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Photocatalytic degradation of Pandurucan River water using Hydroxyapatite from Milkfish bones via calcination

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Abstract

Industrialization, agriculture, urban life, and wastewater have degraded the environment, including the Pandurucan River in San Jose, Occidental Mindoro, leading to significant calamities. High levels of turbidity are one of the results of pollution due to high concentrations of pollutants. Photocatalytic degradation, utilizing UV lights from solar energy, is an efficient, cost-effective, and environmentally friendly wastewater treatment method. Photocatalysis has been studied to increase the efficiency of wastewater treatment. Photosensitizers using hybrid materials extend their light absorption into the visible spectrum, complementing limited UV light absorption. Hydroxyapatite (HAp) is studied as one of the photocatalysis used to degrade water pollutants because of its absorption properties. In this study, HAp was produced from Milkfish bones via calcination and was characterized using Fourier Transform Infrared Spectroscopy (FTIR). Using the Turbidity Meter, the 100 ml of Pandurucan River water in a 1-hour time exposure shows a result of a 359 Nephelometric Turbidity Unit (NTU). Photocatalytic degradation showed a reduced result of 102.5 NTU, and applying the different concentrations of 250mg and 500mg of HAp showed a depletion rate of 79.8 NTU and 25.75 NTU, respectively. The application of HAp as photocatalysis in the degradation of Pandurucan River water showed that the 500mg of HAp was loaded in a 100 ml sample in a 1-hour time exposure, producing a percent degradation of turbidity with approximately 92.38%. Overall, this study provided insights on an eco-friendly way of handling wastewater, using a waste material, particularly Milkfish bones, as a source of HAp.

Keywords: photocatalytic degradation, turbidit, hydroxyapatite, Pandurucan River, milkfish bones

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1. Introduction

The environment has been degraded and polluted due to industrialization, agricultural production, wastewater, and urban life. This harms the vital water bodies (rivers and oceans), which harms human health and long-term social development. When dangerous chemicals or microbes enter a stream, river, lake, ocean, aquifer, or other body of water, they cause water quality to deteriorate and make the water poisonous to environmental organisms (Xu et al., 2022). In the Philippines, three million people use contaminated water sources daily, endangering their health. Additionally, 7 million people need better sanitation services (Filipenco, 2022). Water pollution affects various elements, including the environment, industry, and human health. It is a serious issue not just in the Philippines but around the world. Numerous bodies of water, including lakes, rivers, and seas, are heavily contaminated in the Philippines due to human activity in multiple provinces. An example is the Pandurucan River in San Jose, Occidental Mindoro, which encloses the town and has many residential areas along its shores. The river's abundance of aquaculture had been a contributing factor to the river's pollution and agricultural and industrial activities. Despite this, the province is well known for its agriculture and bodies of water. However, as a result of increased industrial and agricultural action brought on by population growth, the river turned into a disposal area for many businesses and residents, which resulted in a significant decline in the security of food and water as well as a financial crisis for fishermen as a result of the loss of their primary source of income. Additionally, the destruction of the ecosystem and environment led to significant calamities in the town, such as a major flood and increased waterborne diseases due to contaminated water.

Different parameters are being tested to measure the quality of the water, such as Dissolved Oxygen level, conductivity, pH level, total dissolved solids (TDS), color, turbidity, and many more (Atlas Scientific Environmental Robotics, 2023). Out of all the mentioned parameters, turbidity is more likely to be tested in river waters. The cloudiness in a lake or river is measured by its turbidity. Turbidity is a function of anything that makes the water murky. Chemicals in the water or the company of silt, muck, algae, plant fragments, melting glaciers, sawdust, or wood ashes can all contribute to high turbidity. Floating algae, soil that has washed into rivers and lakes from the banks, fires, or industrial activities like mining, logging, or dredging are the leading causes of increased turbidity in these bodies of water. Due to a large amount of mud floating in the water, it is pretty turbid and appears dirty and brown. For this reason, turbidity readings can indicate potential pollution in a water body (Water Science School, 2018). Excessive water turbidity can have adverse implications for both the environment and human well-being, summarized as follows: 1.) Suspended materials can obstruct or harm fish gills, reducing fish growth rates, susceptibility to diseases, egg and larvae maturation, and the effectiveness of fishing methods. 2.) Elevated turbidity can elevate water temperatures because suspended particles absorb more solar heat, ultimately reducing the availability of food resources. 3.) Heavy metals such as mercury, chromium, lead, and cadmium, along with hazardous organic pollutants like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and numerous pesticides, can all become attached to suspended particles. In conclusion, addressing and mitigating the adverse effects of water turbidity is essential for safeguarding both our environment and the well-being of human populations dependent on clean and clear water sources (Omer, 2020).

Turbidity is one of the most critical parameters because it influences other factors, including high temperature and dissolved oxygen. Heat absorption causes a high-temperature level, reducing light penetration into the water and the amount of dissolved oxygen. High temperatures and low oxygen levels can harm fish and other aquatic species. The amount of oxygen in water decreases with increasing temperature; in other words, the warmer the water, the more it can hold less oxygen (When Things Heat Up, 2021). Fish may develop "gas bubble disease" or “emphysema” in waters with too much-dissolved gases. The bubbles, or emboli, cause mortality by obstructing blood flow through blood vessels; they can be visible on fins, skin, and other tissues. Gas bubble illness also affects aquatic invertebrates but at higher concentrations than those fatal to fish (Lenntech, 2018). That is the main reason the researchers want to treat the parameter turbidity rather than the others because turbidity significantly impacts river water. This impact can also be seen in the Pandurucan River. By treating turbidity in wastewater, we can reduce its effects on humans, the environment, and aquatic ecosystems, reducing its impact on human health and industrial aspects, environmental concerns, and the production and living of marine organisms such as fish. Methods were developed to lessen the water turbidity, one of the most critical parameters in determining the water quality. Although some process helps in treating the water in terms of its turbidity, such as coagulation-flocculation, which is a treatment process where colloids in water are destabilized so they can aggregate and be physically removed, it can effectively reduce turbidity when combined with sedimentation and filtration; it is not a practical way of wastewater treatment due to its excessively high operational costs (Soros et al., 2019). Another efficient method, according to Water Color Management (2018), is using ultrafiltration. Specialized membranes are used in this procedure to apply hydrostatic pressure and separate water from suspended particulates. As a result, it also has certain disadvantages because this procedure needs more energy to run an ultrafiltration plant.

