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TiO_2 as an Oxidant for Removal of Chemical Oxygen Demand from Sewage

Narendra Toke*, A. Oza, S. T. Ingale

School of Environmental & Earth Sciences, North Maharashtra University, Jalgaon, 425001

***Corresponding author: narendratoke@gmail.com**

Abstract:

Photo-catalysis of wastewater using titanium dioxide is an advanced oxidation process (AOP) for environmental remediation. Advanced Oxidation Process can mineralize a wide range of organic compound and convert it into carbon dioxide, water and inorganic ions. Recently Advanced Oxidation Process is an emerging technology for the water purification. Advanced Oxidation Process uses different type of oxidants. Titaniumdioxide has been widely studied on lab scale for decontamination of drinking water. This paper deals with the problem of water contamination due to the sewage and also relates with the photo-catalysis of sewage using titanium dioxide as an oxidant. Photo-catalysis of sewage is mainly depending on the oxidation reduction reaction. For the removal of organic waste form the sewage oxidation reduction reaction is used and this reaction is accelerated using titanium dioxide as a strong oxidizing agent. Changes in different physical and chemical characteristics of sewage after application of Advanced Oxidation Process were observed using titanium dioxide as a strong oxidizing agent. The photo catalysis of sewage has been studied for removal COD reduction. The influence of TiO_2 catalyst and pH on COD removal efficiency was recorded. Maximum COD removal of the sewage achieved was 78% after catalyst dosage of 0.25 g/50ml at alkaline pH 8 and at ambient temperature. Effective contact time is 50 minutes for 80% COD removal with optimum catalyst and pH. The photocatalytic degradation process using TiO_2 as an irradiation source showed potential application for the COD removal of the sewage.

Keywords: Advanced Oxidation Process (AOP), Sewage, Ttitanium dioxide, photocatalysis

1.0 Introduction:

Problem of the sewage and industrial discharges into the surface waters remains unsolved. Adverse effects of sewage contaminated water are normally chronic or fatal and are realized only after long exposures (John fawell *et.al.,*2003). Contamination of natural water bodies by sewage has become a major environmental as well as health issue. The sewage discharged from the domestic as well as commercial areas includes certain pollutants which may have the potential to accumulate in the ecological species (Subramani *et.al.,*2004). However, uncontrolled sewage production directly mix in the rivers and nalls and spoil the water quality of the same by changing the physical and biological parameters. Contamination of fresh surface water by sewage is non-controllable issue(Aboyeji *et.al.,* 2013). To overcome the problem of water pollution and water contamination researchers and scientist are always focusing on low cost and sustainable technologies (Willems *et.al.,*2005). Various physical and chemical techniques like coagulation, adsorption, chemical oxidation and froth flotation processes have been used for the removal of organics as well as inorganic from wastewaters(Bailey *et.al.,* 1999).As compared to other technologies photo catalysis is a well-established technique for pollutant degradation. Advanced Oxidation Processes (AOP) are of special interest for the treatment of water and wastewater due to their efficiency in mineralize a great variety of pollutants, including recalcitrant compounds, through the oxidation by generated hydroxyl radicals. AOPs are divided into homogeneous and heterogeneous systems in which hydroxyl radicals are generated with or without UV irradiation. Due to its high reactivity, hydroxyl radicals can react with a great variety of organic compounds (Lazar *et.al.,* 2012.,Jain *et.al.,* 2008).Photo catalytic detoxification has been focused as an alternative method to clean

up polluted water. This technique adopts the possibility of combining the heterogeneous catalysis with solar/UV light to achieve mineralization of toxic pollutants present in effluents. This technique appears to offer a great deal of hope in handling hazardous and toxic chemical wastes into harmless end-products at ambient temperature. Many catalysts like Titanium di-oxide. ZnO, WO_3, SnO_2, ZrO_2, CeO_2 and CdS have been attempted for the photo catalytic oxidation of water borne environmental contaminants. However, $Ti0_2$ has proved to be an excellent catalyst in the photo oxidation of many organic pollutants (Murugesan 2001)

