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Oxidation of total organic content in lake water samples: A case study

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ABSTRACT

The oxidation of total organic content (TOC) present in the two selected Bangalore city lake (Medahalli and Ulsoor lakes) water samples at two different seasons of the year 2010 using photocatalyst TiO_2 as been studied. The different forms of TiO_2 such as natase, rutile and mixed form (Degussa P25) are used for the study. The mixed form (mixture of natase and rutile) has given better results in photooxidation than the individual TiO_2 forms. The oxidation of these pollutants present in the wastewater will be oxidized by photo/ photocatalysis and the extent of contamination and oxidation are measured by COD and BOD tests. The photooxidation studies were made under natural sun light illumination. The efficiency and the rate constants for the oxidation of TOC are calculated and presented. The TOC oxidation reactions are found to follow first order kinetics. The rate constants for photocatalytic oxidation of TOC of the Medahalli lake samples of June and December months are 0.333 and 0.49 (x 10^{-4} s^{-1}) and for Ulsoor lake samples are 0.52 and 0.666 (x 10^{-4} s^{-1}) respectively.

KEYWORDS

Photooxidation;
TiO_2;
BOD;
COD;
Lakewater contaminants.

INTRODUCTION

Degradation of waste water contaminants of urban water bodies or outside (rural /natural) water bodies is one of the challenging areas of the environmental pollution control as our hydrosphere is getting contaminated with significantly high concentrations of various chemicals. These chemicals may include the pesticides domestic or agricultural use, dyes used in domestic and textile fabrics, laboratory reagents, etc. Many of these chemicals persist for long periods causing contamination of water, soil and air environment. However these chemicals are mostly the organic compounds. Many of these are highly toxic, carcinogenic, mutagenic etc. The contamination of water by these chemicals has become a major and serious problem globally and removal of these contaminants has become very challenging.

There are several techniques of removal of contaminants from the water[1-4] and some of them are found to be inefficient procedures. Biological oxygen demand (BOD) and the chemical oxygen demand (COD)[5-7] are among the waste water quality indicators, which are essentially laboratory tests to determine the pollutant content. Any oxidizable material present in a natural waterway or in an industrial or wastewater will be oxidized both by biochemical (bacterial) or chemical processes. Recent developments in the domain of chemical water treatment have led to improved oxidative degradation procedures, which are generally referred to as advanced oxidation processes (AOP). Among AOP the photooxidation has attracted much attention for the degradation of large variety and organic pollutants in contaminated water[8-11]. Photooxidation is that uses the energy in the form of light to destroy environmental contaminants, applicable as both a waste clean-up and a pollution control technique.

In photocatalysis TiO_2 based catalysts are widely used[8-11]. A wide range of photo efficiencies are observed among various TiO_2 phases and formulations. Studies have shown that mixtures of anatase and rutile TiO_2 perform better than either individual rutile or anatase phases of TiO_2[12] and the high photoactivity is reported in some mixed-phase TiO_2 preparations such as Degussa P25. The commercial Degussa P25 TiO_2 contains 80 to 90% of anatase and 10 to 20% of the rutile[12]. The lower activity of pure-phase rutile is due in part to rapid rates of recombination. In mixed-phase $TiO_{2,}$ charges produced on rutile by visible light are stabilized through electron transfer to lower energy anatase lattice trapping sites. These results suggest that within mixed-phase titania (P25) there is a morphology of nanoclusters containing a typically small rutile crystallites interwoven with anatase crystallites. The transition points between these two phases allow for rapid electron transfer from rutile to anatase. Thus, rutile acts as an antenna to extend the photoactivity into visible wavelengths[13] and the structural arrangement of the similarly sized TiO_2 crystallites creates catalytic “hot spots” at the rutile-anatase interface. Hence the commercial Degussa P25 TiO_2 photocatalyst has been chosen for the photocatalytic oxidation study in order to compare with mere photooxidation and chemical oxidation.

The ideal photocatalyst should process the properties such as photoactivity, chemical and biological inertness, stability towards photo corrosion suitability towards visible or near uv, low cost, non-toxicity, etc.[14]. TiO_2 is known to have such excellent properties due to high ultraviolet absorption and photocatalytic degradation of chemicals in water and air[15-17]. Titanium dioxide has different crystallite forms and the most common forms are anatase & rutile. The third crystalline form is brookite which is un common and unstable. Anatase is the most stable form[18] which can be converted to rutile by heating to temperatures ~ 70 °C[19], the density of rutile is greater of about 4.26 gm/ml while anatase has density 3.9 gm/ml. In the photocatalysis applications it is known that, anatase is more efficient than rutile, having an open structure compared with rutile.