By this, the researchers came up with an idea to propose a way to treat wastewater in a more effective, cost-efficient, and environmentally friendly way, which is the Photocatalytic Degradation of River Waters, specifically the Pandurucan River using Hydroxyapatite from Milkfish Bones. The hydroxyapatite that will be produced from Milkfish bones through calcination will catalyze the process of photocatalytic degradation. The hydroxyapatite was characterized by X-ray analysis, Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) to reveal its phase content, morphology, and bond types. Hydroxyapatite (HA, Ca10(PO4)6(OH)2) possesses a low solubility. It can induce the formation of a bone-like apatite layer in the body environment, which makes it a potential reinforcement for increasing the biodegradation resistance of Mg alloys (Cahyaningrum et al., 2018). This aims to reduce the level of turbidity in the water. The effects of turbidity water treatment for drinking and food processing may become more expensive. It can harm fish and other aquatic species because it decreases food sources, deteriorates spawning grounds, and interferes with gill function (Minnesota Pollution Control Agency, 2023). The results of this study will provide information on the potential of Milkfish bones' hydroxyapatite as a photocatalyst in pollutant degradation in water. The cleanliness of the bodies of water they would depend on would benefit both wildlife and people. Employing milkfish bones' hydroxyapatite as a photocatalyst would be a helpful substitute that might reduce the cost of water treatment for cities and communities, particularly in regions with limited resources. The study will also increase the researcher's understanding of the photocatalytic degradation process, making it easier to change treatment parameters and improve the procedure's efficacy. Also, the issue of using byproducts from widely consumed fish, such as Milkfish, would be resolved. It supports environmentally sustainable approaches to managing water resources and backing global initiatives to guarantee everyone has access to clean and safe water.

Statement of the Problem - This study aimed to produce a wastewater treatment which is the Photocatalytic Degradation of River Water using Hydroxyapatite from Milkfish Bone via Calcination, specifically the Pandurucan river water, and test its effectiveness in water's turbidity. Specifically, the researchers sought to answer these questions: (1) What is the level of turbidity of water before the use of Photocatalytic Degradation using Hydroxyapatite from Milkfish bones? (2) What is the level of turbidity of water after the use of Photocatalytic Degradation? (3) Is there a significant difference in the level of turbidity of the water before and after the use of Photocatalytic Degradation? (4) Does the concentration of Hydroxyapatite affect the effectiveness of Photocatalytic Degradation using 250 mg of hydroxyapatite and 500 mg of hydroxyapatite? (5) Is the use of Photocatalytic Degradation using Hydroxyapatite from Milkfish bones effective as a wastewater treatment?

Significance of the Study - The significance of this study becomes evident in its critical role in addressing the pressing global challenge of water pollution. By exploring novel wastewater treatment techniques, this research has the potential to safeguard water resources, protect ecosystems, and enhance public health, thereby contributing to a more sustainable and cleaner environment for all. The various sectors that will benefit from the study are as follows: The environment: this study will help enhance the environment regarding water pollution in the Pandurucan River. This could increase the health of aquatic systems and reduce harmful algae growth caused by water pollution, aquatic recreational activities, and conservation of water resources. The study's findings can be helpful to our industry because a less expensive wastewater treatment process holds significant importance in the industry by lowering business operational costs, improving financial sustainability, and facilitating compliance with environmental regulations compared to an effective water plant treatment. To the community, this study is made to provide the residents with a source of living. The abundance of aquaculture could be a source of income for the people living near the area and boost the community's economic performance. For waste management, this study will help make the waste, specifically milkfish bone, into a recyclable material. This will reduce the debris, such as fishbones, in our local market. Lastly, this research will be a valuable reference for future researchers who plan to conduct any related study regarding wastewater treatment.

Scope and Delimitation of the Study - This study aimed to produce wastewater with the potential use of hydroxyapatite derived from milkfish bone through calcination as a cost-effective and sustainable method for reducing turbidity in Pandurucan River water. This research study is scheduled to commence in September 2023 and is anticipated to conclude in February 2024. The research intends to develop practical insights and guidelines for the community to implement this photocatalytic process locally, focusing on improving water quality in the San Jose Community. The study not only analyzes the scientific effectiveness of the technique but also considers its socioeconomic implications and benefits for the community, including improved access to clean and clear river water for various uses. This study's restriction implies that the photocatalytic degradation method using hydroxyapatite for Pandurucan River water is not intended or recommended for producing drinking water. This study's discussion of financial resources is delimited by the absence of an in-depth financial analysis or cost-effectiveness assessment, focusing primarily on the technical feasibility and efficacy of hydroxyapatite's photocatalytic degradation method. The study on the photocatalytic degradation of Pandurucan River water using hydroxyapatite from milkfish bone via calcination primarily emphasizes turbidity reduction as the key objective, prioritizing it over other water quality parameters. This study seeks to benefit the Pandurucan River community and the residents who live in Barangay 4 (near the Pandurucan River) by providing insights into an environmentally friendly turbidity reduction method while recognizing the need for a community-centric approach to address water quality challenges.

2. Methodology

Research Design - This study used an experimental research design to test the effectiveness of the wastewater treatment, which is the Photocatalytic Degradation of Pandurucan river water using Hydroxyapatite from Milkfish bones via Calcination. This design allowed the researchers to control the independent variables and measure the dependent variable. The researchers used this design to determine the effectiveness of HAP derived from milkfish bone via calcination for the photocatalytic degradation of Pandurucan River water. With the help of this experimental research design, the researchers were able to answer the research questions and develop conclusions and recommendations for future researchers in line with a similar research topic. According to Sirisilla (2023), the foundation of an experimental research design is a set of guidelines and processes for conducting a scientific comparison between the two study variables. The researchers also identified the optimal conditions for photocatalytic degradation, such as the HAP loading, calcination temperature, and water turbidity. Due to this, the researchers defined and compared the results to determine the efficacy of the focused variables of this study, especially concerning the development of new and sustainable technologies for wastewater treatment.