This paper deals with the use of Advanced Oxidation Processes (AOP) using the well-known oxidant TiO_2 for the removal of COD from the sewage. Paper also focus on the optimized condition for use of TiO_2 with reference to catalyst dose, exposure time , optimum temperature and the pH for the better removal of inorganic contaminates and removal of Chemical Oxygen Demand (COD). Activation of TiO2 particles with photons of energy equal to, or greater than, the band gap energy results in the shifting of an electron from the valence band (vb) to the conduction band (cb) of the particle. The resulting output of this process is a formation of positive charge, hole (h^+), in the valence bond(vb) and a free electron (e^-) in the conduction band (cb). The reaction is as (Nor AqilahMohdFadzil*et al,*2013., Jain *et al.,* 2008).

$$TiO_2 + h\nu \longrightarrow TiO_2 (e^- cb + h^+ vb)$$

The mechanism of radical's generation (•OH and•$O2^-$) is presented as follows

$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+)$

$H_2O + TiO_2(h^+) \rightarrow TiO^2 + {}^{\bullet}OH + H^+$

$O_2 + TiO_2(e^-) \rightarrow TiO_2 + {}^{\bullet}O_2^-$

2.0 Material and Methods:

For the present study the photocatalystanatase titanium dioxide (325 mesh) were obtained from M/s Merck. For photocatalytic degradation, the powder was dried at 105^{o}C for an hour followed by experimental evaluation for optimization of the process parameters and efficiencies. Batch processes were used for the study. In batch experiments, known amounts of fresh effluents were taken in conical flasks and subjected to optimization of individual efficiency parameters such as pH, contact time, initial COD load, catalyst concentration and temperature. All laboratory reagents were of analytical grade. Study was carried out by equilibrating the effluents with the sorbent at different pH from 4 to 10. The pH was adjusted to the required range with HCl and/or NaOH using pH meter prior to the addition of sorbent. The experiments for sorption studies were performed in rotary shakers by varying desired parameter of study. The reaction mixture consisted of 100ml of fresh sewage collected from the study area having variable COD loads determined separately each time and a particular dose of adsorbent. The flasks were withdrawn from the shaker at different time intervals followed by adsorbent separation using membrane filtration/centrifugation and the COD was determined as per the APHA standard method of analysis.

Fig. 1. Experimental setup of sorption studies

Fig.2. Experimental setup for photo-catalysis studies

2.1 COD Reduction using photo catalytic oxidation with Titanium di-oxide

Photo catalysis is a mechanism in which pair of electron holes is generated on exposing the semiconducting material to particular wavelength. The chemical reactions that can happen in the presence of a semiconductor and light are collectively termed as photo catalytic reactions. Organic and inorganic contaminants can be mineralized by irradiation in presence of semiconductor, Titanium di-oxide. Photo catalytic detoxification has conducted as an alternative method to clean up polluted water due to the sewage. This technique works on the possibility of combining the different heterogeneous catalysis with different light source with different wavelength like solar/UV light to achieve mineralization of organic and inorganic pollutants present in effluents. Many catalysts like Titanium di-oxide, ZnO, WO_3, SnO_2, ZrO_2, CeO_2 and CdS have been attempted for the photo catalytic oxidation of water borne environmental contaminants.

Photo catalysis is a new technique, which has been successfully used to for removal of organic and inorganic compounds. Many researchers have been trying to use the photo catalytic dissociation of water borne environmental contaminants with different semiconductors employing different light source like solar/UV light. Titanium di-oxide is found to exhibit excellent photo catalytic activity in breaking down organic and inorganic compounds. Extensive research has been reported the ability of photo catalyst to promote the degradation and total mineralization of various organic and inorganic pollutants. The photo-generated holes are highly oxidizing and the photo-generated electrons are reducing enough to produce super oxide from oxygen. This oxidation and reduction procedure is used for the removal of organic and inorganic load which is due to sewage. Removal of Chemical Oxygen demand (COD) by photo catalysis works on the principal of oxidation and reduction of inorganic material by using TiO_2 as a catalyst. Conducted experiment evaluate the optimized condition for the maximum COD removal by varying pH, dose of TiO_2, Temperature and exposure time.

