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Heterogeneous Photocatalytic Treatment of Textile Effluent using Semiconductor Oxide under UV Irradiation

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Abstract

The present work deals with the photocatalytic degradation as a method for pre-treatment of the effluent from a textile industry containing various dyes and their intermediates which are non-biodegradable. The textile effluent was subjected to photocatalytic degradation under UV irradiation in the presence of TiO_2 as catalyst and the process parameters for maximum degradation were determined. Optimisation of catalyst dose and pH was carried out and the effect of addition of oxidant H_2O_2 on the degradation efficiency was also studied. The effectiveness with which the photocatalyst can be recycled was also assessed to ensure the economic viability of the process.

Keywords: Heterogeneous Photocatalysis, Semiconductor Oxide,Textile Effluent,Titanium Dioxide

1. Introduction

Advanced oxidation processes have been established as a promising option to degrade persistent pollutants from contaminated water when conventional water treatment processes fail to furnish significant outcome. Among the various types of advanced oxidation processes heterogeneous photocatalysis [1]in the presence of semiconductor oxides has been widely used to decolorize and mineralize many organic pollutants [2,3]. Heterogeneous semiconductor photocatalysis has been proved to be of a significant importance for treatment of the highly polluted effluent from textile industries. The photocatalysed degradation of organic substances employing semiconductor oxides such as Titanium dioxide with simultaneous irradiation results in complete mineralisation small environmentally benign substances like carbon-dioxide, water or inorganic acids. The significant advantages of this technology include lack of mass transfer limitations, operation at ambient conditions and the possibility of harnessing solar irradiation. The catalysts are affordable, non-toxic and also possess commercial availability and photochemical stability [4]. Among the different photocatalysts used TiO_2has a wide band gap and therefore can effectively be used as a photocatalyst for the degradation of dye pollutants [5–7].

In the present study a highly polluted textile effluent has been treated by photocatalytic degradation under UV irradiation in the presence of TiO_2 and the process parameters for maximum degradation were determined. Since the lifetime of the catalyst is a crucial factor of the process, the efficiency with which the photocatalyst TiO_2 can be reused was also checked.

2. Experimental

Raw wastewater was collected from Textile Unit at Erode, Tamilnadu, India located at about 8 Km away from Erode City on the way to Bhavani town. The area has a cluster of textile industries located close to the Kalingarayan Canal which serves as a main source of irrigation. Wastewater was collected from the flow equalization tank. It was highly concentrated. In order to get the values within the measurable range, the sample was diluted with water to the ratio of 1:1. The initial pH of the sample was noted. The effluent was subjected to UV irradiation in the immersion well type photoreactor using TiO_2 as the photocatalyst

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[8]. Process parameters such as catalyst dose, initial pH etc. were optimised and the effect of addition of H_2O_2 as oxidant was examined.

3. Results and Discussion

The treatment of the textile effluent using TiO_2 as photocatalyst under UV irradiation could bring about significant degradation of the pollutants in the effluent as discussed in the subsequent sections.

3.1 Characteristics of the Effluent

The effluent was deep blue in colour and it was subjected to analysis of important quality parameters and the values obtained are presented in Table 1.

These parameters reveal that the wastewater is highly polluted, has low biodegradability and needs to be subjected to some pre-treatment so as to be safely discharged without posing serious threats to the environment.

3.2 Absorption Spectrum of the Raw Effluent

The absorption spectrum of the raw effluent is shown in Fig.1. The effluent shows several peaks in the Ultra Violet and visible region. This indicates the presence of various compounds of organic nature in the effluent water. The low biodegradability value (BOD_5/COD =0.2- 0.25) of the effluent due to this fact is supported by the presence of large number of peaks in the absorption spectrum of the effluent. This emphasises the need for treatment of the effluent for complete mineralization.

