

ENHANCED PHOTODEGRADATION OF TEXTILE DYE USING DOPED TiO₂

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Abstract: Dyestuffs are the materials which extensively used in the textile and other printing industries. The colour and toxicity which dyes impart to water bodies are very undesirable and harmful to the water users for aesthetic and environmental reasons. About 20% of the overall dye production of the world is discharged from various industries such as dyestuff manufacturing, dyeing, printing, and textile finishing. In this study, Methylene blue (MB) which is a cationic dye, used extensively for dyeing cotton, wool and silk is used. The risk of the existence of this dye in waste water may be arisen from the burns effect of eye, nausea, vomiting and diarrhea. The traditional treatment techniques are not a complete solution to the problem. So, Advanced Oxidation Processes (AOP's), like Photo-catalytic degradation processes with doped Fe-TiO₂, could be a good option to treat and eliminate textile dyes.

It has been studied that Photo-catalytic degradation of methylene blue and real dye wastewater over doped Fe-TiO₂ in presence of light. The progress of the reaction is monitored spectrophotometrically and Chemical Oxygen Demand (COD) removal for dye wastewater is also analyzed. The efficiency of two Catalyst I (Fe-doped TiO₂) and Catalyst II (FeC-doped TiO₂) is used for the removal of textile dye wastewater. The effects of some parameters affecting the rate of reaction, such as pH, dye concentration, amount catalyst, light intensity, contact time were also studied.

Index Terms: Photo degradation, catalyst, textile dye.

I. INTRODUCTION

Dyes are used mostly in the textile (fabric used in clothing) industry and paper industry. Recent development in the realm of chemical water treatment techniques has led to the improvement in oxidative degradation by photochemical methods. Photocatalytic oxidation is cost effective and capable of degrading any complex organic chemicals when compared to other purification techniques. The formation of transient hydroxyl radicals (OH⁻) during photo oxidation are highly reactive than any oxidation agent. The photodegradation are generally classified into two categories such as homogeneous and heterogeneous processes. Homogeneous processes occur in presence of UV light in conjunction with oxidants such as ozone and hydrogen peroxide. Heterogeneous processes occur in presence of oxidants and solid photocatalyst. Photocatalytic degradations are very sensitive to pH, catalyst dosage, type of effluent, effluent concentration and the charges between the effluent and the catalyst [1-2].

The process of photodegradation starts when TiO₂ absorbs a UV radiation of energy equal or higher than its band gap (3.2 eV for anatase; 3.0 eV for rutile). This leads to the formation of free electrons in the conduction band and holes in the semiconductor valence band. The energized electrons can both recombine with the holes (and then dissipate the absorbed energy as heat) or the electron-hole pairs can participate in redox reactions. They can react with electron acceptors/donors adsorbed on the surface of the photocatalyst. Alternatively, the solid side at the semiconductor/liquid junction creates an electrical field that separates the electrons- holes pairs that fail to recombine. The electron field allows the holes to migrate to the illuminated part of the TiO₂ and the electrons to migrate to the unlit region of the TiO₂ particle surface. Essentially, it is accepted that the initial steps of photocatalytic degradation of a species is the reaction with extremely reactive but short-lived hydroxyl radicals (OH[•]) or direct hole trapping. The OH[•] is formed either in the highly hydroxylated semiconductor surface or by direct oxidation of the pollutant molecules under UV radiation. There is also a possibility that both methods of forming OH[•] occurs in these situation simultaneously. The reduction of adsorbed oxygen species occurs immediately after this process. Dissolved oxygen molecules (in the aqueous system), or other electron acceptors available in the aqueous system can cause this reduction [3-9].

II. EXPERIMENTAL INVESTIGATION

The following equipments were used to conduct the experiments at the laboratory:

2.1 XRD (X-Ray Diffraction)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Crystalline nature confirmed by sharp peaks observed in XRD pattern. In this paper all sharp peaks of XRD pattern belong to anatase phase of TiO₂.

