PHOTOCATALYTIC DEGRADATION OF COMMONLY USED ORGANIC DYE IN NEPAL USING NANOPARTICLES

A MINI RESEARCH REPORT

SUBMITTED TO

DEAN'S OFFICE

INSTITUTE OF SCIENCE AND TECHNOLOGY

TRIBHUVAN UNIVERSITY

KIRTIPUR, KATHMANDU, NEPAL

BY

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Mini Research Report

Submitted to

Dean's Office
Institute of Science and Technology
Tribhuvan University
Kirtipur, Kathmandu, Nepal
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RECOMMENDATION LETTER

This is to certify that the research work entitled **“Photocatalytic Degradation of Commonly Used Organic Dye in Nepal Using Nanoparticles”** has been carried out by **Situ Shrestha Pradhanang** as a mini research grant of Dean’s Office, Institute of Science and Technology, Tribhuvan University under my supervision. To the best of my knowledge, this work has not been submitted to any other institute.

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Mentor

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DECLARATION

I, ***Situ Shrestha Pradhanang***, hereby declare that the work presented herein is genuine work done originally by me under the supervision of Asst. Dr. Rajesh Pandit and has not been published or submitted elsewhere for the any other purpose. Any literature, data or works done by others and cited in this project work have been specifically acknowledged and listed in the references section.

Situ Shrestha Pradhanang

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Situ Shrestha Pradhanang

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Abstract

The utilization of organic dyes across various industries has significantly contributed to the vibrant colors in fabrics, papers, and wools. However, the release of these dyes into water bodies poses a significant environmental challenge due to their persistent nature as pollutants. To address this issue, researchers have been exploring different methods for the removal of dye pollutants from water, with nanoparticles emerging as promising catalysts for degradation processes under light exposure. In this research work, zirconia (ZrO_2) and hydroxyapatite (HAp) nanomaterials were investigated as photocatalysts for degrading methylene blue, a prevalent dye in Nepal. Employing an eco-friendly green synthesis route, both nanomaterials were successfully prepared and characterized using techniques such as X-ray diffraction (XRD), Fourier Transmission-Infrared spectroscopy (FT-IR), and UV-Visible spectroscopy. FTIR analysis confirmed the successful green synthesis of zirconia and hydroxyapatite, while XRD results indicated their nanometric size range. The degradation of methylene blue was conducted using the synthesized nanomaterials under sunlight exposure, with degradation efficiency dependent on nanoparticle dosage and dye concentration. Notably, both ZrO_2 and HAp nanoparticles exhibited significant efficacy in dye degradation, with ZrO_2 demonstrating superior performance at low dye concentrations and HAp exhibiting remarkable effectiveness at higher nanoparticle doses. This research underscores the promising potential of ZrO_2 and HAp nanoparticles as efficient catalysts for mitigating organic dye pollution in water bodies, offering a sustainable approach to address this pressing environmental challenge.

Keywords: zirconia, hydroxyapatite, organic dyes, degradation

1. Introduction

1.1 Introduction

A group of color-bearing chemicals known as dyes are widely used in various industrial processes such as fabric, textile, leather, cosmetics, pharmaceuticals, food processing, and distillation. The exact global usage of dyes is unknown, but it was estimated to be around 700,000 tons in 2008, and this amount has been increasing annually (Huitle and Brillas, 2009). Studies indicate that 10-15% of the total dyes are lost during synthesis and dyeing processes (Cho and Zoh, 2007), with almost all of this loss entering water bodies directly or indirectly. The disposal of dye-laden wastewater into water sources significantly impacts aquatic life (Gita et al., 2017), and human consumption of contaminated water can cause respiratory issues, central nervous system problems, eye and skin allergies, and other health concerns (Chequer et al., 2011).

In Nepal, there are 156 textiles, 9 tanning, 5 pulp and paper, and 11 paint industries in operation (Iswori et al., 2005). Waste from these industries is often discharged directly into water sources without proper treatment. This wastewater contains various reactive chemicals and dyes from the dyeing and printing processes. Proper treatment plants are required to manage such dyes and chemicals before their release into the environment (Ramesh et al., 2007). According to the World Bank, 17-20% of industrial waste comes from textile dyeing and finishing treatments (Roshan, 2016). The annual production of toxic waste from the textile, tanning, pulp and paper, and paint industries in Nepal is 5,346 tons, 28,621 tons, 22,852 tons, and 11,386 tons respectively, with these amounts increasing yearly. The average wastewater discharge from these industries is 54.77, 70, 115.65, and 1 m^3/ton respectively (Iswori et al., 2005).

Given the increasing threat dyes pose to human health and aquatic life, various methods such as ultrafiltration, reverse osmosis, ion exchange on synthetic adsorbent resins, and electrochemical oxidation/reduction are employed to decolorize dye effluents. However, most of these methods are non-destructive, converting dyes into other compounds that still cause pollution (Konstantinou and Albanis, 2004). Chlorination and ozonation are also used for dye removal, but these methods are slow, costly, and limited in effectiveness regarding carbon content reduction. To address these limitations, advanced oxidation processes (AOPs) have gained attention. AOPs rely on producing highly reactive hydroxyl radicals (OH^-) using solar or chemical energy. These radicals oxidize a broad range of pollutants quickly and non-selectively (Konstantinou and Albanis, 2004). Among AOPs, the photocatalytic process is particularly attractive due to its efficiency, low cost, non-toxic nature, and chemical stability. Various photocatalysts, including metal oxides, metal sulfides, and metal phosphides, have been studied for their effectiveness (Lu et al., 2018).

Nanotechnology has emerged as a significant field, particularly in surface science and semiconductor materials, with nanomaterials being considered potential candidates for photocatalytic activities due to their stability, low cost, and high photoactivity (Lu et al., 2018). This research focuses on using nanoparticles, specifically zirconium dioxide (ZrO_2) and hydroxyapatite (HAp), synthesized via green routes for the degradation of organic dyes.

Dyes are extensively used to enhance the appearance of materials, with global demand expected to increase by 4% between 2019 and 2023 (www.businesswire.com/news). Nepal is not exempt from this global trend. Despite this, research on dye degradation in Nepal is limited. While international research can provide valuable insights, developing methods and materials using local resources will significantly enhance our capacity to address wastewater management challenges with recent low-cost techniques.

1.2 Objective

General objective

The general objective of this research is to synthesize ZrO_2 and Hap nanomaterials using green route and study the degradation behavior of these materials

Specific Objectives

- Synthesis of ZrO_2 and HAp nanoparticles using green route.
- Characterization of the ZrO_2, and HAp nanoparticles using FTIR, XRD and UV-Visible spectrophotometer for their dye degradation behavior.

- Analysis of the efficiency rate and effectiveness of these materials in photocatalytic dye degradation.

2. Literature Review

2.1 Dyes and their degradation

Industrial development plays a crucial role in improving the social status of people and boosting a country's economy. Various industries contribute to making our lifestyle more convenient and comfortable. However, their waste and wastewater often have negative impacts on public health and the environment. Wastewater discharged from industries such as pharmaceuticals (Rizzo et al., 2009), carpet manufacturing (Saroj et al., 2015), and pulp and paper production (Ashrafi et al., 2015), among others (Rauf et al., 2011), contaminates water with organic dyes, posing severe environmental threats. These dyes not only pollute surface and groundwater but also affect aquatic life (Berradi et al., 2019), public health (Lessis et al., 2019), and cause environmental imbalances (Tayade et al., 2007). According to the World Health Organization (WHO), around 1.8 billion people globally still use contaminated water (Abhilash et al., 2019). Thus, the international community faces the challenge of providing pure water through sustainable wastewater treatment processes (Abinaya et al., 2021).

Organic dyes such as methylene blue (MB), methyl orange (MO), and malachite green (MG) are widely used in textile coloring, fishery (Matpang et al., 2017), and medical sectors (Oz et al., 2011). MB, in particular, can cause carcinogenic diseases (Srivastava et al., 1995; Wang et al., 2010). These dye pollutants have strong chemical structures and stability, making them difficult to degrade in the environment. Various methods, including physical (Shohel et al., 2015), chemical (Bouazizi et al., 2017), and biological methods (Bhatia et al., 2017; Kamoros and Lyberatos, 2006), have been employed for dye degradation.