3.3 Effect of Catalyst Dosage

Catalyst dosage is a significant factor in photodegradation which can strongly influence the degradation of textile effluent. Experiments were carried out to study the

Table 1. Characteristics of raw textile effluent

Characteristics	Value (mg/L)
COD	650-700
Total Solids	4419
Total Suspended Solids	284
Total Dissolved Solids	4135
pH	10.8
BOD_5/COD	0.2 – 0.25

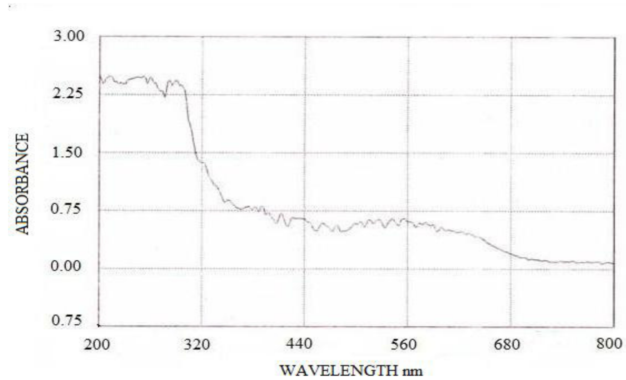

Fig.1. Absorption spectrum of the raw effluent.

degradation of the effluent by varying gradually the catalyst loading up to 7 gm/L under UV irradiation. The extent of COD reduction was determined after every 60 minutes for 5 hours. The results of the study are shown in Fig.2.

As the results infer, maximum COD reduction is observed at the catalyst loading of 5 g/L. The COD decreases from 650 mg/L to 88 mg/L in 5 hours accounting for 86% degradation. Catalyst loading of lesser than 5 g/L or greater than 5 g/L does not cause COD reduction to this much extent. The final percentage of COD reduction for different catalyst loadings after 5 hours is given in Fig.3. The COD reduction percentage is 70% when the catalyst concentration is 1 g/L and it increases to 86% when the catalyst loading is raised to 5 g/L. Increasing the catalyst loading further does not bring about any considerable increase in COD reduction.

Several studies reported earlier confirm that dye degradation increases with increase in TiO_2 concentration up to a value and beyond that optimum value degradation remains practically the same without any change, as plateau [4]. This crucial level of TiO_2dosage depends on geometry of the photo reactor and its operating conditions, wavelength and intensity of irradiation used and also to the point where the full surface of the catalyst is illuminated.

In the present study on the photocatalytic degradation of the effluent, 5 g/L appears to be the optimum amount of catalyst dosage. Hence the same has been fixed as the optimum catalyst dosage for further experiments to study the effect of pH and effect of added oxidant.

3.4 Effect of pH

The effluent from textile industries normally has a varying range of pH values. In general, pH plays a vital role in

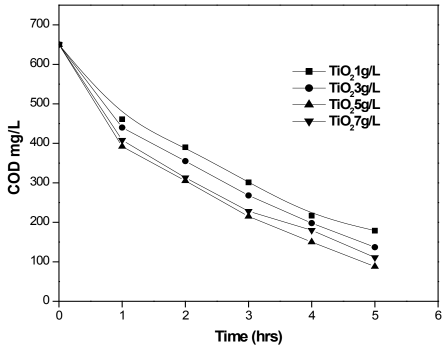

Fig.2. Reduction in COD of the effluent at different catalyst loading.

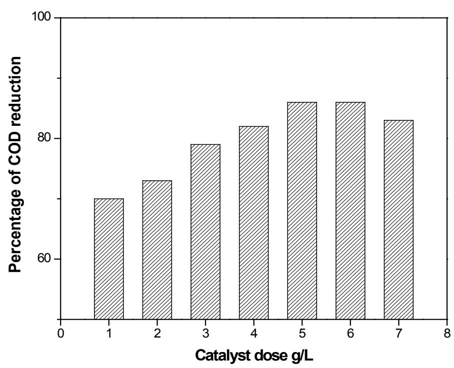

Fig.3. Percentage reduction in COD of the effluent at different catalyst loading in 5 hours.

the quality of textile wastes as well as in the production of hydroxyl radicals [9]. Hence, the influence of pH in the photodegradation of the textile effluent at pH values in the range from pH 4 to pH 10.8 was also studied.

