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# Treatment of highly polluted paper mill wastewater by solar photocatalytic oxidation with synthesized nano $TiO_2$

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ABSTRACT

Photocatalytic processes in the presence of titanium dioxide provide an interesting route to destroy hazardous organic contaminants, being operational in the UV-A domain with a potential use of solar radiation. The solar photocatalytic degradation of paper mill wastewater has been studied over synthesized nano $TiO_2$. The catalyst was characterized by techniques like X-ray diffraction (XRD), gravimetric-differential thermal analysis (TG-DTA) and IR. The enhanced photocatalytic activity of the synthesized catalyst is attributed to the crystallinity, nano-size, large amount of surface hydroxyl species and reduced band-gap.

The results show that prepared $TiO_2$ in the presence of solar light can be employed as an effective photocatalyst for the removal of chemical oxygen demand (COD) from the wastewater but in optimized conditions. The effects of catalyst loading and pH have been investigated. The degradation was strongly enhanced in the presence of electron acceptor such as $H_2O_2$. It was found that the photocatalytic degradation of the paper mill wastewater obeys the pseudo-first order kinetic reaction in the presence of the photocatalyst. At optimum dose of 0.75 g/L $TiO_2$ and pH value of 6.5, 75% COD removal of the wastewater was achieved within 180 min solar irradiation time. A reduction of 80% of total suspended solids (TSS) from the wastewater was also obtained at the same operating conditions. The experimental results have also shown that the non-biodegradable substances can be very effectively degraded by the solar photocatalytic treatment.

The biodegradability of the wastewater treated photocatalytically was measured in terms of $BOD_5$/COD. A substantial improvement in $BOD_5$/COD (0.35) could be achieved, but it required the removal of at least 70.5% of the total organic carbon originally in the water.

## 1. Introduction

Effluents of the pulp and paper industry contain a number of toxic compounds and may cause deleterious environmental impacts upon direct discharge to receiving waters. Pulping processes utilize large amounts of water, which reappear in the form of an effluent. The main treatment process used in paper mill industry is primary clarification, and then succeeded by secondly treatment, generally of a biological nature. But the effluent after biological treatment still contains appreciable concentrations of COD, color and toxicity [1]. The COD, which originates from persistent substances in the wastewater, cannot be further reduced by biological process alone. If the treated effluent is discharged into water streams or land mass without further treatment, it will result in severe environmental pollution [2]. In addition, the paper industry is likely to face more stringent regulations on the quality of effluents entering receiving waters. Thus, the use of tertiary treatment has to be considered in the future.

In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. AOP generates powerful oxidizing agent hydroxyl radicals which completely destroy the pollutants in waste water. Heterogeneous photocatalysis through illumination of UV (or) solar light on a semiconductor surface is an attractive advanced oxidation process for water treatment applications. Heterogeneous photocatalysis is a promising technology for the removal of toxic organic and inorganic contaminates from water. However, the development of a practical photocatalytic system focuses on the cost effectiveness of the process by the use of renewable solar energy source. Photocatalytic degradation of organic contaminants using solar radiation can be highly economical compared with the processes using artificial UV radiation, which require substantial electrical power input. Abundant solar energy can be utilized efficiently in the photocatalytic processes for the degra-

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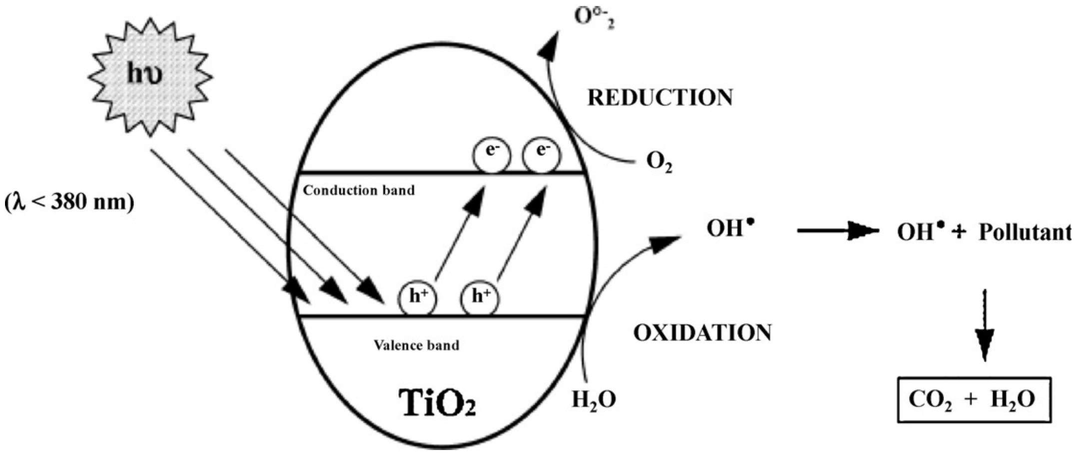