Previously, conventional methods such as coagulation (Ahmad and Puasa, 2007), adsorption (Nasuha, 2010), ion flotation (Shakir et al., 2010), and sedimentation (Zodi et al., 2010) were used to remove dyes from contaminated water. However, these methods were not effective in completely removing dyes from wastewater. Treatments were less effective because the dye adsorbed accumulated in the adsorbent, creating new problems. Kapdan et al. (2000) used the activated sludge method for biologically resistant dye degradation, but it was not effective in dye removal. Kharissova et al. (2013) compared adsorption and photocatalysis techniques for dye pollutant removal, highlighting them as significant methods for wastewater purification.

Given the extensive use of dyes and their environmental threat when disposed into water sources, various methods have been studied to remove dyes from water resources. Among the physio-chemical techniques for effective textile wastewater decolorization, adsorption is a major process. Studies have shown that adsorption effectively removes organic dyes and produces high-quality treated water. However, the challenge lies in selecting the most appropriate adsorbent among those with different adsorption characteristics (Crini, 2006).

Conventional methods are often ineffective in removing dyes from wastewater. Thus, photocatalytic degradation could be an excellent alternative, as reactive species such as hydroxyl radicals and superoxide anions oxidize and reduce organic pollutants (Rochkind et al., 2014). Photocatalysis is gaining attention as a viable solution for wastewater treatment problems (Amin et al., 2014). This process harnesses solar energy to degrade and mineralize organic dyes into harmless products, generating minimal secondary waste or enabling recovery and reuse after the process (Saravana et al., 2017; Kabra et al., 2004).

2.2 Photocatalytic degradation and their activities

Photocatalysis involves using a substance to alter the speed of a chemical reaction, typically speeding it up, under light exposure (solar, UV-visible) (Tahir et al., 2020; Wu et al., 2022). This method is environmentally friendly and effective for removing organo-chemical pollutants (Abhilash et al., 2019). Photocatalytic degradation has become a crucial technique in wastewater treatment, especially for small amounts of refractory organic matter, due to its cost-effectiveness, minimal chemical use, rapid processing, non-toxicity, and sustainability (Miyauchi et al., 2002; Legrini et al., 1993).

In photocatalytic processes, the catalyst decomposes various dyes, organic pollutants, and biological species like viruses and harmful fungi using UV or light irradiation, promoting a cleaner environment (Butt, 2020). This method is economical when sunlight is used as the photon source.

In homogeneous photocatalysis, the photocatalyst and reactants are in the same phase. For example, the Fe+ and Fe+/H_2O_2 photon systems and ozone are commonly used, where reactive species with OH free radical content function effectively (Chung-Hsin et al., 2006). Heterogeneous photocatalysis, on the other hand, involves the reactant and photocatalyst in separate phases. This process is used for water detoxification, metal deposition, hydrogen transfer, alkane oxidation, dehydrogenation, and isotopic exchange, often employing semiconductors and transition metal oxides (Zhu et al., 2021).

Semiconductor photocatalysts, which possess a crystalline structure and an appropriate band gap for generating photon-induced charge carrier pairs (electron/holes), are essential for oxidation-reduction reactions in photocatalytic cycles (Augugliaro, 2019). The efficiency of these photocatalysts depends on the energy positions of the semiconductor bands (HOMO/LUMO) and the redox potential of the adsorbents (Wang et al., 2022).

Various methods have been used for dye degradation, including chemical oxidation, coagulation, flocculation, membrane filtration, and biological degradation (Chanikya et al., 2021). However, Bharath et al. (2020) noted limitations in these methods, such as the need for sophisticated instruments and high costs, hindering their effectiveness in dye degradation. Ghazanfari et al. (2021) recommended an inexpensive and environmentally friendly approach for separating contaminants in wastewater.

Semiconductor photocatalysts like TiO_2, CdS, ZnS, WO_3, and ZnO are highly effective in degrading organic dyes due to their reusability and high degradation efficiency at low pollutant concentrations. The synthesis of Zirconia (ZrO_2) nanoparticles (NPs) has gained attention for their multifunctional properties (Dwivedi et al., 2011).

Biological treatment methods, which use microorganisms like algae, fungi, bacteria, yeast, and enzymes, are also gaining attention due to their availability and eco-friendly nature.

These microorganisms degrade dyes through aerobic, anaerobic, and sequential aerobic-anaerobic processes (Shoukat et al., 2019).

Other methods such as oxidation, electrochemical treatment, coagulation, ion exchange, reduction, and flotation have also been employed for dye treatment (Adamek et al., 2013). However, some of these methods are less efficient or change the dye phase, causing environmental issues. Photocatalytic degradation, using various materials including nanoparticles as catalytic agents, remains a widely used and effective method.

2.3 Nanoparticles for photocatalytic application

Photocatalytic degradation is superior to other methods due to its environmental friendliness, low cost, faster removal rate, and ability to eliminate contaminants in the range of parts per billion (ppb) (Viswanathan, 2018). Over the years, various photocatalysts, including metal oxides, metal selenides, multi-component oxides, and metal-free materials, have been used for dye degradation (He et al., 2018). Nanomaterials are promising photocatalysts due to their stability, high catalytic activity, and low cost. Various methods have been developed to synthesize nanoparticles, such as coprecipitation, hydrothermal, laser ablation, sol-gel, ultrasound, and biological synthesis (Jagpreet et al., 2018).

Among nanomaterials, semiconductor metal oxide nanoparticles such as ZnO, TiO_2, ZrO_2, Fe_2O_3, CdS, and MgO are widely used as photocatalysts for degradation processes due to their wide band gaps, high stability, nontoxic nature, and photosensitivity (Zhang et al., 2019).

Hydroxyapatite (HAp) is an inorganic nanoparticle with broad applications in material science. One of its major applications in wastewater treatment is dye degradation from aqueous solutions, owing to its non-toxic, biodegradable, photooxidative degradation resistance, and eco-friendly nature (Abideen et al., 2018; Selvem et al., 2018).

Zirconia (ZrO_2) nanoparticles (NPs) are attractive for various applications due to their non-toxicity, high chemical and thermal stability, catalytic activity, and a high negative value of conduction band potential (Nayak, 2010; Zheng et al., 2009). Additionally, their large band gap and suitable redox potentials are favorable for degrading a wide range of organic pollutants (Kralik et al., 1998).

This research focuses on using ZrO_2 and HAp NPs for dye removal from water. Nanocomposite materials, which are multi-phase solid materials with one phase in the nanometric range (100 nm), exhibit unique property combinations and design possibilities. These materials are even more effective as they combine the properties of different materials. At the nano-meter level, interactions at the phase interface are significantly improved, enhancing material properties for structural, functional, and cosmetic applications.

In this work, ZrO_2 and HAp nanoparticles are prepared via a green synthesis route. The synthesized NPs are then investigated for their dye degradation efficiency, using visible light as radiation sources for photocatalysis.

3. Materials and Method

3.1. Materials

Turmeric powder (*Curcuma longa*) was purchased from the local market of Kathmandu. Zirconyl chloride octahydrate [$ZrOCl_2 .8H_2O$ (98% purity)] and methylene blue (99% purity) (LOBA Chemie Pvt.Ltd., Mumbai, India) purchased from local suppliers in Kathmandu. All the chemicals (AR grade) used without further purification.

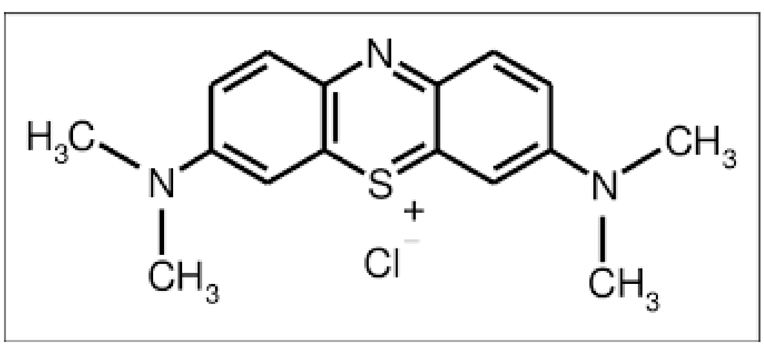

Figure 1: Structure of methylene blue

3.2. Methods

Preparation of Turmeric powder (Curcuma longa) extract

20 g of Turmeric powder (*Curcuma longa*) was taken in 500 mL beaker. 200 mL of distilled water was added and boiled for an hour with continuous stirring with a magnetic stirrer. After that, the boiled mixture was cooled and filtered by using whatsman 40 filter paper. A clear brown colored filtrate was obtained as the working solution (extract).

