Development of AgCuS nanostructures with optimized photocatalytic efficiency under solar irradiation

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Wastewater generated by the textile industry contains high levels of various pollutants. Advanced conventional methods, such as chemical and electrical treatments, are effective in addressing these contaminants. However, the significant operational and capital costs associated with these conventional systems limit their accessibility for industrial stakeholders. In contrast, more economically viable methods tend to be less efficient. This study aims to identify a suitable approach for integrating photocatalytic degradation (PCD) with a low-cost method to enhance the cost-effectiveness of wastewater treatment processes in the textile sector. The study utilized silver copper sulfide (AgCuS) nanocomposites as a photocatalyst, annealed at 200 °C for varying durations. A sustainable and cost-effective approach was implemented by combining photocatalytic degradation with floating treatment wetlands. Initially, the textile wastewater underwent 12 hours of PCD treatment using AgCuS nanocomposites. Subsequently, the entire batch was subjected to FTW treatment. The integrated treatment of wastewater with PCD and FTW achieved compliance with the National Environmental Quality Standards (NEQS) within nine days. Analysis revealed that the integrated system significantly reduced chemical oxygen demand (COD) by 89% and biological oxygen demand (BOD) by 90% in the effluent. Plants in the FTWs receiving PCD-pretreated effluent exhibited reduced stress compared to those in other treatments. Toxicity tests confirmed that the treated wastewater was non-toxic. The combination of photocatalysts and FTWs emerges as a highly suitable approach for optimal wastewater treatment in the textile industry.

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1. Introduction

Water scarcity is a crucial global issue. The growing population, climate change, environmental pollution, and ample water use are the root causes of this issue [1]. The increased demand for water for domestic, agricultural, and industrial purposes over-extraction or the utilization of groundwater for irrigation, industry, and urban usage, depletes aquifers and reduces river flows [2]. One of the recent examples of water scarceness is from Cape Town, South Africa, which is narrowly avoided “Day Zero” [3]. The effects of water scarcity include a lack of access, to clean drinking water, which leads to waterborne infections [4]. Crop yields suffer due to reduced water availability [5, 6]. Conventional wastewater treatment technologies are not practiced due to their high operational and capital cost. So, to develop a wastewater treatment system which is cost effective and sustainable is a dire need of this era. Photocatalytic degradation is an emerging technique, with a high potential to degrade pollutants. It uses light energy, often from sunshine or artificial light sources, to speed up a chemical reaction in the presence of a catalyst [7, 8]. Photocatalysis can degrade organic pollutants and disinfect effluent from pathogens [9, 10]. Photocatalytic water splitting is a promising method for producing hydrogen [11, 12], a clean fuel, by using sunlight to split water molecules into H2 and O2 [13]. A typical photocatalyst process absorbs light with energy equal to its band gap, and electrons in the valence band are excited to the conduction band, creating electron-hole pairs [14].

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The electrons and holes then migrate to the surface of the photocatalyst. Where the electrons and holes participate in redox reactions. Electrons can reduce species (e.g., converting oxygen to superoxide anions), while holes can oxidize species (e.g., converting water to hydroxyl radicals). Silver copper sulfide, AgCuS, is a chemical compound composed of silver (Ag), copper (Cu), and sulfur (S). It belongs to the sulfide mineral group. Silver copper sulfide can exist in various forms, including crystal structures and compositions. Silver copper sulfide can crystallize in different crystal structures, including cubic, orthorhombic, and tetragonal forms. The specific structure depends on factors such as temperature, pressure, and synthesis method. Silver copper sulfide typically appears as a dark gray to black solid with metallic luster. It is insoluble in water but can dissolve in acids. The compound may exhibit semiconducting behavior, making it potentially useful in electronic and optoelectronic applications. Silver copper sulfide nanoparticles may serve as catalysts in chemical reactions [15]. Silver copper sulfide can be synthesized in the laboratory using various methods, including chemical precipitation, solid-state reactions, and hydrothermal synthesis. Overall, silver copper sulfide is a compound of interest for its potential applications in electronics, catalysis, and optoelectronics. Researchers continue to explore its properties and develop new synthesis methods to harness its full potential. Silver has well-known antimicrobial properties, and incorporating silver copper sulfide into materials such as textiles, coatings, or medical devices can impart antimicrobial activity [15, 16].