**Fig. 1.** General mechanism of the photocatalysis.

dation of organic pollutants. Several literatures are available on photocatalytic destruction of various organic and inorganic pollutants using artificial UV radiation [3,4]. Photocatalytic oxidation of these pollutants using sunlight has also been reported [5–12]. The heterogeneous photocatalysis has been studied for degrading the organic matters dissolved in paper mill effluents [13–16]. The basic process of photocatalysis consists of ejecting an electron from the valence band (VB) to the conduction band (CB) of the $TiO_2$ semiconductor creating an $h^+$ hole in the valence band. This is due to UV irradiation of $TiO_2$ with an energy equal or superior to the band gap (>3.2 eV) (Eq. (1)):

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \quad (1)$$

This is followed by formation of extremely reactive radicals (like $OH^\bullet$) at the semi-conductor surface and/or a direct oxidation of the polluting species (R) (Eqs. (2)–(4)): the ejected electrons react with electron acceptors such as oxygen adsorbed or dissolved in water (Eq. (5)). The mechanism is summed up in Fig. 1:

$$h^+_{vb} + H_2O \rightarrow {}^\bullet OH + H^+ \quad (2)$$

$$h^+_{vb} + OH^- \rightarrow {}^\bullet OH_{ad} \quad (3)$$

$$h^+_{vb} + R_{ads} \rightarrow R^+ \quad (4)$$

$$e^-_{cb} + O_2 \rightarrow O_2{}^{\bullet -} \quad (5)$$

Among various semiconducting materials (oxides, sulfides, etc.) most attention has been given to $TiO_2$ because of its high photocatalytic activity, chemical stability resistance to photocorrosion, commercial availability, low cost, non-toxicity and favorable wide band-gap energy (3.2 eV) [17,18]. Titanium dioxide is a solid semiconductor that upon light excitation generates electrons in the conduction band and holes in the valence band [19]. Also in this case the mechanism remains to be fully established: the holes could initiate oxidation of the substrate, generating its radical cation. Alternatively, hydroxyl radicals could be generated from water molecules [20]. As radiation with wavelengths shorter than 380 nm is absorbed by titanium dioxide, the UV fraction of sunlight can be employed in the process. Titanium dioxide is a semiconductor that is particularly promising in this regard [21]. Extensive works have been done elsewhere on solar photocatalytic oxidation of organic compounds [22–25].

The aim of the present work was to test solar photocatalysis for the treatment of wastewaters from paper mill industries. In this work, we focused on the preparation of highly catalytic active nano size anatase structured $TiO_2$. We have synthesized nano $TiO_2$; which absorbs UV and most of the visible light of the solar spectrum. The photocatalytic activity of this catalyst was evaluated by measuring degradation efficiency of the paper mill wastewater under solar irradiation. The catalyst has been characterized using X-ray diffraction (XRD) technique, gravimetric-differential thermal analysis (TG-DTA) and FTIR. For the practical application of the treatment of paper mill wastewater by $TiO_2$–sunlight process, there is a need to determine the optimal conditions of experimental parameters. In the present investigation we have investigated several parameters such as the catalyst loading, pH and the addition of electron acceptor such as hydrogen peroxide under specified climatic conditions (solar intensity and ambient temperature) to find out the optimum conditions for the removal of COD from the wastewater.

## 2. Experimental

### 2.1. Source and the characterization of the wastewater

The original real wastewater used was obtained from Egyptian board paper mill industrial plant and was provided as a material of this study. The plant produces 25 ton/day board paper from recycling wasted paper. Wastewater discharged from the mill amounted to 1000 $m^3$/day was dumped into a pond nearby the factory without any treatment. The wastewater produced was highly contaminated with suspended solids and organic pollutants as well. The samples are taken from the end-of-pipe and were treated without modifications. These effluents were characterized with a high organic load of chemical oxygen demand (COD) and low biological oxygen demand ($BOD_5$) indicating low biodegradability of the organic compounds present in the wastewater requiring advanced treatment. Low ratio ($BOD_5$/COD) of 0.16 proved the non-biodegradability proprieties of the wastewater and the requirement of advanced treatment. In our study the final effluent of the industry was diluted to 4-fold before treatment and its composition was listed in Table 1.