Table 1 XRD result for Catalyst I and Catalyst II

Anatase phase	25.3°	37.7°	48°	53.8°	55.0°	62.69°	Average particle size
Catalyst I Fe-TiO ₂	25.34°	37.87°	48.00°	53.81°		62.85°	0.3-7.4nm
Catalyst I FeC-TiO ₂	25.36°	37.64°	48.1°		55.2°	62.68°	

2.2 Photocatalytic Reactor

The experimental setup in which the dye sample of 200ml is mixed with 0.2gram of doped TiO₂ catalyst and the whole setup is covered with casing. UV lamp and aerator is switch on and time interval for reaction is noted down at the interval of 30, 60, 90 minutes. Before the reactor is started the dye sample initial concentration (C₀) is noted using Digital Spectrometer and after each interval of time the final concentration (C₁, C₂, C₃) are noted down for calculation of percentage removal of dye concentration.

In this investigation, preparation of Doped Fe-TiO₂ catalyst, Characterization of Doped Fe-TiO₂ catalyst, Photo-catalytic degradation of methylene blue and real dye wastewater over prepared doped Fe-TiO₂ in presence of UV light is conducted.

III. ANALYSIS OF RESULTS

3.1 Effect of contact time on removal of dye solution.

Degradation was observed in terms of decrease in wavelength. The percentage (%) degradation was calculated as follows:

$$\text{Percentage Degradation} = 100 * (C_0 - C) / C_0$$

where C_0 = initial concentration of dye solution,

C = concentration of dye solution after irradiation.

As shown in table 2 and figure 1, it has been observed that increase in time has augmented the removal of dye concentration. The dye concentration of 17.62% and 24.35% has been removed in case of Catalyst I (Fe-doped TiO₂) and Catalyst II (FeC-doped TiO₂) after 90 min.

Table 2. Table for Study of the effect of contact time

Sl.no	Dye Dosage (mg/L)	Time (Minutes)	Initial concentration of dye solution (mg/L) (C ₀)	Final concentration of dye solution (mg/L)	Percentage (%) removal of dye concentration $[C_0 - C_f/C_0]*100$
Catalyst I Fe-doped TiO₂					
1	20	0	1.93	0	0
2		30		1.75	9.3%
3		60		1.66	13.98%
4		90		1.59	17.62%
Catalyst II FeC-doped TiO₂					
1	20	0	1.93	0	0
2		30		1.65	14.4%
3		60		1.57	18.6%
4		90		1.46	24.35%

The efficiency of Doped TiO₂ catalyst with respect of contact time is studied and the catalyst Fe-Doped TiO₂ proved its efficiency in removal of dye with increase in contact time. It is evident that the percentage of removal increases with increasing irradiation time. This is because more •OH radicals will be generated when the exposure time is longer. The generation of •OH radicals is crucial in photodegradation process as it oxidizes the organic pollutants to carbon dioxide, water and some simple mineral acids.

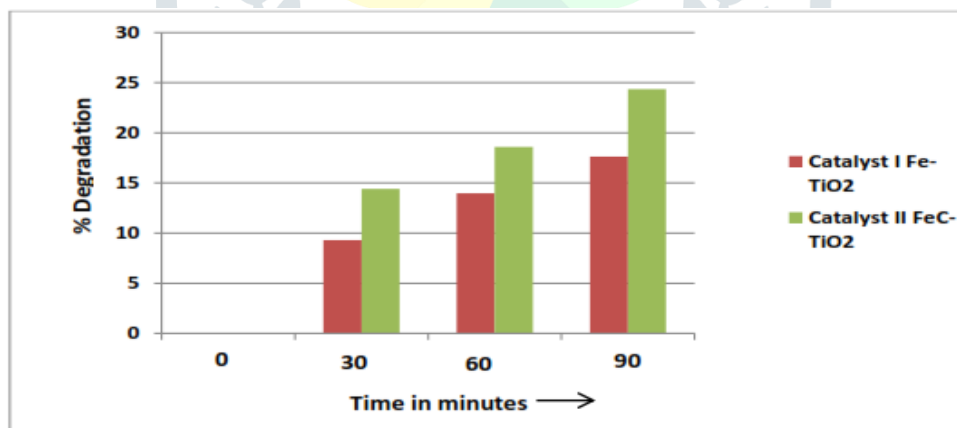


Figure 1. Effect of contact time on two catalysts in degradation of methylene blue

From this study, it is evident that the two catalysts of immobilized TiO₂ are capable in removing methylene blue (MB) under the illumination of UV light. The results revealed that the FeC-TiO₂ is stronger in decolorizing efficiency of MB with contact time.

