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Characteristics Of Photocatalyst Materials Derived From Fish Bones

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Abstract. The most commonly used part of the fish body is meat, while the bone is more often not utilized despite the fact that it contains hydroxyapatite (HAp). HAp minerals as the main constituent of inorganic parts in fish bones have been widely studied for their use as material for bone tissue engineering and for pollutant adsorbent. Moreover, modification of this HAp containing material has also been studied to obtain materials with superior properties such as photocatalytic material. In this research, fish bone was converted into photocatalytic material which is able to degrade methylene blue (MB) dyes. The starting materials were bones of red snapper and skipjack tuna. The bones were dried, calcined at 600 °C and 1000 °C, and ground. The products were then treated in a silver nitrate solution, rinsed, and dried. The materials obtained were analyzed by using the X-ray diffraction (XRD) technique for phase composition determination and Scanning Electron Microscope (SEM) to explore the morphology. Photocatalytic activity of the materials obtained from the red snapper was then confirmed by applying them to MB photodegradation under visible light. The XRD diffraction patterns showed typical characteristics for the bones of each species. Phase identification of the patterns showed that not all the material has metallic silver incorporated. On the other hand, all the materials produced by this new procedure contained silver phosphate (Ag_3PO_4) which is known as visible light photocatalyst. The photodegradation experiment confirmed that most MB was degraded under visible light by materials produced by calcination of bone at 600 °C.

INTRODUCTION

The waters on the surface of the earth store tremendous wealth with enormous utilization potential. There were 34,700 fish species, for example, recorded in the Fishbase database [1] as of August 2021. Part of the fish body that is most utilized is the meat, while the bones are discarded as waste. Fish bones mainly contain hydroxyapatite (HAp) which has been widely studied for its use both in the form of a single material or in the form of composites. In the field of health, this mineral has been assessed for its potential as a biomaterial [2,3,4] and in the environment as an adsorbent for metal pollutants and synthetic dyes [5,6].

Modification on HAp mineral from fish bone was also studied to obtain photocatalyst material [7,8]. Piccirillo *et al*. [7] claimed that their work was the first to synthesize silver phosphate-based material from a natural source, which is cod fish bone. In their study, the crushed fish bone was treated with a solution containing $AgNO_3$ before calcination. A photocatalyst and antibacterial material was obtained by the method. In our work, we apply a slightly different, new method where the red snapper (RS) and skipjack tuna (SjT) fish bones were calcined before being treated with $AgNO_3$ solution. Both of these fish species are widely caught for their meat as food. Most of the bone that is not consumed is not utilized and only a small portion is used as animal feed. By this method, silver phosphate-based photocatalyst materials could also be obtained. The characteristics of the materials are described in this paper, as well as the photocatalytic activity of material derived from RS fish bone. This photocatalytic activity was assessed through the photodegradability of this material against methylene blue (MB) dye. Despite its use as a raw material for medicines, MB can be toxic to the neural system, skin, and reproductive system of living things. The use of MB in the textile industry as a dye, as a consequence, could also cause the problem of pollution to the aquatic environment.

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MATERIALS AND METHODS

Materials

Red snapper (RS) (*Lutjanus sp.*) and skipjack tuna (SjT) (*Katsuwonus pelamis*) fishes were obtained from a fish auction place in Bitung, North Sulawesi, Indonesia. RS having a minimum fork length of 70 cm and SjT with that of 30 cm were the source of fish bones. Reagent grade chemicals were used in this study.

Preparation of Photocatalyst Materials

The bones were separated from the flesh, boiled for 30 minutes, and brushed to remove the remaining fleshy material. After that, they were dried overnight at 105 °C in an oven and the materials were subjected to calcination at 600 °C (designated as RS 600 and SjT 600) and 1000 °C (designated as RS 1000 and SjT 1000) for 5 h with a heating rate of 5 °C/min to extract mineral part of the bones. In the next step, the calcined bones were ground and sieved using a 100-mesh screen. The ground bones were subsequently treated with $AgNO_3$ solution by applying the molar ratio of 5:1 between Ag and HAp. The mixture was stirred at 40 °C for 24 h, filtered, rinsed, and dried in the oven at 100 °C for 24 h.