### 2.2. Preparation and characterization of $TiO_2$

Titanium dioxide ($TiO_2$) powder used in this study was synthesized by a conventional sol–gel process. $TiCl_4$ was first dissolved

**Table 1**
Composition of the paper mill effluent with 4-folds dilution used in this study.

| Parameters | Unit | Value |
|---|---|---|
| pH | – | 6.5 |
| COD | $mgO_2$/L | 2075 |
| $BOD_5$/COD ratio | – | 0.16 |
| TSS | mg/L | 1165 |

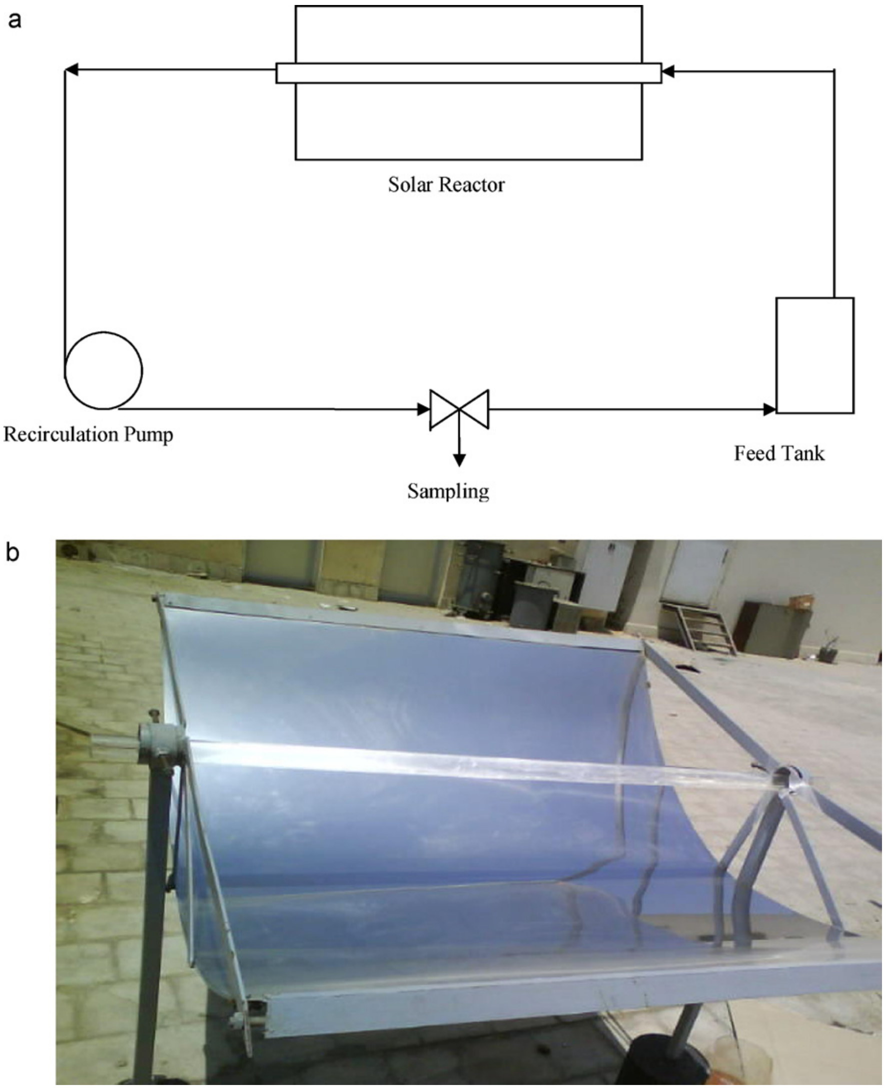

**Fig. 2.** (a) Schematic diagram of solar catalytic oxidation unit. (b) Solar parabolic collector used in the study.

in an ethanol/water (volume ratio of 4:1) solution, and ammonia was then introduced into the solution to induce condensation until pH reached 7.5. The resulted gelatinous precipitate was filtered and washed to remove chloride and then dried at 80 °C in air. The resulted powder was then dried band to make the catalyst. The standard calcinations procedure involved heating the powder at a rate of 50 °C/h to 450 °C, and holding the powder at 450 °C for 3 h, finally the powder being furnace-cooled. The prepared nano powder was characterized X-ray diffraction (XRD), gravimetric-differential thermal analysis (DTA) and infra red (IR). The X-ray diffract meter type Philips, model Brukur $D_8$ Advance-Germany, Target Cu $K_\alpha$, with secondary monochromator $V = 40$ kV, $A = 40$ mA, with Ni filter was used to investigate the crystalline phases of the prepared nano powder. DTA [STERAM Labsys$^{TM}$ TG-DSC1600 °C] apparatus with heating rate 5 °C/min and IR Fourier transform infrared spectroscopy (FT/IR-6300-Jasco spectroscopy) were used to confirm the obtained phases.