Degussa P25 is commercially available, consists of two forms of TiO_2 (closely approximating to 25 % rutile, 75% anatase)[20] and has been used in many studies of photocatalytic degradation. Studies employing P25 have been widely reported because of its chemical stability, ready availability, reproducibility and as a catalyst for oxidation processes[21] it also been suggested as a standard for such studies[22]. Intensive studies are in progress to develop the existing materials or prepare new materials which can be used under solar energy and hence shortening the time needed for degradation.

In the present work, the oxidation of total organic content (TOC) of the urban lake water contaminants by photooxidation and photocatalytic oxidation employing chemical oxygen demand (COD) and biological oxygen demand (BOD) measurement methods is discussed. The study also includes the oxidation of TOC by solar light irradiation and by an oxidizing agent and Microbes in the presence/absence of catalyst.

EXPERIMENTAL

Materials

The materials other than TiO_2 (anatase and rutile forms: surface area 49.5 m^2/g and 50 m^2/g respectively) such as Potassium dichromate, Ferrous ammonium sulphate (FAS), Silver sulphate, Mercuric sulphate, Hydrogen peroxide, H_2SO_4 and Ferroin indicator of Merck chemicals are used for this study. Degussa P-25 TiO_2 as supplied by the company has surface area of about 50 g /m^2 and anatase and rutile ratio is 4:1 (80%: 20%). The BOD test done with the natural population of microbes present in the respective lake water samples.

Analytical methods

Photo/photocatalytic oxidation procedures are employed to study the oxidation of pollutants in lake water under solar illumination. COD and BOD measurements are used as analytical methods to follow the degradation of lake water organic contaminants. The value of COD/BOD indicates the concentration of the organic carbon (OC) in the water sample. The decrease in COD values indicates the extent of degradation of OC under solar illumination.

Reactors

Photoreactor

The photoreactor unit consists of a glass reaction vessel of the circumference 34 cm of 1000 ml capacity which was mounted on a magnetic stirrer. It consists of the optical convergence lens of circumference of 34 cm which was fixed at the appropriate height in such a way that the entire area of the reaction vessel would focused by the sun light and it was maintained carefully throughout the experiment. The entire set up is encased with a cabinet allowing the sun light to fall directly o the lens.

COD reactor

A typical COD experimental setup consists of a round bottom flask fitted with reflux (water cooled) condenser. The heating was done using heating mantle.

BOD (Biological Oxygen demand) reaction setup

A typical BOD experimental setup includes the incubation of the sample for the determination of the BOD over 5 days period. The usual titrimetric method was adopted.

Analytical methods used

The oxidation methods such as COD, BOD, Photooxidation and photocatalytic oxidation (under solar light) are used in the present research. In addition, also the COD and BOD procedures are used as the analytical tools to ascertain the extent of contamination and the extent of organic compound oxidized and/ or the level of OC remained un-oxidized.

Experimental procedure

Photo/photocatalytic oxidation of TOC of the lake water samples have been investigated by solar light irradiation. The lake water samples of about 300 ml were kept under constant stirring during irradiation. The solar irradiation was performed between 11 am to 2 pm during June and December months in 2010. The experimental setup was made on the roof of the research lab in Bangalore, India. The latitude and longitude are 12.58 N and 77.38 E respectively. The average intensity of sunlight was around 1.16 x 10^3 W cm^{-2}. The solar light was concentrated by using convex lens and the reaction solution was exposed to this concentrated solar light. The samples for analysis were withdrawn before the start of irradiation and at 30, 60, 90 and 120 min during irradiation in about 30 ml quantities each time. The similar procedure was involved in photocatalysis, but in the presence of anatase, rutile and Degussa -25 TiO_2 photocatalysts. The samples from the photocatalysis were centrifuged to remove suspended photocatalyst. The process is largely followed by measuring COD of the solution and also BOD measurements. The COD determination, which involves the use of oxidizing agent such as potassium dichromate to oxidize the chemical in acidic aqueous medium. The other reagents such as silver sulfate as catalyst and mercury sulfate in order to avoid the formation of silver halide were added[5-7,23,24].

RESULTS AND DISCUSSION

Characteristics of water collected from lakes

The TABLE 1 gives the characteristics of the lake water samples as obtained from the lakes. These data show the physical contamination of the water which infers us the changes in the physical parameters of the lake waters with seasons. In the month of December

TABLE 1 : Physical properties of the lake water samples as observed and determined.