Characterization of Photocatalyst

Materials treated with $AgNO_3$ were characterized by using the X-Ray diffraction (XRD) technique to determine phase composition. Samples were scanned at a 2θ range of 15°-80° with a step size of 0.01°. We used XRD patterns of HAp (COD ID 9011091), metallic silver, Ag, (COD ID 9008459), silver phosphate, Ag_3PO_4, (COD ID 1007043), and tricalcium phosphate, TCP, (COD ID 9005865) from Crystallography Open Database (COD) [9] and that of whitlockite mineral (R070675.9) from RRUFF database [10] as standards. In addition, the morphology of HAp obtained from RS and SjT fishes was explored using a Scanning Electron Microscope (SEM).

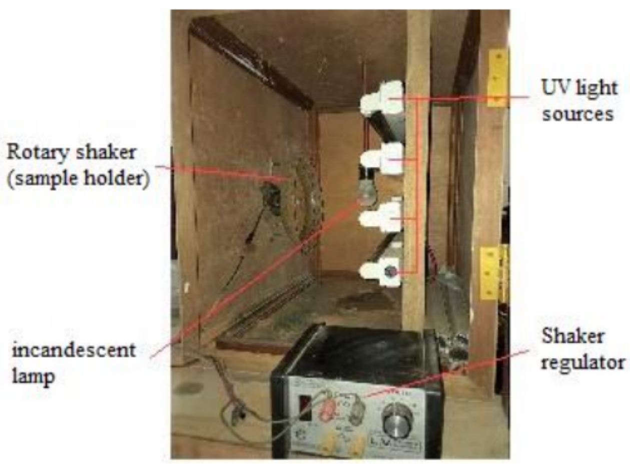

FIGURE 1. Photocatalytic reactor

Photocatalytic Activity Experiments

A batch experiment of MB photodegradation was conducted to explore the potential for the red snapper fish bone-based material as a photocatalyst. A number of glass tubes were filled up with 15 mL of MB solution at a variation of MB initial concentration of 1 to 10 ppm. The selected initial concentration range of MB was established after a preliminary examination and was adjusted to the amount of photocatalyst used. Each tube was then loaded with 50 mg of the sample, sealed, and placed in a rotary shaker under a common 75 W incandescent lamp (Philips) for 180 minutes. The light source was set at a distance of 20 cm from the samples. A picture of the photocatalytic reactor is shown in Fig. 1. At the end of the interaction period, the mixture was centrifuged at 3500 rpm for 30 minutes and the remaining MB in the solution was determined by using UV-vis spectrophotometer at 664 nm to calculate the amount of MB removed from the solution.

RESULTS AND DISCUSSION

Characteristics of Calcined and Ag-Treated Fish Bones

A diffractogram of calcined RS and SjT is shown in Fig. 2. It is revealed that RS and SjT bones contain HAp, while TCP is not formed in these materials. It is observed that RS and SjT calcined at 600 °C contain low crystalline HAp. At a higher calcination temperature, which is 1000 °C, higher crystallinity of HAp is detected. The increased HAp crystallinity in fish bone with the increasing calcination temperature was studied in Japanese sea bream [11] and Atlantic salmon [12] fishes. The interesting figure is the fact that TCP could be formed at higher calcination temperature and it depends on species. In Japanese sea bream fish, part of HAp was transformed into TCP at 1300 °C [11] and in Atlantic salmon. TCP was formed at a calcination temperature of 850 °C [12]. This TCP would probably be formed in RS and SjT if the calcination temperature is increased above 1000 °C.

The other interesting fact is that whitlockite mineral is observed only in SjT calcined at 1000 °C (SjT 1000). Whitlockite ($Ca_{18}Mg_2(HPO_4)_2(PO_4)_{12}$) is the second most abundant mineral in bone and it occupies approximately up to 25 wt% of the inorganic part of human bone [13]. This mineral is a relatively rare mineral in nature with an unusual form of calcium phosphate and an unknown biological role [14].

