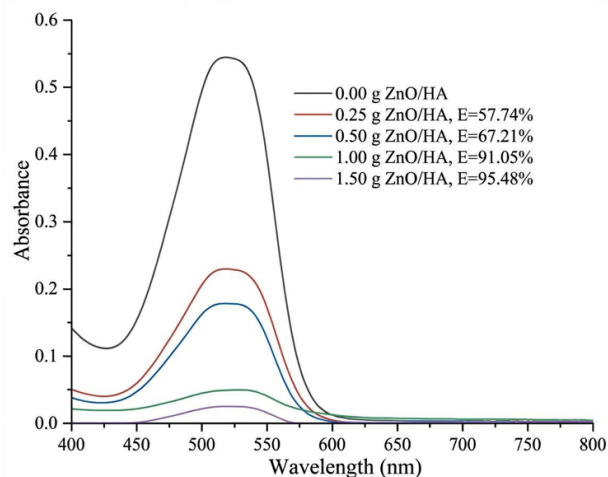


Figure 7. Photodegradation behavior of dyes as a function of dye concentration.

that promote the rate of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radical formation. However, excessive photocatalyst loading induces increased turbidity within the reaction system, which obstructs effective photon–photocatalyst interaction due to enhanced light scattering in the suspension. This phenomenon limits light penetration and reduces the number of photons reaching the catalyst surface, thereby diminishing the photocatalytic degradation efficiency of the dye [39–42]. Moreover, the decline in degradation performance observed at excessive catalyst dosages can also be attributed to photocatalyst agglomeration. Such aggregation decreases the effective surface area and restricts the accessibility of active sites, ultimately impairing the overall photocatalytic reaction efficiency. The photocatalytic degradation performance of the ZnO/HA nanocomposite toward 250 mL of 10 mg/L RRRB dye solution with different amounts photocatalyst (0.25–1.50 g) irradiated with 50 W visible light for 120 min is illustrated in Figure 8. As shown in Figure 8, increasing the ZnO/HA nanocomposite dosage

enhanced the photocatalytic degradation of RRRB. The removal efficiency increased from 57.74% at 0.25 g to 91.05% at 1.00 g, while a further increase to 1.50 g resulted in only a marginal improvement, indicating that the optimum catalyst dosage had been reached. A similar trend was reported by Manikandan *et al.*, who observed that the photocatalytic degradation efficiency of methylene blue using ZnO/HA increased with catalyst dosage up to an optimum of 100 mg, after which it declined at higher dosages due to particle agglomeration and increased light scattering [42]. Likewise, Le and Nguyen, reported that increasing the $\text{TiO}_2/\text{Fe(III)}$ nanocomposite dosage from 0.1 to 0.2 g enhanced the degradation of indigo carmine from 66.9% to 96.7% after 6 h of irradiation, whereas a further increase to 0.3 g reduced the efficiency to 84.7% [43].

3.3.4. Effect of length of irradiation time on photocatalytic degradation efficiency

The photocatalytic activity of ZnO/HA nanocomposite was evaluated for the degradation of RRRB dye solution presence 50-watt a visible light source at different irradiation time. The photocatalytic removal efficiency of RRRB (10 mg/L, 250 mL) in the presence of 1.0 g ZnO/HA nanocomposite at an initial pH of 6 was investigated under varying irradiation times (30–180 min). The variation in the photocatalytic degradation efficiency of the dye as a function of visible-light exposure time is shown in Figure 9.

3.3.5. Proposed role of hydroxyapatite in the ZnO/HA photocatalytic system slightly higher degradation efficiency

The photocatalytic behavior of the ZnO/HA nanocomposite can be interpreted based on the physicochemical characteristics of the composite

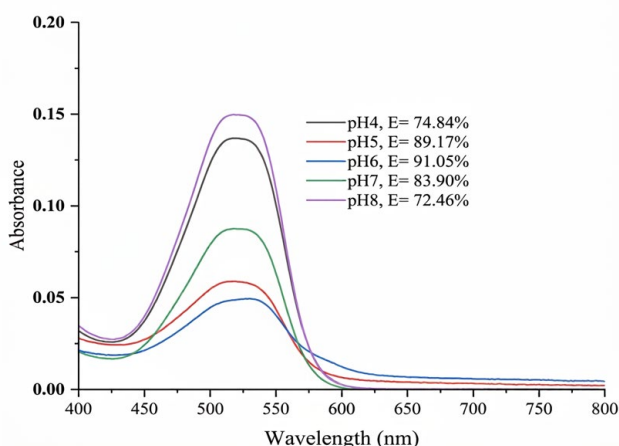


Figure 8. Photodegradation behavior of dyes as a function of ZnO/HA weight.