Artificial wetlands, also known as floating treatment wetlands and constructed wetlands or manmade wetlands, are engineered ecosystems designed to mimic the functions of natural wetlands. These wetlands are created to provide various ecological services, including wastewater treatment, storm-water management, habitat restoration, and biodiversity conservation. One of the primary purposes of artificial wetlands is to treat wastewater. They can effectively remove pollutants such as nutrients (nitrogen and phosphorus), organic matter, heavy metals, and pathogens from domestic, agricultural, or industrial wastewater. This treatment is achieved through physical, chemical, and biological processes occurring within the wetland ecosystem, including sedimentation, filtration, adsorption, and microbial degradation. Artificial wetlands represent a sustainable and nature-based solution for addressing water quality issues, promoting biodiversity, and enhancing the resilience of ecosystems in urban, agricultural, and industrial landscapes [17-20].

This study evaluates the synergistic effects of two cost-effective technologies, namely photocatalytic degradation and floating treatment wetlands (FTWs), in the remediation of wastewater within the textile industry. The synthesized nanocomposite photocatalyst, silver copper sulfide, was annealed at 200 °C for five different durations. To construct the FTWs, a locally available polyethylene mat served as the floating substrate and hydroponic plant Phragmites australis (common reed) was used. In the first phase of photocatalytic degradation (PCD), the pretreated effluent is exposed to silver copper sulfide (AgCuS) photocatalyst, with seven different treatments for comparative analysis. After the PCD pretreatment, the whole batch was transferred to FTWs. The system's total efficiency was increased by the pretreatment of FTWs with a photocatalyst.

2. Material and method

All materials were purchased from Sigma Aldrich Company. The hydrothermal method was used to synthesize AgCuS [21]. Where the powdered silver, copper, and sulfur were utilized as the initial ingredients in the ratio Ag:Cu:S (0.9 : 1.1 : 1). All these materials were mixed into 170ml of distilled water in a 500ml beaker with the help of a magnetic stirrer at 80℃. After mixing the mixture was shifted into a 350ml Teflon lined autoclave and heated for 60 hours at 180℃. The pressure vessel was allowed to cool to room temperature after heating. Distilled water and methanol were used to filter and wash the precipitates several times. The product powders were dried at 60℃ over the night in the oven [22].

The materials' crystal structure was examined using X-ray diffraction (XRD) patterns obtained from the XRD D8 Advance Bruker device (Germany) with Cu Ka radiation (l ¼ 1.540 Å). Fourier-transform infrared (FT-IR) spectroscopy was conducted in a dry environment using Perkin-Elmer Spectrum II instrument. Data were gathered between 650cm−1 and 4000cm−1 at a 4cm−1 resolution and processed with Spectrum-10 software. Here HATR (Horizontal Attenuated Total

Reflectance) method with ZnSe flat plate was utilized for qualitative analysis. A Scanning Electron Microscope (SEM) Cube II from Emcraft South Korea was used to investigate the surface morphology of the samples.

3. Results and discussion

3.1. X-ray diffraction

Prepared samples of AgCuS, X Ray diffraction results Fig. 1 revealed that, XRD peaks at 2θ value 27.8° attributed to the (111) plane, one of the strongest reflections for many sulfide-based compounds. The peak at 32.2° likely corresponds to the (200) plane, representing another prominent crystallographic orientation. At the same time, the peak at 46.2° corresponds to a higher-order reflection, possibly the (220) plane. The 2θ value at 54.9° is related to the (311) plane, indicating complex crystallographic structures. The peak at 57.5° is a minor peak, possibly attributed to (222) or other higher index planes. The presence of other peaks indicates the existence of some impurities in the compound therefore; the results represent a mixed phase instead of a monoclinic one. This suggests that AgCuS exists with some other phases, like Ag2S (silver sulfide) or Cu2S (copper sulfide). An increase in annealing temperature results in a rise in the sharpness of peaks.