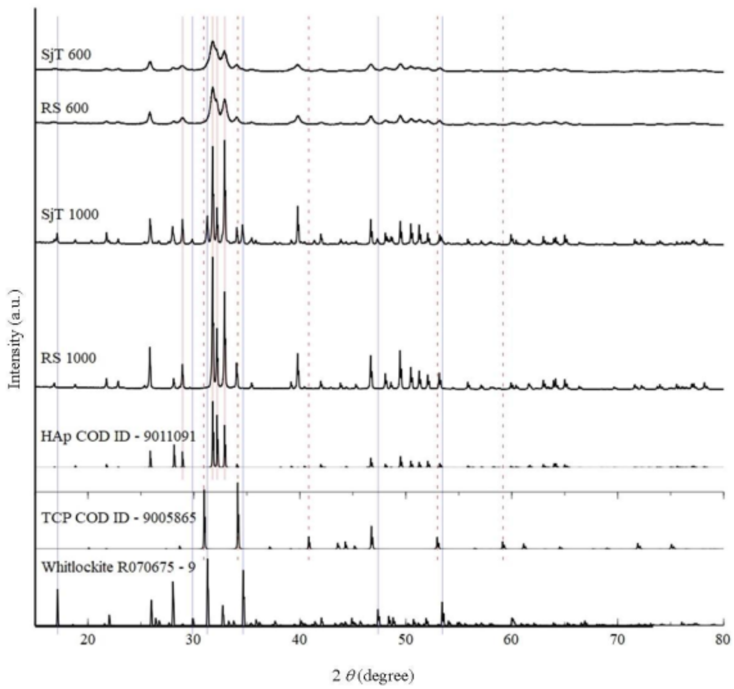

FIGURE 2. XRD patterns of calcined SjT and RS bones at 600 °C and 1000 °C

XRD patterns of Ag-treated calcined bones are shown in Fig. 3. As with Fig. 2, HAp exists on all materials and whitlockite appears only in SjT bone-based material. Ag is observed only in RS 600-Ag and is not detected in RS

1000-Ag and SjT 1000-Ag. Ag_3PO_4 is detected in all materials, and this compound has high crystallinity in SjT 1000-Ag. In contrast to the results from a study by Piccirillo et al. [7] showing that sample calcined at higher temperature gave material containing more Ag_3PO_4, XRD patterns shown in Fig. 3 indicate that treating RS calcined at a higher temperature with $AgNO_3$ would generate material containing less Ag_3PO_4. This may have been favored by higher degree of crystallinity in RS calcined at 1000 °C which prevents Ag ions to react with phosphate groups in converting HAp into Ag_3PO_4. This could explain the existence of Ag_3PO_4 peak that is more intense in RS 600-Ag than in RS 1000-Ag.