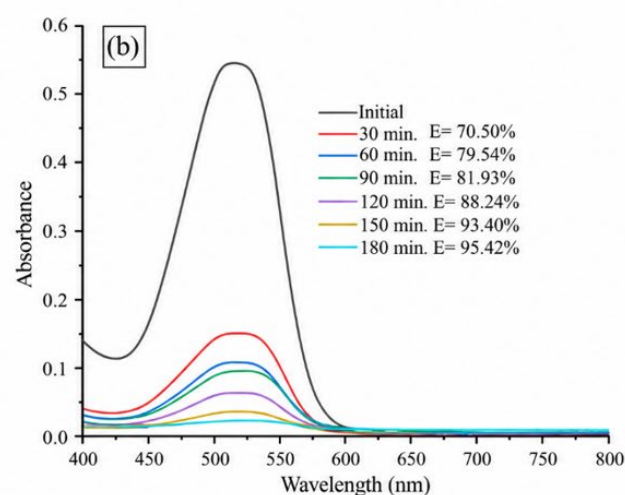
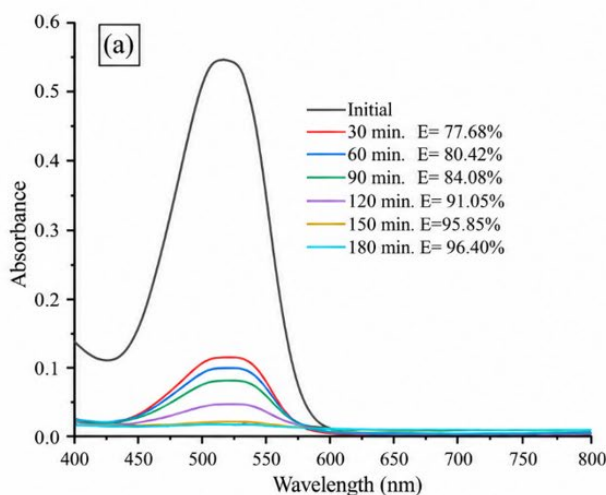


Figure 9. Photocatalytic degradation of RRRB as a function of irradiation time using (a) ZnO/HA nanocomposite and (b) green-synthesized ZnO under otherwise identical experimental conditions.

and the observed degradation results. XRD and FTIR analyses confirmed the coexistence of crystalline ZnO and hydroxyapatite phases, while SEM-EDX indicated the distribution of ZnO particles within the hydroxyapatite matrix. The porous character of the composite may provide additional adsorption sites and improve the dispersion of ZnO particles, thereby increasing the probability of interaction between RRRB molecules and photocatalytically active ZnO surfaces. This interpretation is also supported by the pH-dependent behavior of the system. At pH of 6, which is below the pH_{pzc} of the ZnO/HA composite (8.47), the catalyst surface is expected to possess a predominantly positive charge and thus favor electrostatic interaction with the anionic RRRB molecules.

Under irradiation, the ZnO component can undergo photoexcitation according to the conventional semiconductor photocatalytic pathway, generating electron-hole pairs when photons with sufficient energy are absorbed. The photogenerated charge carriers can participate in interfacial reactions involving adsorbed water, hydroxyl groups, and dissolved oxygen, potentially producing reactive oxygen species that contribute to dye degradation. The presence of hydroxyapatite may facilitate pollutant adsorption and provide a porous support for ZnO, thereby increasing the accessibility of RRRB molecules to the photocatalytically active surface.

However, the present study does not include UV-Vis diffuse reflectance spectroscopy, photoluminescence, electrochemical impedance spectroscopy, or reactive-species scavenging experiments. Therefore, modification of the ZnO band gap, suppression of electron-hole recombination, and the specific contribution of individual reactive oxygen species cannot be experimentally confirmed from the present dataset. The proposed mechanism should consequently be regarded as a plausible interpretation based on the material characterization, surface-charge behavior, and photocatalytic results rather than as a directly demonstrated charge-transfer mechanism.

Overall, as illustrated in Figure 9, the photocatalytic efficiency increased with longer irradiation time. In the initial stage, the degradation rate rose sharply, then the increase slowed down, and finally, the efficiency approached a nearly constant value. The degradation efficiencies obtained with irradiation times of 30, 60, 90, 120, 150, and 180 minutes were 77.68%, 80.42%, 84.08%, 91.05%, 95.85%, and 96.40%, respectively. As irradiation time increases, the number of photons interacting with the photocatalyst surface also increases, thereby enhancing the generation of electron-hole pairs and subsequent formation of $\cdot OH$ and $\cdot O_2^-$.

These reactive species are responsible for breaking down dye molecules, leading to higher degradation efficiencies with prolonged exposure. However, after a certain period, the degradation rate often shows a marked deceleration or approaches a plateau [44,45]. Similar results were reported by Bagheri *et al.* who observed a sharp increase in the photocatalytic degradation of Reactive Blue 203 by UV-irradiated ZnO nanoparticles within the first 20 minutes, followed by only a slight improvement at 25 minutes [46].