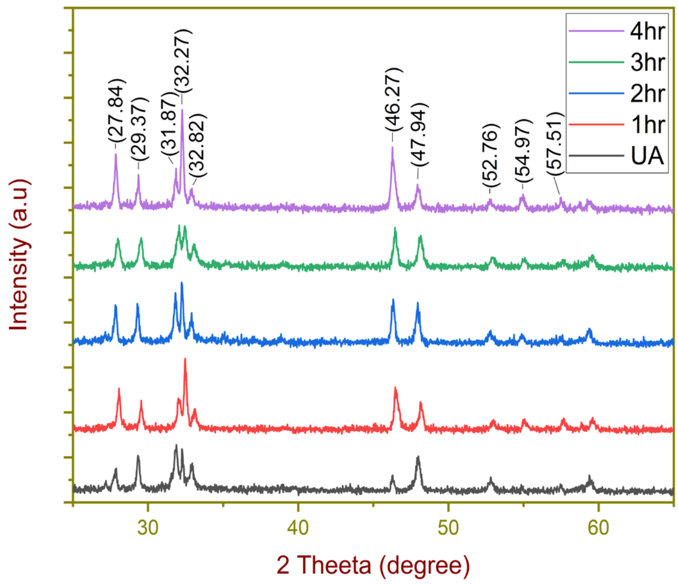


Fig. 1. XRD pattern of AgCuS nanocomposites annealed for different time duration.

The sharpness of peaks in X-ray diffraction (XRD) patterns Fig. 1 is influenced by several factors related to the crystallinity, sample quality, and experimental conditions. An increase in the sharpness of peaks typically indicates a more crystalline or ordered sample, while broader peaks often suggest a more disordered or smaller crystalline size. Here are some of the main factors that can lead to sharper peaks in XRD.

3.2. FTIR analysis

The FTIR analysis of AgCuS nanocomposites was performed with the help of zinc selenide (ZnSe) flat plate as sample holder and horizontal attenuated total reflection (HATR) methodology. In Fig. 2 the characteristic absorption bands related to the S–Ag and S–Cu bonds, typically found in the range of 400–600 cm-1. According to the literature review, there is no prominent peak for AgCuS above the value of 650 cm-1 and the achieved data from FTIR Fig. 2 showed no peak above 650 cm-1. Therefore, from XRD and FTIR results it can be deduced that the particles are of AgCuS.

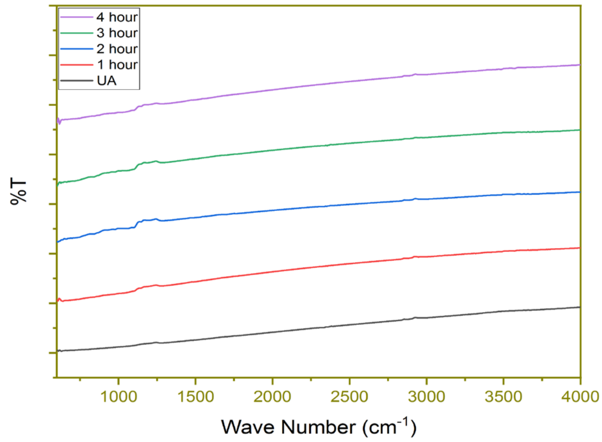
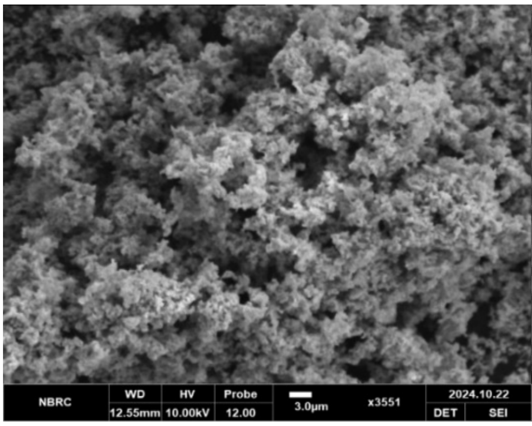
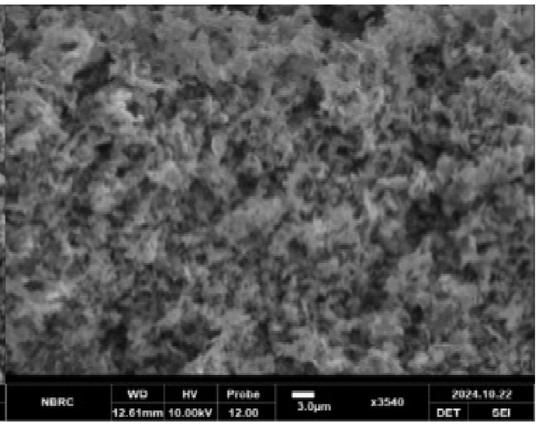


Fig. 2. FTIR pattern of AgCuS nanocomposites annealed for different time duration.