Data Gathering Procedure - During the experiment, the researchers were present in the field to perform the photocatalytic degradation process. The researchers gathered the data and results from the laboratories where the chemical and the process of photocatalytic degradation were tested. The Chemistry Laboratory of Adamson University provided an authorized copy that proved the characterization of Milkfish bones' hydroxyapatite. Mach

Union Laboratory, where the researchers sent the water after the photocatalytic degradation process for testing, was also given an authorized copy of the water quality. The researchers spent 2 days, including the experimentation and the observation. Photocatalytic Degradation of 3 samples, the samples without the Hydroxyapatite and the samples with 250 mg and 500 mg of Hydroxyapatite, were put in a 1-hour process, respectively. For the characterization of Hydroxyapatite using the FTIR, it took 1 hour for the researchers to get the results. Additionally, for the water quality testing of the samples, including the raw samples, it took 3 hours for the researchers to get the final result finally. Since all the data would be provided by an authorized person from Adamson University Laboratory and Mach Union Laboratory, the researchers waited for the results. All the results were proven by the paper and confirmed by the laboratory professionals.

Research Process; Stage 1 Preparation and Gathering of Materials - This research investigates the potential of hydroxyapatite derived from milkfish bones for photocatalytic degradation – a process that utilizes light to break down pollutants – in Pandurucan River water. Readily available materials were prioritized to create a cost-effective and sustainable water treatment method. This study uses organic components, laboratory machines, and equipment to synthesize the product. After determining the most appropriate materials for the products, the researchers investigated to find an appropriate place for the materials and equipment. First, the milkfish bones are derived from the San Jose wet market, and second, the amber bottle used to store the sample water was ordered online. Lastly, all laboratory materials and equipment, like the Furnace, FTIR, Ultraviolet lights, and Turbidity meter, came from the Laboratory of Adamson University and Mach Union Laboratories INC. The raw milkfish bones are given to us for free by kind fish sellers at the San Jose wet market. The two amber bottles cost Php454. All the Laboratory equipment and machines that were used cost PHP 4000. There are also additional causes which are primarily transportation uses, the flat boat used to collect samples from the Pandurucan River water, and the cost of transportation of the samples and the researcher who experimented in Laboratory of Adamson University and Mach Union Laboratories INC, which cost PHP 2850 for transportation. The final product cost is PHP 7304.

The materials used to produce the catalyst Hydroxyapatite are as follows:

Figure 1. Milkfish bones

The milkfish bones were gathered from San Jose wet market, San Jose Occidental Mindoro. This was used to produce the hydroxyapatite photocatalyst. As stated in the study of Pramono et al. (2020), the Milkfish (chanos-chanos forsk/CCF) bones, which are a waste product, contain 32% protein, 3% P, and 4% Ca. To make the most of its use, the waste must be processed into a new product. The milkfish content includes a variety of metallic elements that can be combined metallurgically to create an interface between materials using Titanium (Ti)/Magnesium (Mg) as a wetting element and Aluminium (Al) as a matrix. Because of these benefits, milkfish bones can be used to create composite materials that contain multiple matrix types, thereby creating a hybrid composite material. Material made from milkfish bones calcined at 500–700 OC to produce hydroxyapatite.

Figure 2. Hydroxyapatite.

In this study, all reagents and chemicals were analytically graded and used as received without any further purification. The main catalyst used for the photocatalytic degradation process is Hydroxyapatite (HA)(Ca(10)PO(4)6OH(2) powder which was obtained from the calcined milkfish bone through the Biology Laboratory (Gao et al., 2019). Deionized water was bought from the Chemistry Laboratory which was used for the preparation of the simulated polluted water. Hydroxyapatite has excellent biocompatibility and mechanical properties. Hydroxyapatite is a vital inorganic material widely used in bone grafts, drug-carrying systems, photocatalysts, and adsorbents. Because of its high adsorption capacity for contaminants, high effectiveness, low cost, and high stability under redox conditions, Hap is an ideal material for handling long-term pollutants in water treatment applications.

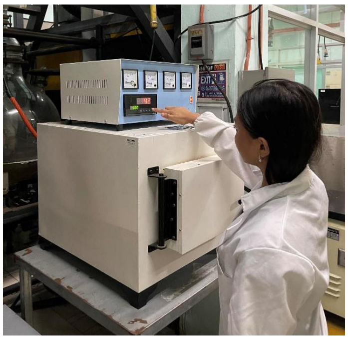

Figure 3. Furnace

This experiment required the use of different laboratory apparatuses. All glass wares such as 250 ml beakers, volumetric flasks, weighing dishes, magnetic stirrers, test tubes, and reagent bottles were borrowed from the Chemistry Laboratory and Chemical Engineering Laboratory. The amber bottle used to store the turbid water was bought online.

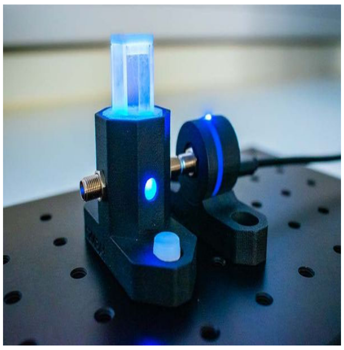

Figure 4. UV/ Light Source (https://g.co/about/zxmtph)

For the identification of the synthesized hydroxyapatite, it was characterized using Fourier Transform Infrared (Spectrum Two-Perkin Elmer). A photocatalytic reactor used for treatment in this study is composed of UV Lamp (UV LED Light with Hi-Power LED Hoenle Point) and is capable of inducing a stirring effect, centrifuge (Clay Adams), and UV-Vis- Spectrophotometer (Lambda 25 UV-Visible Perkin Elmer).