Preparation of Zirconia (ZrO_2) nanoparticles

50 mL, 0.1M zirconyl chloride octahydrate [$ZrOCl_2 .8H_2O$] was taken in a 250 mL beaker.10 mL of prepared Turmeric powder (*Curcuma longa*) extract was added to it. The mixture solution was heated at 80 ^oC with continuous stirred by using magnetic stirrer for two hours. At that moment, the final solution was placed undisturbed for two days and then the solution was filtered. The brownish colored precipitate of zirconia was obtained as a residue. The residue was ultimately calcined at 600 ^oC in muffle furnace and the white powdered zirconia was obtained.

Extraction of hydroxyapatite (HAp) from chicken bones

For defatting and deproteinizing, the raw bone samples were washed in fresh tap water and boiled in 1 L water at one and half hours. The clean bones were dried and grounded by a rotary mill in powder form. The powdered bones were sieved in 450 µm sieve. The sieved powders were calcined first at 600^oC at 3 hr. and then at 900 ^oC for 3 hr. to confirm the removal of the organic matters and the carbonate apatite. Finally, white powder of HAp was obtained. Thus, the synthesized NPs were characterized by the subsequent techniques.

Characterization methods

Fourier Transform Infrared (FT-IR) spectroscopy

FTIR analysis was done for the characterization of synthesized nanoparticle and the instrument was Infrared Spectrophotometer IR Tracer-100 (Shimadzu) within the range of 400 cm^{-1} and 4000 cm^{-1}. This characterization was carried out in Nepal Academy of Science and Technology (NAST).

X-ray diffraction (XRD)

The crystallographic structure, chemical composition and physical properties of materials were analyzed by X-ray diffraction (XRD) which is a non-destructive technique. The samples were characterized by Bruker D2 phaser diffractometer in Nepal Academy of Science and Technology (NAST).

Photocatalytic degradation of dyes

5 ppm solutions of methylene blue dyes were prepared and the prepared nanomaterials (ZrO_2 and HAp) nanomaterials with respect to 15 and 20 mg were used as a photocatalyst in the presence of hydrogen peroxide for the degradation of dyes. The study was conducted in presence of sunlight. The dye degradation was analyzed by using UV-spectrophotometer (Shimadzu) in RECAST. The general photocatalytic dye degradation process is shown in Figure 2.

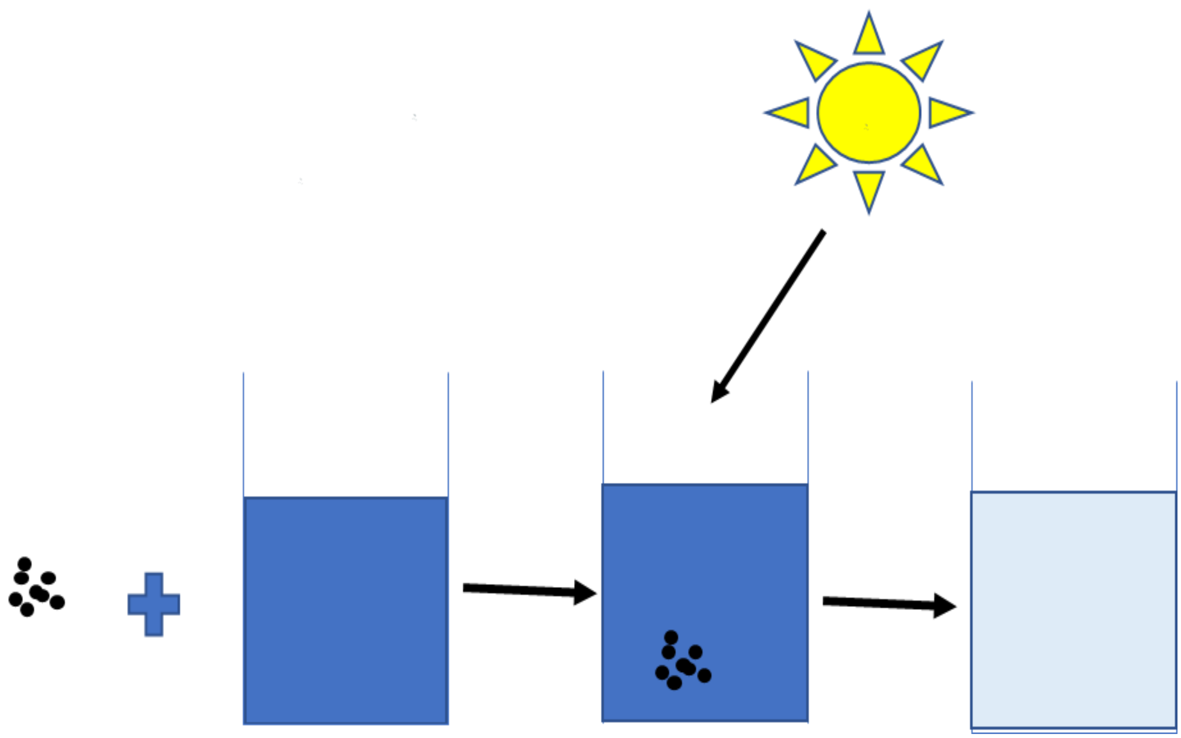

Figure 2: Photocatalytic dye degradation process of Methylene blue

4. Results and Discussion

4.1 FTIR Analysis of Zirconia (ZrO_2) and Hydroxyapatite (HAp) Nanoparticles

The FTIR spectrum of the synthesized zirconia nanoparticles within the range of 400 cm^{-1} and 4000 cm^{-1} is shown in Figure 3.

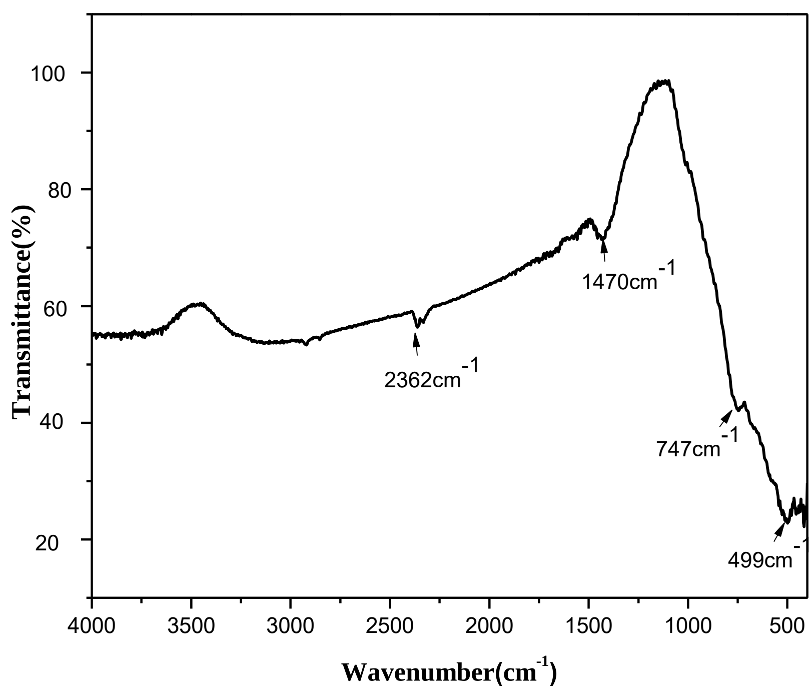

Figure 3: FTIR spectrum of Zirconia (ZrO_2) nanoparticles

In Figure 3, the zirconia nanoparticles showed a characteristic peak particularly at 499 cm^{-1} and 747 cm^{-1} representing to Zr-O stretching modes and Zr-O_2-Zr asymmetric respectively, which confirms the formation of ZrO_2 phases. Similar results had been reported by Bishwokarma et al. by using *curcuma longa* extract. Peaks at about 1430 cm^{-1} representing the C-H bending of the alkane.

Thus, it can be concluded that the ZrO_2 was successfully synthesized using green route.

The structural analysis of hydroxyapatite nanoparticles was characterized by the FTIR spectroscopy. The FTIR spectrum of synthesized HAp is shown in Figure 4.