Physical properties	Medahalli lake		Ulsoor lake	
	June	December	June	December
Colour	Colorless	Greenish	Light Green	Greenish
Odour	Fishy odour	Fishy odour	Fishy Odour	Fishy odour
pH	7.5	7.6	7.2	7.4
Conductivity (mho /cm)	0.79	0.8	0.67	0.73
Density (kg /m^3)	0.99832	0.99922	0.99853	0.99948
COD (mg/l)	78.0	85.0	92.0	55.0
BOD (mg/l)	12.7	13.5	14.3	5.8

due to less raining, the water accumulation and concentration due to water evaporation takes place and the values of physical parameter increases when compared to month of June.

COD analysis of medahalli and ulsoor lake water

The extent of oxidation is followed by chemical oxygen demand (COD) measurements. The samples from photooxidation and photocatalytic oxidation experiments were subjected for COD measurements. In general the COD value indicates the extent of contamination by chemically oxidizable organic matter. In this study, it also implies the concentration or amount of organic contaminants (OC) oxidized. The general reaction of potassium dichromate with OC solution is given by:

$$C_xH_yZ_p + 2\ Cr_2O_7^{2-} + 2\ H_2SO_4\ CO_2 + 14H_2O + + 2Cr_2SO_4 \qquad (1)$$

The COD calculations are made using following relation:

$$COD = 8000\ (V_2 - V_1)\ N/\ V \qquad (2)$$

Where V_2 is the volume of FAS used in the blank sample, V_1 is the volume of FAS in the original sample, and N is the normality of FAS. If milliliters are used consistently for volume measurements, the result of the COD calculation is given in mg/L.

Contaminated water sample is oxidized by using a strong oxidizing agent, $K_2Cr_2O_3$. The COD values for water samples are determined. Oxidation of water sample was done with using two different catalysts and without catalyst. Initially COD values are recorded without catalyst and then with different catalysts. A COD value of a sample from the experiment without catalyst was compared with the COD value from the experiment with catalyst and found that there is a considerable change in it. The water sample was filtered to remove course material 25ml of water sample was taken in a COD reactor (round bottomed flask fitted a reflux condenser) and 10ml of 0.1m $K_2Cr_2O_7$, 10ml of 1:1 H_2SO_4 4-5 dps of indicator is added to it. Refluxed for about 2h and COD values were calculated.

On treating any particular waste water (of particular concentration) the COD should decrease[25]. Here COD test itself is considered as the chemical oxidation. However this method itself introduces lots of toxicants such as chromium ions, acid, etc. along with the degradation of OC. Hence a suitable environmental friendly method is essential for removal of water contaminants. In this regard photo oxidation by natural or artificial light irradiation is prominent and hence the experiments were performed as discussed in the experimental section.

First of all after sampling from the lakes the water was filtered to remove suspended coarse substance and the COD of the sample was determined. The Figure 1 depicts the COD values for the water samples from Medahalli Lake. The lake is situated somewhere outskirt at a distance of about 15 km from Bangalore city core towards east. It will receive the waters from various sources from the city at two different seasons. The COD values of sample, tested in the month of June 2010 is found to be less, on contrary the value for the sample tested in the month of December is found to be high. The reason could be the less contamination of water as the rain water enters the lake, which dilutes the water and fresh water sweeps the stagnant contaminated water where as in the month of December the rain was found to be less and the streams, drainages carrying the waste accumulate in the lake and the sample would get polluted since the lake is more open to receive the water from urban streams. Hence COD values are found to be high.

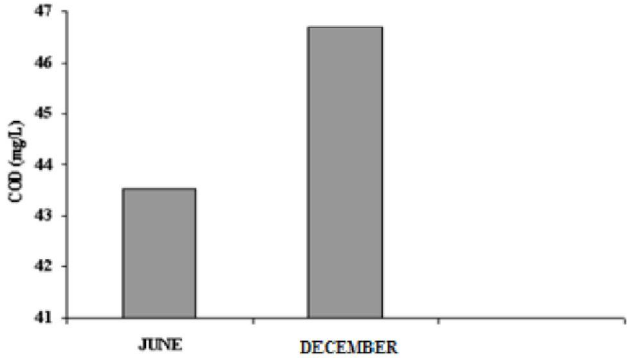

Figure 1 : Bar diagram of COD values (mg/L) versus sampling season for medahalli lake

The COD values are found to be in contrast with Ulsoor lake water (the lake is situated at core of city. It will receive only the rain washings in rainy season. The Lake is maintained by the concerned (corporate) authority. Figure 2 is the plot of COD values as a function of season in which the sample tested in the month of June is high compare to that for the Month of December. The run off waste waters, during the rainy seasons enters the lake and water gets more contaminated where as in the month of December since it receives no runoff water the contamination level is less and hence COD values are found to be high. However it is to be noted that the COD of both lake waters is found to be less, within the permissible limit as set by the Pollution Control Board.