### 2.3. Configurations of the solar collector

The parabola cylindrical concentrator solar photoreactor configuration, as shown in Fig. 2(a), was used to perform heterogeneous photocatalysis oxidation of the paper mill wastewater under solar irradiation in a total recirculation loop with a feed tank by a peristaltic pump. The solar reactor is consisted of one UV transparent glass tube with 3.5 m long and internal diameter of 40 mm as a receiver. An irradiated surface of 3.7 m$^2$ from borosilicate glass is placed on fixed support as a parabolic concentrating collector that is to be oriented about a horizontal east-west axis so as to constantly minimize the angle of incidence and thus maximum the incident beam radiation [26].

### 2.4. Solar irradiation experiments

All solar photocatalytic experiments were carried out under similar conditions on sunny days of summer (August) under clear skies between 11 a.m. and 3 p.m. The intensity of solar radiation and ambient air temperature were measured using a weather station erected in the outdoor test field of the Solar Energy Department of NRC, Giza, Egypt. The problem of variation of intensity of sunlight even under a clear sky is overcome by conducting experiments in sets simultaneously and comparing the results. At this time, the UV intensity ranged from 35 to 45 W/m$^2$, which corresponds to the 30% of the power of the solar irradiation. The photocatalytic oxidation was carried out in aqueous suspensions of the prepared $TiO_2$ irradiated by sunlight which was focused on the photoreaction system. The wastewater and the catalyst at definite concentrations were continuously fed to the solar reactor from the feed tank by

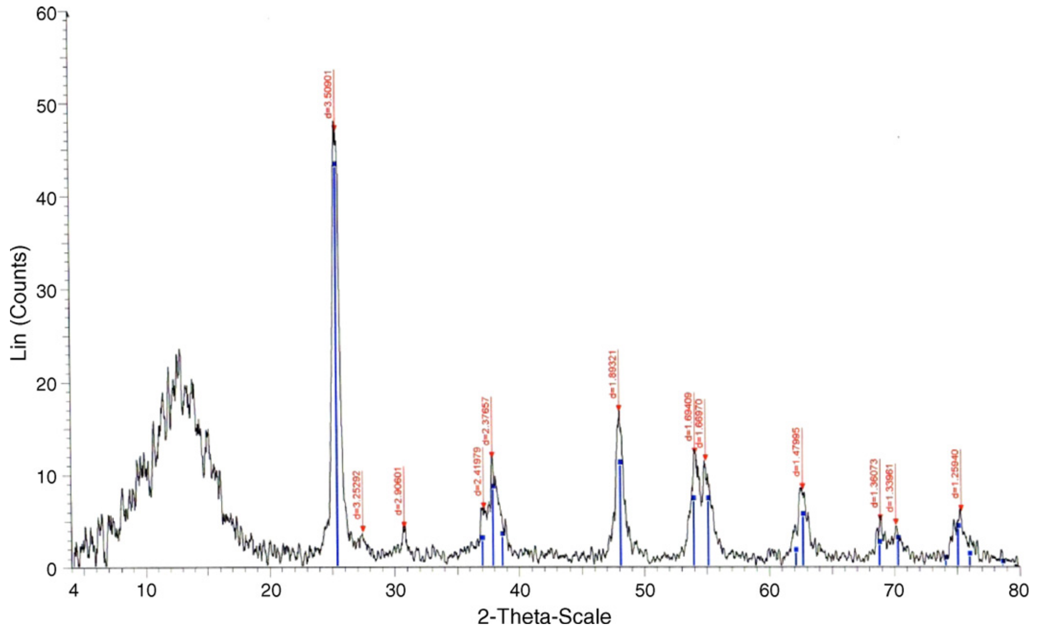

**Fig. 3.** XRD of the prepared $TiO_2$ photo catalysis calcined at 450 °C.

means of a peristaltic pump as batch process. The solution flow rate, maintained constant for all of the runs, was 60 L/h. The total irradiated volume was 3.5 L. The schematic diagram of the experimental set-up is shown in Fig. 2(b).

