

# Synthesis of Ag<sub>3</sub>PO<sub>4</sub>/HAp from Red Snapper Bone (*Lutjanus spp.*) For Photodegradation of Methylene Blue

*by Henry Aritonang 26*

---

**Submission date:** 09-May-2022 07:40AM (UTC+0700)

**Submission ID:** 1831479847

**File name:** b.\_Synthesis\_of\_Ag<sub>3</sub>PO<sub>4</sub>HAp\_from\_Red\_Snapper\_Bone.pdf (684.09K)

**Word count:** 2852

**Character count:** 13831

## Synthesis of $\text{Ag}_3\text{PO}_4/\text{HAp}$ from Red Snapper Bone (*Lutjanus spp.*) For Photodegradation of Methylene Blue

V P J Lairah, A D Wuntu and H F Aritonang

Department of Chemistry, Faculty of Natural Science and Mathematics, Sam Ratulangi University, Manado, Indonesia

Corresponding author: vanialairah08@gmail.com

**Abstract.** Fish bone is one part of the fish body that is often not used in the fish processing industry, so it needs to be used as HAp. For the composite material to be used in the study of the photodegradation kinetics model of methylene blue, it must go through synthesis. This research went through a calcination process to obtain fish bone powder at a temperature of 600°C. The purpose of this study was to determine the kinetics model of the photodegradation of methylene blue by  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites from 600°C calcined fish bones with a ratio of Ag:HAp = 5:1 and 2.5:1. The synthesis was carried out by reacting HAp with acid and  $\text{AgNO}_3$  and then characterized by the *X-Ray Diffraction (XRD)* method. The results showed that the composite formed was  $\text{Ag}_3\text{PO}_4/\text{HAp}$  and at the peak of the 2 $\theta$  samples diffraction patterns with standard diffraction patterns were very similar. The determination of this kinetics model resulted in the highest  $R^2$  value in the second order kinetics model with a mole ratio of Ag:HAp = 2.5:1, namely 0.001 so that the photodegradation of methylene blue took place following the second order kinetics model.

### 1. Introduction

North Sulawesi is one of the places that has marine biological resources with various types of fish contained in it. Fish bones are more often not used in the fish processing industry and fish bones contain the highest calcium content among fish body parts [1]. Fish bones contain 60-70% minerals such as HAp and 30% organic components in the form of collagen protein [2].

In Indonesia, there are several types of snapper, including (*Red snapper, Lutjanus sanguine*) and dark greenish red snapper, known as giant (*Seaperch or seabass, Lates calcarifer*). The red snapper comes from the *Lutjanidae* tribe, while the snapper is from the *Centropomidae* family [3]. Red snapper (*Lutjanus spp.*) Is one type of marine fish that has important economic value and has the potential to be cultivated. The red snapper, *Lutjanus argentimaculatus* or "red snapper", spreads across Indo-Pacific waters, Line islands in North Africa to Australian waters and Ryukyu Islands, Japan [4].

Dyestuff waste produced from the textile industry is generally non-biodegradable organic compounds, which can cause environmental pollution, especially the aquatic environment. The types of dyes used in the textile industry today are very diverse, and usually do not consist of one type of dye, therefore handling textile waste becomes very complicated and requires several steps until the waste is completely safe to be released into the aquatic environment [5].

Methylene blue can reduce the intensity of light entering the waters and slow down the photosynthesis of aquatic biota, besides that, methylene blue can cause serious health problems if it enters the human body. Therefore, a waste treatment technology is needed that is able to accelerate the decomposition of dye waste [6].

As an alternative, a photodegradation method was developed using a photocatalyst material and light radiation whose energy is equal to or greater than the band gap energy of the photocatalyst. With this photodegradation method, the dye will be broken down into simpler components that are safer for the environment [7].