Figure 5. Photocatalytic Reactor

The reactor is built with three UV lamps to serve as the light source. Two fans are installed in the back of the reactor to maintain the room temperature in the system. The inside part of the reactor is covered with silver wrappings for the equal distribution of light during the process. Four magnetic stirrers are constructed in the reactor to be occupied by four 250 mL beakers filled with the mixture of polluted solution and catalyst during the photodegradation.

Figure 6. Control Panel of the Reactor

The pilot lamp (green light) signals when the system is fully operating and in good condition. The five on-off switches are used to operate the UV lamps and fans in the system while the four black turning buttons are used to control the rotation speed through the magnetic stirrers.

Based on the study conducted by Mohd Pu'ad et al. (2019), natural hydroxyapatite is typically obtained from biological wastes or sources, including marine or aquatic environments (e.g., fish bone and fish scale), shells (e. g. cockles, clams, eggshell, and seashell), plants and algae, and animal bones (e. g. Bovine, Camel, and Horse) through the application of various methods of HAp extraction. Using HAp extracted from natural sources is considered a cost-effective, sustainable, and ecologically friendly method to create these materials because they are widely accessible.

Stage 2: Construction and Development of the Project - The figure below is the summary of the flow of the process during the experiment and the process of Photocatalytic Degradation.

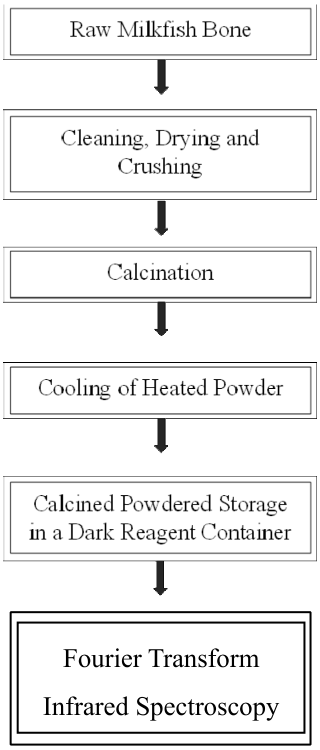

Figure 7. Process of calcination

Figure 7 shows the process of calcination. It was started first with the use of raw Milkfish bones, Milkfish is known as "bangus", a type of fish that is high in protein and unsaturated fats (National Nutrition Council, 2022). In this study it is the source of hydroxyapatite. The raw milkfish bones were cleaned, dried, and crushed by the researchers. Moreover, calcination is procedure that involves heating an object to a high temperature under the melting point of metal in absence of air or limited supply of air. It is the process needed to produce hydroxyapatite. The researchers delve into the multifaceted process of calcination, exploring its widespread applications in diverse industries, from the production of metals and ceramics to the manufacturing of cement, focusing on the removal of volatile substances, moisture, and impurities through the application of high temperatures. One research investigates the phase transformation of alumina and silica minerals in coal gangue, showing that high-temperature calcination leads to the release of active silica minerals, which can be separated through caustic leaching, with potential applications in water purification (Xie et al., 2021). The dried Milkfish bone was put in a furnace at 900 Degrees Celsius for several hours and was characterized by the Fourier Transform Infrared Spectroscopy (FTIR). It is the most popular type of infrared spectroscopy used to identify organic, polymeric, and occasionally inorganic materials. According to Kumar et al. (2021). FTIR spectrum revealed the presence of major constituents of bone carbonate, phosphate groups and the degradation of organic matters.

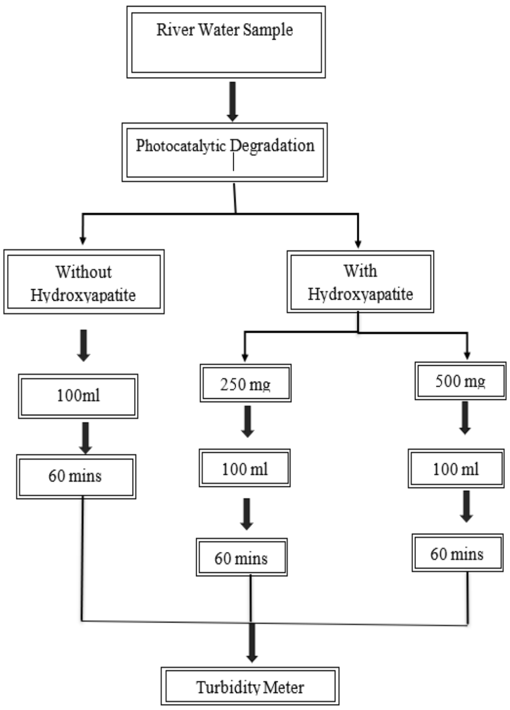

Figure 8. Process of Photocatalytic Degradation

Figure 8 shows the process of Photocatalytic Degradation. The figure shows that there are 3 water samples that were experimented. The first one is the Pandurucan River water sample without the use of Hydroxyapatite. The next one is the water sample using Hydroxyapatite but with different dosages of 250 and 500 mg. The samples were put in the photocatalytic reactor for a 1-hour process. Pollutants that are complex, highly concentrated, and non-biodegradable can be broken down using an advanced oxidation technique termed photocatalytic degradation. In photocatalytic degradation, light energy speeds up the breakdown of pollutants. The molecules of pollutants are hydrolyzed and oxidized by photons in the ultraviolet (UV) (Guamung et al., 2021).

Stage 3: Experimental Stage - Calcination of Hydroxyapatite from Milkfish Bones- Milkfish bones were collected and washed thoroughly with water to remove any dirt or debris. The cleaned bones were dried under the sun for several hours until completely dry. Drying removes any remaining moisture from the bones, which could prevent the formation of HAp during calcination. The dried bones were crushed into a fine powder using a mortar, pestle, or ball mill. Crushing the bones increases their surface area, facilitating the reaction between calcium and phosphorus during calcination. The crushed bone powder was placed in a furnace and heated to a temperature of 900 °C for several hours. The calcined HAp powder was cooled overnight. The cooled powder is stored in a dark reagent container to prevent contamination.