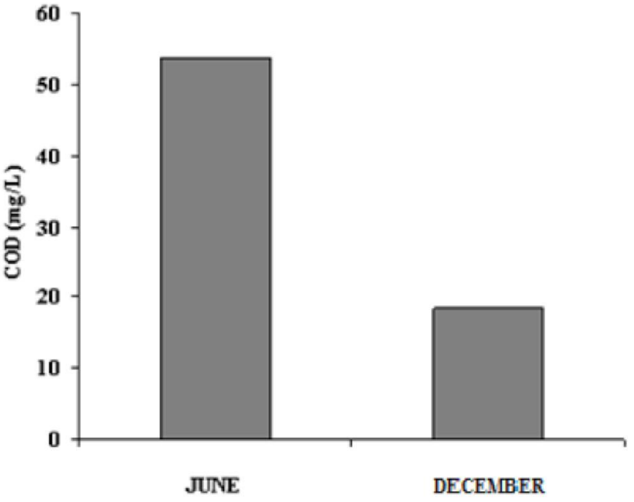

Figure 2 : Bar diagram of COD values (mg/L) versus sampling season for ulsoor lake.

BOD analysis of medahalli and ulsoor lake water

The BOD is an important measure of water quality. It is a measure of the amount of oxygen needed (in milligrams per liter or parts per million) by bacteria and other microorganisms to oxidize the organic matter present in a water sample over a period of 5 days. The so called BOD method of treatment is to allow the undissolved solids in raw sewage to settle out of suspension forming sludge. Such primary treatment removes only one-third of the BOD. In secondary treatment, the effluent is brought in contact with oxygen and aerobic microorganisms. They break down much of the organic matter to harmless substances such as carbon dioxide.

The BOD_5 Procedure includes the use of well cleaned 14 cleaned 300 mL BOD bottles for the test which were numbered. Each sample was prepared as a duplicate as the Winkler DO method[7]. Two of the bottles were used for the blank, six for the three different dilutions of the sample, two for a duplicate of one of the dilutions and two each for the G/GA (glucose-glutamic acid) and KHP (potassium hydrogen phthalate)[7]. The initial pH of each sample was recorded. Some dilution water to each BOD bottle was added, and then the necessary amount of well mixed sample using a serological pipette (with a wide opening tip) was withdrawn and the corresponding amount was recorded. Each bottle was filled to the top with dilution water and Stoppard so that no bubbles are visible in the sample. Each bottle was placed with a water seal and a plastic cap over the stopper.

One set of bottles were placed in the incubator in the dark for 5 days at 20 ± 1° C. The temperature, date and time of the beginning of the incubation were recorded. The DO on the duplicate set of bottles was with the Winkler titration[7] at the end of the incubation period, the temperature, date and time were recorded. The DO on each bottle was determined by Winkler titration the BOD for the samples were calculated.

To compare the COD value with BOD value, the solution was prepared with tap water, since the BOD experiment has to be carried out in the presence of microorganisms (which were present in the tap water). TABLE 2 shows the higher COD values for the samples collected in the month of June with Ulsoor lake and of December with Medahalli lakes. The BOD values are also in accordance with COD but they are found to be 6- 8 times lesser than the COD values as one can expect due to the limited capability of microorganisms in oxidizing pollutants and also may be due to insufficient population of microorganisms to oxidize the TOC. Hence the BOD experiments were performed by increasing the microbial concentration. This was done by adding the stored sump water of 25 ml to each bottle. The BOD values thus obtained are also tabulated in the TABLE 2.

TABLE 2 : COD and BOD values for the samples from ulsoor and medahalli lake in two different seasons (June and December 2010).

Test method	Ulsoor lake		Medahalli lake	
	June	December	June	December
COD (mg/L)	92.0	55.0	78.0	85.0
BOD (mg/L)	14.3	5.8	12.7	13.2
BOD (mg/L) (with increased Microbial Population)	45.2	17.4	40.6	47.5

Photocatalytic oxidation of lake water samples

A large variety of reactions can take place on the semiconductor surface under light illumination. Some of the commomon reactions are as given below.

$$TiO_2 + hv \longrightarrow e^-_{cb} + h^+_{vb} \qquad (3)$$

$$O_2 + e^-_{cb} \longrightarrow O_2^- \qquad (4)$$

$$H_2O + h^+_{vb} \longrightarrow OH^{\cdot} + H^+ \qquad (5)$$

The $OH^{\cdot}$ radicals formed on the illuminated semiconductor surface are very strong oxidizingagents with an oxidation potential of 2.8 V. These can easily attack adsorbed organic molecules or those located close to the surface of the catalyst mostly by hydrogen abstraction. This reaction generates the organic radicals, which by the addition of molecular oxygen yield peroxy radicals[26]. These intermediates initiate chain reactions of oxidative degradation leading finally to carbon dioxide and water as given in the following scheme.

