International Journal of Architectural, Civil and Construction Sciences
ISSN: 2415-1734
Vol:2, No:1, 2008

Photocatalytic Detoxification Method for Zero Effluent Discharge in Dairy Industry : Effect of Operational Parameters

Janhavi Inamdar and S.K. Singh

***Abstract*—**Laboratory experiments have been performed to investigate photocatalytic detoxification by using TiO_2 photocatalyst for treating dairy effluent. Various operational parameters such as catalyst concentration, initial concentration, angle of tilt of solar flat plate reactor and flow rate were investigated. Results indicated that the photocatalytic detoxification process can efficiently treat dairy effluent. Experimental runs with dairy wastewater can be used to identify the optimum operational parameters to perform wastewater degradation on large scale for recycling purpose. Also effect of two different types of reactors on degradation process was analyzed.

***Keywords*—**Photocatalytic detoxification, TiO_2 photocatalyst, Solar flat plate reactor, Zero effluent discharge.

I. INTRODUCTION

A. Zero Effluent Discharge: To cater to increased water demand due to urbanization & industrialization, reduced rain falls, increase in standard of living, depletion in natural water resources, water recycling is necessary which is known as zero effluent discharge. Zero effluent discharge reduces the water pollution also by following ways. a) Disposal of inadequately cleaned waste water contaminates other fresh water resources. b) The waste water generating company will recycle water properly only if they are forced to generate their fresh water resource from the waste water generated by them. c) It is economical to use recycled water than to pay for consuming fresh water & wasting waste water.

Water is scarce due to clustering of industries in the industrial belts. Hence the existing water supplies must be used frugally and any effluents must not be allowed to pollute the exiting water sources. The users are becoming more demanding for an unpolluted environment [1].

Dairy industry produces milk, milk products like butter, cheese, condensed milk and ice creams. Dairy effluent is white in color and mostly alkaline in nature. It has very high Biochemical Oxygen Demand (BOD) value but low Chemical oxygen Demand (COD). Dairy effluent decomposes rapidly and depletes dissolved oxygen of receiving streams, resulting in anaerobic conditions and release of strong foul odors. Due to this flies and mosquitoes increase and also toxicity increases.

B. Conventional Treatment of dairy effluent: As evident from the low COD: BOD ratio, Dairy wastes can be treated efficiently by biological processes and also because it contains nutrients for micro-organisms in sufficient quantities. Biological treatments like Activated sludge process (ASP) and Trickling Filter (TF) requires economy while oxidation ditch, aerated lagoon, stabilization ponds are low cost. These conventional treatment methods do not degrade the effluent up to the limit it can be recycled and also require detention time of several days. However Photocatalytic detoxification is a process where a semiconductor upon adsorption of a photon acts as a catalyst in producing reactive radicals, mainly hydroxyl radicals, which in turn can oxidize organic compounds and totally neutralize them. It completely destroys the organic and inorganic compounds in the water instead of simply removing or displacing them. Since the Photocatalytic Detoxification process is driven by light, outdoor facilities can be constructed that make use of a free source of energy supplied by the sun. The combination of light and catalysts has proven very effective for water purification. Photocatalytic oxidation, using solar energy as a photon source, was demonstrated in the mid-1980s by Ahmed and Ollis [2]. The use of solar radiation for the photocatalytic oxidation of organic contaminants in waste water is fast developing application [3-6]. In some cases, such as, removal of color and reduction of chemical oxygen demand (COD) in industrial wastewater, photocatalytic oxidation may be the only environmentally benign, effective treatment available [7]. There are two types of reactor designs generally used for photocatalytic detoxification method – Concentrating and Nonconcentrating. Nonconcentrating solar reactors make use of both direct and diffuse components of solar ultraviolet radiation and have the potential for low cost development and greater efficiency [8-10]. So flat plate reactor was used for experiments as it utilizes both direct and diffuse radiation. It is simple in design and easy to maintain.