Under identical experimental conditions, the ZnO/HA nanocomposite achieved 95.85% RRRB degradation after 150 min, whereas the green-synthesized ZnO achieved 93.40%. Thus, the incorporation of hydroxyapatite resulted in an absolute improvement of 2.45 percentage points. Although this improvement is relatively modest, it indicates that the addition of hydroxyapatite did not impair the photocatalytic activity of ZnO and provided a measurable additional contribution to dye removal.

The improvement can reasonably be associated with the physicochemical role of hydroxyapatite as a porous mineral support and adsorptive phase. The positive surface character of ZnO/HA at pH of 6, as indicated by its pH_{pzc} of 8.47, favors interaction with the anionic RRRB dye. In addition, the incorporation of HA may improve ZnO dispersion and increase the accessibility of pollutant molecules to active surface sites. These effects provide a plausible explanation for the higher removal obtained with ZnO/HA. Nevertheless, because the increase in degradation efficiency was relatively small and no direct charge-carrier or optical measurements were performed, the present results do not establish a strong synergistic photocatalytic effect or a modification of the intrinsic ZnO electronic structure. The contribution of HA is therefore better interpreted as a combined adsorption-support effect that complements the photocatalytic function of ZnO.

3.3.6. Catalyst stability and practical applicability

Catalyst reusability is an important consideration for the practical application of heterogeneous photocatalysts because repeated use can influence catalytic activity, structural integrity, and treatment cost. In the present study, the ZnO/HA nanocomposite was evaluated for photocatalytic performance under different operating conditions; however, repeated-cycle experiments were not included in the experimental design. Consequently, the retention of photocatalytic activity after repeated use and the possible leaching or structural alteration of

the catalyst cannot be quantitatively established from the present data.

The absence of recycling data represents a limitation of the present study, particularly in relation to the practical implementation of the material for continuous or repeated wastewater treatment. Nevertheless, the use of hydroxyapatite derived from seashell waste as a support provides a potentially useful material platform because of its mineral stability and surface functionality. Further investigation should therefore include multiple adsorption–photocatalysis cycles, post-use XRD and FTIR characterization, and analysis of Zn leaching to determine catalyst stability and environmental safety. Such experiments would provide essential information for evaluating the long-term feasibility of the ZnO/HA system in practical textile wastewater treatment.

4. Conclusions

This study demonstrated the feasibility of preparing a ZnO/hydroxyapatite (ZnO/HA) nanocomposite using two renewable biowaste resources, namely Balinese shallot peel and seashell waste, for visible-light-assisted degradation of Remazol Red RB (RRRB) dye. XRD, FTIR, and SEM-EDX analyses confirmed the coexistence of crystalline ZnO and hydroxyapatite phases in the composite, with an average crystallite size of 24.80 nm and crystallinity of 80.20%. The ZnO/HA nanocomposite exhibited a pH_{pzc} of 8.47, which contributed to favorable electrostatic interaction with the anionic RRRB dye under acidic to near-neutral conditions.

Among the investigated operating conditions, the highest degradation efficiency obtained was 95.85% for 10 mg/L RRRB in 250 mL solution using 1.0 g of ZnO/HA at pH of 6 after 150 min of irradiation with a 50 W visible-light source. Under identical conditions, green-synthesized ZnO achieved 93.40% degradation, corresponding to an absolute improvement of 2.45 percentage points upon incorporation of hydroxyapatite. The improvement is interpreted primarily in terms of the adsorptive and supporting roles of hydroxyapatite, including enhanced pollutant–surface interaction and improved ZnO dispersion.

The present results demonstrate the potential of combining shallot peel and seashell wastes to produce a functional ZnO/HA material for dye treatment. However, because UV–Vis diffuse reflectance, charge-carrier characterization, reactive-species identification, and catalyst-reusability tests were not conducted, modification of the ZnO band gap, detailed charge-transfer pathways, and long-term catalyst stability cannot be conclusively established. Further studies should therefore focus on optical characterization,

photocatalytic mechanism verification, catalyst recycling, and metal-leaching assessment to determine the practical applicability of the material for repeated textile wastewater treatment.

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CRedit Author Statement

Author Contributions: I Nyoman Sukarta: Conceptualization, Design of methodology, Resources, Investigation, Writing-initial draft preparation; I Dewa Ketut Sastrawidana: Design of methodology, Resources, Investigation, Data presentation, Review and editing manuscript; Dewi Oktifa Rachmawati: Software, Formal analysis, Review and editing of manuscript. All authors have read and agreed to the published version of the manuscript.

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