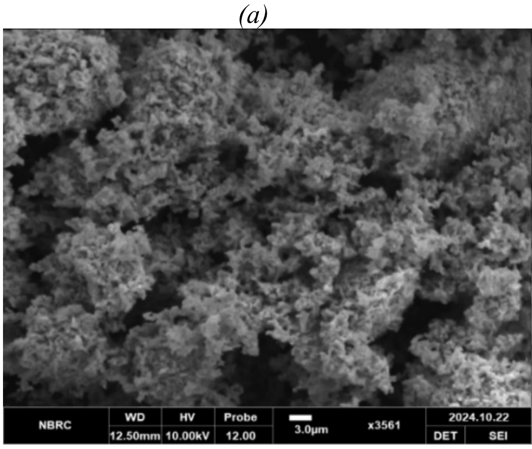
3.3. SEM analysis

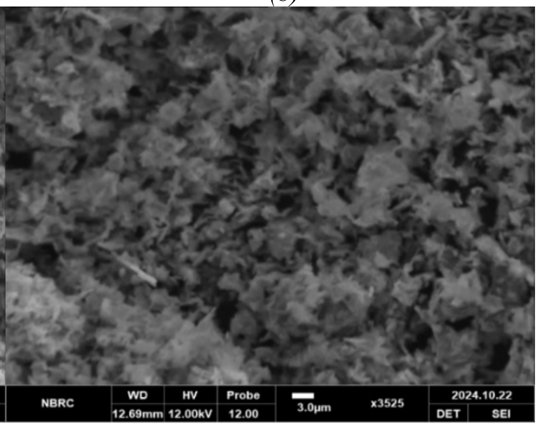
The keen observation of SEM images Fig. 3 can reveal that as the annealing temperature increased crystal structure, grain size, and overall material morphology improved. These improvements can be observed through fig. 3a to fig. 3e. It is because the elevation of annealing temperature provides more kinetic energy to atoms in the material, results in improved movement and rearrangement. The elevated temperatures enhance the nucleation of crystalline phases, promotes the formation of well-defined crystal structures.



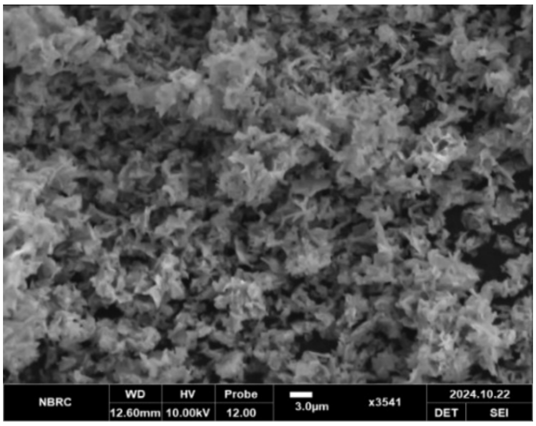


(a) *(b)*





(c) *(d)*



(e)

Fig. 3. a) SEM image of Ag CuS Unannealed nanoparticles b) SEM image of Ag CuS nanoparticles annealed for 1hr c) SEM image of Ag CuS nanoparticles annealed for 2hr d) SEM image of Ag CuS nanoparticles annealed for 3hr e) SEM image of Ag CuS nanoparticles annealed for 4hr.

3.4. Development of photocatalytic degradation (PCD) setup

For the PCD process, small containers with a 750ml capacity and a 0.110 ft² surface opening were utilized. These containers were positioned outdoors in direct sunlight. The control sample, labeled "without any treatments" (NL), was shielded from sunlight using aluminum foil. Each container was filled with 700ml of wastewater. A 300mg quantity of photo-catalysts (AgCuS), annealed at various temperatures, was added to the mesocosm. Seven experimental setups, each replicated three times, were monitored for 24 hours (01 Day) to observe the PCD effects. The whole PCD mesocosm was subjected to forced aeration, to avoid settling of photocatalysts in mesocosm and to provide oxygen for PCD reaction. The locally available Jumbolon role (insulation material) was used as a floating material to develop FTWs as described earlier [23, 24]. Briefly, the hole was made in the center of the material, and the saplings of Phragmites australis were vegetated in it with the help of coconut shaving and soil, and allowed to grow for two months in tap water. Then the tap water was replaced with textile industry wastewater. The plant, P. australis, has been extensively documented for its efficacy in removing different organic pollutants from industrial wastewater [25-27]. Following the guidelines set forth by the American Public Health Association (APHA), wastewater samples were taken from a textile industry in Khurianwala, Faisalabad, Pakistan, and examined for several physiochemical attributes. 23rd edition [28].