This paper explores the feasibility of using Solar Flat

J.I. Professor, Department of Civil Engineering, Sinhgad Institute of Technology, Lonavala, Pune-410401, India. Tel.: +912114304355; Fax: +912114280210, Email-id:- janhavi3127@rediffmail.com

S.K.S. Professor & Head of department, Delhi College of Engineering, New Delhi, India, Email:- sksingh@email.com

Plate Reactor (SFPR) for treating dairy effluent by photocatalytic detoxification. Various operational parameters affecting the degradation such as catalyst concentration, initial concentration of effluent, angle of tilt of SFPR and flow rate were investigated.

C. Theory of Solar photocatalytic Detoxification: Many semiconductors like TiO_2, ZnO, CdS, etc., have been employed as photocatalysts. TiO_2 is most preferred one due to its chemical and biological inertness, high photocatalytic activity, photodurability, mechanical robustness and cheapness. Of all the commercial sources of TiO_2, Degussa P25 TiO_2 has become widely recognized as the 'gold-standard', due to its high specific surface area (typically 50 $m^2 g^{-1}$) and photocatalytic activity [11]. When a photon with an energy equal to or more than the band gap of TiO_2 is absorbed on its surface, it causes excitation of an electron from the valence band (vb) to conduction band (cb), forming a 'positive hole' in the valence band and valence band holes can then migrate to the surface and participate in interfacial oxidation-reduction reactions. The oxidative degradation of an organic pollutant is attributed to indirect reaction at the positive hole where adsorbed water or hydroxyl groups are oxidized to hydroxyl radicals (*OH), which then react with the pollutant molecule [12].

D. Kinetic Model: Factors affecting degradation are dosage of catalyst, flow rates, UV radiation intensity, tilted angle of the reactor. Among all other kinetic models, Langmuir- Hinshelwood (L-H) kinetics seems to describe many of the reactions well. [13-15].

The rate of destruction is given by

$$C = C_0 e^{-kt} \quad (1)$$

where C - solute concentration at time t, C_0 - initial solute concentration, k—the apparent reaction rate constant, t—solar exposure time

$$C/C_0 = e^{-kt}$$
$$\ln C/C_0 = -kt$$
$$k = \frac{\ln C/Co}{t}$$

The degradation process monitored follows approximately pseudo first-order kinetics according to the Langmuir–Hinshelwood model [16,17,18].The photocatalytic oxidation process with a Solar Flat Plate Reactor (SFPR) was found to be effective in degradation process. This study confirms that first-order kinetics is adequate for a simplified characterization of this process in engineering applications [19].

II. EXPERIMENTAL

A. Materials

The titanium dioxide powder used for measurements was Degussa TiO_2 (P25) powder specified as having 80/20 anatase/rutile composition, primary particle size~ 30 nm and BET surface area 50 m^2g^{-1}.Effluent from Katraj Dairy industry, Pune was collected after secondary and tertiary stages of treatment.

B. Preparation of SFPR and Shallow Solar Pond Reactor (SSPR)

Two different types of nonconcentrating photoreactors have been fabricated and tested over a range of operational parameters. Solar Flat Plate Reactor (SFPR) was designed, developed and used for investigations is shown schematically in Fig.1 and shallow solar pond reactor (SSPR) is shown schematically in Fig.2

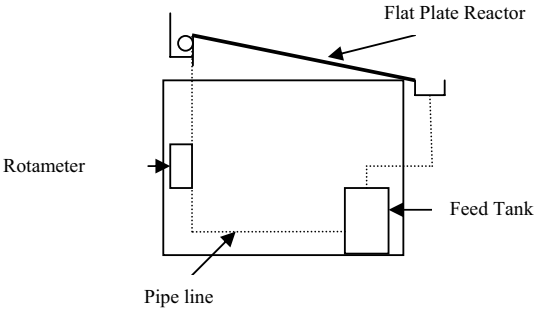

Fig. 1: Schematic diagram of solar flat plate reactor

The SFPR reactor size was 1000 mm x 750 mm. A feed tank size (320mm x 320mm x 260mm) of 26.624 l capacity was used to store effluent and mix the photocatalyst TiO_2 by a circulation pump. The feed tank was left open to the atmosphere and it was continuously stirred by pump to get air dissolved in aqueous TiO_2 dispersion. Oxygen is a necessary agent for the heterogeneous photocatalytic reaction because it suppresses the recombination of photogenerated electrons (e^-) and holes (h^+). A sufficiently high dissolved oxygen concentration level in the photoreactor renders the photocatalytic reaction more effective and the kinetics more favorable.[20]

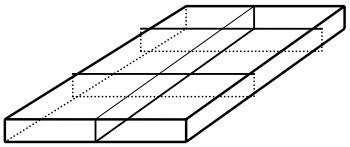

Fig. 2: Schematic diagram of shallow solar pond reactor

The SSPR reactor size was 90cm x 60 cm x 6 cm having six separate compartments for testing the wastewater for various depths and catalyst concentrations.