In this research, the synthesis of  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites from calcined red snapper bone treated with acid and  $\text{AgNO}_3$  with different Ag:HAp ratio, namely 5:1 and 2.5:1 was carried out for later use in the study of photodegradation kinetics using methylene blue dye. This study aims to determine the kinetics model of the photodegradation of methylene blue by calcined  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites with a ratio of Ag:HAp = 5:1 and 2.5:1.

## 2. Methodology

### 2.1. Sample Preparations

Preparation of fish bones begins with boiling the fish bones. Boiling is carried out at a temperature of 100 °C for 60 minutes. After that, the remaining meat is cleaned by brushing it. The fish bones are then air-dried for about 1 day to reduce the water content during the steaming process. The dried fish bones are then in the oven at 100 °C for 24 hours. After the fish bones were dry, they were calcined at 600 °C for 5 hours. Fish bones crushed and sieved with a 100 mesh sieve.

### 2.2. Composite Synthesis $\text{Ag}_3\text{PO}_4/\text{HAp}$

Synthesis of  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites using the modified [8] method. Fish bones that have been processed into 600 °C flour weigh 2.8519 g, mixed into 100 mL  $\text{HNO}_3$  0,01 M solution and stirred for 2 hours then filtered with filter paper and rinsed with distilled water until the pH returns to neutral, after in an oven with a temperature of 105 °C for approximately 2 hours, after drying the material is put 100 mL of 0,15 M  $\text{AgNO}_3$  solution. This mixture is a mixture with a mole ratio of Ag:HAp = 2.5:1. The mixture is then stirred using a magnetic stirrer for 24 hours. Furthermore, the mixture is filtered with filter paper, then in the oven for 1 night with a temperature of 100 °C. The same procedure was carried out using 100 mL of 0.28 M  $\text{AgNO}_3$  solution to produce a material with an Ag:HAp = 5:1 ratio. The material was further characterized by XRD and used for the photodegradation of methylene blue.

### 2.3. Photodegradation Kinetics of Methylene Blue

The photodegradation kinetics experiment of methylene blue was carried out following the procedure of [9]. The composites were weighed 0,03 g each and put in 6 glass bottles, then added 15 mL of 6 ppm of methylene blue. The mixture was then placed in a photodegradation box and exposed to a commercial 100 W incandescent lamp (Phillips E27 220-240V A55 CL) for a time range of 10 minutes to 240 minutes. After the specified time, the mixture was centrifuged and the remaining methylene blue concentration in the solution was determined using a UV-Vis spectrophotometer (Shimadzu UV-1800) at a wavelength of 664 nm. Existing data were then analyzed using kinetics models of order-1 and order-2 [10].

The first order kinetics model is expressed in the following equation:  $-\ln \frac{C_t}{C_0} = k t$ .

The second order kinetics model is expressed in the following equation:  $\frac{1}{C_t} = \frac{1}{C_0} + k t$ .

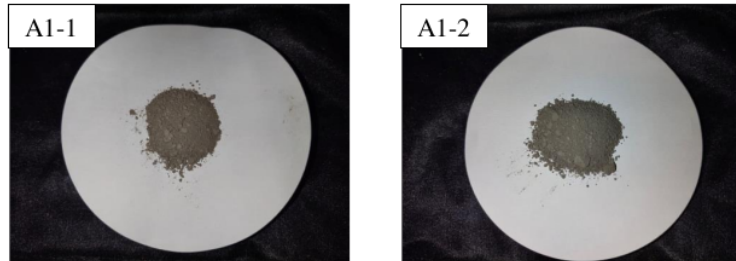
## 3. Results and Discussion

### 3.1. Preparation and Synthesis

Calcination of red snapper bones aims to remove organic compounds contained in the bones by heating at a temperature of 600 °C. Uncalcined bones generally contain approximately 30% organic

material and 70% inorganic material in the form of hydroxyapatite (HAp). Organic material will burn out at heating 550 C [11] and leave inorganic material in the bones.