The experimental runs were carried out by using the following procedure: firstly the suspensions were magnetically stirred in the dark for 10 min to attain adsorption–desorption equilibrium between the wastewater and $TiO_2$, the aqueous suspension containing the wastewater and the $TiO_2$ powder was circulated in the reacting system.

Since the literature reports that the presence of strong oxidant species can greatly enhance the photooxidation rate of organic compounds [27]. The influence of the presence of hydrogen peroxide ($H_2O_2$ solution, 35% (w/w) in stable form provided by Merck) on the photocatalytic oxidation rate was also investigated. In these experiments, hydrogen peroxide was injected before the start of the solar catalytic oxidation. Samples were taken at regular time intervals from the solar reactor and first were centrifuged to get ride off the residual catalyst and then were analyzed immediately to avoid further reaction. In the experiments with the addition of hydrogen peroxide, the reaction was stopped instantly by adding NaOH to the reaction samples to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with the organic compounds present in the wastewater during the analysis, since hydrogen peroxide cannot proceed at pH >10. The initial pH to the desired value was adjusted with $H_2SO_4$ or NaOH. The dependence of solar photooxidation rate of the wastewater on catalyst amount, pH and the addition of hydrogen peroxide was investigated.

### 2.5. Analysis

The wastewater effluents were characterized and analyzed for COD, $BOD_5$, TSS and other physical chemical analysis, according to the procedures described in Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, 1995) [28].

The pH was measured by means of a WTW pH-meter 537 equipped with a pH combination electrode E56. Chemical oxygen demand (COD) was carried out via a Hach-2000 spectrophotometer using a dichromate solution as the oxidant in strong acid media using closed reflux, colorimetric method according to APHA, 1995 section 5220-D. Total suspended solids (TSS) in samples were measured by the gravimetric method according to APHA, 1995 section 2540-D. Hydrogen peroxide was detected by a modified iodometric titration method [29]. $BOD_5$ was measured using a respirometry system by 5-day BOD test according to APHA, 1995 section 5210-B. All values of COD and the other parameters of the wastewater are presented in Table 1.

## 3. Results and discussion

### 3.1. Characterization of the prepared $TiO_2$ nanoparticles

X-ray diffraction (XRD) was used to investigate the crystalline phases (anatase or rutile) of the $TiO_2$ powder. XRD of the prepared $TiO_2$ photo catalysis calcined at 450 °C is shown in Fig. 3. Peaks characterizing anatase with minor amount of rutile phases are detected in the pattern. The broadness of the peaks indicates the lack of complete crystallinity of the obtained phases at such calcinations temperature.

Two major structural forms of titanium dioxide can exhibit photocatalytic activity: anatase and rutile [30]. Anatase (chains of $TiO_6$ octahedral sharing two edges) has a wider optical band gap of 3.2 eV, and the band gap of rutile (chains of $TiO_6$ octahedral sharing four edges) is 3.0 eV [31]. It is important to develop methods for the selective preparation of $TiO_2$, because anatase and rutile are often formed at the same time during the formation of $TiO_2$ and it is desired to synthesize anatase nanoparticle $TiO_2$ since the anatase form has a higher photocatalytic activity than rutile $TiO_2$ [37]. Different preparation methods and conditions yield different particle sizes and phase compositions of the nanostructured $TiO_2$ that display different morphological, structural, and surface physiochemical properties, and also give different photocatalytic activities [32]. These conditions include the types of precursors, the concentration and molar ratio of reactants, the polarity of the solvent, the pH, and the temperature of the reacting solution.

