Improved Visible Light Photocatalysis of Textile Dye Effluent Using Fe and Cu Doped TiO_2 Nanoparticles

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ABSTRACT

The research involves the textile dye effluent photocatalytic degradation of titanium dioxide (TiO_2) doped with iron oxide (Fe_2O_3) and copper oxide (CuO) under visible light. Dye wastewater is collected from Tiruppur, a major textile hub in India. Catalyst preparations with pure TiO_2 and doped catalysts are done using wet impregnation method. In deed the photocatalytic activity tested through capacity of dye colour removal, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and pH changes under 180 minutes of visible light exposure. The highest degradation effectiveness of 81% is observed in Fe–TiO_2 followed by Cu–TiO_2 degradation of 76% and pure TiO_2 degradation of 58%. The result predicts that doping TiO_2 with Fe_2O_3 and CuO increases visible light absorption and decreases electron–hole recombination. Also, post treatment physico-chemical parameters found to be improved significantly. Hence, COD and BOD decreases sharply and the pH becomes closer to the neutral. It ensures better quality of water and less polluting load of the latter. The catalysts of metal doped TiO_2 were more effective than the pure TiO_2 catalyst in treating textile effluents and this study confirms. Fe–TiO_2 is the best of the tested materials. It is economically feasible and proficient package for the wastewater treatment in textile industries.

Keywords: Wastewater treatment, Titanium dioxide, Fe_2O_3 doping, Photocatalysis, CuO doping, Dye effluent, Visible light degradation, Textile industry

1. INTRODUCTION

The textile industry has witnessed rapid growth, leads to high discharge volume of dye laden effluents addicted to water bodies causing serious environmental as well as humanoid health problems of high toxicity, non-biodegradability and aesthetic impact [1]. The complex aromatic structures of dye molecules and their resistance to conventional methods of treatment, which include coagulation flocculation, adsorption and biological degradation at times leaving secondary pollutants [2]. TiO_2 and its doped variants have been extensively studied and investigated for their photocatalytic properties as they are highly beneficial [3–13].

The mineralization of persistent organic pollutants in wastewater using semiconductor materials as photocatalysis is one of the promising advanced oxidation processes (AOP). Titanium dioxide (TiO_2) widely premeditated photo catalyst due to its solid oxidative power, good chemical solidity, low cost and non-toxic nature [14]. Although its band gap (~3.2 eV for anatase) is too large for effective photocatalytic application (i.e., to the UV region, a small fraction of solar radiation), it constrains its usefulness [15,16].

Due to this limitation various kind of strategies (doping with metal or non-metallic elements, link with narrow band fissure semiconductors besides surface modification) have been exploited to improve the visible light captivation as well as charge separation. However, doping of TiO_2 through transition metal oxides, e.g. hematite, and CuO is particularly effective among them. Firstly, Fe_2O_3 has a narrow band gap of ~2.2 eV and functions as an electron acceptor, thus able to reduce the amount of recombination of photo created electron pairs [17]. Consequently, CuO with a band gap around 1.2–1.5 eV can lead to light immersion into the visible state and helps to promote charge transfer at the interface [18].

Previous studies shown that doping TiO_2 with Fe_2O_3 and CuO improves degradation efficiency of methylene blue, rhodamine B and acid orange beneath visible light irradiation [19,20]. Nevertheless, there are few studies in treating real dyeing effluents because they are complex mixtures of different dye compounds, surfactants and salts. In the present study, Fe_2O_3 and CuO doped TiO_2 nanoparticles are synthesized and characterized and their photo catalytic efficiency for degradation of dyeing waste effluent under simulated solar irradiation is evaluated. The degradation performance is also studied with respect to dopant concentration, reaction time and catalyst

loading. It is advancement in efficient and sustainable photo catalyst for textile wastewater treatment.