The pH affects the activity of TiO_2 to a significant extent, including the charge possessed by the particles, the size of the aggregate particles formed and the position of the bands. Extensive results have already been published related to the effect of pH on photocatalytic degradation of various compounds [10]. For charged species, the photocatalytic degradation efficiency considerably depends upon the pH value. This is because the surface charge and therefore the adsorption characteristics of TiO_2 particles depend very much on the pH of the solution [11]. Alkaline pH is favourable for the degradation of the cationic substrates, while negatively charged particles are effectively degraded in the acidic media when the photocatalyst surface is having positive charge.

In fact, in the degradation of effluent, it is not the initial pH but it is the final pH which is the deciding pH. Because it has to be subjected to biological treatment after the photocatalytic pre-treatment. During the biological treatment the pH of the wastewater should be neutral so that effective biodegradation can take place leading to complete mineralization. Hence the effluent was subjected to photocatalytic degradation at different initial pH values. Adjustment of pH was done by adding suitable amount of 0.02N H_2SO_4 or 0.02N NaOH solution. The final pH of the solution as well as the percentage of COD reduction was determined after the treatment. The results of the study are presented in Table 2.

It is revealed from the experimental results that when the photocatalytic treatment is carried out at an initial pH of 8.5, the final pH obtained after the treatment is 7.2 and the percentage of COD reduction at this pH is 83%. This shows that the water after the photocatalytic treatment can directly be subjected to the biodegradation so that further mineralization can take place. The other pH values, especially in the alkaline range, also respond to good degradation rates. In fact highest COD reduction is achieved during the degradation at the initial pH of 10.8 and the final pH of the treated solution in this case is 8.2. But, since the final pH of the treated effluent is vital in case of photocatalytic treatment so as to facilitate effective biological treatment at the subsequent stage, treatment at the initial pH of 8.5 appears to be suitable for the effluent.

3.5 Effect of Addition of H_2O_2

Another important parameter which affects the degradation of wastewater significantly is the amount of H_2O_2

Table 2. Change in pH and COD Reduction of the Effluent after Photocatalytic Treatment at different initial pH

pH before treatment	pH after treatment	Percentage of COD reduction aftertreatment
4.0	6.7	73
5.5	6.9	78
7.0	8.4	83
8.5	7.2	83
10	8.3	85
10.8	8.2	86

added. Therefore experiments were conducted to study the effect of H_2O_2 on the degradation of the effluent so as to determine the optimum H_2O_2 concentration for the effective degradation to take place. The results of the experiments performed by adding varying the amount of hydrogen peroxide from 0.5 to 3.0 ml/L of the effluent are presented in Fig. 4. The best results are obtained when the amount of H_2O_2 addition is 2.0 ml/L. The percentage degradation of the effluent containing 5 gm/L of TiO_2 at the initial pH of 8.5 increases gradually as the amount of H_2O_2 added is increased. In the absence of H_2O_2 the final COD of the effluent is 111 mg/L accounting for 83% degradation. The COD reduction percentage increases with the added H_2O_2 and reaches 88% when the amount of added H_2O_2 reaches 2.0 ml/L of the effluent. The final COD in the presence of 2.0 ml/L of H_2O_2 is 72 mg/L.When 3.0 ml/L of H_2O_2 is added the extent COD reduction decreases to 87.5%. Hence 2.0 ml/L can be considered as the optimum amount of H_2O_2 required for the effective degradation of the dye effluent by the addition of 5 g/L of TiO_2 at the pH 8.5.

3.6 Characteristics of the Effluent and Absorption Spectrum after Photodegradation

The reaction conditions were optimized for the degradation of the effluent so as to maximise the economic benefits of the process. The characteristics of the effluent after the photocatalytic degradation using TiO_2 photocatalyst under UV irradiation were determined and the results are shown in Table 3.