3.2 Effect of Catalyst Dosage on removal of dye solution.

Many reports suggest that the amount of catalyst plays a major role in the degradation of organic compound or dyes in photocatalytic degradation. To avoid the use of excess catalyst, it is necessary to find the optimum loading for the efficient removal of dye or organic compound. So it is necessary to optimize the amount of catalyst to obtain the highest photocatalytic activity. To study the effect of the amount of catalysts, varied amounts of catalysts from 1 to 5g/L is examined. The concentration of methylene blue dye (20mg/L) was kept the same in all these experiments. Figure 2 shows the effect of the amount of catalyst on the degradation of dye in the presence of UV light irradiation.

The experiments were conducted by varying catalyst doses from 1g/L to 4g/L for the dye solution of 20mg/L as well as increasing contact time. The combination of increasing catalyst dosage (1 to 4 g/L) and contact time (minutes) in dye solution increases percentage of removal of dye concentration. The maximum percentage of removal of dye concentration is found at catalyst dosage 3 g/L with 210 minutes at 92.2% in case of catalyst I.

The result demonstrated that the increase in percentage decolorization and degradation of MB dye was lowest in the case of 1g/L catalyst and it was increased up to 3 g/L sharply from 44% to 92% in 240 minutes in the case of Catalyst I and 45% to 94% in 240 minutes in the case of Catalyst II. This is due to the catalyst load increases, the turbidity of the solution increases, resulting in a decrease in UV light penetration and photo activated volume. When the photocatalyst amount surpassed 3 g/L, the degradation rate decreased because a further increase in catalyst loading caused light scattering and a screening effect while reducing the specific activity of the catalyst. Part of the catalyst surface probably became unavailable for photon absorption and dye adsorption under such conditions, thus bringing little stimulation to catalytic reaction. The results suggest that an optimal amount of the catalyst is necessary for enhancing the degradation rate and reducing needless waste, and in this experiment the optimal amount is 3 g/L as shown in figures 2 and 3.

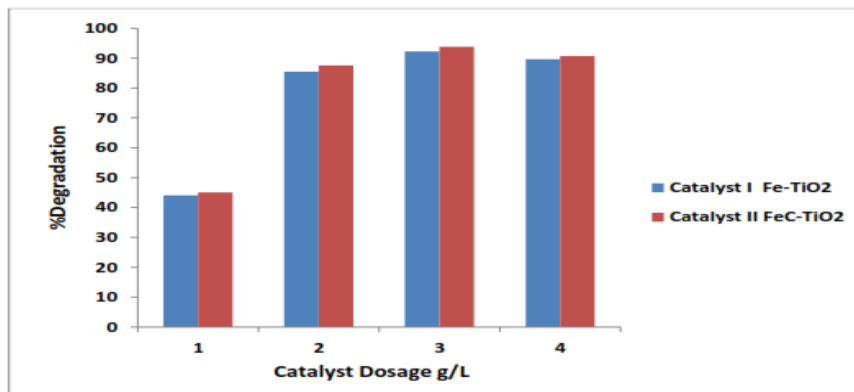


Figure 2. Comparison of two catalysts in case of Dosage of Catalyst.

Figure 2 clearly explained that catalyst II FeC-doped TiO₂ has more capability and higher efficiency in removal of dye colour within specified irradiation times. In the two cases of catalysts same amount of dye concentration, Catalyst dosage and pH are maintained throughout the experiment.

Table 3 Increasing Catalyst I Dosage and contact time effect on removal of dye solution

Dye dosage	Catalyst Dosage (gm/L)	Time (Minutes)	Initial concentration of dye solution (mg/L) (C ₀)	Final concentration of dye solution (mg /L)	Percentage(%) removal of dye concentration [C ₀ – C _f /C ₀]*100
Fe-doped TiO₂ Catalyst					
20mg/L	1g/L	0	1.93	0	0
		30		1.75	9.30%
		60		1.66	13.98%
		90		1.59	17.62%
		120		1.49	22.79%
		150		1.38	28.49%
		180		1.27	34.20%
		210		1.12	41.95%
		240		1.08	44.04%
20mg/L	2g/L	0	1.93	0	0
		30		1.67	13.47%
		60		1.48	23.32%
		90		1.35	30%
		120		1.24	35.75%
		150		0.98	49.22%
		180		0.62	67.78%
		210		0.43	77.72%
		240		0.28	85.49%
20mg/L	3g/L	0	1.93	1.93	0
		30		1.66	13.98%
		60		1.37	29%
		90		1.12	42%
		120		0.98	49.22%
		150		0.68	64.76%
		180		0.42	78.23%
		210		0.32	83.42%
		240		0.15	92.22%
20mg/L	4g/L	0	1.93	1.93	0
		30		1.65	14.50%
		60		1.368	29.11%