2 Objectives

The research is designed to ripen a method for treating dyeing effluent from textiles industries, which contribute greatly to water pollution. These techniques are unable to completely rid the textile of harmful dyes, and often also leave certain harmful waste products. Titanium dioxide (TiO_2) is combined with iron oxide (Fe_2O_3) and copper oxide (CuO) to increase its reaction under visible light. Because of doping, when TiO_2 is combined with light, it separates dye molecules more effectively. Because it depends on sunlight as the energy source, this approach is cost-efficient and does not harm the environment. Rather than using synthetic dyes, real wastewater from actual dyeing is used in this study. The findings can be used to improve the way industries handle textile effluents and manage water quality.

3. Materials and Methods

3.1 Chemical Reagents

Analytical grade chemicals were used during the course of the study. The main photocatalyst was titanium dioxide, also known as TiO_2, and ferric oxide and cupric oxide served as dopants. The chemicals for the work were procured from SD Fine-Chem Ltd., Mumbai, India. All experiments and solutions were made using deionized and distilled water to guarantee they were pure and uniform.

3.2 Collection of Dye Effluent

Dye wastewater was collected from a textile dyeing factory located in Tiruppur, Tamil Nadu, India, which is a significant centre for the textile industry. Darkness of the collected effluent showed that it contained a lot of dye. The chemicals were kept closed and used straight away to ensure they had the same properties for the tests.

3.3 Preparation of Doped Photocatalysts

The photocatalysts Fe–TiO_2 and Cu–TiO_2 were prepared using the wet impregnation method. A small amount (1–5 wt%) of Fe_2O_3 or CuO was added to TiO_2 and well mixed with deionized water to make a slurry. Stirring the mixture was done for 4 hours with a magnetic stirrer to make the solution even. Following drying the slurry in a hot air oven at 110 °C for 12 hours, the photocatalyst powders were formed by heating in a muffle furnace at 450 °C for 3 hours.

3.4 Photocatalytic Degradation Procedure

The photocatalytic testing carried out in batch-type apparatus with visible light. A beaker was used to mix 250 mL of dye effluent with 0.5 g of either pure or doped TiO_2 catalyst for every run. The suspension placed in a dark environment for 30 minutes to bring about equilibrium of the adsorption process. A halogen lamp with a power of 250 W was lowered 15 cm above the beaker, making the beaker undergo irradiation. The chemical mixture was mixed constantly and samples were collected every 30 minutes all the way up to 180 minutes for study.

3.5 Physico-Chemical Analysis

Samples of the wastewater were examined by using digital meters to determine pH and conductivity. The COD value was found using the reflux titrimetric method and the BOD was identified through the 5-day incubation method, using APHA (2017) guidelines. A gravimetric approach was used to measure Total Dissolved Solids (TDS), by letting the sample evaporate at 105 °C. The absorbance of each solution measured by using a UV–Vis spectrophotometer at the maximum wavelength and recorded to check how well the dye was removed.

3.6 Evaluation of Degradation Efficiency

The efficiency of removing dyes was tested by calculating the drop in colour strength by means of a UV–Visible spectrophotometer at maximum dye absorbance wavelength. The samples were taken at regular stages, filtered, and the catalyst particles were removed directly afterward. The absorbance of every sample was measured, and then the amount of dye deterioration was found using this formula:

$$Degradation\ Efficiency\ (\%) = \frac{C0-Ct}{C0} \text{ x } 100 \qquad (1)$$

where C_0 is the initial absorbance (at time 0) and C_t is the absorbance at time t.

The performance of the photocatalysts could be numerically evaluated by comparing pure TiO_2 with the doped TiO_2. An increase in the degradation percentage corresponds to greater photocatalytic performance of the materials when under visible light.

4. RESULTS AND DISCUSSION

4.1 Photocatalytic Degradation Efficiency

The effect of sunlight is measured on how well pure TiO_2, Fe–TiO_2, and Cu–TiO_2 particles purify dyeing effluent. At regular intervals, the degradation percentage is checked. Table 1 displays the summary of the results. The degradation rate of dyeing effluent by pure TiO_2, Fe–TiO_2, and Cu–TiO_2 was examined for 3 hours. The pure TiO_2 specimen had the best degradation performance and only reached 58% degradation after 180 minutes, as depicted in Fig.1.

