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Enhancing the Photocatalytic Degradation of Pulp & Paper Mill Wastewater through ZnO Photocatalyst Application

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Abstract— In this study, the photocatalytic degradation of pulp & paper mill wastewater using a ZnO photocatalyst was investigated. The objective was to reduce pollutants in the effluent through an environmentally friendly heterogeneous photocatalysis process. The study aimed to determine the optimal pH and catalyst dose for enhanced degradation efficiency. The photocatalytic process offers complete degradation of contaminants without the transfer of hazardous compounds. By manipulating various parameters such as pH, irradiation time, catalyst dose, and UV light intensity, the degradation process was analyzed. The results demonstrated that at an optimum pH of 7.0, a catalyst dose of 1.2 g/500 ml, and a contact time of 6 hours, degradation efficiencies of 97% for BOD, 90% for COD, and 83% for color removal were achieved.
Keywords— Photocatalysis, ZnO, Pulp & Paper Mill Effluent, Artificial UV.

INTRODUCTION

The discharge of wastewater from various industries, including agricultural fertilizers, chemical industries, and landfills, remains a global concern due to the contamination of water bodies with contaminants. Conventional treatment processes face challenges in effectively removing trace and toxic contaminants present in the wastewater. The development of modern techniques is needed to overcome the technical limitations and treat toxic and trace elements in a cost-effective manner. The untreated effluent discharged from industries and agricultural processes, such as fertilizers and chemicals, poses a significant threat to the environment. Chlorination during treatment processes can transform a large number of compounds into harmful substances. In the context of pulp and paper wastewater, decolorization is a prominent concern. The presence of toxic pollutants makes the treatment of pulp and paper mill wastewater challenging using physical, chemical, and biological methods (Reference 1).

Conventional methods have several limitations as they often convert contaminants from one form to another without fully solving the initial problem. To overcome these limitations, advanced treatment methods have been developed (Reference 2). The paper industry, which utilizes a substantial amount of water and chemicals, makes the decolorization of pulp and paper mill wastewater an interesting subject. This approach can help save significant amounts of water, considering the large amount of pollutants produced by these industries. The pulp and paper industry is a major source of aquatic pollution in India, and the pollutants released from these processes can cause various diseases and mutations in aquatic life (References 3 and 4). Black liquor, a byproduct of various processes in the industry, contains high levels of BOD and COD (Reference 5).

A. **Photocatalysis Photocatalysis** is a light-based acceleration of photoreaction in the presence of a semiconductor catalyst. In this process, electron-hole pairs are generated, and the activity of the photoreaction depends on the generation of these pairs, leading to the formation of free radicals that undergo secondary reaction processes. Non-toxic semiconductor catalysts such as TiO2 and ZnO are commonly used in photocatalysis. Semiconductors possess properties such as light absorption, excited state lifetime, and charge transport that make them suitable for photo catalysis (References 6 and 7). Photocatalysis

offers advantages over conventional treatment methods like oxidation, biological treatment, and activated carbon adsorption, which have their limitations. In a typical photocatalytic system, the photo-induced transformation occurs on the surface of the photocatalyst. The photocatalytic reaction involves the formation of electron-hole pairs in the semiconductor and their interaction with organic matter. The catalyst initially absorbs light of different colors based on the band gap energy of the semiconductor (Reference 8). The choice of semiconductor as a photocatalyst is based on properties such as electronic configuration, charge carrying capacity, charge transport property, excited state lifetime, and light absorption ability (Reference 9).