The fish bones that have been calcined at 600°C are crushed and sieved with a 100 mesh sieve to obtain fish bone powder which is then reacted with HNO<sub>3</sub> and AgNO<sub>3</sub> so that a composite Ag<sub>3</sub>PO<sub>4</sub>/HAp at 600°C with a mole ratio of Ag:HAp 5:1 (A1-1) and 2.5:1 (A1-2) shown in Figure 1.



**Figure 1.** Ag<sub>3</sub>PO<sub>4</sub>/HAp composite at 600°C at a mole ratio of Ag:HAp = 5:1 (A1-1) and 2.5:1 (A1-2)

9

### 3.2. Analysis of X-Ray Diffraction (XRD)

The *X-Ray Diffraction* (XRD) method provides information about the structure and degree of crystallinity of a solid produced in the form of a diffraction pattern (diffractogram). XRD testing was conducted to determine two types of data, namely qualitative and quantitative. XRD analysis aims to determine the presence of a peak at 2θ position of the HAp sample and the dispersion of Ag<sub>3</sub>PO<sub>4</sub> on the red snapper bone, the dispersion of the sample can be determined by comparing the sample with HAp and Ag<sub>3</sub>PO<sub>4</sub> standards. On the diffractogram, the sample and standard diffraction patterns are clearly visible in the presence of peaks in the 2θ region, as shown in Figure 2.



**Figure 2.** Composite Ag<sub>3</sub>PO<sub>4</sub>/HAp diffractogram at 600°C at the mole ratio of Ag:HAp (5:1 and 2.5:1) with HAp and Ag<sub>3</sub>PO<sub>4</sub> standards

The diffraction patterns of the samples were compared with the standard diffraction patterns from the *Crystal Open Database* (COD). Qualitatively Figure 2 shows the presence of HAp and Ag<sub>3</sub>PO<sub>4</sub> in the sample by looking at the 2θ peaks very similar to the standard. In addition to the peaks of HAp and Ag<sub>3</sub>PO<sub>4</sub>, the sizes of HAp and Ag<sub>3</sub>PO<sub>4</sub> particles can be calculated using *Full Width at Half* data. X-ray diffraction can be used to determine the crystallite size with a certain phase [12]. The determination refers to the main peaks of the diffractogram pattern through the Debye Scherrer equation approach which is formulated in Equation (1).

$$D = \frac{K \lambda}{\beta \cos \theta} \tag{1}$$

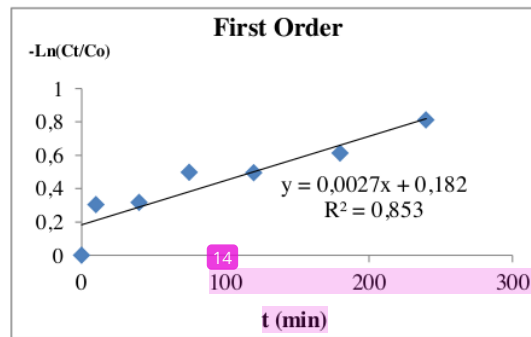
Based on the results of the XRD data, the particle size was obtained by calculating FWHM (Full width Half Maximum). The combined particle sizes of HAp and Ag<sub>3</sub>PO<sub>4</sub> found in the samples are presented in Table 1.

**Table 1.** The size of the HAp and Ag<sub>3</sub>PO<sub>4</sub> particles in the sample

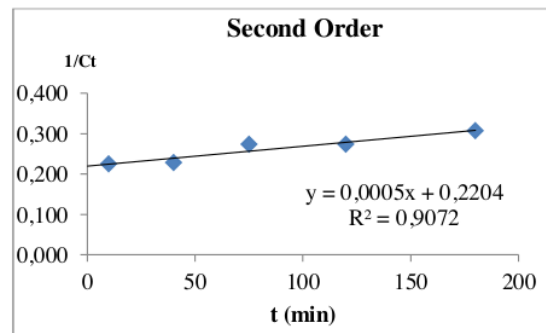
Ratio	D <sub>(nm)</sub>	
	HAp	Ag <sub>3</sub> PO <sub>4</sub>
5 : 1	426.7283738	380.526588
2.5 : 1	405.139647	320.9982077