Following 12 hours of sunlight exposure, the suspended matter in all containers was allowed to settle for a further 12 hours, ensuring nanoparticles would not be transferred to the next phase. Approximately 90% of the PCD-treated wastewater was then moved to FTWs containers. A skimming technique was employed to prevent the transfer of settled particles. The wastewater transferred from PCD containers to FTW containers followed the batch transfer principle, where the entire treated volume was moved to the next stage.

The PCD-treated wastewater was further processed in the FTWs during the second phase. To assess the effectiveness of FTWs, eight treatment configurations were built. Samples from the FTWs were taken every three days and examined for the different pollution indicators COD, BOD, pH, and TDS [28]. During the PCD process, samples were collected twice. The first sample was obtained at the start time (0 Day), and the second sample was collected 24 hours later (1 Day), before being transferred to the FTW pots. The PCD pretreated sample was considered the FTW initial sample, followed by three-day intervals for a total of 15 days. Samples were collected using 10 mL glass vials.

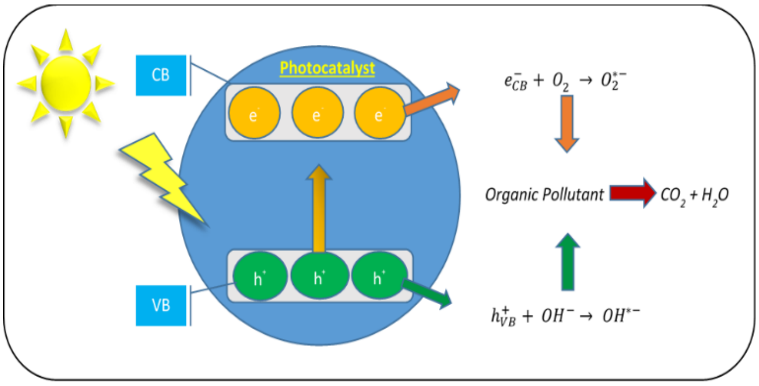
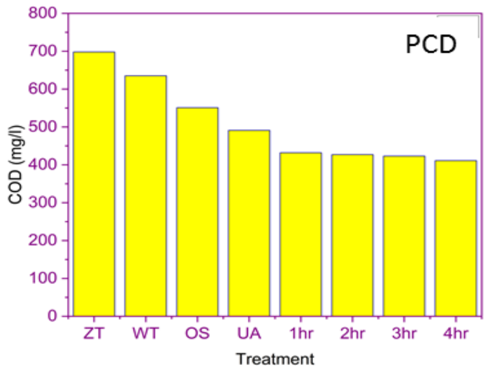


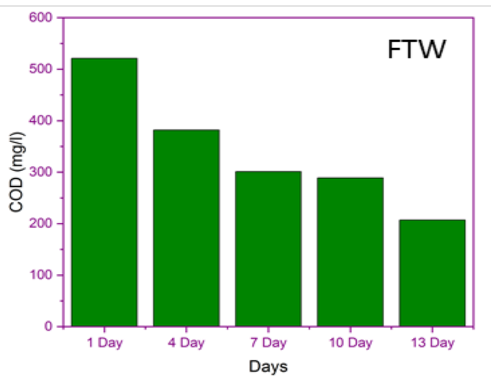
Fig. 4 Represents the mechanism for photocatalytic degradation (pcd) of organic pollutants.

Fig. 5(a, b, c) and Fig. 6(a, b, c) present the results of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) for different treatments. These figures represent a comparative analysis between photocatalytic degradation (PCD), floating treatment wetland (FTW), and their combination. It is evident that after one day of PCD treatment, the reduction in COD and BOD is substantial. However, it fails to meet discharge standards. In PCD treatment, it was observed that maximum chemical variation occurs within the first three hours, after which further variation diminishes. The graph in green (Fig. 5b and Fig. 6b) illustrates the COD and BOD results for FTW treatment, indicating that when applying only FTW treatment discharge standards were not achieved after 13 days of treatment. Fig. 6c and Fig. 7c depict treatments where PCD was utilized as a pretreatment before FTW treatment. It demonstrates that effluent pretreated with AgCuS nanocomposites annealed for 4 hours achieved discharge standards before all other treatments. These results can be corroborated by the SEM results in Fig. 5e and XRD results in Fig. 3, where AgCuS annealed for 4 hours exhibits a well-defined crystal structure, consequently resulting in an improved surface area for PCD. Fig. 8(a, b, c) illustrates the impact of PCD, FTW, and combination of PCD and FTW on the total dissolved solids (TDS) of wastewater. The TDS value for various dyeing water was 2750 mg/L. It was observed that no significant change was made in the value of TDS by all treatments used over here.