B. Process Variables

1. Catalyst Dose: The catalyst dose or catalyst mass directly influences the photocatalytic reaction and is proportional to it. Increasing the catalyst dose increases the number of active sites available on the catalyst, promoting the formation of OH- and superoxide radicals, and thus accelerating the reaction rate. However, when the catalyst dose is excessively high, it can scatter UV light, reducing penetration and reaction rates (Reference 10).
2. Light Intensity: The photocatalytic reaction rate depends on the amount of energy absorbed by the catalyst. Higher light intensity leads to an increased degradation rate of pollutants. The form or nature of the radiant source does not significantly affect the photo-degradation reaction pathway; the band-gap sensitization process remains unaffected (Reference 10).
3. pH: In the presence of a photocatalyst, electron-hole formation occurs on the semiconductor surface due to UV light irradiation. The high oxidative potential holes can directly oxidize the pulp

EXPERIMENTAL PROGRAMME

A. **Experimental Setup and Materials**: The wastewater samples were collected from a paper mill located in Saharanpur, Uttar Pradesh, India. The collected effluent was promptly stored under appropriate conditions after collection and kept at a temperature of 4°C. Prior to experimentation, the wastewater samples were analyzed for various parameters including COD, BOD, color, turbidity, and pH to ensure reproducibility of the results. The photocatalyst used in the study was ZnO, obtained from CDH in New Delhi. All chemicals used in the experiments were of analytical reagent grade and employed without any additional purification. The pH of the pulp and paper mill effluent was adjusted using different normalities of HCl and NaOH solutions. A 50 mL sample was taken in a measuring cylinder and diluted by a factor of 10 before transferring it to the reaction vessel for further processing.

B. **Photoreactor Design:** The photoreactor used in the study consisted of a wooden body with specific dimensions of 100 cm × 76 cm × 60 cm (length × width × depth). It was equipped with four UV tubes (λ = 365 nm) placed on the top side of the reactor, each having a power rating of 18 W (OSRAM). The UV tubes were positioned at a distance of 30 cm from the sample. The photo-degradation experiments were conducted in an 800 mL borosilicate glass bowl. The reaction mixture was subjected to UV light irradiation while being continuously stirred. Two fans were installed on the side walls of the reactor to dissipate the heat generated by the UV lamps. All experiments were performed in a completely mixed and batch mode configuration. Samples were collected at regular intervals of 1 hour and filtered before analysis of parameters such as BOD, COD, dissolved oxygen (DO), pH, and turbidity.

RESULTS & DISCUSSION

The photocatalytic degradation of pulp and paper mill effluent using ZnO catalyst was carried out in a photo reactor at a temperature of 25°C. A series of experiments were conducted by varying the catalyst dose, pH, UV exposure time, and UV light intensity, and their effects on the degradation process were evaluated.

TABLE I Initial Characteristics of Pulp & Paper Wastewater

Sr. No.	Parameter	Value
1	Colour	Dark Yellow
2	pH	7.82
3	COD	820 mg/l
4	BOD	590 mg/l
5	Absorbance	0.455
6	%Transmission	36.03 %

A. Effect of pH on Photocatalytic Treatment

Pulp & Paper industries generate wastewater with a pHvalue greater than neutral. Pulp & paper effluent sample.

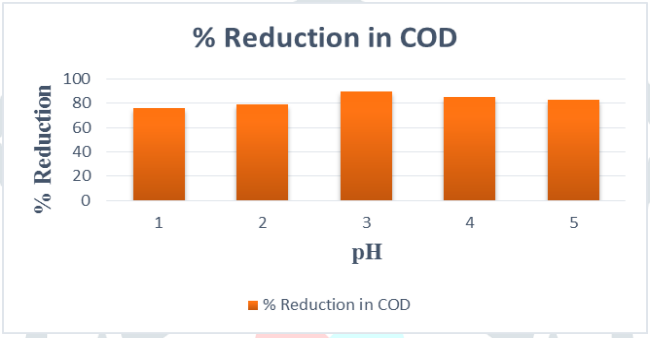


Fig 1: Effect of Initial pH on %Reduction In C.O.D of Pulp & Paper Wastewater

Effect of Catalyst (ZnO) Dose on Degradation

In the experiment, the ZnO catalyst dose was varied from 0.2 g/500ml to 1.6 g/500ml while maintaining a constant pH of 7.0. The initial pH of the collected pulp and paper mill effluent was measured at 7.82. The pH value plays a vital role in the photocatalytic oxidation process as it affects the production of OH- ions, which are strong oxidizing agents. To investigate the influence of pH on degradation efficiency, the pH of the solution was adjusted from 3.0 to 9.0, with a catalyst dose of 1.2 g/500ml, and a contact time of 6 hours.