	90	1.13	41.45%
	120	0.99	48.70%
	150	0.67	65.28%
	180	0.46	76.16%
	210	0.3	84.45%
	240	0.2	89.63%

Table 4 Increasing Catalyst II Dosage effect on removal of dye solution

Sl.no	Dye Dosage(mg/L)	Catalyst Dosage g/L	Initial concentration of dye solution (mg/L) (C ₀)	Final concentration of dye solution (mg /L)	Percentage(%) removal of dye concentration [C ₀ – C _f /C ₀]*100
Catalyst II FeC-doped TiO₂					
1	20	1	1.93	1.06	45
2		2		0.24	87.56
3		3		0.12	93.78
4		4		0.18	90.67
5		5		0.21	89.12

3.3 Effect of pH value in Dye wastewater.

pH is most important parameter to study because wastewater containing dyes is discharged at different pH. Therefore the role of pH on the decolourisation was examined at different pH values 2, 4, 6 and 8 with optimum dosage of catalyst.

pH of solution is one of important factor effecting on efficiency of photocatalytic process. To evaluate the optimum value of pH solution, the experiments was carried out with pH value from 2 to 8 with dye concentration of 20mg/L and 3g/L catalyst dosage. Figure.3 and Figure 4 show the results of MB degradation, which higher at acidic solution (pH at 4.0) after 2 hr using 20 mg/l as initial concentration. To explain effects of pH solution, the zero point charge (pH_{zc}) of TiO₂ is between 5.8-6.8, which the adsorption of MB molecules onto the surface of TiO₂ catalyst as important step to start photo-oxidation reaction. According to zero point charge (pH_{zc}) of TiO₂, the surface is positively below pH_{zc} and negatively charge of MB molecules. For this reason, the strong adsorption of MB onto TiO₂ surface at pH solution of 4.0 and highest degradation was found.

Table 5 Table for Study of the effect of pH of Dye wastewater

Dye dosage	Catalyst Dosage (gm/L)	pH value	Initial concentration of dye solution (mg/L) (C ₀)	Final concentration of dye solution (mg /L)	Percentage(%) removal of dye concentration [C ₀ – C _f /C ₀]*100
Catalyst I Fe-doped TiO₂ (Time 60 minutes)					
20mg/L	3g/L	2	1.63	1.45	11
		4	1.77	1.05	40.67
		6	1.73	1.31	24.27
		8	1.93	1.63	15.54
Catalyst II FeC-doped TiO₂ (Time 60 minutes)					
20mg/L	3g/L	2	1.63	1.25	23.3
		4	1.77	0.98	44.63
		6	1.73	1.02	41
		8	1.93	1.59	17.62

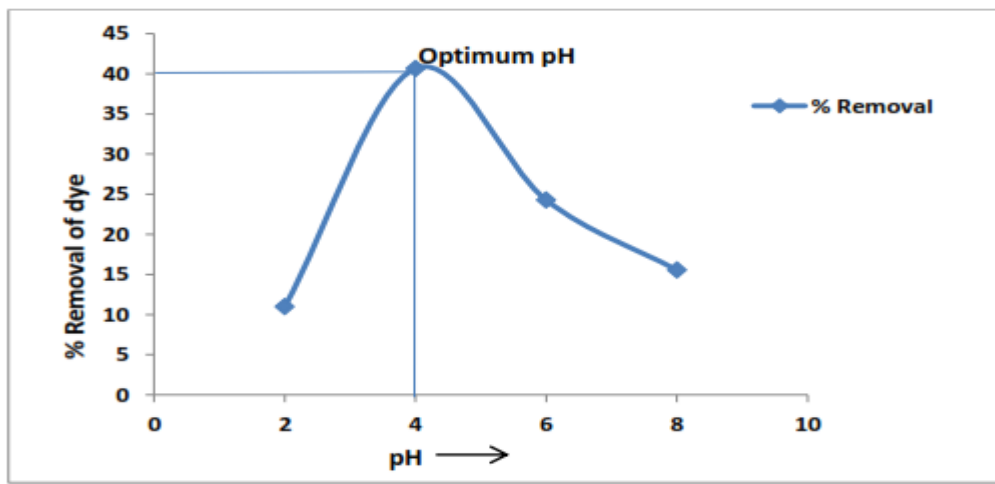


Figure 3 Study of the effect of pH for efficiency of Catalyst I Fe-TiO₂.