### 3.3. Photodegradation Kinetics of Methylene Blue

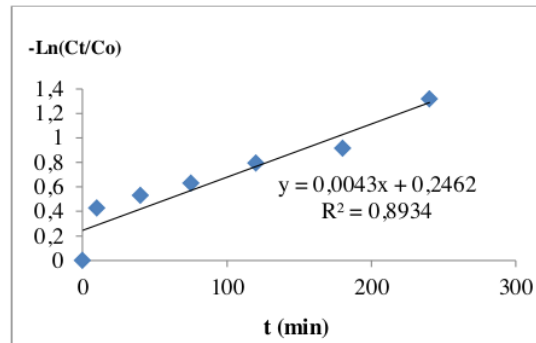
Photodegradation kinetics were used to determine the rate of photodegradation of methylene blue which was influenced by time. The rate test was carried out by estimating the reaction order by plotting  $-\ln C_t/C_0$  vs t for the 1st order reaction kinetics model and  $1/C_t$  vs t for the 2nd order reaction kinetics model (Figures 3, 4, 5 and 6).



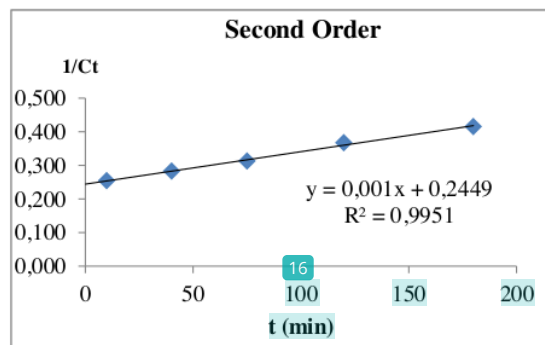
**Figure 3.** Kinetics model of 1st order photodegradation of methylene blue by Ag<sub>3</sub>PO<sub>4</sub>/HAp composite from 600°C calcined fish bone with Ag:HAp mole ratio (5:1)



**Figure 4.** Kinetics model of 2nd order photodegradation of methylene blue by Ag<sub>3</sub>PO<sub>4</sub>/HAp composite from 600°C calcined fish bone with Ag:HAp mole ratio (5:1)



**Figure 5.** Kinetics model of 1st order photodegradation of methylene blue by  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composite from  $600^\circ\text{C}$  calcined fish bone with Ag:HAp mole ratio (2.5:1)



**Figure 6.** Kinetics model of second order photodegradation of methylene blue by  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composite from  $600^\circ\text{C}$  calcined fishbone with Ag:HAp mole ratio (2.5:1)

The calculation results show that the  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composite material with a mole ratio of Ag:HAp 5:1 and 2.5:1 degrades methylene blue following the second order kinetics model. The determination of this kinetics model is based on the linearity of the curve according to the equation of the 1st and 2nd order kinetics models where the curve in the 2nd order kinetics model produces the greatest  $R^2$  (coefficient of determination) Table 2.

**Table 2.** Reaction rate constants for the photodegradation of methylene blue by  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites

Composite	Orde 1		Orde 2	
	$R^2$	K	$R^2$	K
5 : 1	0.853	0.0027	0.9072	0.0005
2.5 : 1	0.8934	0.0043	0.9951	0.001

In general, the reaction order for a certain substance is not the same as the coefficient in the stoichiometric equation of the reaction [12] and a second-order kinetics model of the reaction rate which is directly proportional to the square of the concentration of the reactants. The values of the photodegradation reaction rate constants and the kinetics model determination coefficients for the two  $\text{Ag}_3\text{PO}_4/\text{HAp}$  composites with a temperature of  $600^\circ\text{C}$  in the Ag:HAp mole ratio (2.5:1 and 5:1) are shown in Table 2.