The results showed that the maximum degradation of the wastewater occurred at pH 7.0. As the pH increased beyond 7.0, the degradation efficiency started to decrease. At pH 7.0, a remarkable degradation of 97% in B.O.D and 90% in C.O.D was achieved. After the photocatalytic treatment, the final pH of the effluent was measured at 7.25, which falls within the permissible limit for biological treatment and safe disposal of wastewater into water bodies.

These findings highlight the importance of pH optimization in the photocatalytic degradation process, as it significantly influences the efficiency of pollutant removal. pH 7.0 was identified as the optimal condition for achieving high degradation efficiency in the treatment of pulp and paper mill effluent. The results support the use of photocatalysis as an effective method for wastewater treatment, contributing to the removal of harmful pollutants and the preservation of water quality.

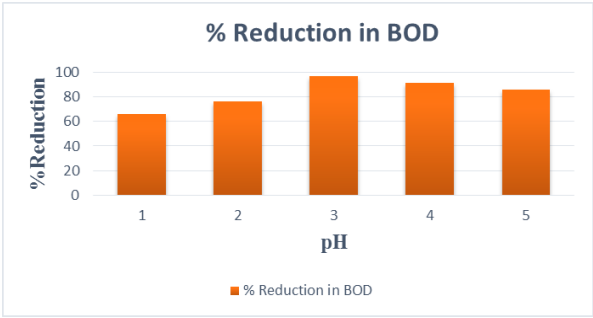


Fig 2: Effect of initial pH on % Reduction in B.O.D of Pulp & Paper wastewater

During the experiment, the degradation efficiency initially increased up to a catalyst dose of 1.2 g/500ml, beyond which it started to decrease. The highest degradation efficiency was observed at a catalyst dose of 1.2 g/500ml. This trend suggests that the degradation efficiency is influenced by the catalyst dose.

The increase in degradation efficiency with an increasing catalyst dose is attributed to a greater number of active sites available on the catalyst surface. This leads to an increased formation of reactive species, such as OH- and superoxide radicals, which enhance the reaction rate. However, as the catalyst dose exceeds a certain limit, the efficiency becomes constant and eventually decreases. This decrease is caused by the agglomeration of catalyst particles, forming clusters that reduce the number of available active sites on the catalyst's free surface. Consequently, the efficiency of the photo-reactor is diminished.

At higher catalyst doses, the cloudiness of the solution increases, resulting in increased UV light scattering. This impedes the passage of UV radiation through the sample, further contributing to the decrease in the photo-reactor's efficiency. While a larger catalyst dose allows for the absorption of a greater number of photons, accelerating the reaction rate and increasing the degradation efficiency, once all the pollutant particles/molecules have been absorbed by the catalyst, no further degradation occurs in the sample. Therefore, adding additional catalyst beyond this point would only increase the cost of the treatment without yielding any additional degradation.

In summary, optimizing the catalyst dose is crucial to strike a balance between efficient degradation and cost-effectiveness. The results indicate that a catalyst dose of 1.2 g/500ml maximizes degradation efficiency, beyond which adding more catalyst becomes economically unfavorable and hinders UV light penetration.