3.0 Result and Discussion:

Wastewater treatments has become an very expensive and time consuming process, to avoid this obstacles and get faster treatments scientists are engaged to develop new advanced process. Photocatalytic treatment for the sewage waste assisted by semiconductor based photocatalysts is well known and accepted method for the same.(Mils *et.al.,* 1997, Moshe *et al.,* 2009). The effect of photodegradation experimental factors on the removal of Chemical Oxygen Demand (COD) degradation in the sewage was studied using TiO_2 as photocatalyst. Experiment was designed with reference to similar work carried out by different scientist. Prime goal of the work was removal of COD from the sewage and develop a non-conventional method of sewage treatment which is economically viable and easily applicable to a wide range of organic loadings. Observed results in the reduction of COD at different condition are as follows.

3.1 Effect of Catalysts Concentration

For economic and fast degradation of pollutants from the municipal sewage water, it is necessary to find optimum amount of catalyst and find the efficiency with reference to catalyst load. The initial COD of the sewage sample was 204mg/l. The initial reaction rates were found to be directly proportional to catalyst mass. The optimum catalyst dosage required for maximum COD reduction for the effluents is found to be 2.5 g/50ml. However, above a certain value, i.e. 2.5 g/50ml, the reaction rate levels off and becomes independent of catalyst mass.

Table 1: **Effect of Catalyst Concentration on COD reduction**

Sr. No	TiO_2 Conc. (g/50 ml)	Final COD (mg/l)	%COD Reduction
1	0.5	189±4.35	7.13
2	1	165±4.35	19.27
3	1.5	136±4.94	33.34
4	2	61±2.64	69.8
5	2.5	44±3.53	78.00
6	3.0	46±3.46	77.6

(Values are ± Standard deviation of three estimations)