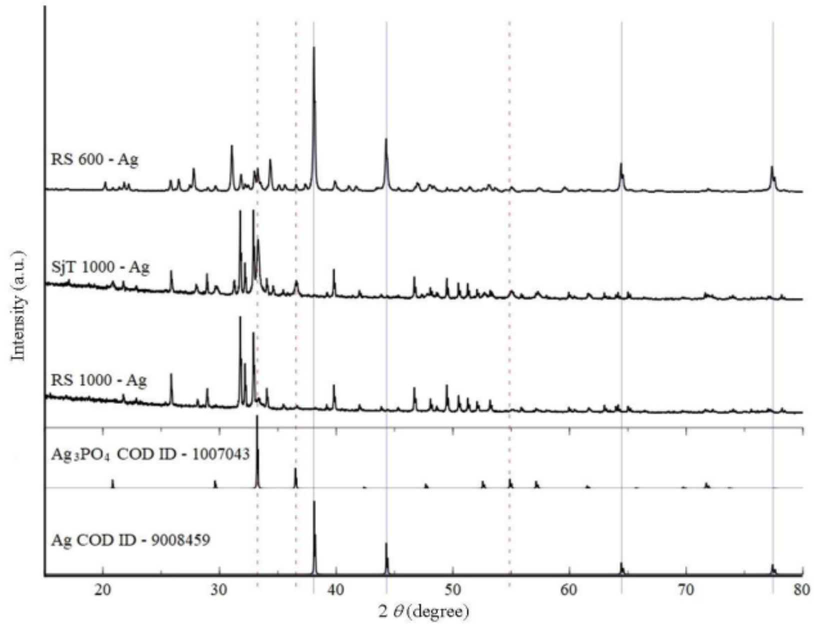

FIGURE 3. XRD patterns of Ag-treated calcined RS and SjT

SEM images of HAp obtained from RS and SjT calcined at 600 °C and 1000 °C are shown in Fig. 4. Calcination of fish bones leaves the particles in the form of granular which has a size of approximately 1 μm. It is clearly seen that the calcined materials having higher crystallinity can be obtained at higher temperatures up to 1000°C.

Photocatalytic Activity Experiments

The ability of calcined RS and Ag-treated calcined RS bones in degrading synthetic dye MB is depicted in Fig. 5 showing the amount of MB removed from solution by the materials under visible light. It is clear that RS 600-Ag has the highest ability in removing MB than the other materials. This result is in accordance with the finding above that treating RS calcined at 600 °C with $AgNO_3$ generates more intense Ag_3PO_4 in the material. It is known that Ag_3PO_4 is a photocatalytic material that can be activated under visible light [15]. However, this result does not fully reflect the ability of the material as a photocatalyst to remove MB because calcined bone treated with $AgNO_3$ still contains HAp which can also act as an adsorbent. In fact, the ability of RS 1000-Ag to remove MB from solution is not much different from the ability of RS 1000 due to the lack of $AgNO_3$ formation.