C. Method

The dairy effluent was stored in a feed tank in which a

catalyst TiO_2 powder (P25 Degussa) was mixed in slurry mode in varying proportions of 0.5 gm/l, 1gm/l, 2gm/l, 3gm/l. TiO_2 was used as slurry type instead of fixed mode type even if slurry type faces problem of removal of catalyst because slurry type is more efficient for bacterial inactivation. J.F.Klausner tested by using slurry type TiO_2 catalyst and as fixed catalyst mode on fiberglass mesh and found reaction rate constants for fixed catalyst mode were typically 50% lower than the 0.1 % TiO_2 slurry results [21].

Readings were taken at different retention time from 1 hour to 4 hrs. The tests were started one hour prior to the solar noon and lasted for four hours. Some sample was taken out for testing after stipulated time and tested for Chemical Oxygen Demand (COD) and was measured by reflux method titrating against FAS solution. The photoreactor faces south and in addition, as the angle between the horizontal and the reactor plate can affect the amount of solar radiation received, the angle was taken as constant 25^0 from the horizontal. A flow meter (Rotameter -Eureka Company to measure flow rate from 0 to 100 L/h) was used to record the system flow rate. The flow rate was taken as 60 l/h and pH 6.5. The fluid was pumped into the reactor where it formed a thin layer so that the fluid comes in contact with the solar radiation and this partially treated water coming out of the reactor is mixed with the water in the tank. The process continues until the mixed concentration in the tank reaches an acceptable level. A complete description was previously reported by Wyness [8].

To determine the optimum proportion of catalyst concentration, the graph of COD v/s degradation time was plotted. Similarly by keeping all other parameters same, effect of one parameter was studied. Thus the effect of initial concentration of effluent, effect of angle of tilt of SFPR, effect of flow rate i.e. depth of water on degradation was investigated. For analyzing the effect of initial concentration, dairy effluent after secondary and tertiary stages was taken for experiments and was tested for Biochemical Oxygen Demand (BOD) and COD by Winkler's Iodite Azide method and reflux method respectively.

III. RESULTS AND DISCUSSION

The effect of operational parameters, including catalyst concentration, initial concentration, angle of tilt of flat plate reactor and flow rate was examined using SFPR and adopting the procedures described above.

A. Effect of catalyst concentration on photocatalytic degradation of dairy effluent

To investigate the effect of catalyst concentration, employing commercial TiO_2 (Degussa P25), in which photocatalyst loading in the dispersion was varied between 0.5 gm/l to 3 gm/l. Results obtained are presented in Fig. 3.

It is observed that irradiation time required for degradation of effluent decreases with increasing catalyst concentration, until 1gm/l. Further increase in catalyst concentration decreases the degradation rate. This behavior is due to effect caused by the suspended TiO_2 particles closer to radiation, which reduce the penetration of light. Obviously the effect becomes more pronounced as the photocatalyst concentration increases. So optimum dosage of catalyst found out was 1gm/l i.e. (0.1 %).

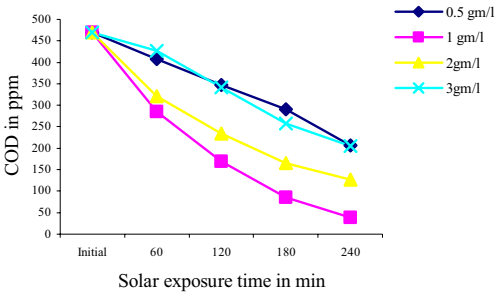

Fig. 3: Effect of catalyst concentration on degradation of dairy effluent at Initial concentration= 470 ppm, Angle of tilt =25 degree, Discharge = 60 l/h, pH=6.5, Catalyst :-P25 Degussa TiO_2, Direction of solar flat plate reactor: - South

B Effect of Initial concentration on photocatalytic degradation of dairy effluent

The influence of the initial concentration on degradation of dairy effluent is presented in Fig. 4 where both the parameters BOD and COD were plotted as a function of time of irradiation. The initial concentration was 1250 ppm for effluent collected after secondary treatment and concentration was 325 ppm for effluent collected after tertiary treatment.