Hydroxyapatite Characterization- Hydroxyapatite from milkfish bones typically involves several techniques to assess its properties and suitability for biomedical applications. These techniques include Fourier transform infrared spectroscopy (FTIR). FTIR identifies the functional groups present in HAp, such as phosphate and hydroxyl groups. These groups' peak positions and intensities can provide information about the crystalline and purity of the HAp.

Preparation of River Water Sample- The researchers collected a water sample from the Pandurucan River. A clean container (Amber Bottles 150ml and 2liter, respectively) was used to collect the water sample. Stored the water sample in a clean container away from direct sunlight until it is ready to be used.

Photocatalytic Degradation Process- The photocatalytic degradation process is a water treatment process that uses light to break down pollutants. The photocatalyst is irradiated with light, which causes it to generate electrons and holes. The electrons and holes can then react with the pollutants in the water, breaking them down into harmless byproducts. The river water sample with and without hydroxyapatite underwent photocatalytic degradation simultaneously. Both water samples were processed for 60 minutes; for the photocatalytic degradation of the other river water sample using hydroxyapatite, two (2) samples were tested but with different catalyst dosages. This is to help the researchers determine if the hydroxyapatite concentration affects the photocatalytic degradation's effectiveness.

After all of the samples were tested, a turbidity meter was used. The use of this meter helped the researchers determine if there is a significant difference in the level of turbidity of the water after using photocatalytic degradation with hydroxyapatite and without using hydroxyapatite. Also, the researchers were able to identify if the dosage of the photocatalyst affects the photocatalytic degradation of the turbid water.

Observation and Data Recording - The researchers conducted a comprehensive data gathering and observation study to analyze the effectiveness of photocatalytic degradation using hydroxyapatite from milkfish bone as a wastewater treatment. The result was tested in a laboratory, and the researchers recorded every detail systematically. The researchers determined if there is a difference regarding the effectiveness of the photocatalytic degradation process with and without hydroxyapatite in the same period of 60 minutes. To do that, first is the photocatalytic degradation without hydroxyapatite and with hydroxyapatite with different dosages of catalyst, 250 mg and 500 mg simultaneously. Aside from the records that the laboratory had provided, the researchers also took down notes and observations to make sure that no information was left out.

Statistical Treatment of the Data - The researchers used a T-test and weighted mean to statistically analyze the data. The t-test is a vital statistical tool for comparing the means of two groups, determining if differences are likely due to chance or actual effects. This study used it to test wastewater quality post-photocatalytic treatment with and without hydroxyapatite. The t-test analyzes variability within each group and compares it to the difference between group means. Moreover, the weighted mean was used to calculate the water's turbidity level and to regulate and measure the degree of photocatalytic degradation. When comparing wastewater quality before and after photocatalytic treatment using the material, a significant change in the pollutant levels calculated using the weighted mean indicates increased efficacy of photocatalytic degradation. The weighted mean analysis considers the distribution of data points within each group and compares it to the difference between group means.

3. Results and Discussions

Table 1

Level of turbidity of water before the use of Photocatalytic Degradation using Hydroxyapatite from Milkfish bones

Trial	Turbidity (NTU)
1	358
2	360
Average	**359**

The goal of this project is to treat the water in the Pandurucan River in an efficient, economical, and environmentally responsible manner. To determine the difference in water turbidity between the controlled and using photocatalytic degradation, the researchers collected a sample of water from the Pandurucan River as the initial turbidity level or control. As stated in Bright & Mager's study (2020), a measure of light side scattering called turbidity is reliant on the mass concentration of suspended sediment in the water. The presence of suspended particle matter controls the turbidity of river water, which is used to detect changes in appearance in reaction to organic and inorganic particles of the river water. In explaining this outcome, the table above displays turbidity levels before photocatalytic degradation using hydroxyapatite from Milkfish bones. Two tests were conducted on 150 mg of Pandurucan River water to find out how turbid the sample water was. Throughout the two tests, the turbidity level obtained from the initial test was 358. In contrast, the second test yielded 360 both before the use of photocatalytic degradation, arriving with the mean score of 359, which is the average of trials 1 and 2, and came up with that level of turbidity without the use of photocatalytic degradation using Hydroxyapatite from milkfish bone.

Table 2

Level of turbidity of water after the use of Photocatalytic Degradation

Trial	Control	Photocatalytic Degradation
1	358	105
2	360	100
Average	**359**	**102.5**

The researchers used the process of calcination to determine the level of turbidity after the use of photocatalytic degradation using hydroxyapatite from milkfish bones without a catalyst. Table 2 shows the data gathered after the process. During the procedure, researchers examine the water's turbidity level variation after photocatalytic degradation without a catalyst using a sample of 150 mg of Pandurucan river water for 1 hour under UV light. The information shows that the amount of turbidity in water significantly decreases upon completing photocatalytic degradation without a catalyst. Photocatalytic Degradation as a de-pollution method has limited efficacy, but from the environmental point of view, it has great significance because the sun is a cheap and endless source (Afanasiev et al., 2023). Given the fact that the level of turbidity changed after a distinct process, the researchers have concluded that the level of turbidity from 2 sample tests of photocatalytic degradation without hydroxyapatite obtained; (1) initial test: 100, and (2) second test: 105–reaching the of 102.5 mean. The findings have proved that the conducted process was highly influential in lowering the water's turbidity level despite its small differences.