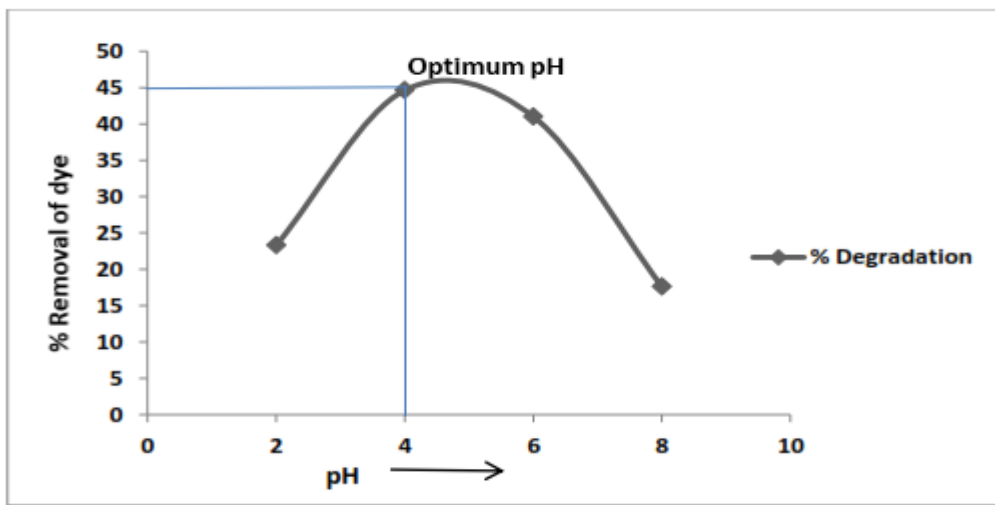


Figure 4 Study of the effect of pH for efficiency of Catalyst II FeC-TiO₂

st on Textile Dye wastewater.

Textile Dye wastewater is collected from Dying Centre and is tested for the efficiency of effect of the two catalysts at room temperature. The characteristics of the wastewater collected are shown in table 6. Wastewater collected is diluted with distilled water for testing and examination. The efficiency of the catalyst in removal of colour is checked spectrophotometrically and COD removal is checked. It has been observed as shown in the table 7 and figure 5 that catalyst is efficient at 3g/L with contact time of 120 minute in case of Catalyst I and II for removal of colour. The percentage of removal of COD is higher in Catalyst II as shown in the figure 6 and table 8. Therefore, Catalyst II has higher value in term of efficiency for the removal of colour and COD.

Table 6. Characteristics of raw Textile dye wastewater sample.

Parameters	Values
pH	11.75
Chemical Oxygen Demand (mg/L)	680
Total Suspended Solids (mg/L)	60
Total dissolved solids (mg/L)	2965

Table 7. Catalyst efficiency for dye Colour Removal.

Sl.no	Dye Dosage (mg/L)	Time (Minutes)	Initial concentration of dye solution (mg/L) (C ₀)	Final concentration of dye solution (mg /L)	Percentage (%) removal of dye concentration [C ₀ – C _f /C ₀]*100
Catalyst I Fe-doped TiO ₂			Catalyst dosage – 3g/L		
1		0		0	0

2	20	30	2.1	1.83	12.5
3		60		1.72	18.09
4		90		1.42	32.38
5		120		1.06	49.52
Catalyst II FeC-doped TiO₂			Catalyst dosage – 3g/L		
1	20	0	2.1	0	0
2		30		1.8	14.28
3		60		1.42	32.38
4		90		1.02	51.42
5		120		0.62	71.42

Table 8. Catalyst efficiency for removal of COD.