$$OH^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O \qquad (6)$$

$$R^{\cdot} + O_2 \longrightarrow RO_2 \qquad (7)$$

$$OH^{\cdot} + RX \longrightarrow RX^{\cdot +} + H_2 \qquad (8)$$

The Lake water samples were filtered to remove course materials such as sticks, leaves, dung, paper, etc. About 300 ml of the water sample was taken in a glass photoreaction vessel. It was subjected to sunlight irradiation. The experiment was carried out in bright sunlight as discussed earlier. The samples were with drawn at 0, 30, 60, 90 and 120 minutes and they were subjected for COD analysis. Similar experiments were carried out with both the lake water samples. The COD values are tabulated in the TABLE 3. The COD values for Medahalli lake water without and with catalyst in the month of June decreases as we move from left to right as given in the TABLE 3. In case of photocatalyst TiO_2 and its different phases (anatase and rutile) the COD values decrease comparably whereas with Degussa P-25 TiO_2 the values decrease much faster when compare to the other cases and hence it implies that Degussa P-25 TiO_2 is a better photocatalyst when compared to other TiO_2 catalyst phases. Figure 3 is a plot of COD values versus irradiation time in which the line a represents that the COD values remains same even after 2h of irradiation, the line b shows the decrease in COD values and the line c represents the decrease of COD values faster than the lines a or b however the rate of decrease in COD values is much faster with the experiment with Degussa-P25 TiO_2 when compared to all the other experiments.

TABLE 3 : COD values for medahalli lake water without/ with catalyst the month of June

Irradiation Time in min	COD Values			
	Without catalyst	Rutile – TiO_2	Anatase-TiO_2	DegussaP25-TiO_2
0	78.0	78.0	78.0	78.0
15	77.4	75.1	72.2	70.8
30	76.2	73.6	67.1	62.5
60	75.3	72.0	60.4	53.6
90	74.1	64.1	55.3	46.7
120	73.1	62.2	50.8	41.2

The TABLE 4 shows that the COD values are slightly high in the Month of December due to fewer rains and also the accumulation of large amount of waste has been expected since it is an open type of lake to receive the waste from various sources and it has no maintenance. COD values for sample tested for without catalyst under solar irradiation are found to be decreased moderately. Where as in case of photocatalyst TiO_2 phases (rutile or anatase) the decrease in COD values is more indicating the faster photodegradation of TOC. The degradation rate is found to be much faster with Degussa

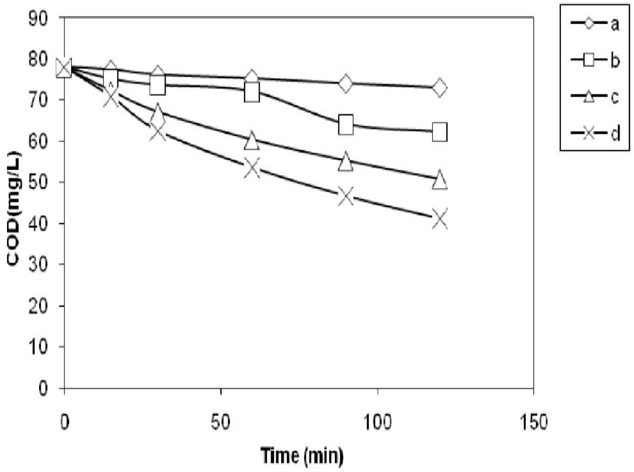

Figure 3 : Plot of COD values versus time in which the curves a, b, c and d are correspond to the experiments without catalyst, catalyst Rutile- TiO_2, Anatase- TiO_2, and Degussa-P25-TiO_2 for the TOC oxidation of medahalli lake water sample sampled in the month of June.

P-25 TiO_2 (mixed phases). Figure 4 shows the plots of COD values as a function of solar irradiation time for oxidation of TOC from the contaminated lake water. The experiments are carried out in presence of photocatalyst TiO_2 and its phases and also in absence of photocatalyst. The COD removal with Degussa-P25-TiO_2 is found to be least abut >30% for medahalli lake water sample tested in the month of December whereas in other cases it is about 50% of the initial COD of the samples of both the lakes and both seasons. This indicates the presence of more stable organic matter and in the higher concentration than that in the month of June.