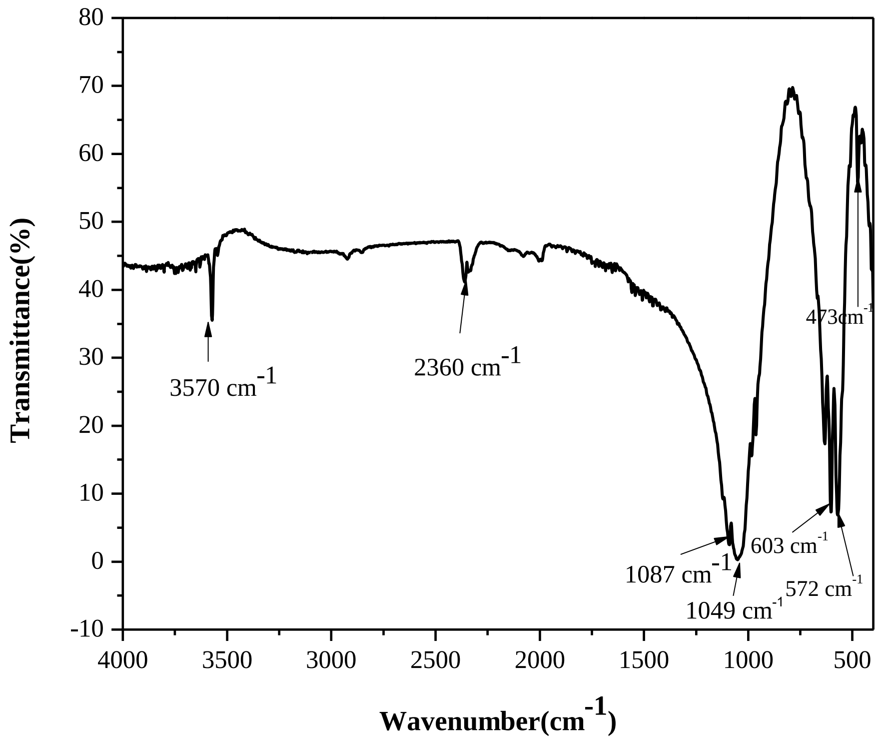

Figure 4: The FTIR spectrum of hydroxyapatite (HAp)

The FTIR spectrum showed the characteristic peaks around 473, 572, 603, 1049, 1087, 2360 and 3570 cm^{-1} was recorded in the Figure 3. The 473, 572, 603, 1049 and 1087 cm^{-1} representing the phosphate ion of the hydroxyapatite. The peaks around 473, 572, 603 cm^{-1} corresponding the symmetrical stretching of the phosphate group whereas the sharp peak around 1049, 1087 cm^{-1} representing the asymmetrical stretching of the phosphate group. The peak at 3570 cm^{-1} representing the hydroxyl group present in the hydroxyapatite. Similar results were reported on the literatures (Boujaady et al. 2016, Shah et al. 2021). Thus, the hydroxyapatite was successfully synthesized by calcination.

4.2 XRD Analysis of Zirconia (ZrO2) and Hydroxyapatite (HAp)

The zirconia and hydroxyapatite particles were analyzed by the XRD analysis. The XRD diffractogram of zirconia is shown in Figure 5. The diffraction peaks were observed at 28.8°, 30.6°, 41°, 50.7°, and 60.6° 2θ positions are indexed as (-111), (101), (-112), (220) and (-203) respectively. The monoclinic structure of zirconia is indicated by peaks (-111), (-112), (220) and (-203) whereas peak (101) indicates the tetragonal structure of zirconia (Gauna et al. 2015, Lydia et al., Liu et al, 2017). The sharpness of XRD peaks indicates that the particles are having crystalline nature (Gnanasangeetha & SaralaThambavan, 2013).

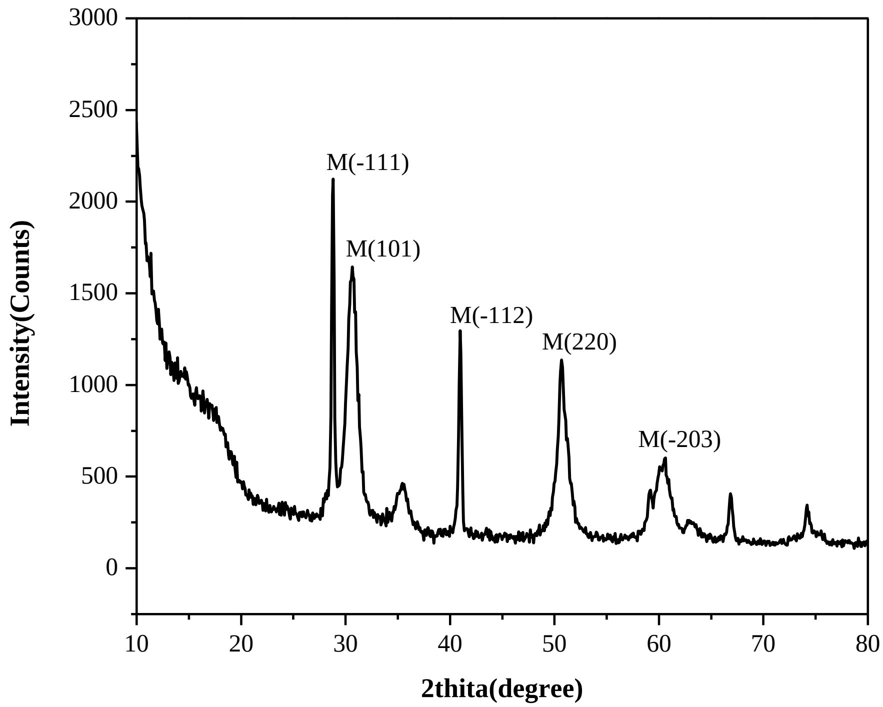

Figure 5: XRD diffractogram of zirconia (ZrO_2) particles

The average crystallite size was calculated by Scherrer's equation, as 14.57 nm. Similarly, the zirconia was found the mixed phase of monoclinic and tetragonal in structure.

Similarly, structural analysis was carried out using XRD diffractogram. XRD pattern of HAp nanoparticles prepared by calcination from chicken bone at 900 ^oC is shown in Figure 6.

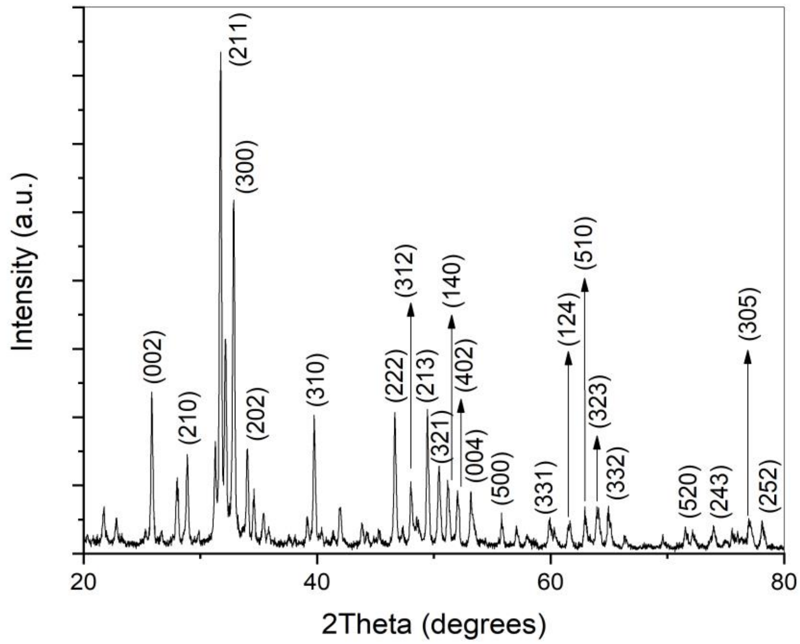

Figure 6: XRD diffractogram of hydroxyapatite (HAp) particles

The diffraction peaks appear at 2θ values of approximately 25.79º, 28.81º, 31.37º, 32.76º, 34.05º, 62.91º, 39.75º, 46.62º, 48.02º, 49.41º, 50.47º, 51.16º, 51.97º, 53.13º, 55.81º, 60.00º, 61.63º, 63.04º, 63.97º, 65.01º, 71.64º, 73.97º, 76.88º and 78.17º corresponding to (002), (210), (101), (211), (300), (202), (310), (222), (312), (213), (321), (140), (402), (004), (500), (331), (124), (510), (323), (332), (520), (243), (305) and (252) planes (JPCDS card number: 09-0432), indicating the sole existence of HAp using Bragg's law. From the peaks of the XRD diffraction pattern, the synthesized HAp sample was found to be in hexagonal space group and these peaks give references to find the crystalline structure of synthesized HAp. (Boujaady et al. 2016, Shah et al. 2021). The crystallite size of the HAp nanoparticles calculated from the average of the most intense peak was approximately 50.4 nm. The diffraction revealed that the nanoparticles were crystalline.