It can be studied from the graphs in Fig. 4 and Fig. 5; effluent after tertiary treatment has undergone almost complete degradation in only 12 hours of solar exposure which corresponds to 2 days of solar exposure which shows this water can be recycled in the dairy industry. Even for effluent after secondary stage of treatment as seen in Fig 4 the COD values dropped down from 1200+ ppm to 200+ ppm in only 2 days. It can further drop down if circulated on SFPR for more no of days. This method gives better results at low initial concentration i.e. after tertiary treatment. This was because at higher initial concentration, the organic molecules obstruct the penetration of light.

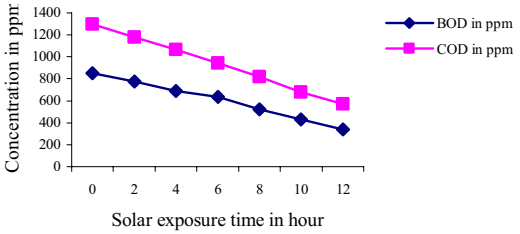

Fig. 4: Effect of Initial concentration on degradation of dairy effluent after secondary stage. At Catalyst concentration= 1 gm/l, Angle of tilt =25 degree, Discharge = 60 l/h, pH=6.5, Catalyst:-P-25 Degussa TiO_2, Direction of solar flat plate reactor:- South

Laboratory studies of the TiO_2 catalyzed photodegradation

of phenol showed a similar decrease in the apparent first-order reaction rate constant as the initial concentration of phenol increased [22].

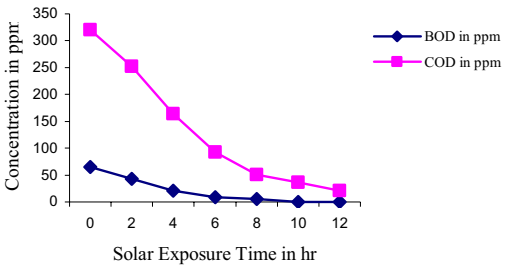

Fig. 5: Effect of Initial concentration on degradation of dairy effluent after tertiary stage. At Catalyst concentration= 1 gm/l, Angle of tilt =25 degree, Discharge = 60 l/h, pH=6.5, Catalyst: - P-25 Degussa TiO_2, Direction of solar flat plate reactor:- South,

C. *Effect of angle of tilt of solar flat plate reactor on degradation dairy effluent*

Solar irradiation received by SFPR depends on the angle of tilt. To investigate this, experimental results are plotted for 15^0, 25^0, 35^0, 45^0 angle of tilt in Fig. 6. The figure indicates that although very little effect on degradation was observed due to change of angle of tilt, the optimum angle of tilt found was 25^0 which is near about to the latitude of the place of experiment.

D. Effect of flow rate on photocatalytic degradation of dairy effluent.

It was tested by taking flow rate from 30 l/h to 90 l/h and the results are shown in Fig 7.The film thickness in the reactor is more for more flow rate. When the film is above certain thickness, only TiO_2 particles within the upper layer of liquid can receive photons. So the degradation is slower with increase in flow rate.

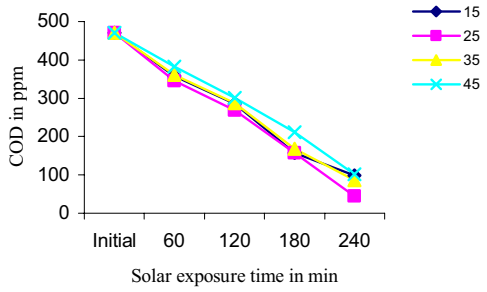

Fig. 6: Effect of angle of tilt of flat plate reactor on degradation of dairy effluent- At Initial concentration= 470 ppm, Catalyst concentration = 1gm/l, Discharge = 60 l/h, pH=6.5, Catalyst:-P25 Degussa TiO_2, Direction of solar flat plate reactor:- South