TABLE 4 : COD values for medahalli lake water without/ with catalyst the month of December

Irradiation Time in min	COD Values			
	Without catalyst	Rutile – TiO_2	Anatase- TiO_2	Degussa P25- TiO_2
0	85.0	85.0	85.0	85.0
15	84.2	82.3	82.8	80.1
30	83.3	80.2	78.2	74.8
60	82.0	77.2	74.3	69.5
90	80.1	74.3	70.2	65.6
120	76.2	71.0	66.2	60.2

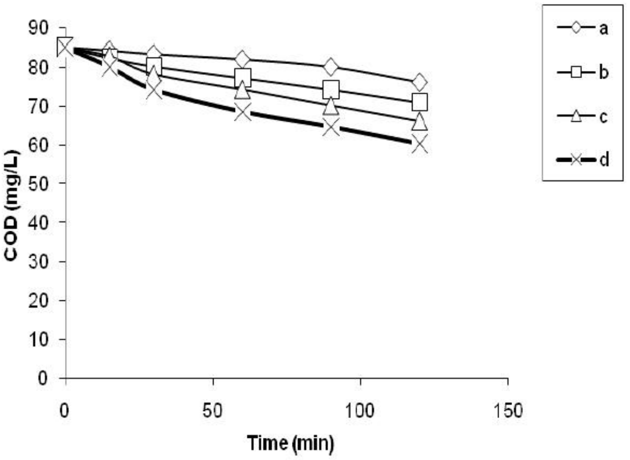

Figure 4 : Plot of COD values versus time in which the curves a, b, c and d are correspond to the experiments without catalyst, catalyst Rutile- TiO_2, Anatase- TiO_2, and Degussa-P25- TiO_2 for the TOC oxidation of medahalli lake water sample sampled in the month of December.

The COD values in the TABLE 5 are found to be decreased comparably faster with the TABLE 4 and these values are found to be more when compared to all the samples in both seasons. The higher COD is due to the accumulations of the contaminants due to rain wash of the urban ground. Though the COD is higher the other lake sample, the degradation rate is found to be faster. This could be due to the contaminants largely of simple organic molecules, because the urban domestic usage might involves the simple environmentally least stable chemicals. Hence the photodegradation of these chemicals becomes faster when compared to the contaminants of the other lake. The other lake is located at about 15 km from the centre of the city. It may receive the chemicals from other sources like industries, etc. These chemical molecules may be of stable kind and their photodegradation becomes slow.

TABLE 5 : COD values for ulsoor lake water without/with catalyst the month of June

Irradiation Time in min	COD Values			
	Without catalyst	Rutile – TiO_2	Anatase- TiO_2	Degussa P25- TiO_2
0	92	92	92	92
15	90.2	88.2	83.5	80.5
30	88.3	83.5	76.4	72.8
60	86.1	78.6	69.5	63.6
90	84.2	73.8	61.7	55.8
120	82.3	67.9	52.1	48.7

TABLE 6 shows the least initial COD value, however almost similar COD removal rate is observed as in the other cases. On the whole the contaminants are degraded more effectively in case of Degussa P-25 TiO_2 than the other forms of TiO_2. On the whole TABLES 3, 4, 5 & 6 clearly indicates that the TOC is more in the month of December and will be less in the month of June. And the Degussa P-25 TiO_2 is more efficient in catalyzing the solar degradation of organic carbon present in the lake water this may be due to the mixture of both phases as discussed in earlier section. In this study the samples tested in the month of June shows less COD values indicating

TABLE 6 : COD values for ulsoor lake water without/with catalyst the month of December

Irradiation Time in min	COD Values			
	With out catalyst	Rutile – TiO_2	Anatase- TiO_2	Degussa P25- TiO_2
0	55	55	55	55
15	54.1	53.2	52.1	49.0
30	53.2	51.0	49.1	43.1
60	52.0	49.1	46.2	37.2
90	51.2	46.2	43.1	30.1
120	50.0	44.0	40.2	25.1

less contamination where as the samples tested in the month of December show high COD values due to large concentration of contaminants.

Figure 5 and Figure 6 are the plots of COD values versus time as in the Figures 3 and 4 for the TOC oxidation of Ulsoor lake water sample sampled in the month of June and December respectively. In the figure 5 the initial COD is 92 mg/L which is higher than that with the COD of sample of December. This is due to the reason as explained earlier the entry of chemical contaminants trough rain washings in the month of June (rainy season). On the other hand in December since there was no entry of rain washings the only existing contaminants will be concentrated due the water evaporation under hot sun. Hence the COD will be less, about 55 mg/L however a similar rate of COD removal is found in both the cases. The COD has reduced to almost 50% and the rate of oxidation of TOC is more with Ulsoor lake sample than the Medahalli lake water sample.