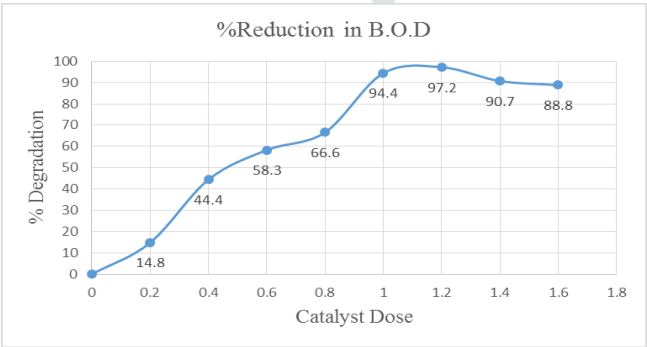


Fig 3: Effect of catalyst dose on B.O.D

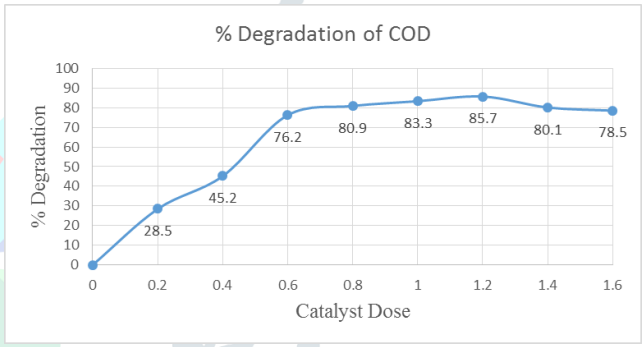


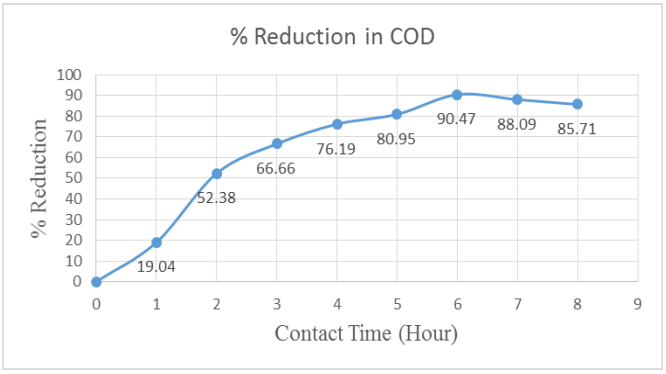
Fig: 4: Effect of catalyst dose on C.O.D

The degradation efficiency of B.O.D and C.O.D in the wastewater reached its maximum at a catalyst dose of 1.2 g/500ml. Initially, as the catalyst dose (ZnO) increased, the rate of degradation also increased. However, beyond the optimum dose of 1.2 g/500ml, the degradation efficiency started to decrease. This observation is consistent with previous studies. Kumar et al. (2011)[12] reported a maximum degradation efficiency at a catalyst dose of 0.75 g/L (54.5% C.O.D and 83.7% color removal), and as the catalyst concentration increased, the degradation efficiency decreased. Similarly, Hussein (2010)[1] observed a similar trend, where an increase in catalyst mass initially led to an increase in process efficiency, but further increasing the catalyst mass resulted in a constant degradation efficiency followed by a decrease.

Effect of Irradiation Time on Degradation Efficiency

The effect of irradiation time, or reaction time, was also investigated at the optimum catalyst dose of 1.2 g/500ml. The reaction time was varied from 2 hours to 8 hours to assess the degradation efficiency at the optimal catalyst dose.

During the initial two hours, a rapid degradation of C.O.D, B.O.D, and color was observed in the sample. However, after 6 hours, the rate of degradation slowed down and became approximately constant. This behavior can be attributed to the formation of a thin layer of ZnO catalyst, which hinders the supply of oxygen to the catalyst surface, consequently slowing down the photo-degradation process. At the 6-hour mark, a significant reduction of 90% and 97% in C.O.D and B.O.D, respectively, was achieved.