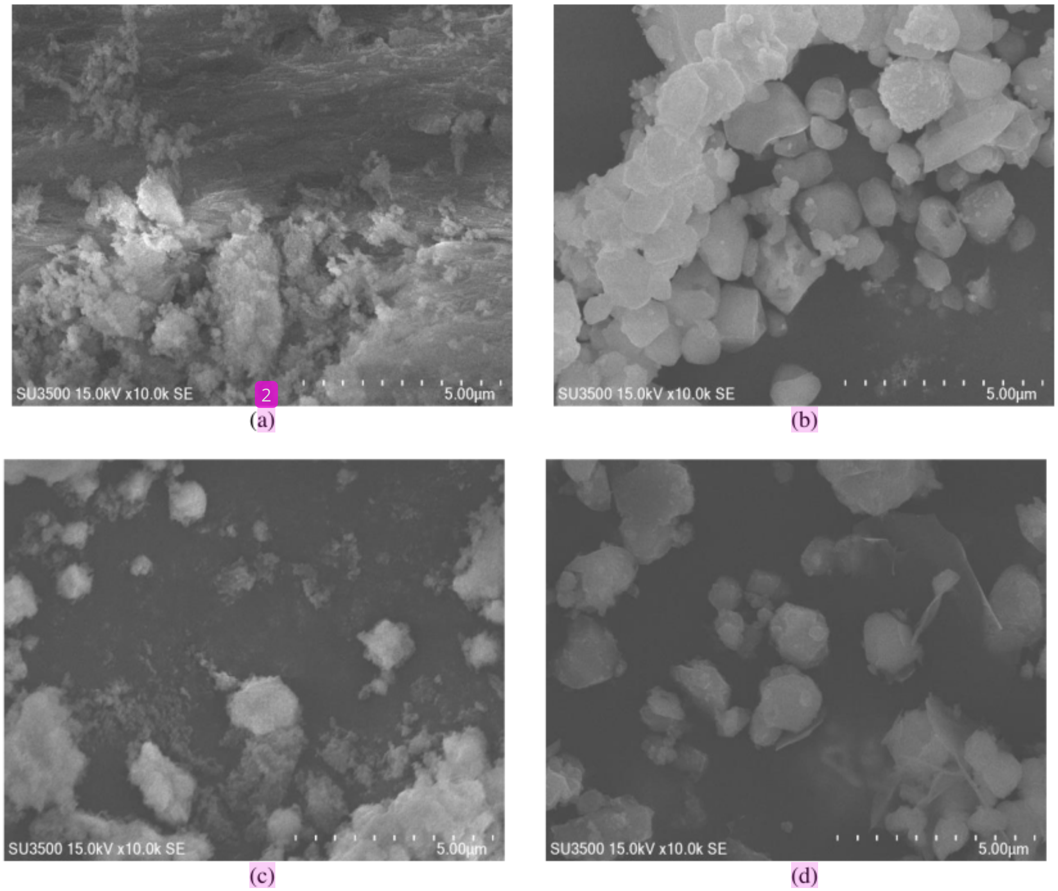

FIGURE 4. SEM images of calcined fish bones of (a) RS at 600 °C, (b) RS at 1000 °C, (c) SjT at 600 °C, and (d) SjT at 1000 °C

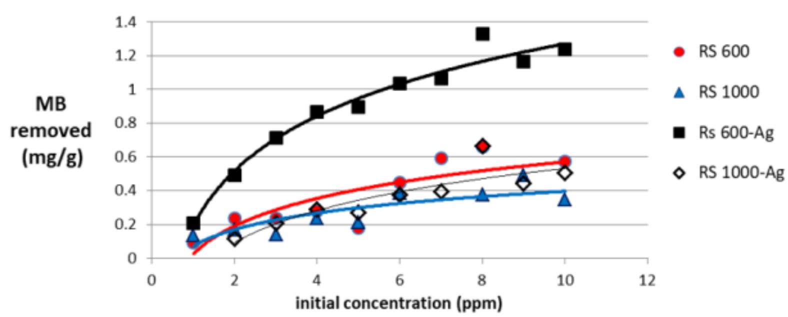

FIGURE 5. MB removed from solutions by calcined RS and Ag-treated calcined RS bones under visible light

To explore further the ability of Ag-treated calcined RS bones in degrading MB, an experiment of MB photodegradation under UV light was set up and the result is presented in Fig. 6. UV light provides higher energy than visible light to activate the photocatalyst Ag_3PO_4 and, as a result, a remarkable increase in the amount of MB removed from solutions is observed for RS 600-Ag. A slight increase in the amount of MB removed is shown by RS 1000-Ag.

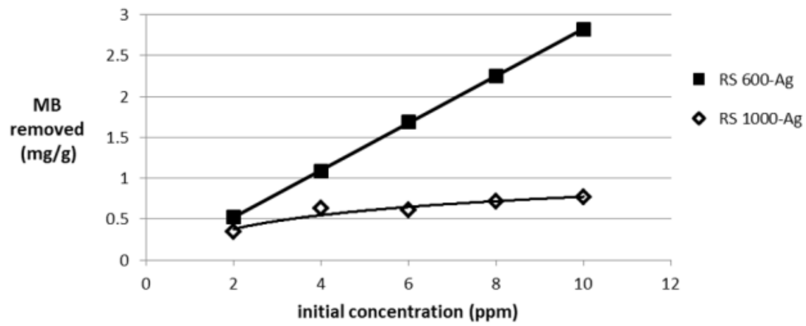

FIGURE 6. MB removed from solutions by Ag-treated calcined RS bones under UV light

CONCLUSION

A new procedure of synthesizing a silver phosphate-based material from fish bone is described here. Phase identification by using XRD showed the formation of Ag_3PO_4 to produce a composite with hydroxyapatite mineral. Whitlockite, the second abundant mineral in bone, was identified only in skipjack tuna fish bone. The synthesized silver phosphate-based material from red snapper fish bone showed photocatalytic properties and was able to remove methylene blue from the solution under visible light. The best performance was shown by this material under irradiation of UV light.

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