To assess the treatment system's capacity for detoxification, the water collected from the PCD and FTWs treatment pots was subjected to phytotoxicity assay as explained earlier [29, 30]. Briefly, the seeds of wheat (Triticum aestivum) were exposed to the treated water, and seed germination and growth parameters of the saplings were monitored. Seeds irrigated with untreated wastewater did not germinate as well as seeds irrigated with purified water Fig. 9. The substantially high germination rate with treated water indicates the extensive detoxification and the removal of contaminants, improving the waterbody's or ecosystem's compatibility with fauna and flora.



(a)



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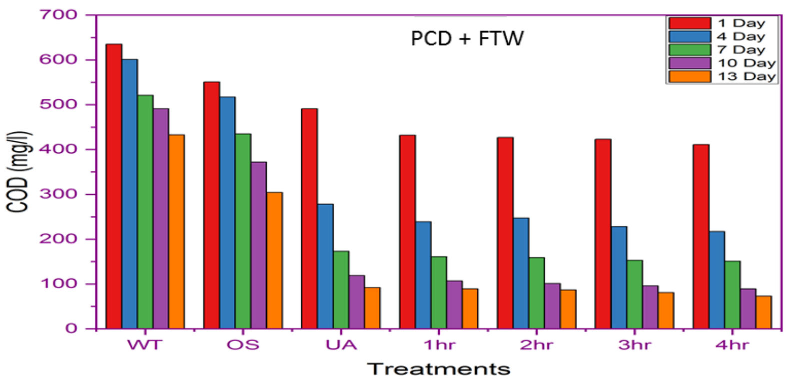
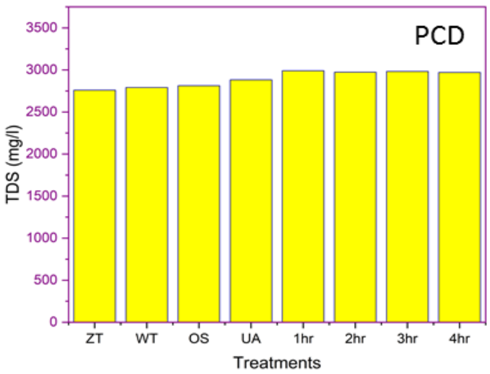
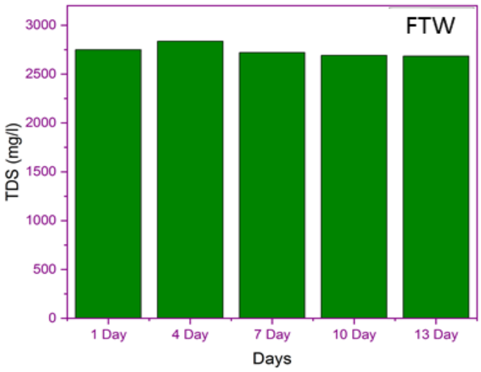


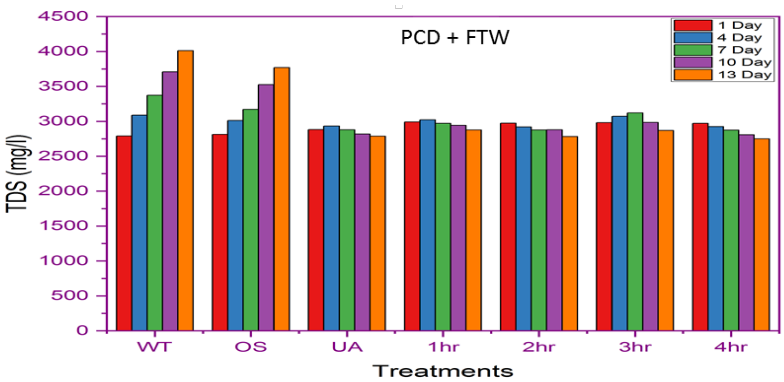
(c)

Fig. 5. a) Effect of PCD on the COD of wastewater, b) Effect of FTW on COD of waste water, c) combine effect of PCD and FTW on COD of textile wastewater.