4.3 Effect of Catalytic Dose on Methylene Blue

During photodegradation, one of the key elements that can affect how well methylene blue (MB) degrades is the loading of the photocatalyst. For this reason, it is critical to get the ideal level of catalyst loading during the photocatalytic process. The effect of catalytic dose was observed in low concentration of Methylene blue (MB). The degradation of MB 15 mg and 20 mg/L ZrO_2 and HAp NPs was added in 5 ppm aqueous solution of MB and degradation was recorded for 50 min in sunlight.

Zirconia (ZrO_2) NPs as photocatalyst

To observe the effect of catalyst loading on dye solution 5 ppm concentration of MB kept constant and the amount of ZrO_2 was took 15 mg and 20 mg. Figures 7 and 8 shows the UV spectra evolution of degraded sample solution of MB for 15 mg and 20 mg ZrO_2 respectively.

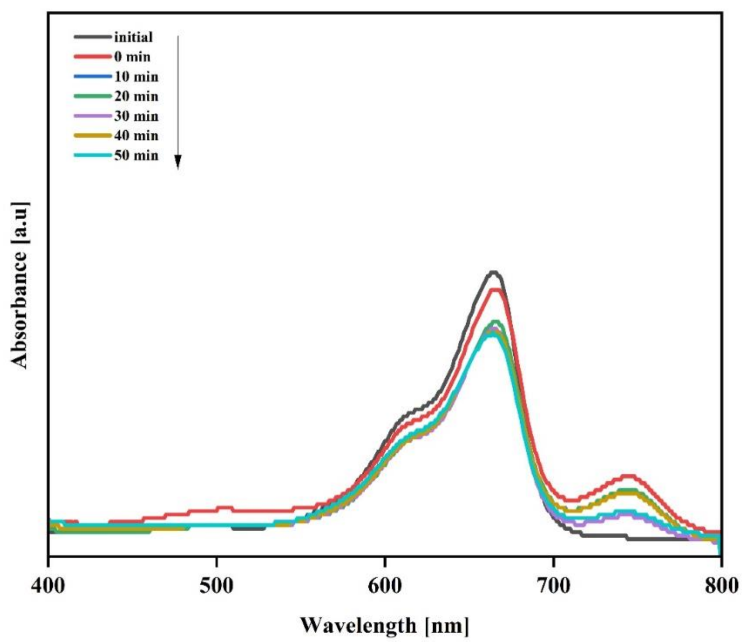

Figure 7: UV spectra of photodegradation of MB (MB: 5ppm, ZrO_2: 15 mg)

In Figure 7, the UV spectra shows the photodegradation of MB over the time. The decrease in absorbance indicates the decrease in concentration of MB. The UV -spectra of photocatalytic degradation of 5 ppm MB using 5 mg of ZrO_2 was analyzed from 0 to 50 min and the photocatalytic efficiency (%) is calculated by change in the absorbance with respect to time. The UV spectra from 0 to 50 min showed the decrease of absorbance with increase in irradiation time which indicated that the concentration of MB decrease. Similar spectral evolution was observed for 20 mg ZrO_2 NPs.

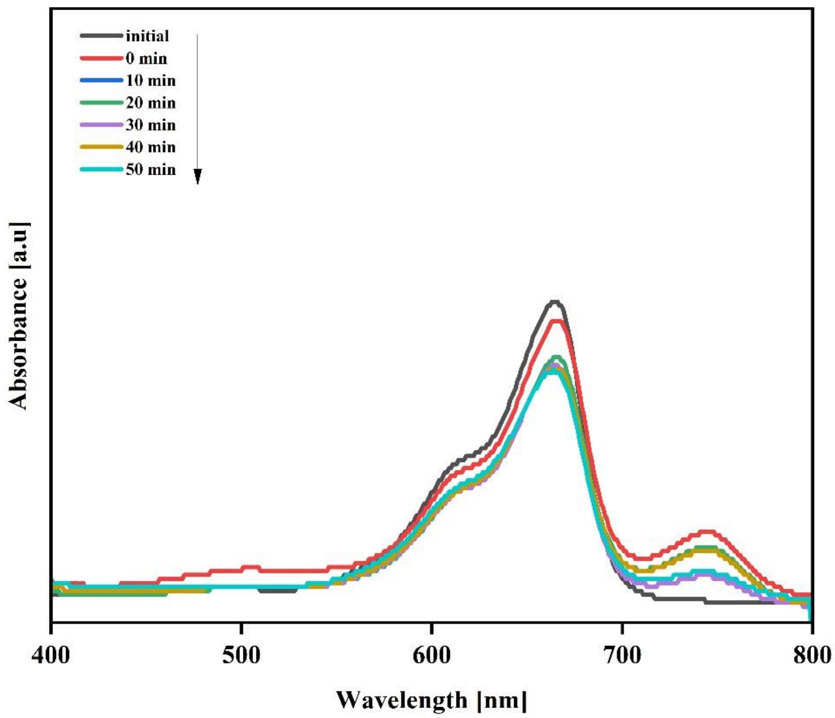

Figure 8: UV spectra of Photodegradation of MB (MB: 5ppm, ZrO_2: 20 mg)

The photocatalytic degradation efficiency of MB within 50 min using 20 mg and 15mg ZrO_2 was recorded 53.39 % and 40.77%. Comparing the efficiency of both dosages of ZrO_2, the higher amount showed the higher photocatalytic activity, whereas the lowest amount showed low efficiency

The impact of catalytic dosages was observed on the decomposition of methyl orange (20 ppm) and methylene blue (5 ppm) under UV radiation was studied by Shinde et al. They reported that when the amount of catalyst is increased from 0.5 to 1.5 g/dm^3, the degradation efficiency of both MB and MO dyes initially rises from 38 to 56 and 17 to

29%, respectively (Shinde et al., 2018). Thus, the higher amount of zirconium oxide shows higher degradation efficiency and vice versa.

Hydroxyapatite (HAp) as photocatalyst

The photocatalytic degradation of MB on changing the amount of HAp (15 mg and 20 mg) in was also observed in present work. The UV spectral evolution of degraded sample solution of MB for 15 mg and 20 mg HAp is shown in Figure 9 and 10, respectively. The UV spectra evolution over the period indicate the decrease in concentration of MB.

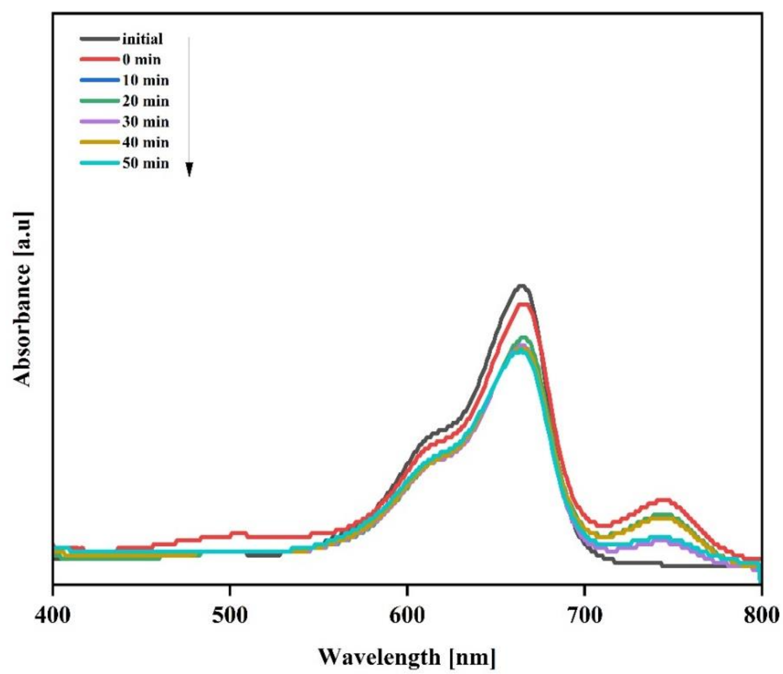

Figure 9: UV spectra of Photodegradation of MB (MB: 5ppm, HAp: 15 mg)