E. Effect of two different types of reactors on degradation of dairy effluent

To investigate the effect of reactor type, two types of reactors i.e. solar flat plate reactor shown in Fig. 1 and shallow solar pond reactor in Fig. 2 were experimented and the results are plotted in Fig. 8. The same solution was tested on two different reactor setups. First on Solar Flat Plate Reactor, second on shallow solar pond reactor having depth of water of 2 cm and third on the same as second but varying the depth to 4 cm. It was found from the graph that shallow solar pond having depth of 2 cm gives the best results. This may be because the length of the SFPR is comparatively small giving very less time for solar exposure to continue the photocatalytic reaction. In third case, depth being more, sun's radiation can not reach the bottom of reactor for photocatalytic reaction.

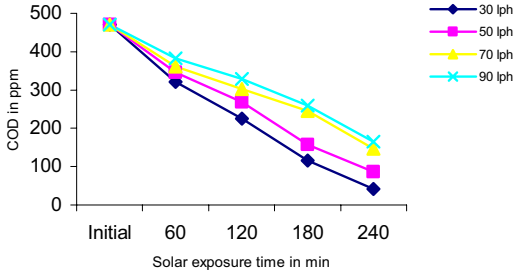

Fig. 7: Effect of flow rate on degradation of dairy effluent. At Initial concentration= 470 ppm, Angle of tilt =25 degree, Catalyst concentration =1gm/l, pH=6.5, Catalyst:-P-25 Degussa TiO_2, Direction of solar flat plate reactor:- South

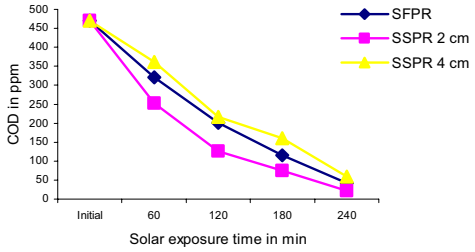

Fig. 8: Effect of two different types of reactors on degradation of dairy effluent. At Initial concentration= 470 ppm, Angle of tilt =25 degree, Catalyst concentration = 1gm/l, pH=6.5, discharge =60lph, Catalyst:-P-25 Degussa TiO_2, Direction of solar flat plate reactor:- South

IV. CONCLUSION

Photocatalytic Detoxification with the use of TiO_2 photocatalyst can be efficiently applied for degradation of dairy effluent. Complete degradation can be achieved with the use of optimal operational parameters. In particular following conclusions can be made from the experiments done in this study. Optimal catalyst concentration worked out as 1gm/l i.e. (0.1%). Complete degradation is observed for effluent at lower initial concentration i.e. after tertiary treatment so if photocatalytic detoxification is used after tertiary treatment zero effluent discharge can be achieved for dairy industry.

Optimal value of angle of tilt of solar flat plate reactor found out to be 25^0 which is near to the latitude of the place. It was revealed that the degradation is faster for low flow rates. Shallow solar pond reactor with 2 cm depth of effluent gave better results than Solar Flat plate Reactor.

REFERENCES

[1] C. A. Buckley, C. J. Broukaert and G.E. Rencken, "Waste Water Reuse ,The South African experience", *Water Science and Technology,* Vol.41: 10-11, 2000, pp. 157-163.

[2] S. Ahmed, D. F. Ollis, "Solar Photoassisted catalytic decomposition of the chlorinated hydrocarbons Trichloroethylene and Trichloromethane," *Solar Energy*, Vol.32 (5), 1984, pp.597-601.

[3] D. F. Ollis, E. Pelizzetti, N. Serpone, "Photocatalyzed destruction of water contaminants." *Environmental Science and Technology*, Vol. 35, 1991, pp. 971-976.

[4] K. Vinodgopal, I. Bedja, S. Hotchandani, P. V. Kamat, "A photocatalytic approach for the decolorization of textile azo dyes in colloidal semiconductor suspensions." *Langmuir*, Vol.10 (6), 1994, pp.1767-1771.

[5] D.Roche, K.Baskaran, "A preliminary investigation of colour removal from dyeing operation wastewater." *WaterTECH Conference*, 2000.