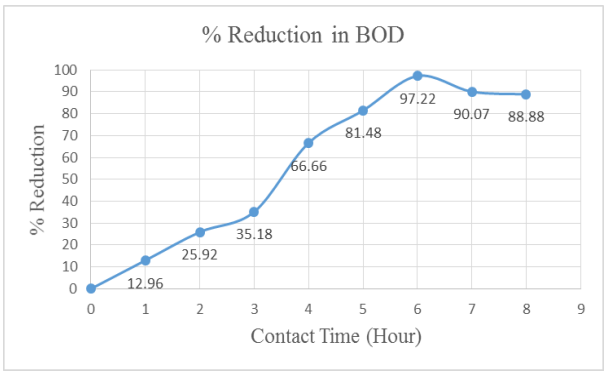


Fig: 5: Effect of contact time on COD reduction.

Fig: 6: Effect of contact time on BOD

Fig: 7: Effect of Irradiation Time on Decolouration

Effect of Decolouration Rate

The decolouration rate of the wastewater was determined by measuring the absorption and %Transmission using a spectrophotometer. Since the effluent was highly polluted and colored, it exhibited high light absorption and low %Transmission initially. As the photocatalytic reaction proceeded, the color of the effluent gradually decreased, resulting in a decrease in absorption and an increase in %Transmission. The reaction was conducted at the optimum pH, time, and catalyst dose. After 6 hours of reaction, a decolouration rate of 83% was achieved.

Effect of UV Light Intensity on Degradation Efficiency

The experiment also investigated the influence of UV light intensity, specifically the number of UV lamps, on the degradation efficiency. It was observed that increasing the light intensity led to an increase in degradation efficiency. This can be attributed to the higher number of photons striking the ZnO catalyst per unit area as the light intensity increased. The higher light intensity generated more excited electrons and electron-hole pairs, resulting in an increased production of OH- ions, which play a crucial role in pollutant degradation.

The effect of UV light intensity on the reaction was studied at the optimum pH (pH 7), catalyst dose (1.2 g/500ml), and contact time (6 hours). Initially, the degradation experiment was conducted using 2 out of 4 UV lamps. The degradation rate was approximately half compared to when all 4 lamps were used.

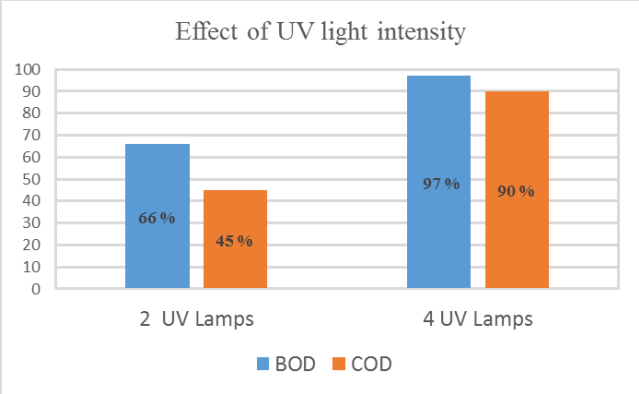


Fig:8: Effect of UV light intensity on Degradation

Harshal Nagpure et al (2013) [6], *Savtri Lodha et al. (2011)* [13] also observed same results, they observed the direct relation between Light intensity and the Degradation.They recorded that the Light intensity and degradation are directly propotional to each other.

CONCLUSION

By varying parameters such as pH, irradiation time, catalyst dose, and UV light intensity, the degradation process of the pulp and paper mill effluent was studied. Optimum conditions of pH 7.0, catalyst dose of 1.2 g/500ml, and a reaction time of 6 hours resulted in significant degradation percentages of 97%, 90%, and 83% for BOD, COD, and color, respectively. The final pH of the treated solution was measured to be 7.25, which is within the neutral range. The COD and BOD levels after UV photocatalytic treatment were determined to be 120 mg/L and 15 mg/L, respectively, meeting the limits specified by the National Environmental Quality Standards (NEQS).

Based on these results, it can be concluded that photocatalysis is a suitable and cost-effective process for the degradation of pulp and paper mill effluent.

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