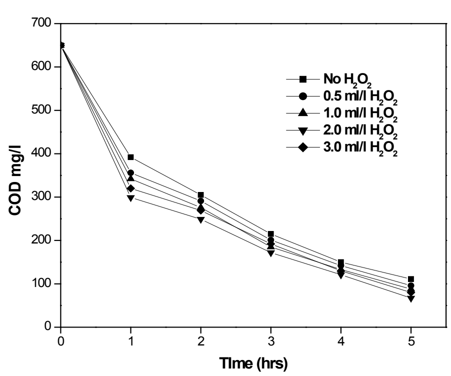

Fig. 4. Effect of addition of H_2O_2 on the degradation of the effluent.

Table 3. Characteristics of the effluent before and after treatment

Characteristics	Before treatment (mg/L)	After treatment (mg/L)
COD	650-700	80-90
Total Solids	4419	1853
Total suspended solids	284	0
TotalDissolved Solids	4135	1853
pH	10.8	7.2
BOD_5/COD	0.2 – 0.25	0.8 – 0.9

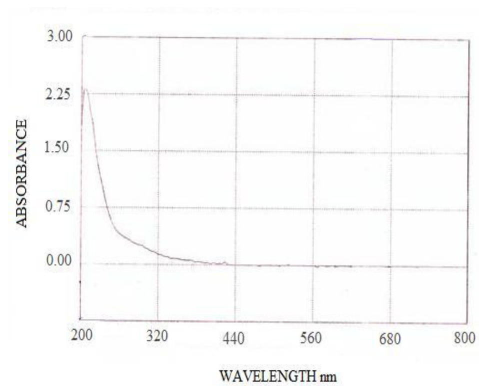

Fig. 5. Absorption Spectrum of the effluent after photocatalytic treatment.

The ratio of BOD_5/COD in wastewater is generally indicates the extent to which the wastewater is biodegradability. BOD_5/CODvalue greater than 0.3 indicates that the wastewater is of good biodegradability. If the ratio is less than 0.3, then it is not easily biodegraded [12]. The characteristics of the effluent before the photocatalytic treatment and after the treatment as given in Table 3 show that the COD value of the effluent decreases significantly after the treatment. Hence the BOD_5/COD ratio increases from 0.2-0.23 to 0.8-0.9. This clearly suggests that the textile effluent which was initially non-biodegradable becomes biodegradable after the photocatalytic treatment.

The UV-Vis spectrum of the effluent after the photo catalytic degradation under irradiation of UV light is shown in Fig.5. The peaks corresponding to the dyes have vanished during the photocatalytic process indicating the complete degradation of the dyes. Moreover, no new absorption bands especially those of aromatic species or other similar intermediates appear in either the visible or ultraviolet regions.

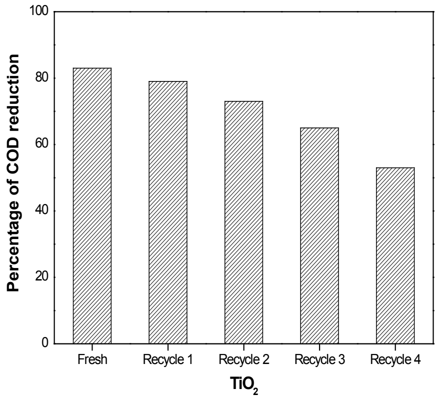

Fig. 6. Recyclability of TiO_2 for the degradation of the effluent.

This shows the complete mineralisation of the dyes and their intermediates by the photocatalytic degradation.