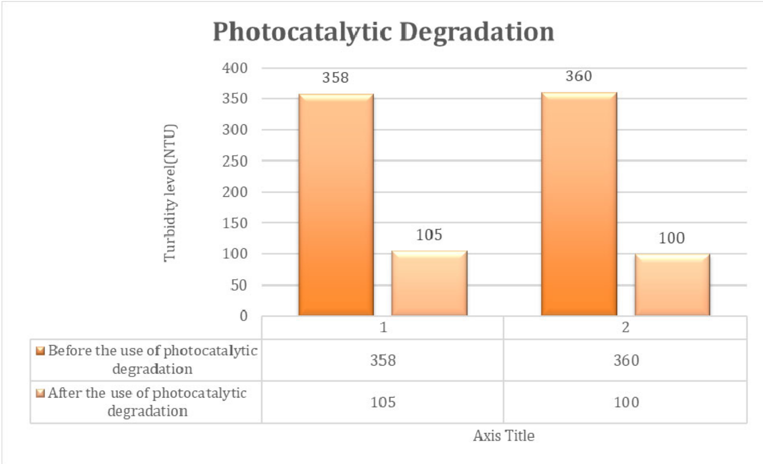

Figure 9. Graph of Photocatalytic Degradation

A distinct experiment was conducted to evaluate the effectiveness of the process in testing the turbidity level before and after the use of photocatalytic degradation. Throughout the experiment, researchers tested the efficacy of Photocatalytic Degradation in reducing water turbidity. The data reveals a significant difference in turbidity levels before and after Photocatalytic Degradation. Furthermore, a comparative study between UV light and visible light was also conducted at optimum conditions, whereby the UV light was demonstrated to be highly effective for turbidity and COD removal (Munien et al., 2023).

Table 3

*T-test r*esults in the level of turbidity of water before and after the use of Photocatalytic Degradation

	Control	**Photocatalytic Degradation only**
Mean	359	102.5
Variance	2	12.5
Observations	2	2
Pearson Correlation	-1	
Hypothesized Mean Difference	0	
Df	1	
t Stat	73.28571429	
P(T<=t) one-tail	0.00434314	
t Critical one-tail	6.313751515	
P(T<=t) two-tail	0.00868628	
t Critical two-tail	12.70620474	

Legend: p-value ≤ 0.05- Significant, reject Ho.

Based on the provided data and statistical analysis, the p-value (P(T<=t) two-tail) is 0.00868628, which is less than the typical significance level of 0.05. Therefore, this study rejects the null hypothesis (Ho) and accepts the alternative hypothesis (Ha). This suggests a significant difference in the water's turbidity level before and after the use of Photocatalytic Degradation. In photocatalytic degradation, light energy speeds up the breakdown of pollutants. The molecules of pollutants are hydrolyzed and oxidized by photons in the ultraviolet (UV) (Guamung et al., 2021). The mean turbidity decreased from 359 to 102.5, indicating that the Photocatalytic Degradation process effectively reduced the turbidity of the water. Bright & Mager's (2020) study states that a measure of light-side scattering called turbidity relies on the mass concentration of suspended sediment in the water. The presence of suspended particle matter controls the turbidity of river water, which is used to detect changes in appearance in reaction to organic and inorganic particles of the river water. A study conducted by Prihatinningtyas (2019) found a substitute treatment for coagulation-flocculation: removing turbidity in water treatment using a natural coagulant from Lemna perpusilla. Lemma perpusilla (duckweed) is an aquatic plant that quickly spreads. This plant contains high protein and is proven to remove 85.02%; 88.89%, and 92:48% from water, having turbidities of 50, 150, and 300 TV, respectively. He added that natural coagulants that are safe for human health and biodegradable should be used instead of these chemical coagulants.

Table 4

T-test results in the effectiveness of Photocatalytic Degradation using 250mg and 500 mg of Hydroxyapatite

	Control	**Photocatalytic Degradation with 250 mg of HAp**	**Control**	**Photocatalytic Degradation with 500 mg of HAp**
Mean	359	79.8	359	25.75
Variance	2	0.08	2	0.125
Observations	2	2	2	2
Pearson Correlation	1		1	
Hypothesized Mean Difference	0		0	
Df	1		1	
t Stat	349		444.3333333	
P(T<=t) one-tail	0.00091206		0.000716375	
t Critical one-tail	6.313751515		6.313751515	
P(T<=t) two-tail	0.00182412		0.00143275	
t Critical two-tail	12.70620474		12.70620474	

Legend: p-value ≤ 0.05- Significant, reject Ho.

Table 4 shows the T-test results in the effectiveness of Photocatalytic Degradation using 250 mg and 500 mg of Hydroxyapatite. Another experiment was carried out to examine hydroxyapatite concentration's impact on photocatalytic degradation's effectiveness. The controlled variable was compared to 250 and 500 mg of hydroxyapatite throughout two observations on each of its factors to assess the process' effectiveness. In using 250mg Hydroxyapatite, with a mean of 359 for Variable 1 compared to 79.8 for Variable 2, there appears to be substantial variance in the degradation performance between the two scenarios. The low p-value of 0.00091206 indicates that this difference is statistically significant, further supported by the t-statistic of 349, exceeding the critical value of 6.31. This suggests that the concentration of hydroxyapatite does indeed affect the effectiveness of photocatalytic degradation, with higher concentrations potentially resulting in more efficient degradation processes. Therefore, there is a significant difference in the effectiveness of photocatalytic degradation using 250 mg of hydroxyapatite. According to Gao et al. (2019), Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, Hap) has excellent biocompatibility and mechanical properties. It is a vital inorganic material widely used in bone grafts, drug-carrying systems, photocatalysts, and adsorbents. Because of its high adsorption capacity for contaminants, high effectiveness, low cost, and high stability under redox conditions, Hap is an ideal material for handling long-term pollutants in water treatment applications. In using 500mg, the data suggests a significant difference in the effectiveness of photocatalytic degradation between the control variable (359) and the variable with 500 mg of hydroxyapatite (25.75). The mean concentration of hydroxyapatite substantially decreased the effectiveness of photocatalytic degradation compared to the control. This is evident from the sizeable t-stat value of 444.3333333, indicating a considerable difference between the two variables.

Additionally, the p-value obtained (0.000716375) is well below the typical significance level of 0.05. The data implies that higher concentrations of hydroxyapatite negatively impact the efficiency of photocatalytic degradation, suggesting a non-linear relationship between hydroxyapatite concentration and degradation effectiveness. Turbidity can be easily removed from turbid water using a bridging mechanism with a rate of 95% from 178 NTU to 14.1 NTU with an ideal dosage of 0.8 mg/l (Zahraa, 2021). Furthermore, according to Deshmukh (2021), there is a relationship between concentration of catalyst and reaction rate. As the catalyst concentration increases, the rate of the reaction also increases. Thus, it is evident that variations in hydroxyapatite concentration play a crucial role in determining the efficiency of photocatalytic degradation processes.