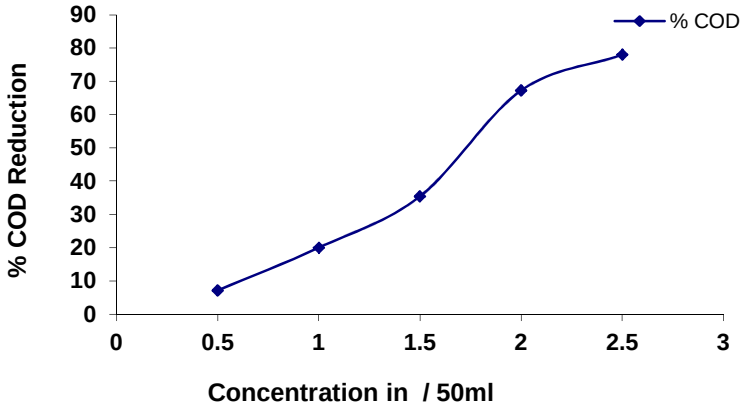

Fig. 3 Effect of Catalyst Concentration on COD reduction

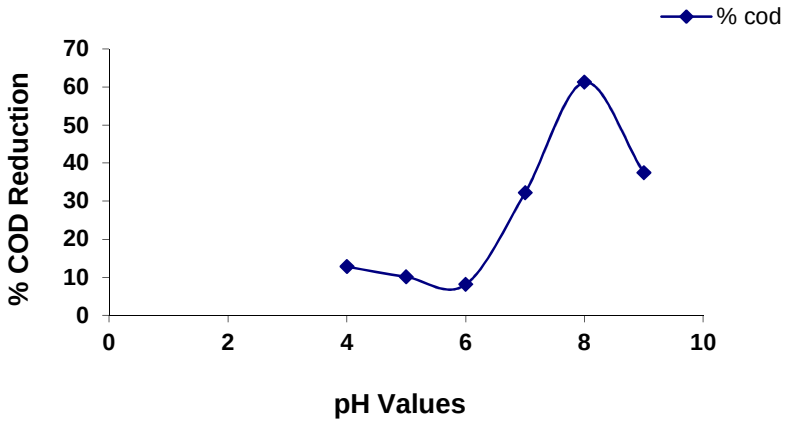

Fig. 4 Effect of pH on COD reduction

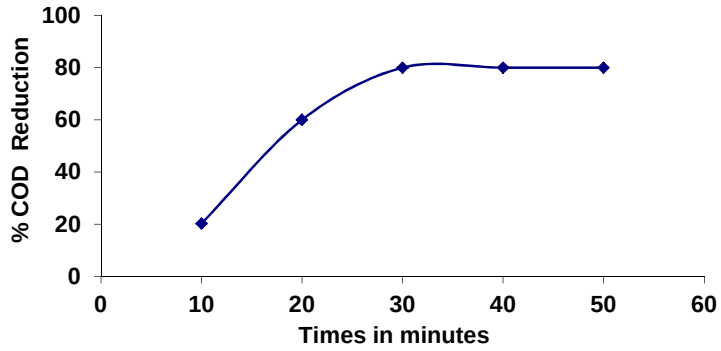

Fig. 5 Effect of contact time on COD reduction

3.2 Effect of pH

A common feature of Photo catalytic reactions occurring on metal oxide as a semiconductor powders suspended in aqueous solution is the weak dependence of the reaction on solution pH. The surface charge density distribution for these TiO_2 catalyst clusters is highly dependent on the operating pH (Kormann*et. al.,*1992). The particle size, surface charge and band edge positions of Titanium di-oxide are strongly influenced by pH (Siffert B *et. al.,*1992). The isoelectric point of Titanium di-oxide in water is about pH6 and positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH values. The COD reduction is found to be within the range of pH 7.2 to 7.8, however, Effect of pH on COD reduction is found to maximum at pH 7.9. A maximum COD reduction of 61% is achieved for colored effluent collected from the study area.

Table2: Effect of pH on COD reduction

Sr. No	TiO_2 Conc. (g/50 ml)	pH	%COD Reduction
1	0.5	4	12.79±0.55
2	1	5	10.1±0.36
3	1.5	6	8.11±0.22
4	2	7	32.2±1.96
5	2.5	8	61.23±1.13
6	3.0	9	37.43±1.32

(Values are ± Standard deviation of three estimations)

3.3 Effect of Contact Time

As noticed any absorption process is proportional to the contact time. Initially the COD reduction seems to be directly proportional to time. However, after a particular time, the system achieves a stationary phase, and any further increase in contact time does not affect the activity of Titanium di-oxide. The equilibrium time in case of effluents is found to be 30 minutes. The effect of contact time on the COD reduction for the effluents is presented in Table 3. The reason for such behavior is the saturation of the active groups on the surface. However, as the oxidation proceeds, less and less of the surface of the Titanium di-oxide particles are covered as the contaminant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photo catalytic rate is to be expected with increasing illumination time. This is confirmed from the gradual reduction in the COD reduction rate with increase in contact time.

Table 3: Effect of Contact Time on %COD reduction

Sr. No	TiO_2 Conc. (g/50 ml)	Contact Time	%COD Reduction
1	0.5	10	15±2.0
2	1	20	23±3.24
3	1.5	30	80±2.0
4	2	40	80±2.0
5	2.5	**50**	**80**±2.0
6	3.0	60	78±2.0

(Values are ± Standard deviation of three estimations)

3.3 Effect of Temperature

Like most photoreactions, photo catalytic reactions are not dramatically sensitive to minor variations in temperature. It has been reported that the rate of photo assisted decomposition of aliphatic alcohols was insensitive to temperature variation (Pichat *et.al.,* 1982). As a consequence, the optimum reaction temperature for photo-mineralization is reported to be in the range of 20-80^{0}C (Malato *et.al.,* 2009). As noted from the research the maximum demineralization of a pollutant occurs at normal temperature. The highest reduction in COD was found at Ambient Temperature. Due to photonic activation, the system does not require heating and hence operates at ambient temperature. The true activation energy is nil whereas the apparent activation energy is often very low (a few KJ/mol) in the medium temperature range. The activity is reported to be lowered at very low temperatures.

Table 4: Effect of Temp. on COD reduction

Sr. No	TiO_2 Conc. (g/50 ml)	Temp(^{o}C)	%COD Reduction
1	0.5	5	15±2.0
2	1	11-20	23±1.73
3	1.5	21-30	52±1.73
4	2	Ambient 30-35	79±2.64
5	2.5	Hot Water Bath 60	61±2.64

(Values are ± Standard deviation of three estimations)