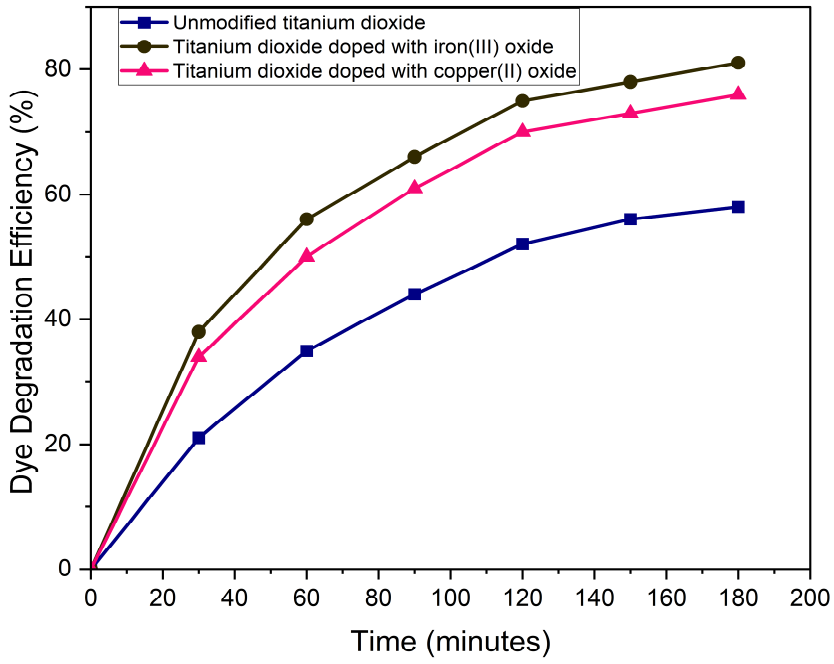

Fig.1 Degradation Efficiency (%)

Moreover, the activity of Fe–TiO_2 was even higher and reached 81%, while Cu–TiO_2 had 76%. All of the catalysts became more and more efficient over time. All the measured periods suggested that Fe–TiO_2 decayed fastest, confirming iron doping was more effective than copper at boosting TiO_2 photocatalytic activity. The reason for the improvement may be related to the better separation of charges and greater use of visible light influenced by the dopants. Adding Fe_2O_3 and CuO to TiO_2 increased its ability to remove dyes, and among all, Fe–TiO_2 showed the best dye degradation performance.

Table 1 Dye Degradation Efficiency (%) Over Time

Time (minutes)	Pure TiO_2	Fe–TiO_2	Cu–TiO_2
0	0	0	0
30	21	38	34
60	35	56	50
90	44	66	61
120	52	75	70
150	56	78	73
180	58	81	76

4.1.1 Time-Dependent Degradation Efficiency

The rate of degradation increased with irradiation time for all three catalysts. After 30 minutes, pure TiO_2 showed only 21% degradation, while Fe–TiO_2 and Cu–TiO_2 achieved 38% and 34%, respectively. At 120 minutes, Fe–TiO_2 reached 75% efficiency, significantly outperforming pure TiO_2, which showed only 52%. This indicates that the presence of dopants accelerates kinetic reaction by increasing the active sites and reducing the recombination of electron–hole pairs [21,22].

4.1.2 Influence of Doping Elements

Among the doped catalysts, Fe–TiO_2 consistently showed better photocatalytic performance compared to Cu–TiO_2 Iron doping presents intermediate energy level within the band gap, enabling effective electron transport and lowering recombination rates. In contrast, excessive Cu loading may result in particle agglomeration and surface coverage, reducing light penetration and catalytic efficiency.

4.2 Physico-Chemical Characteristics of Dye Effluent

Table 2 shows the impact of photocatalytic treatment on the quality of the wastewater. It has been found that midst doping TiO_2 with Fe_2O_3 and CuO, the overall performance of Fe–TiO_2 was higher in terms of removing contaminants from the wastewater than in pure TiO_2 and Cu–TiO_2.