Sl.No	Irradiation time	Volume of FAS	Initial COD Mg/L	Final COD Mg/L	% Removal of COD
Catalyst I Fe-doped TiO₂					
1.	30	14.5	680	580	14.7
2	60	12.3		492	27.65
3	90	10.3		412	39.41
4	120	8.2		328	52
Catalyst II FeC-doped TiO₂					
1	30	13.6	680	544	20
2	60	11.4		456	32.94
3	90	9.2		368	45.88
4	120	6.2		248	63.53

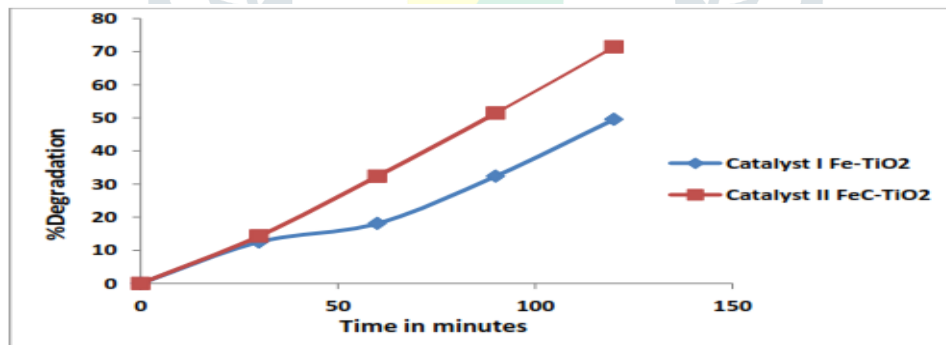


Figure 5. Activity of two Catalysts in removal of dye color in raw wastewater.

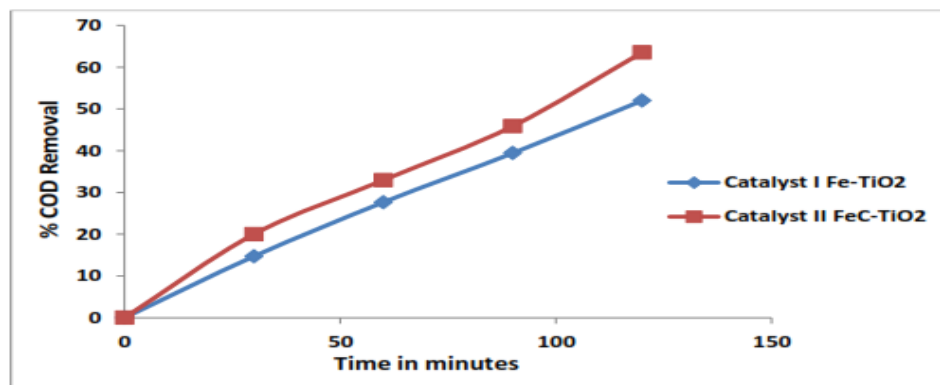


Figure 6. Activity of two Catalysts in percentage removal of COD in raw wastewater.

IV. CONCLUSIONS:

1. The catalyst Fe-doped TiO₂ is synthetically prepared and characterization of catalyst is done with XRD. The result of XRD shows that prepared TiO₂ is in pure anatase phase and from the Powder XRD spectrum the average crystallite size is found to be 0.3-7.4nm. This confirms that the prepared samples are in pure form.
2. It was found that optimum dosage of catalyst was 3g/L and the highest percentage of colour removal is achieved as high as 92% with irradiation time of 240 minutes.
3. The dye removal was inversely proportional to the initial methylene blue concentration in all processes. It was found that the optimum pH for the reaction is 4.
4. According to zero point charge (pH_{zc}) of TiO₂, the surface is positively below pH zero point charge and negatively charge of MB molecules. For this reason, the strong adsorption of MB onto TiO₂ surface at pH solution of 4.0 and highest degradation was found. It is also found that the percentage of colour removal increase with increase in contact time.
5. The catalysts have capability to remove dye colour and have efficiency for removal of COD from raw textile wastewater.
6. Fe-doped TiO₂ catalyst proved that it has good capability and efficiency for removal of dye colour and COD in synthetic dye wastewater and raw textile dye wastewater.
7. Catalyst II (FeC-doped TiO₂) has more capability and higher efficiency than catalyst I (Fe-doped TiO₂) in removal of dye concentration within specified irradiation times.

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