Table 2 shows that the fastest photodegradation of methylene blue occurred in composites synthesized from calcined fish bones at a temperature of 600°C ikan at an Ag:HAp ratio of 2.5: 1. This characteristic seems to be related to the particle size produced by the different Ag:HAp ratios. The ratio of Ag:HAp = 2.5:1 resulted in smaller particles Table 1 which were estimated using the Debye Scherrer equation. The smaller particle size provides a larger contact surface area between this Ag<sub>3</sub>PO<sub>4</sub>/HAp composite and methylene blue. This allows more methylene blue to interact with the catalyst surface and undergo photodegradation on the photocatalyst surface per unit time so that the photodegradation process takes place faster.

#### 4. Conclusion

Ag<sub>3</sub>PO<sub>4</sub>/HAp composites which act as photocatalysts can be synthesized by treating nitric acid and AgNO<sub>3</sub> on calcined red snapper bone 600°C tulang. Treatment Ag:HAp ratio = 2.5:1 resulted in composites with smaller particle sizes and Photodegradation of methylene blue by composite Ag<sub>3</sub>PO<sub>4</sub>/HAp took place following the second order reaction kinetics model and the photodegradation of methylene blue was faster in composites that were synthesized using a ratio of Ag/HAp = 2.5: 1.

#### References

- [1] Jayathilakan K, Sultana K, Radhakrishna K and Bawa A S 2012 Utilization of byproducts and waste materials from meat, poultry and fish processing industries: a review *Journal of food science and technology* **49** (3) 278-293
- [2] Mery D, Lillo I, Loebel H, Riffo V, Soto A, Cipriano A and Aguilera J M 2011 Automated fish bone detection using X-ray imaging *Journal of Food Engineering* **105** (3) 485-492
- [3] Carter C H R I S, Glencross B R E T T, Katersky R S and Bermudes M 2010 The snooks (family: centropomidae) *Finfish Aquaculture Diversification*. CABI, Oxfordshire 323-336
- [4] Andriyono S, Alam J, Kwak D H and Kim H W 2018 Complete mitochondrial genome of brownstripe red snapper, *Lutjanus vitta* (Perciformes: Lutjanidae) *Mitochondrial DNA Part B* **3** (2) 1129-1130
- [5] Rai H S, Bhattacharyya M S, Singh J, Bansal T K, Vats P and Banerjee U C 2005 Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment *Critical reviews in environmental science and technology* **35** (3) 219-238
- [6] Hanafiah M A K M, Ngah W S W, Zolkafly S H, Teong L C and Majid Z A A 2012 Acid Blue 25 adsorption on base treated *Shorea dasyphylla* sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis *Journal of Environmental Sciences* **24** (2) 261-268
- [7] Corrent S, Cosa G, Scaiano J C, Galletero M S, Alvaro M and Garcia H 2001 Intrazeolite photochemistry. 26. photophysical properties of nanosized TiO<sub>2</sub> clusters included in zeolites Y, β, and Mordenite. *Chemistry of materials* **13** (3) 715-722
- [8] Piccirillo C, Pinto R A, Tobaldi D M, Pullar R C, Labrincha J A, Pintado M M E and Castro P M L 2015 Light induced antibacterial activity and photocatalytic properties of Ag/Ag<sub>3</sub>PO<sub>4</sub>-based material of marine origin *Journal of Photochemistry and Photobiology A: Chemistry* **296** 40-47
- [9] Taringan A K, Wuntu A D and Aritonang H F 2017 Kinetika Fotodegradasi Remazol Yellow Menggunakan Fotokatalis ZnO dan ZnO-Ag *Jurnal MIPA* **6** (2) 68-71
- [10] Wu C H and Chern J M 2006 Kinetics of photocatalytic decomposition of methylene blue *Industrial & engineering chemistry research* **45** (19) 6450-6457
- [11] Hafiludin H 2011 Karakteristik Proksimat dan Kandungan Senyawa Kimia Daging Putih dan Daging Merah Ikan Tongkol (*Euthynnus affinis*) *Jurnal Kelautan: Indonesian Journal of Marine Science and Technology* **4** (1) 1-10
- [12] Zak A K, Majid W A, Abrishami M E and Yousefi R 2011 X-ray analysis of ZnO nanoparticles by Williamson–Hall and size–strain plot methods *Solid State Sciences* **13** (1) 251-256

Reproduced with permission of copyright owner. Further reproduction prohibited without permission.