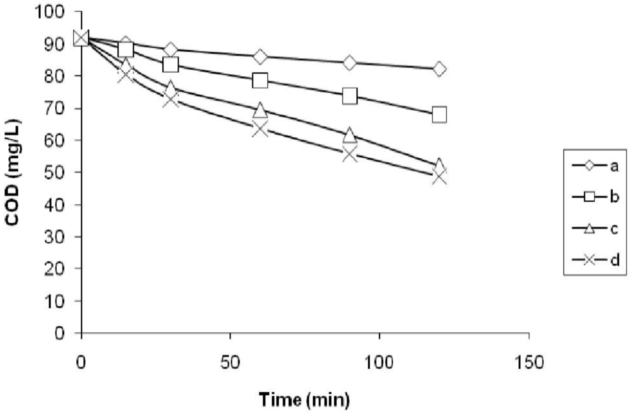

Figure 5 : Plot of COD values versus time in which the curves a, b, c and d are correspond to the experiments without catalyst, catalyst Rutile- TiO_2, Anatase- TiO_2, and Degussa-P25- TiO_2 for the TOC oxidation of ulsoor lake water sample sampled in the month of June.

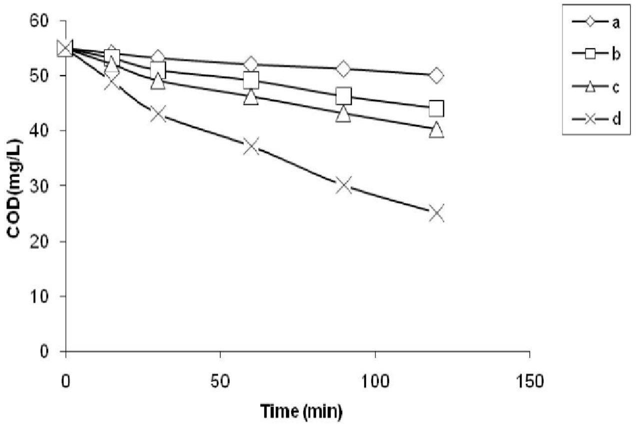

Figure 6 : Plot of COD values versus time in which the curves a, b, c and d are correspond to the experiments without catalyst, catalyst Rutile- TiO_2, Anatase- TiO_2, and Degussa-P25- TiO_2 for the TOC oxidation of Ulsoor lake water sample sampled in the month of December.

Efficiency of oxidation of TOC

The efficiency 'η' of photo/photocatalytic oxidation is defined by percentage efficiency as follows:

$\eta(\%)=(COD_0"COD)/COD_0\times100$ **(7)**

Where, COD_0 and COD denote the concentrations at initial (zero) time and given time *t* during irradiation, respectively. Figure 7 is a plot of η (%) versus irradiation time, which imply the percentage of oxidation of TOC for the samples from Medahalli lake (curves a and b) and for the samples from Ulsoor lake (Curves a and b) respectively in the presence of Degussa P25 TiO_2. The high efficiency is found with Ulsoor lake sample in the month of December and the lowest is with Medahalli lake sample of December month. The june month samples from both the lakes found to be intermediate. The lowest efficiency of the medahalli lake could be due to the reason as explained earlier the presence of more stable chemicals in higher concentration from industries and other urban wasteson contrary the high efficiency of ulsoor lake in the month of December could be due to the presence of less stable organics of domestic use. The Degussa P25 TiO_2 has found to be better than the other TiO_2 forms.

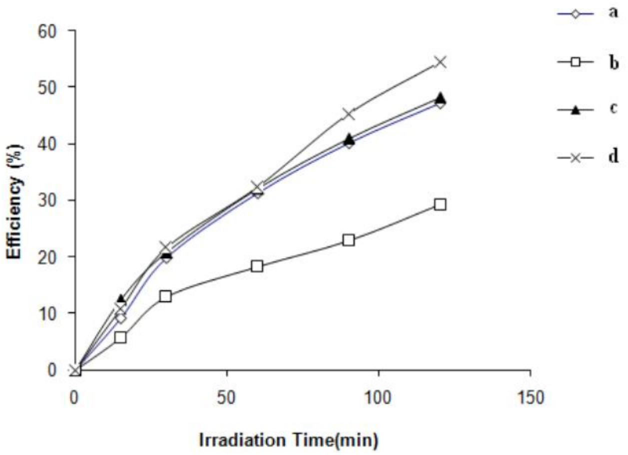

Figure 7 : Efficiency of oxidation of TOC as a function of irradiation time.

Kinetics of photo/photocatalytic of TOC of lake water samples

The kinetics generally includes the study of rate of a reaction, order of reaction, etc. Similarly in the present study a lot of rate of oxidation of TOC of lake water samples has been discussed in terms of decrease in COD on solar irradiation in the above sections. The plot of (COD)/ $(COD)_0$ versus irradiation time (Figure 8) is another way of expressing rate of degradation TOC. This figure implies the residual TOC as a function of time during irradiation. It shows the minimum residual concentration is high about 0.4 which means the maximum TOC oxidized is about 0.6 (or 60%) in 120 min of irradiation in the presence of Degussa P25 TiO_2 photocatalyst.