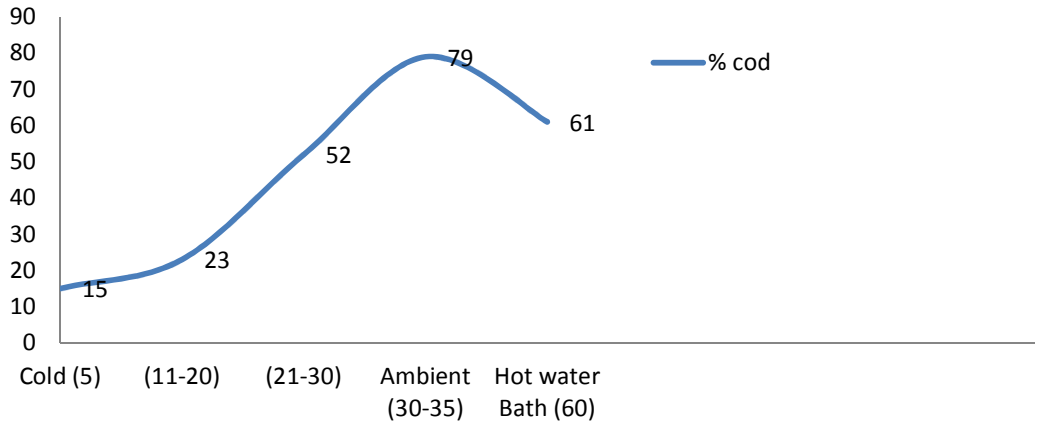

Fig. 6 Effect of temperature on COD reduction

A large number of studies have reported the effect of TiO_2 loadings on the process efficiency (Gaya *et. al.,*2008; Chong *et al.,* 2009,Yao-Hsuan*et al.,* 2006). These results are mostly independent and a direct comparison cannot be made, as the working geometry, radiation fluxes, intensity and wavelengths used were different. It was reported that the optimum catalyst loading for photo mineralization and photo-disinfection are varied.One of the most important features of photo catalysis, is that when it is used for the decontamination of water, intermediate products are generated which might behave differently depending upon pH concentration of the solution. It was also observed that Titanium di-oxide remained in dispersed phase in the effluents at pH 8.0. Thus, the reduction in COD at different pH is varying to great extent since the sewage subjected to Titanium di-oxide photo catalysis. Different study carried reveals that the photo-catalytic degradation of effluent increases with variation in pH i.e. from 8-12. In the instant study the highest COD reduction was observed at pH 8.0 (Shivaraju, 2011).The initial reaction rates were found to be directly proportional to catalyst mass. This is indicative of a truly heterogeneous regime. where the amount of TiO_2 is directly proportional to the overall photo catalytic reaction rate (Gaya *et.al.,* 2008).The same behavior is seen in case the present system under consideration. The increase in temperature increases the photo-catalytic degradation of a pollutant in the effluent is also revealed, during the study of decolorization of textile effluent, (F. H. Hussein,2010.,T. A. Abbas, 2010).Considering the above results and output from conducted work explain the optimum condition for the COD removal with variation in dose, pH, exposure time and temperature. This optimized condition will show the maximum COD removal in sewage as well as at industrial application level also.

4.0 Conclusion:

From the above study it can be concluded that the advanced oxidation process using Titanium di-oxide as photo catalyst seems to be very much economical, cost effective and moreover eco friendly in nature. The main photo catalytic oxidation process doesn't use any external energy source helpful in carbon footprint. The most impressive factor making the use of this system for application is the operation at ambient temperature. The optimum catalyst dosage required for maximum COD reduction for the effluents is found to be very less i.e. 5 mg/ml. However, above a certain value, i.e. 2.5 gm/50ml, the reaction rate levels off and becomes independent of catalyst mass. The COD reduction is found to be within the range of pH 7.2 to 7.8, however, Effect of pH on COD reduction is found to maximum at pH 8.0. One of the most important features of photo catalysis, is that when it is used for the decontamination of water, intermediate products are generated which might behave differently depending upon pH concentration of the solution. It was also observed that Titanium di-oxide remained in dispersed phase in the effluents at pH 8.0. Thus, the reduction in COD at different pH is varying to great extent since the sewage subjected to Titanium di-oxide photo catalysis. As noticed any absorption process is proportional to the contact time. Initially the COD reduction seems to be directly proportional to time. However, after a particular

time, the system achieves a stationary phase, and any further increase in contact time does not affect the activity of Titanium di-oxide.

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