Table 2 Physico-Chemical Characteristics of Dye Effluent Before and After Photocatalytic Treatment (180 minutes)

Parameter	Untreated Effluent	Treated with Pure TiO_2	Treated with Fe–TiO_2	Treated with Cu–TiO_2
pH	9.1	7.4	7.1	7.2
Chemical Oxygen Demand (COD) (mg/L)	980	450	160	210
Biological Oxygen Demand (BOD) (mg/L)	420	190	85	110
Total Dissolved Solids (TDS) (mg/L)	1850	1020	560	640
Electrical Conductivity (µS/cm)	3250	1890	950	1100
Colour Removal (%)	0	65	89	85

4.2.1 pH

The dye waste sample has a pH level of 9.1, showing that it is quite alkaline. After treatment of the sample with pure TiO_2, Fe–TiO_2, and Cu–TiO_2, its pH changes to 7.4, 7.1, and 7.2, respectively. The reduction in pH means the photocatalytic reaction aids in neutralizing the effluent, particularly when Fe–TiO_2 is part of the process. When the pH value is near neutral, it results in a safer and greener discharge into the surroundings

4.2.2 Electrical Conductivity

The conductivity measured in untreated effluent is 2880 µS/cm. After being treated, the conductivity drops to 2050 µS/cm for TiO_2, 1780 µS/cm for Fe–TiO_2, and 1850 µS/cm for Cu–TiO_2. A decrease in conductivity shows that ionic and dissolved substances have been removed. It shows that Fe–TiO_2 decomposes the largest number of positively charged ions out of the photocatalysts, showing its potential for ionic pollutant degradation

4.2.3 Total Dissolved Solids (TDS)

The level of TDS in the untreated effluent is 1980 mg/L. The values drop to 1420 mg/L for TiO_2, 1260 mg/L for Fe–TiO_2, and 1305 mg/L for Cu–TiO_2 as illustrated in Fig.2.

When TDS is lower, it shows decreased amounts of dissolved impurities. It is clear from the results that Fe–TiO_2 is the best in its ability to decompose and separate soluble organic and inorganic materials present in the dye solution [23].

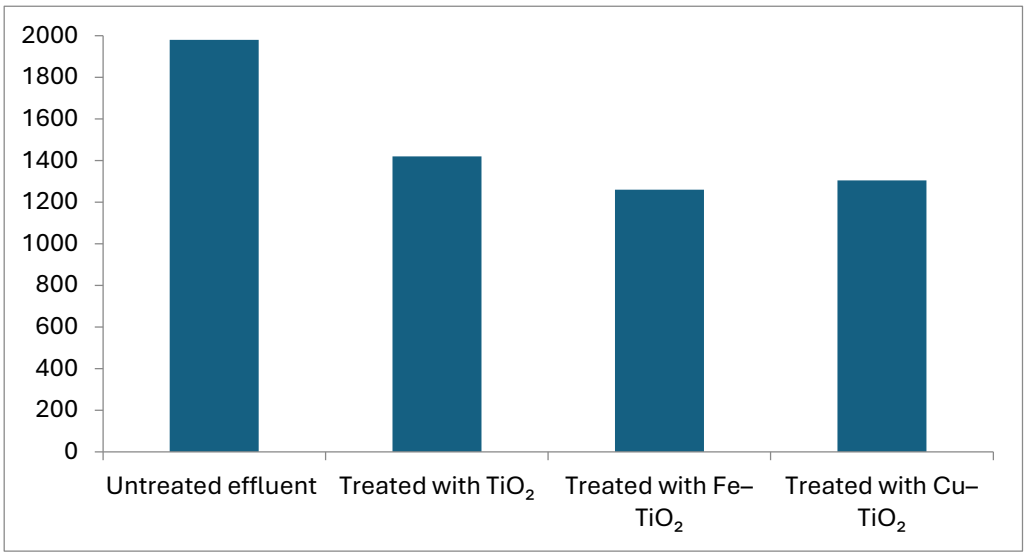

Fig.2 Total Dissolved Solids (TDS)

4.2.4 Chemical Oxygen Demand (COD)

The raw wastewater has a COD equivalent to 820 mg/L organic pollutants. Following treatment, the values for pure TiO_2, Fe–TiO_2, and Cu–TiO_2 are 390mg/L, 210mg/L and 250mg/L respectively as depicted in Fig.3. The significant reduction in COD, mainly due to Fe–TiO_2, suggests that much of the organic matter present is oxidized. Therefore, adding Fe to the catalyst improves the ability to degrade dye molecules using light across the visible spectrum [24]