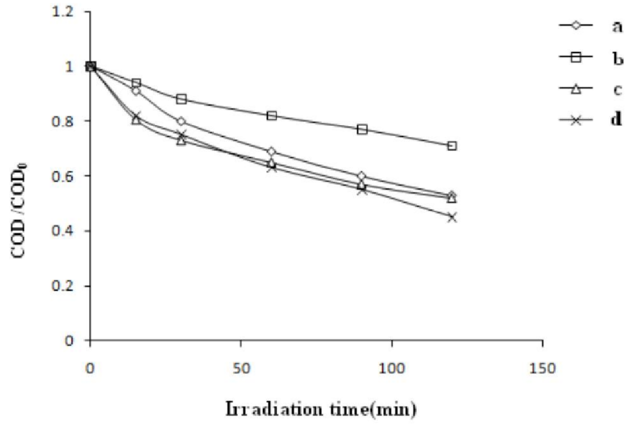

Figure 8 : Plot of COD_0/ COD as a function of irradiation time showing the kinetics of oxidation.

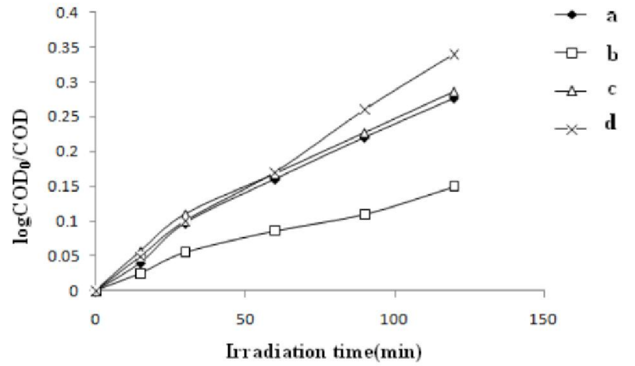

Figure 9 : Plot of log COD_0/ COD as a function irradiation time showing the rate constants for the oxidation reactions.

The COD concentration can be fitted well by the following apparent first-order kinetics,

$$\ln (COD_0/COD)=kt \tag{9}$$

Where, *k* is the apparent first-order reaction rate constant for the oxidation of lindane. Consider the Figure 8, which is a plot of log $(COD)_0$ / (COD) versus irradiation time, in which the initial rate of oxidation is fast as the lines are more linear in the beginning up to about 30 min of irradiation and deviate slightly showing the gradual increase in the oxidation rate. The rate constants for photocatalytic oxidation of TOC of the Medahalli lake samples of June and December months are 0.333 and 0.49 (x 10^{-4} s^{-1}) and for Ulsoor lake samples are 0.52 and 0.666 (x 10^{-4} s^{-1}) respectively for the curves a, b, c and d respectively. The highest rate is found for the oxidation of TOC of Ulsoor lake in the month of December and the lowest is found for Medahalli lake in the in the month of December.

CONCLUSION

In this study the oxidation of TOC of the water samples from two different Bangalore city (India)lakes by COD, BOD and photo/phtocatlytic oxidation under solar light has been conveniently performed at two different seasons. The samples tested in the month of June show less COD values indicating less contamination and the samples tested in the month of December have shown significantly high COD values due to large concentration of contaminants. The higher COD values in the Month of December could be due to fewer rains, large amount of waste has been expected to accumulate in lake as it is an open type of lake to receive the waste from various sources and unmaintained. COD values for sample tested in the absence of catalyst catalyst under only solar light irradiation are found to decrease moderately. Where as in case of photocatalyst TiO_2 phases (rutile or anatase) the decrease in COD values is more indicating the faster photodegradation of TOC. The degradation rate is found to be much faster with Degussa P-25 TiO_2(mixed phases). In mixed-phase TiO_2, charges produced on rutile by visible light are stabilized through electron transfer to lower energy anatase lattice trapping sites. Hence the Degussa p 25 TiO_2 has shown better efficiency in oxidizing the TOC of the lake water samples.

The decrease in COD with Degussa-P25-TiO_2 is found to be high (up to >30%) for medahalli lake water sample tested in the month of December whereas in other cases it is about 50% of the initial COD of the samples of both the lakes and seasons. This indicates the presence of more stable organic matter and in the higher concentration than that in the month of June in the Medahalli lake water sample. This study will provide a useful procedure to study the lake water TOC oxidation under natural light in rainy and summer seasons using TiO_2 based photocatalysts.

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