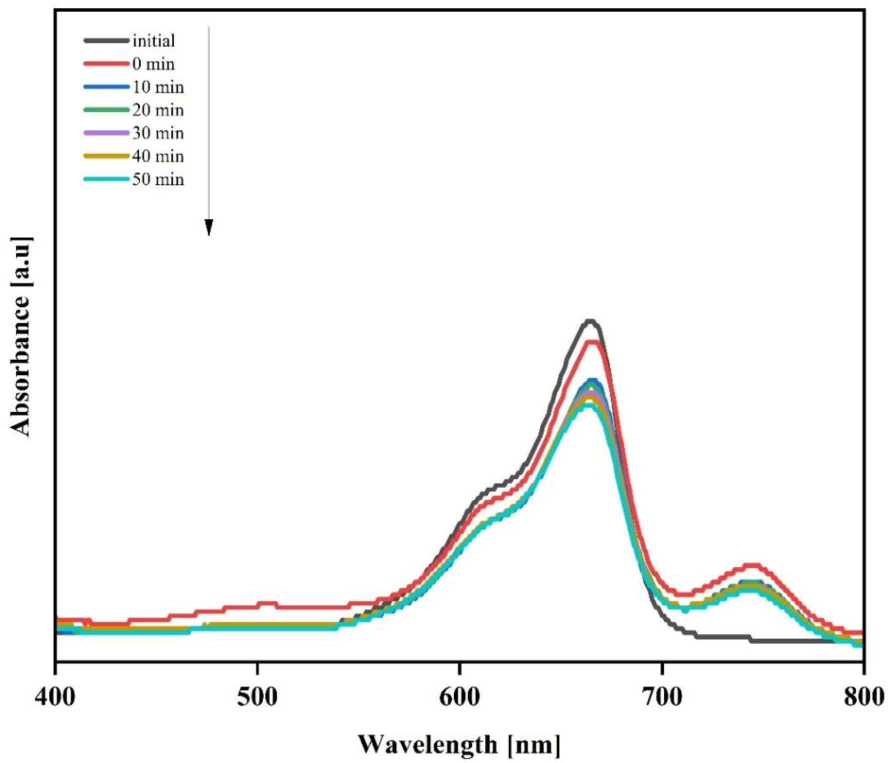

Figure 10: UV spectra of photo degradation of MB (MB: 5ppm HAp: 20mg)

The photocatalytic degradation MB in sunlight within 50 min, by using 15 mg and 20 mg HAp was found 23.65% and 26.32% respectively. The effect of amount of HAp on degradation of dye was observed by Valizadeh et al., they reported the removal of DR23 increased with increasing HAP quantity up to 1 g/L. The increase in degradation percentage is explained by the availability of adsorptive sites and a larger surface area (Valizadeh et al., 2016).

5. Conclusion

In our study, zirconia (ZrO_2) and hydroxyapatite (HAp) were successfully synthesized using green route. The FTIR spectra of ZrO_2 and HAp indicated that an absorption peak particularly at about 747 cm^{-1} and about 499 cm^{-1} corresponding to Zr-O_2-Zr asymmetric and Zr-O stretching modes respectively and the characteristic peaks at 473, 572, 603, 1049 and 1087 cm^{-1} representing the phosphate ion of the hydroxyapatite. The peak at 3570 cm^{-1} representing the hydroxyl group present in the hydroxyapatite.

The XRD patterns showed the ZrO_2 and HAp showed the crystallite size in the nanometric range. The average crystallite size of ZrO_2 was found in 14.57 nm and was noted the mixed phase of monoclinic and tetragonal in structure. Similarly, the crystallite size of the HAp nanoparticles calculated from the average of the most intense peak was approximately 50.4 nm.

From the result obtained, it was found dye degradation efficiency increases as the dose of catalysts increases. However, in the case of the initial concentration of dye, it was found to be reversed. The efficiency of both dosages of ZrO_2 was compared, the higher amount showed the higher photocatalytic activity, whereas the lowest amount showed low efficiency. Similarly, higher amount of HAp nanoparticles increases the degradation rate of MB. Thus, with increase in the amount of HAp nanoparticles the degradation of MB also increases.

Therefore, it is concluded that ZrO_2 and HAp can be effectively used as a photocatalyst to degrade dye from wastewater which could solve the problem created by dye contaminated water.

References

Augugliaro, V., Palmisano, G., Palmisano, L. and Soria, J. **(2019).** Heterogeneous photocatalysis and catalysis. *Heterogeneous Photocatalysis*, Elsevier: Amsterdam, The Netherlands, 1-24 ISBN 9780444640154

Adeogun, A. I. Ofudje, E. A., Idowu, M. A., Kareem, S. O., Vahidhabanu, S., Babu, B. R., **(2018).** Biowaste-derived hydroxyapatite for effective removal of reactive yellow 4 dye: equilibrium, kinetic and thermodynamic studies. *ACS Omega* ,3, 1991 – 2000. DOI:10.1021/acsomega.7b01768

Abhilash, M. R., Gangadhar. A. and Srikantaswamy, S. **(2019).** Photocatalytic dye degradation and biological activities of the Fe_2O_3/Cu_2O nanocomposite. *RSC Advances,* 9,8557-8568. DOI:10.1039/C8RA09929D

Abhilash, M. R, Gangadhar, A., Krishnegowda, J., Chikkamadaiah, M. and Srikantaswamy, S., **(2019).** Hydrothermal synthesis, characterization and enhanced photocatalytic activity and toxicity studies of a rhombohedral Fe_2O_3 nanomaterial. *RSC Advances*, 9, 25158-25169. DOI:10.1039/C9RA04978A

Abinaya, S., Kavitha, H. P., Prakash, M. and Muthukrishnaraj, A., **(2021).** Green synthesis of magnesium oxide nanoparticles and its applications: A review. *Sustainable Chemistry and Pharmacy* ,19,100368. DOI: 10.1016/j.scp.2020.100368

Amin, M., T., Alazba, A., A. and Manzoor, U. **(2014).** A review of removal of pollutants from water / wastewater using different types of nanomaterials. *Advances in Materials Science and Engineering*, ,24. DOI:10.1155/2014/825910

Adamek, E., Baran, W., Ziemianska, J. and Sobczak, A., **(2013).** The comparison of photocatalytic degradation and decolorization process of dyeing effluents. *International Journal of Photoenergy*, 5-6. DOI:10.1155/2013/578191

Ahmad, A, L and Puasa, S., W. **(2007).** Reactive dyes decolorization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process. *Chemical Engineering Journal*, 132(1), 257-265. DOI: 10.1016/j.cej.2007.01.005

Akshatha, G., Abhilash, M. R., Jagadish, K. and Srikantaswamy, S. **(2021).** Photo – catalytic dye degradation of methylene blue by using ZrO_2/MWCNT nanocomposites. *Water Practice and Technology*, London, 16(4), 1265-1276. DOI:10.2166/wpt.2021.066

Ashrafi, O., Yerushalmi, L., and Haghighat, F. **(2015).** Wastewater treatment in the pulp and paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of Environmental Management*, 158, 146-157. DOI: 10.1016/j.jenvman.2015.05.010

Balaji, S., Mandal, B. K., Ranjan, S., Dasgupta, N. and Chidambaram R. **(2017).** Nano−zirconia-evaluation of its antioxidant and anticancer activity. *Journal of Photochemistry and Photobiology B: Biology*,170,125 – 133. DOI: 10.1016/j.jphotobiol.2017.04.004

Baudot, C., Tan, C.M. and Kong, J. C. **(2010).** FTIR spectroscopy as a tool for nano-material characterization. *Infrared Physics and Technology*, 53(6), 434-438. DOI: 10.1016/j.infrared.2010.09.002

Berradi, M., Hsissou, R., Khudhair, M. Assouag, M., Cherkaoui, O., EI Bachiri, A. and EI Harfi, A. **(2019).** Textile finishing dyes and their impact on aquatic environs. *Heliyon*,5(11), e02711 DOI :10.1016/j.heliyon.2019.e02711

Bishwokarma, M., Bhujel, A., Baskota, M. and Pandit, R. **(2021).** Green synthesis of zirconia (ZrO2) nanoparticles using curcuma longa extract and investigation of compressive strength of epoxy resin (EP)/ ZrO2 nanocomposites. *Journal of Nepal Chemical Society*,42(1),45-50 DOI :10.3126/jncs, v42i1.35328

Bhatia, D., Sharma, N., R., Singh, J. and Kanwar, R., S. **(2017).** Critical reviews in environmental science and technology ,47(13),1836-1876 DOI:10.1080/10643389.2017.1393263

Bouazizi, A., Breida, M., Achiou, B., Ouammou, M., Calvo, J. I., Aaddane, A. and Younssi, S.A**. (2017).** Removal of dyes by a new nano-TiO2 ultrafiltration membrane deposited on low-cost support prepared from natural moroccan bentonite. *Applied Clay Science.*149,127-135. DOI: 10.1016/j.clay.2017.08.019

Boujaady, H. E., Mourabet, M., Abdelhadi, E. R., Bennani-Ziatni, M., Hamri, R.E. and Abderrahim, T. **(2016).** Adsorption of a textile dye on synthesized calcium deficient hydroxyapatite (CDHAp) : Kinetic and thermodynamic studies. *Journal of Materials and Environmental Science*, *7*(11), 4049-4063. https://www.jmaterenvironsci.com.