# Synthesis of Ag<sub>3</sub>PO<sub>4</sub>/HAp from Red Snapper Bone (*Lutjanus spp.*) For Photodegradation of Methylene Blue

## ORIGINALITY REPORT

16%

SIMILARITY INDEX

13%

INTERNET SOURCES

11%

PUBLICATIONS

4%

STUDENT PAPERS

## PRIMARY SOURCES

1	<a href="https://repository.usd.ac.id">repository.usd.ac.id</a> Internet Source	4%
2	<a href="https://repository.unja.ac.id">repository.unja.ac.id</a> Internet Source	2%
3	<a href="https://ejournal.undip.ac.id">ejournal.undip.ac.id</a> Internet Source	2%
4	G Pasau, G H Tamuntuan, A Tanauma, D P Pandara, F Ferdy, A As'ari, C Maramis. "Empirical Attenuation Model for Predicting Peak Ground Acceleration in North Arm Sulawesi, Indonesia", IOP Conference Series: Materials Science and Engineering, 2021 Publication	1%
5	<a href="https://aip.scitation.org">aip.scitation.org</a> Internet Source	1%
6	<a href="https://nozdr.ru">nozdr.ru</a> Internet Source	1%
7	A. U. L. S. Setyadi, F. Nurosyid, Y. Iriani. "Influence of holding time annealing process	1%

on the microstructure and optical properties of barium titanate (BaTiO<sub>3</sub>) thin film using the sol-gel method", AIP Publishing, 2019

Publication

8

Submitted to University College Technology Sarawak

Student Paper

1 %

9

[ro.uow.edu.au](http://ro.uow.edu.au)

Internet Source

1 %

10

Chun-Hsing Wu, Jia-Ming Chern. "Kinetics of Photocatalytic Decomposition of Methylene Blue", Industrial & Engineering Chemistry Research, 2006

Publication

<1 %

11

Dong, Zheng, Hong Xu, Zhishan Bai, Huizhi Wang, Li Zhang, Xiaojiao Luo, Zhiyong Tang, Rafael Luque, and Jin Xuan. "Microfluidic synthesis of high-performance monodispersed chitosan microparticles for methyl orange adsorption", RSC Advances, 2015.

Publication

<1 %

12

[tudr.thapar.edu:8080](http://tudr.thapar.edu:8080)

Internet Source

<1 %

13

Dadrasnia, A., and P. Agamuthu. "Organic wastes to enhance phyto-treatment of diesel-

<1 %

# contaminated soil", Waste Management & Research, 2013.

Publication

---

14 [home.hiroshima-u.ac.jp](http://home.hiroshima-u.ac.jp) <1 %  
Internet Source

---

15 Anthony J. Hurford. "Standardization of fission track dating calibration: Results of questionnaire distributed by International Union of Geological Sciences Subcommittee on Geochronology", International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements, 1986 <1 %  
Publication

---

16 [aaltodoc.aalto.fi](http://aaltodoc.aalto.fi) <1 %  
Internet Source

---

17 [neptjournal.com](http://neptjournal.com) <1 %  
Internet Source

---

18 [rmiq.org](http://rmiq.org) <1 %  
Internet Source

---

19 [sutir.sut.ac.th:8080](http://sutir.sut.ac.th:8080) <1 %  
Internet Source

---

Exclude quotes On

Exclude matches Off

Exclude bibliography On