3.7 Effect of Recycling of TiO_2

The lifetime of the catalyst is a crucial parameter of the photocatalytic process. This is because the use of catalyst for a longer period leads to a considerable reduction in the cost of the treatment. To determine the efficiency with which TiO_2 can be recycled for the treatment of the effluent, the catalyst after use was recovered by filtration and activated at 100°C and used again. The results of the experiments on the recyclability of the catalyst using 5 gm/L of the catalyst at pH 8.5 are shown in Fig. 6. It shows that TiO_2 can be recycled effectively. Though the extent of COD reduction decreases on successive reuse of the catalyst significant COD reduction of 52% was observed in the 4^{th} time reuse also. The efficiency of the catalyst is decreased by 37% on repeated reuse for four times.

4. Conclusion

The results of the present study show that heterogeneous photocatalytic treatment of the textile industry effluent can be efficiently carried out using TiO_2 as photocatalyst under UV irradiation. The degradation rate depends upon the process parameters like catalyst concentration and pH. Maximum degradation is observed at an optimum catalyst dose 5/l. To facilitate effective biological treatment of the effluent at the subsequent stage, photocatalytic treatment at the initial pH of 8.5 appears to be suitable for the effluent and significant COD reduction of 83% is also achieved at this range. The COD reduction percentage increases with the added H_2O_2 and reaches 88% when the amount of added H_2O_2 reaches 2.0 ml/L of the effluent. Studies on recyclability of the catalyst confirm that it could be reused for 4 times, though with decreased efficiency thereby increasing the economic viability of the process.

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6. References

1. Prevot A.B., Baiocchi C., Brussino M.C., Pramauro E., Savarino P., Augugliaro V., "Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO_2 suspension", *Environ. Sci. Technol,* vol. 35, p. 971–976, 2001.
2. Vinodgopal K., Kamat P.V.,"Photochemistry of textile azo dyes. Spectral characterization of excited state reduced and oxidized forms of acid orange 7", *Photochem Photobiol A: Chem.,* vol. 83, p. 141–146, 1994.
3. Hachem C., Bocquillon F., Zaharaa O., Bouchy M., "Decolorization of textile industry wastewater by the photocatalytic degradation process", *Dyes Pigments,* vol. 49, p. 117–125, 2001.
4. Konstantinou I.K., Albanis T.A., "TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review", *Appl.Catal. B: Environ*., vol. 49, p. 1–14.
5. Poulios I., Aetopoulou I., "Photocatalytic Degradation of the Textile Dye Reactive Orange 16 in the Presence of TiO_2 Suspensions", *Environ. Technol*., vol. 20, p. 479–488,1999.
6. Epling G.A., Lin C., "Photoassisted bleaching of dyes utilizing TiO_2 and visible light", *Chemosphere*, vol. 46, pp. 561–570, 2002.
7. Tang W.Z., Zhang Z., An H., Quintana M.O., Torres D.F., "TiO_2/UV Photodegradation of Azo Dyes in Aqueous Solutions", *Environ Technol*., vol. 18, p. 1–12,1997.
8. KavithaS. K., Palanisamy P.N., "Photocatalytic degradation of Vat yellow 4 under UV/TiO_2", *Modern Applied Sci*., vol.4, p. 90–142, 2010.
9. Neppolian B., Choi H.C., Sakthivel S., Arabindoo B., Murugesan V., "Solar light induced and TiO_2 assisted degradation of textile dye Reactive Blue 4", *Chemosphere*, vol. 46, p. 1173–1181, 2002.

10. Arslan I., Balcioglu I.A., Tuhkanen T., Bahnemann D. "H_2O_2 /UV-C and Fe^{2+}/ H_2O_2/UV-C versus TiO_2/UV-A treatment for reactive dye wastewater", *J. Environ. Engg.*, vol. 126, p. 903–911, 2000.
11. Bahnemann D.W., Cunningham J., Fox M.A., Pelizzetti E., Pichat P., Serpone N., Helz G.R., Zepp R.G., Crosby D.G., *Acquatic and Surface Photochemistry*, CRC Press, Boca Raton, Florida, p. 261–316, 1994.
12. Chun H., Yizhong W., "Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastewater", *Chemosphere*, vol. 39(12), p. 2107–2115, 1999.