Babu, B. R., Parande, A. K., Raghu, S. and Kumar, T. P. **(2007)**. An overview of wastes produced during cotton textile processing and effluent treatment methods. *The Journal of Cotton Science*, 11(1), 110 – 122. http://journal cotton.org.

Cho, I. H. and Zoh, K. D. **(2007).** Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: optimization and modeling using a response surface methodology (RSM) based on central composite design. *Dyes and Pigments*, 75(3),533-543. DOI: 10.1016/j.dyepig.2006.06.041

Crini, G. **(2006).** Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour Technol*, 97(9), 1061-85. DOI: 10.1016/j.biortech.2005.05.001

Chequer, F. M. D., Dorta, D. and de Oliveira, D.P. **(2011).** Azo dyes and their metabolites: Does the discharge of the azo dye into water bodies represent human and ecological risks, *Advances in Treating Textile Effluent*, 27- 48. DOI:10.5772/19872

Dwivedi, R., Maurya, A., Verma, A., Prasad, R., and Bartwal, K. S. **(2011).** Microwave assisted sol-gel synthesis of tetragonal zirconia nanoparticles. *Journal of Alloys and Compounds*, 509(24), 6848-6851. DOI: 10.1016/j.jallcom.2011.03.138

Gnanasangeetha, D. and Sarala Thambavani, D. (**2013).** Biogenic production of zinc oxide nanoparticles using *acalypha indica*. *Journal of Chemical, Biologica, and Physical Sciences*, *4*(1), 238-246. www.jcbsc.org.

Gauna, M., Conconi, S., Gomez, S., Suarez ,G., Aglietti, E. F. and Rendtorff, N. M., (**2015).** Monoclinic-tetragonal zirconia quantification of commercial nanopowder mixtures by XRD and DTA. *Ceramics-Silikaty*, *59*(4), 318-325.

Ghazanfari, S. Z., Jaafari, J., Ashrafi, S. D. and Taghavi, K. **(2021).** Decolourisation of direct red dye 81 from aqueous solutions by SnO_2/H_2O_2 hybrid process. *International Journal of Environmental Analytical Chemistry*,103(16), 4016-4030. DOI: 10.1080/ 03067319.2021.1921758

Samchetshabam, G., Hussan, A. and Choudhory, T. G. **(2017).** Impact of textile dyes waste on aquatic environments and its treatment. *Environment and Ecology*, 35(3c), 2349-2353. www: environmentanology.com ISSN 0970-0420

He, R., Xu, D., Cheng, B., Yu, J. and Ho, W. **(2018).** Review on nanoscale bi-based photocatalysts. *Nanoscale Horizons*, 3(5), 464-504. DOI:10.1039/C8NH00062J

Huitle, C. A. M. and Brillas, E., (**2009**). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A General Review. *Applied Catalysis B: Environmental*, 87(3-4), 105-147. DOI: 10.1016/j.apcatb.2008.09.017

Iswori. S., Anjita. R., Sudhir T. and Dipendra, J. **(2005).** Final report: Development of profile of toxic waste products in Nepal. *Nepal Health Research Council (NHRC*), 1–63. DOI:103.69.126.140:8080/20.500.14356/230

Konstantinou, I. K. and Albanis, T. A., **(2004).** TiO_2-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution:Kinetic and Mechanistic Investigations. A Review, *Applied Catalysis B: Environmental*,49(1),1-14. DOI: 10.1016/j.apcatb.2003.11.010

Kapdan, I. K., Kargi, F., McMullan, G. and Marchant R. **(2000).** Decolorization of Textile Dyestuffs by A Mixed Bacterial Consortium. *Biotechnology Letters*, 22(14),1179-1181. DOI:10.1023/A:1005641430613

Kralik, B., Chang, E. K. and Louie, S. G. **(1998).** Structural properties and quasiparticle band structure of zirconia, *Physical Review B*,57(12-15),7027. DOI:10.1103/PhysRevB.57.7027

Kharissova, O. V., Dias, H. V. R., Kharisov, B. I, Perez, B. O. and Perez, V .M, J. **(2013). The** greener synthesis of nanoparticles. *Trends in Biotechnology*,31(4),240-248. DOI: 10.1016/j.tibtech.2013.01.003

Kabra, K., Chaudhari, R. and Sawhney, R. L. **(2004).** Treatment of hazardous organic and inorganic compounds through aqueous phase photocatalysis: A review. Industrial *and Engineering Chemistry Research*,43, 7683 -7696. DOI:10.1021/ie0498551

Khan, M. M., Pradhan, D. and Sohn, Y., Editors **(2017)** Nanocomposites for visible light-induced photocatalysis. Springer Series on Polymer and Composite Materials; springer.com. /book/10.1007/978-3-319-62446-4

Kafle, R. **(2019).** Implementing clean technology in pashmina industry, A Project Report Submitted in partial fulfillment of the requirements for the Degree of bachelor's in technology in Environmental Engineering, *Department of Environmental Science and Engineering, School of Science, Kathmandu University*. (Unpublished)

Lellis, B., Favaro-Polonio, C. Z., Pamphile, J. A. and Polonio, J. C. **(2019).** Effects of Textiles Dyes on Health and the Environment and Bioremediation Potential of Living Organisms. *Biotechnology Research and Innovation*,3,275-290. DOI:10.1016/j.biori.2019.09.001

Liu, C., Xiang, Q., Yang, M., Wang, S., Wang, L., Zhang, J., and He, Y. (**2017).** One-step preparation of hydrogenated ZrO_2 microspheres by cathode plasma electrolysis. *Materials Research Express*, *4*(7),076204. DOI:10.1088/2053-159/aa8046

Lydia, I. S., Rani, S. E. G. D., Radhika, N., and Selvin, S. S. P. **(2013).** Green synthesis of ZrO_2 nanoparticle using nyctanthes arbor-tristis leaf extract. *Recent Advances in Surface Science*, 274-275. ISBN 978-93-82338-36-9

Lu, J., Batjikh, I., Hurh, J., Han, Y., Ali, H., Mathiyalagan, R., Ling, C., Ahn, J. C. and Yang, D. C., **(2019).** Photocatalytic degradation of methylene blue using biosynthesized zinc oxide nanoparticles from bark extract of kalopanax septemlobus. *Optik* ,(182),980-985. DOI: 10.1016/j.ijleo.2018.12.016

Mallesh, B., Krishna, B. M. and Kumar, B. M. **(2020).** Degradation and biodegradability improvement of the landfill leachate using electrocoagulation with of iron and aluminum electrodes: A comparative study. *Water practice & Technology*, 15(2),540-549. DOI:10.2166/wpt.2020.041

Matpang, P., Sriuttha, M. and Piwpuan, N. **(2017).** Effects of malachite green on growth and tissue accumulation in pak choy (Brass chinensis Tsen and Lee). *Agriculture and Natural Resources,*51(2) ,96 -102. DOI: 10.1016/j.anres.2016.10.008

Miyauchi, M., Nakajima, A., Watanabe, T. and Hashimoto, K. **(2002).** Photocatalysis and photoinduced hydrophilicity of various metal oxide thin films. *Chemistry of Materials*,14(6) 2812-2816. DOI:10.1021/cm020076p

Nayak, A.K. **(2010)**. Hydroxyapatite synthesis methodologies: An overview. *International Journal of Chemical Technology Research*, 2(2), 903-907.