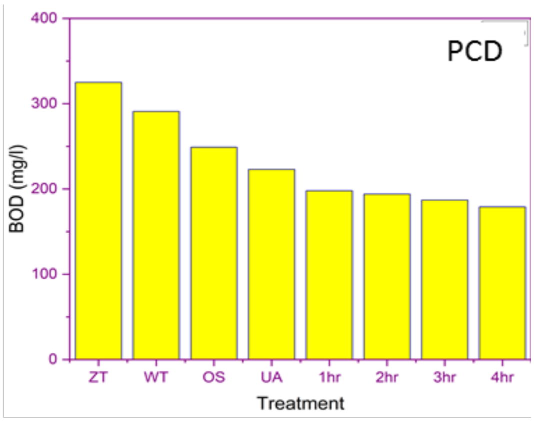


(a) *(b)*

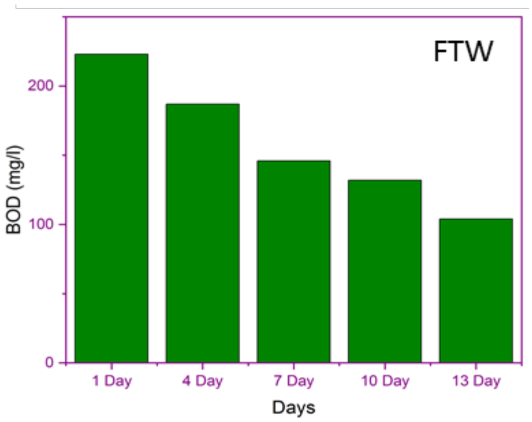


(c)

Fig. 6. a) Effect of PCD on the TDS of wastewater, b) Effect of FTW on TDS of waste water, c) combine effect of PCD and FTW on TDS of textile wastewater.



(a)



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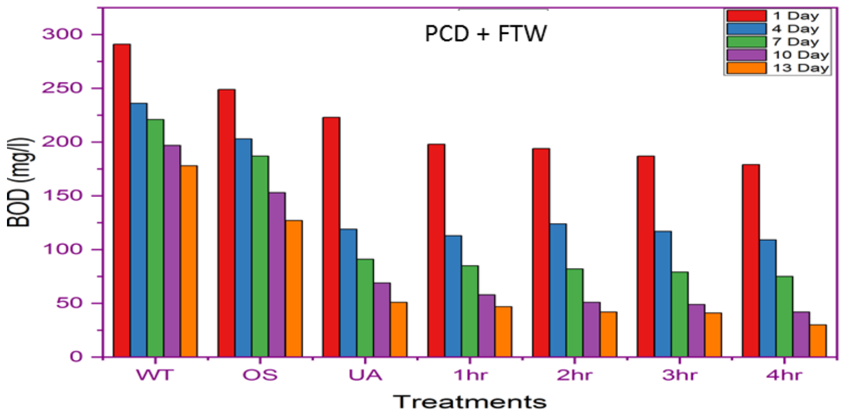

(c)

Fig.7. a) Effect of PCD on the BOD of wastewater, b) Effect of FTW on BOD of waste water, c) combine effect of PCD and FTW on BOD of textile wastewater.

4. Conclusions

This study reveals that an efficient and cost-effective wastewater treatment system can be developed by integrating photocatalytic degradation with the conventional, low-cost, and less efficient wastewater treatment processes like; FTW, anaerobic treatment and constructed wetland, etc., used in the textile industry. When this pretreated water through PCD is introduced to Floating Treatment Wetlands (FTWs), a rapid reduction in Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) is observed. This is attributed to the oxidation and reduction processes during PCD treatment, which break down the long chains of dye molecules into smaller ones facilitating further degradation by the synergism of plant and bacterial activity. Consequently, the treatment incorporating PCD and FTW achieved the National Environmental Quality Standards (NEQS) within nine days. In contrast, treatments lacking photocatalytic pretreatment failed to meet NEQS within 25 days. Therefore, the combination of Photocatalytic Degradation (PCD) with FTWs offers a cost-effective, environmentally friendly, and sustainable method for treating textile wastewater. The primary challenge for the widespread implementation of this technique is preventing the discharge of the photocatalyst with the effluent. To address this issue, we propose the development of effective thin-film photocatalysts that can be contained within the treatment ponds, thereby eliminating concerns regarding their release in the outflow.

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