[6] Y. Zhang, G. Wang, L. Yang, "Photocatalytic oxidation of dye wastewater" *Fine Chemicals*, Vol. 17(2), 2000.

[7] D.Y.Goswami., 1997, "A Review of Engineering Developments of Aqueous Phase Solar Photocatalytic Detoxification and Disinfection Processes." *Journal of Solar Energy Engineering*, Vol. 119(2), 1997, pp.101-107.

[8] P. Wyness, J. F. Klausner, D. Y. Goswami, K. S. Schanze, "Performance of concentrating solar photocatalytic oxidation reactors, part 1: flat-plate configuration." *Journal of Solar Energy Engineering*, Vol.116, 1994, pp. 2-7

[9] M. March, A. Martin, C. Saltiel, (1995), "Performance Modeling of Nonconcentrating Solar Detoxification systems", *Solar Energy*, Vol.54 (3), 1995, pp. 143-151.

[10] R. F. P. Nogueira, W.F. Jardim,"TiO2-fixed-bed-reactor for water decontamination using solar light." *Solar Energy*, Vol. 56, 1996, pp.471-477.

[11] A. Mills, S. N. Elliott, I. P. Parkin, S.A. O'Neill, R.J.Clark, "Novel TiO2 CVD films for semiconductor photocatalysis" *Journal of Photochemistry Photobiology A: Chemistry.* Vol.151, 2002, pp.171-179.

[12] C. S Turchi, D.F.Ollis, "Photocatalytic Degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, *Journal of Catalysis*. Vol.122, 1990, pp. 178-192.

[13] C. S. Turchi, D.F.Ollis, "Mixed Reactant photocatalysis: Intermediates and Mutual Rate Inhibition," *Journal of Catalysis*, Vol. 119, 1989, pp. 483-496.

[14] M. Abdullah, G. Low, R.W. Matthews, "Effects of Common inorganic Anions on rates of Photocatalytic oxidation of Organic carbon over illuminated Titanium Dioxide," *Journal of Physical Chemistry*, Vol.94(17),1990, pp. 6820-6825.

[15] H. Al-Ekabi, N. Serpone, "Kinetic studies in Heterogeneous Photo-catalysis", *Langmuir*, Vol.5,1989, pp. 250-255.

[16] B. Pare, S.B. Jonnalagadda, H. Tomar, P. Singh, V.W. Bhagwat, "ZnO assisted photocatalytic degradation of cridine orange in aqueous solution using visible irradiation", *Desalination*, Vol. 232(1-3), 2008, pp. 80-90.

[17] S. D. Sharma, K.K. Saini, C. Kant, C.P. Sharma, S.C. Jain, "Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films" *Applied Catalysis B: Environmental,* Vol.84(1-2), 2008, pp. 233-240.

[18] C.H. Chiou, C.Y. Wu, R.S. Juang, "Photocatalytic degradation of phenol and m-nitrophenol using irradiated TiO2 in aqueous solutions" *Separation and Purification Technology*, Vol. 62(3), 2008, pp. 559-564.

[19] Linda Zou, Y. Li , E. Hu , "Photocatalytic Decolorization of Lanasol Blue CE Dye Solution Using a Flat Plate reactor" *Journal of Environmental Engineering ,* Vol. 131(1),2005, pp.102-107.

[20] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, H. Hidaka, N. Serpone, "Assessment and influence of operational parameters on the TiO_2 photocatalytic degradation of sodium benzene sulfonate under highly concentrated solar light illumination" *Solar Energy*, Vol. 71(5), 2001, pp. 305-313.

[21] J.F. Klausner, A. R. Martin, D.Y.Goswami, K.S. Schanze, "On the accurate determination of reaction rate constants in batch type solar photocatalytic oxidation facilities," *Journal of Solar Energy Engineering*, Vol.116 (1), 1994, pp.19-24.

[22] H. Al-Ekabi, N. Serpone, "Kinetic studies in Heterogeneous Photo-catalysis: 1. Photocatalytic Degradation of Chlorinated Phenols in Aerated Aqueous Solutions over TiO_2 Supported on a Glass Matrix," *Journal of Physical Chemistry*, Vol. 92, 1988, pp.5726-5731.