Nasuha, N., Hameed, B. H. and Din, A. T. M. **(2010).** Rejected Tea as a Potential Low-Cost Adsorbent for the Removal of Methylene Blue. *Journal of Hazardous Mater*ials,175(1-3),126-132. DOI: 10.1016/j.jhazmat.2009.09.138

Pinapala, C., Nidheesh, P.V., Davuluri, S.B., Gopinath, A. and Kumar, M. S. **(2020.)** Treatment of dyeing wastewater by combined sulfate radical based electrochemical advanced oxidation and electrocoagulation processes. *Separation and Purification Technology* ,254:117570. DOI: 10.1016/j.seppur.2020.117570

Rizwan, A. **(2020).** Nanotechnology and Wastewater Treatment. In book: Nanoagronomy. Springer, 153-177.

Rauf, M. A., Meetani, M. A. and Hisaindee, S. **(2011).** An Overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals. *Desalination*, 276, 13-27. DOI: 10.1016/j.desal.2011.03.071

Rail, R., Tahoces, P. G., Hassan, N., Cordero, M. L., Liu, Z. and Ruso, J. M. **(2019).** Noble microfluidic system for bioceramic nanoparticles engineering. Materials *Science and Engineering:* C., 102, 221-227. DOI: 10.1016/j.msec.2019.04.037

Rochkind, M., Pastemak, S. and Paz, Y. **(2014).** Using dyes for evaluating photocatalytic properties: A critical review. *Molecules,* 20(1), 88-110 DOI:10.3390/molecules20010088

Rahmawati, F., Permadani, I., Pasha, D. A. and Pratiwi, A. W. **(2016).** The composite of ZrO_2-TiO_2 produced from local zircon sand used as a photocatalyst for the degradation of methylene blue in a single batik dye wastewater. *Bulletin of Chemical Reaction Engineering and Catalysis*,11(2),133-139. DOI:10.9767/bcrec.11.2.539.133-139

Singh, J., Dutta, T., Kim, K. H., Rawat, M., Samddar, P. and Kumar, P. **(2018)**. Green synthesis of metals and their oxide nanoparticles: applications for environmental remediation. *Journal of Nanobiotechnology*, 16(1):84. DOI:10.1186/s12951-018-0408-4

Saroj, S., Singh, S.V. and Mohan, D. **(2015).** Removal of colour (direct blue 199) from carpet industry wastewater using different biosorbents (maize cob, citrus peel and rice husk), *Arabian Journal for Science and Engineering*,40,1553-1564.

Shinde, H. M., Bhosale, T. T., Gavade, N. L., Babar, S. B., Kamble, R. J., Shirke, B. S., and Garadkar, K. M. **(2018).** Biosynthesis of ZrO_2 nanoparticles from ficus benghalensis leaf extract for photocatalytic activity. *Journal of Materials Science: Materials in Electronics*, *29*, 14055–14064. DOI: 10.1007/s10854-018-9537-7

Shoukat, R., Khan, S. J. and Jamal, Y., **(2019)**. Hybrid anaerobic- aerobic biological treatment for real textile wastewater. *Journal of Water Process Engineering*, 29, 100804 DOI: 10.1016/j.jwpe.2019.100804

Sathiyavival, S., Vasantharaj, S., Bharathi, D., Saravanan, M., S., Manikandan, E., Kumar, S. S. and Pugazhendhi, A., **(2018).** Biogenesis of copper oxide nanoparticles (CuONPs) using sida acuta and their incorporation over cotton fabrics to prevent the pathogenicity of gram negative and gram-positive bacteria. *Journal of Photochemistry and Photobiology B: Biology*,188, 126-134. DOI: 10.1016/j.jphotobiol.2018.09.014

Srivastava, S. J., Singh, N. D, Srivastava, A. K. and Sinha, R. **(1995).** Acute toxicity of malachite green and its effects on certain blood parameters of a catfish, heteropneustes fossilis. *Aquatic Toxicol*ogy,31(3),241-247. DOI: 10.1016/0166-445X (94)00061-T

Shohel, M., Miran, M. S., Susan, M. A. B. H. and Mollah, M. Y. A. **(2016).** Calcination temperature-dependent morphology of photocatalytic ZnO nanoparticles prepared by an electrochemical-thermal method. *Research on Chemical Intermediates,*42,5281-5297 link.springer.com. /article/10.1007/s11164-015-2358-x

Shakir, K., Elkafrawy, A. F., Ghoneimy, H. F., Elrab Beheir, S. G. and Refaat, M. **(2010).** Removal of rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater stimulants by ion flotation. *Water Research*,44(5), 1449-1461 DOI: 10.1016/j.watres.2009.10.029

Shah, S., Joshi, R., Rai, N., Adhikari, R. and Pandit, R. **(2022).** Microstructural analysis of biowaste-derived hydroxyapatite-chitosan nanocomposites. *Micro and Nano Letters,*17, 369–376. DOI:10.1049/mna2.12143

Singh, J., Dutta, T., Kim, K. H., Rawat, M., Samddar, P. and Kumar, P. **(2018).** Green synthesis of metals and their oxide nanoparticles: applications for environmental remediation. *Journal of Nanobiotechnology*,16:84,1-24. DOI: 10.1186/s12951-018-0408-4

Tayade, R. J., Surolia, P. K., Kulkarni R. G. and Jasra R.V. **(2007).** Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO_2.

*Science and Technology of Advanced Mater*ials, 8, 455-462. DOI: 10.1016/j.stam.2007.05.006

Tahir, M. B., Riaz, K. N., Rafique, M., Rafique, M. S., Yousaf, N. and Sagir, M.**(2020).** Nanotechnology and Photocatalysis for Environmental Applications, Micro and Nano Technologies. Elsevier,57-64. DOI: 10.1016/B978-0-12-821192-2.00004-8

Valizadeh, S., Rasoulifard, M. H., and Dorraji, M. S. S. **(2016)**. Adsorption and photocatalytic degradation of organic dyes onto crystalline and amorphous hydroxyapatite: Optimization, kinetic and isotherm studies. *Korean Journal of Chemical Engineering*, *33*, 481–489. DOI:10.1007/s11814-015-0172-1

Vani P., Manikandan N. and Vinitha G., **(2017).** A green strategy to synthesize environment friendly metal oxide nanoparticales for potential applications: A review. *Asian Journal of Pharmaceutical and Clinical Research*,10(13),337-343 DOI:10.22159/ajpcr. 2017.v10s1.19751.

Wu, C. H. and Chang, C. L. **(2006).** Decolorization of reactive red 2 by advanced oxidation processes: Comparative studies of homogeneous and heterogenous systems. *Journal of Hazardous Mater*ials, 128(2-3), 265-272. DOI: 10.1016/j.jhazmat.2005.08.013

Wang, H., Li, X., Zhao, X., Li, C.; Song, X., Zhang, P., Huo, P. and Li, X. **(2022).** A review on heterogeneous photocatalysis for environmental remediation: From semiconductors to modification strategies. *Chinese Journal of Catal*ysis, 43(2), 178−214. DOI:10.1016/S1872-2067(21)63910-4

Wu, S. C., Hsu, H. C, Hsu, S. K., Tseng, C. P. and Ho, W. F. **(2017).** Preparation and characterization of hydroxyapetite synthesized from oyster shell powders. *Advanced Powder Technology*,28(4),1154 -1158. DOI: 10.1016/j.apt.2017.02.001

Zhang, D., Ma, X. L., Gu, Y., Huang, H. and Zhang, G. W. **(2020).** Green synthesis of metallic nanoparticles and their potential applications to treat cancer. *Frontiers in Chemistry*,8,799. DOI:10.3389/fchem.2020.00799

Zhang, F., Wang, X., Liu, H., Liu, C., Wan, Y., Long, Y. and Cai, Z. **(2019).** Recent advances and application of semiconductor photocatalytic technology. *Applied Sciences*, 9(12), 2489. DOI:10.3390/app9122489

Zheng, H., Liu, K., Cao, H. and Zhang, X. **(2009).** L-Lysine-assisted synthesis of ZrO_2 nanocrystals and their application in photocatalysis. *Journal of Physical Chemistry C*, 113(42), 18259-18263. DOI:10.1021/jp9057324

Zhu, J., Luo, G., Peng, X., Wen, W., Zhang, X. and Wang, S. (**2021**). Visible light mediated self-powdered sensing based on target induced recombination of photogenerated carriers. *Journal of Hazardous Materials*, 407, 124765. DOI: 10.1016/j.jhazmat.2020.124765

Zodi, S., Potier, O., Lapicque, F. and Leclerc, J-P. **(2010).** Treatment of the industrial wastewaters by electrocoagulation; Optimization of coupled electrochemical and sedimentation processes. *Desalination*, 261,186-190. DOI: 10.1016/j.desal.2010.04.024