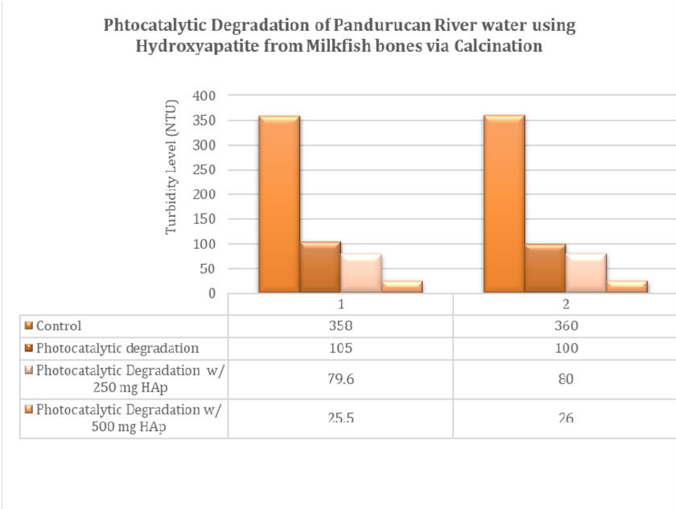

Figure 10. Comparison of turbidity of the water before and after the use of Photocatalytic Degradation using Hydroxyapatite from Milkfish bone

Based on Figure 10, data shows the result of trials in each experiment. The 150 ml water sample from Pandurucan was tested, and the result says that the first trial of the first turbidity test experiment had 358 NTU and the second had 360 NTU with an average of 359 NTU serving as the control variable. Another 2 trials were conducted by the researchers with the same amount of water sample from Pandurucan River that had undergone the process of photocatalytic degradation without using hydroxyapatite and tested its turbidity level. The result of the first trial was 105 NTU, and the second trial was 100 NTU with an average of 102.5 NTU. Furthermore, the researchers performed the third experiment of turbidity testing, in which the water samples underwent the process of photocatalytic degradation but with the use of hydroxyapatite as a photocatalyst. The results of the first two trials using 250 mg of hydroxyapatite were 79.6 NTU and 80 NTU, with an average of 79.8 NTU. The second set of trials with 500mg of hydroxyapatite resulted in 25.5 NTU and 26 NTU, with 25.75 NTU as the average. After the trials conducted by the researchers, it is clearly shown on the graph that the turbidity level of the water was successfully reduced with hydroxyapatite. The first turbidity testing reduced it from 359 NTU to 102.5 NTU with the photocatalytic degradation. 102.5 NTU to 79.8 with 250 mg of Hap, and successfully reduced to 25.75 NTU with 500 mg of Hap. It only proves that Hydroxyapatite is an effective catalyst in Photocatalytic degradation by reducing the turbidity of the water. The findings of this study are similar to those of Mustafa et al. (2015), who stated in their study that Hydroxyapatite is one of the most essential materials and is mainly used in the clinical area of the biomedical field. Similarly, since hydroxyapatite's chemical composition is similar to that of human bone and teeth, it is the most widely used calcium phosphate ceramic in biomedical applications. Chemical precursors, particularly calcium and phosphorus, can be used to synthesize hydroxyapatite by a variety of techniques, such as dry, wet, thermal, or a combination of these (Mohd Pu'ad et al., 2020).

Table 5

Degradation rate of water's turbidity

Water Sample	Turbidity (NTU)	Degradation Rate (%)
Panduruan River Water	359	
Without HAp	102.5	71.45%
With 250 mg HAp	79.8	77.77%
With 500 mg HAp	25.75	92.83%

The provided data presents a study on the impact of Hydroxyapatite (HAp) on the turbidity and degradation rate of water samples taken from the Panduruan River. Turbidity is measured using the Turbidity Meter. The result shows a 359 Nephelometric Turbidity Unit. After applying Photocatalytic Degradation, the turbidity of the river water stands at 102.5 NTU, with a corresponding degradation rate of 71.45%. With the use of HAp as photocatalysis, the turbidity degradation is highly improved. The application of 250mg of HAp resulted in a 79.8 NTU, corresponding to a 77.77% degradation rate, while using a more high concentration of HAp further increased the rate of degradation, the application of 500mg concentration of HAp dramatically reduced the turbidity to 25.75 NTU, with a drastic degradation rate of turbidity to approximately 92.83%. The data suggests a clear correlation between the dosage of HAp and its efficacy in reducing turbidity and enhancing the degradation rate of the river water samples.

The observed decrease in turbidity indicates that HAp is effective in precipitating suspended particles and clarifying the water. Moreover, the notable increase in degradation rate with higher HAp concentrations signifies its potential to facilitate the removal of pollutants or impurities from the water. These findings underscore the promising role of HAp as a water treatment agent for improving water quality in rivers, potentially benefiting ecosystems and human populations reliant on clean water sources. However, further investigation is warranted to elucidate the mechanisms underlying the observed phenomena and to assess any potential adverse effects or limitations associated with the use of HAp in water treatment applications. Additionally, factors such as HAp stability, cost-effectiveness, and scalability should be considered to evaluate its practical feasibility and implementation on a larger scale for water treatment purposes. Nonetheless, the data provides valuable insights into the potential efficacy of HAp as a solution for mitigating water pollution and enhancing water quality in river ecosystems. The findings are also proven by Mohd Pu'ad et al. (2019), who state that using HAp extracted from natural sources is considered a cost-effective, sustainable, and ecologically friendly method and is widely accessible. This may lead to beneficial effects on the economy, both to the environment and overall health.