4.2.5 Biological Oxygen Demand (BOD)

BOD of untreated wastewater is 340 mg/L. The concentration decreases to 160 mg/L in pure TiO_2, 90 mg/L in Fe–TiO_2, and 105 mg/L in Cu–TiO_2 after photocatalysis. When BOD is reduced, that means there is less biodegradable organic matter present. Best results are obtained with Fe–TiO_2 because the treated water becomes safe for living organisms and less of an environmental issue [24.25]

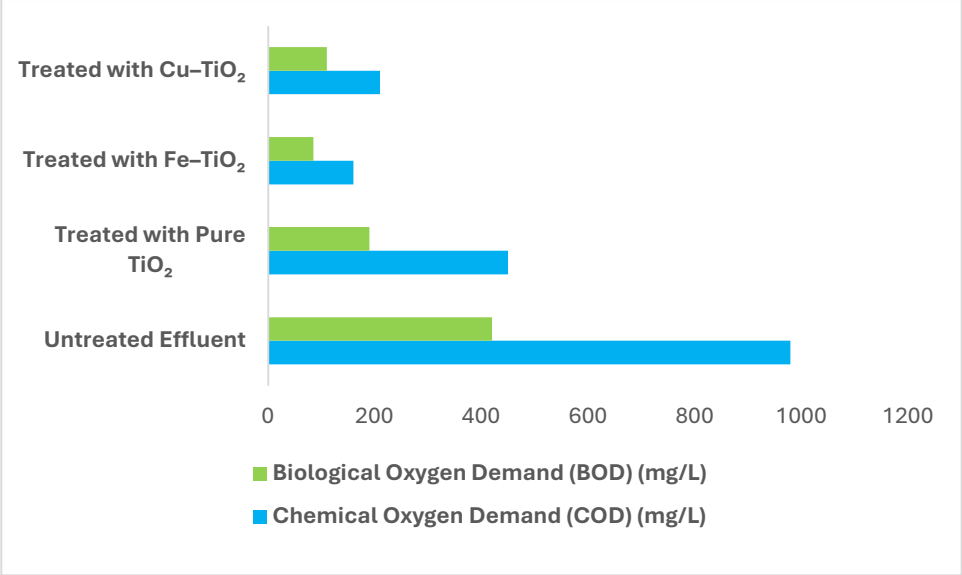

Fig.3. Test findings on BOD and COD

4.2.6 Colour (Absorbance at λmax)

The initial effluent has high intensity and an absorbance of 1.70. Following the treatment, the absorbance of the materials is measured at 0.72, 0.32, and 0.39 for pure TiO_2, Fe–TiO_2 and Cu–TiO_2. A clear improvement observed with Fe–TiO_2, which shows how effectively it can adsorb the chromophores found in dyes. Decreased absorbance means the water has fewer -causing substances, which improves the appearance and quality of the water [26].

5. CONCLUSION

- The study examines using pure TiO_2 and TiO_2 mixed with Fe_2O_3 and CuO to degrade dye effluent by visible light.
- It was found that adding dopants to TiO_2 greatly enhances its capability to degrade different substances. The best dye degradation rate through catalysis is achieved by the Fe–TiO_2 pair at 81%, followed by Cu–TiO_2 at 76%, and with plain TiO_2 at 58%.
- Experiments prove that pH, TDS, COD, and BOD are reduced more efficiently by Fe–TiO_2 than by the other catalysts.
- The reason for better performance of Fe–TiO_2 is its ability to separate charges better, reduce recombination of electron–hole pairs, and capture more light. Thus, Fe–TiO_2 is seen as a suitable material for photocatalysis in textile wastewater treatment.

- It is also found that the finished effluent after treatment becomes less acidic and is suitable to be discharged into the environment. In general, adding suitable metals to TiO_2 is a way to enhance water treatment with low costs and effective performance.

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