Figure 11 shows the FTIR characterization of Hydroxyapatite; the resorption process and dissolution of bone have been assisted by a modest part of the hydroxyl groups. The intensity of the OH single bond band was found to be decreased in both samples after thermal calcination treatment, which was attributed to the dihydroxylation process in extracted HAp material. FTIR spectra analysis showed HAp has some functional groups, such as –OH, -(PO4)6, and -CO3 2. The FTIR result of the hydroxyapatite is shown in Figure 11. The acquired spectrum confirmed the presence of various functional groups of hydroxyapatites compared with the results of Kumar et al. (2021). The bond peaks 3439.92 cm^1, 3424.22cm, and 620.92 cm fall between the ranges 3405.30 cm to 3437.27 cm, 3641cm to 3543 cm, and $646cm^3$ to 606 cm^3 correspondingly, are known to verify the existence of hydroxyl (OH) group which indicates the presence of hydroxyapatite (Kumar et al. 2021) The strongest peaks at 557.94 cm and 561.94cm that fall to the range of 611.33cm to 552.62cm and 470.63cm to 634.58cm correspond to the stretching vibrations of the phosphate (PO) group. The presence of phosphate groups is also validated by vibrational modes at 655.42cm and 572.25 cm. In addition, the aforementioned piece of literature also confirmed the peak at 582.05 cm as the vibration peak for phosphate ions (Kumar et al., 2021).

The bands at 1025.01cm and 1239.88 cm-1 were attributed to CO3 Asymmetric stretching (carbonate group). The carbonate content in higher concentrations helps in the solubility and resorbability process that occurs in bone.

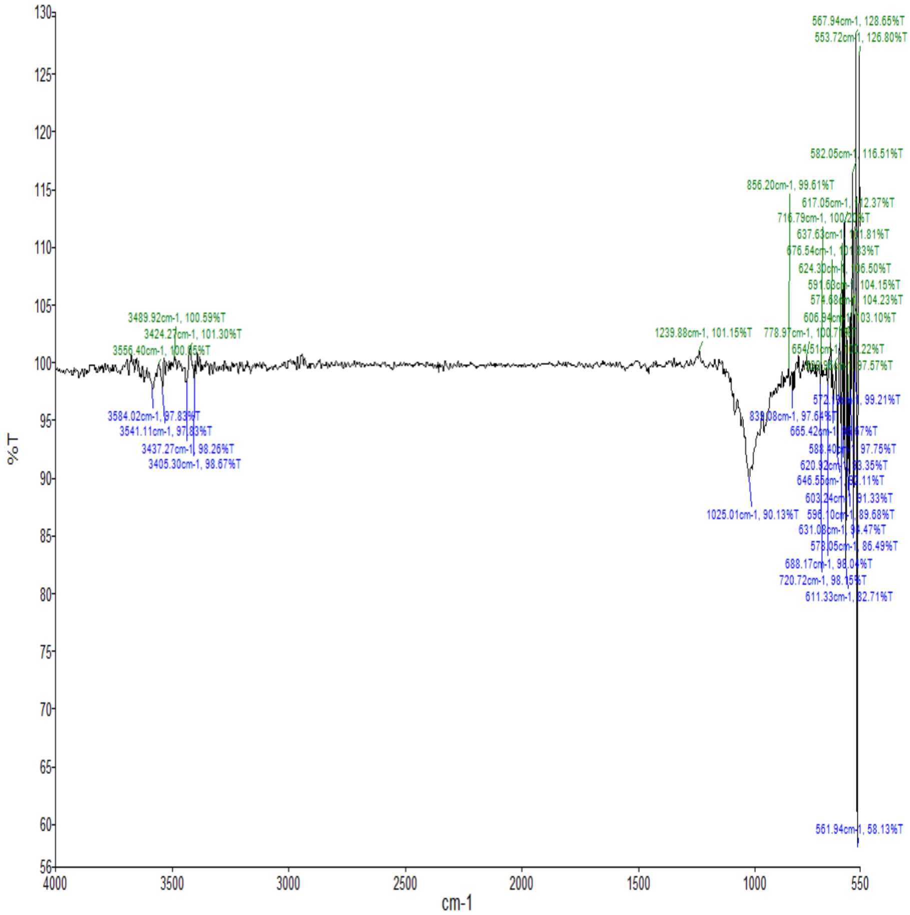

Figure 11. FTIR characterization of Hydroxyapatite

4. Conclusions

The study's findings led the researchers to formulate conclusions, such as the Pandurucan River water sample utilized as a control, which had an initial turbidity level of 359 NTU. It is evident that photocatalytic degradation using hydroxyapatite from milkfish bones, even without a catalyst, effectively lowers the turbidity level in wastewater. The findings indicated that the Photocatalytic Degradation process effectively reduced the turbidity of the water. With the use of two samples, this study found that the higher the concentration of hydroxyapatite, the more effective it is in lowering the turbidity of the water. The research findings led to the acceptance of the alternative hypothesis (Ha) and rejection of the null hypothesis (Ho), which stated that treating wastewater with hydroxyapatite from milkfish bones by photocatalytic degradation is ineffective. The researchers' trials have demonstrated the efficacy of hydroxyapatite derived from milkfish bones as a catalyst for photocatalytic degradation in wastewater treatment.

4.1 Recommendation

In line with the findings and the conclusions of both the study itself and the data gathered, here are the recommendations for future researchers: they may increase the amount of control (raw sample) before using photocatalytic degradation, they may prolong the reaction time for photocatalytic degradation from 1 hour; you can make it up to 2 hours or more based on the laboratory recommendations because the reaction time affects the result of photocatalytic degradation, they may collect a sample of water on a rainy, cloudy, or sunny day because the results of the photocatalytic process differ depending on the weather, they may increase the dosage of hydroxyapatite from 500mg to 750mg or more because the higher the dosage of hydroxyapatite being used, the higher the percentage of hydroxyapatite being an effective wastewater treatment, they may use the hydroxyapatite derived from milkfish bone as a wastewater treatment for other parameters like pH level, concentration of dissolved oxygen, and other concentrations of pollutants. Future researchers may investigate hydroxyapatite photocatalysis for wastewater treatment across diverse weather conditions and dam-influenced water sources. Expanding water quality analysis beyond turbidity to include pH, dissolved oxygen, and specific pollutants is also crucial. This comprehensive approach will yield a clearer picture of the method's effectiveness and environmental impact, paving the way for more sustainable wastewater treatment solutions.

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