Fig. 4 shows TGA thermograph of the calcined $TiO_2$ at 550 °C. About 0.5% weight loss at 165 °C was obtained due to the loss physically adsorbed and entrapped moisture from the surrounding medium. IR spectrum of the calcined $TiO_2$ is shown in Fig. 5. The binding vibration H–O–H at 1624 and weak stretching vibra-

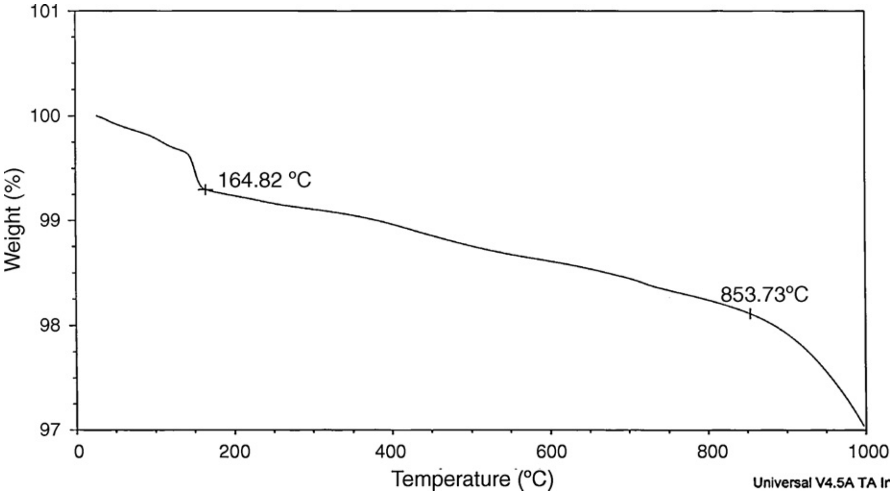

**Fig. 4.** TGA of the prepared $TiO_2$ photo catalysis at calcinations temperature of 450 °C.

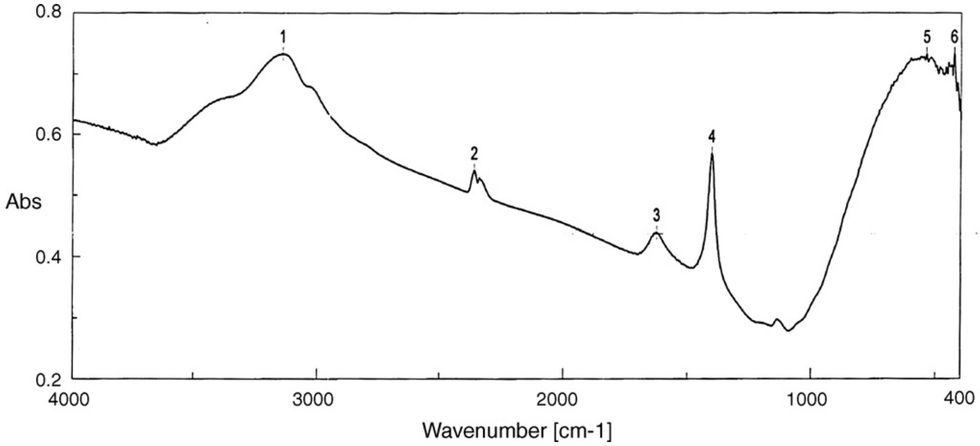

**Fig. 5.** IR spectra of the prepared $TiO_2$ photo catalysis at calcinations temperature of 450 °C.

tion O–H at 3372 cm$^{-1}$ indicate the existence of a small amount of water and hydroxyl group. The absorption peak at 1405 cm$^{-1}$ observed for freshly prepared $TiO_2$ powder by wet process. The wide peak from 410 to 1000 cm$^{-1}$ is assigned to Ti–O–Ti starching vibration.

### 3.2. Photodegradability

Fig. 6 shows the results of photodegradation with and without $TiO_2$–solar light. In the absence of photocatalyst the wastewater, on irradiation with the solar light, has been found to be nearly stable. In the presence of $TiO_2$ (0.75 g/L) and in the absence of solar light, about a 12% only of COD removal was observed within 180 min reaction time. This is due to the adsorption of the organic pollutants present in the wastewater on the surface of $TiO_2$. Simultaneous solar irradiation caused 70.5% COD removal of the wastewater at catalyst dos of 0.75 g/L and pH value of 6.5 within 180 min solar irradiation time. The results indicated that the observed high decomposition in the presence of both solar light and $TiO_2$ process is exclusively attributed to the photocatalytic reaction of the semiconductor particles. On the other hand, these experiments demonstrated that both solar light and a photocatalyst, $TiO_2$, were needed for the effective treatment of the paper mill wastewater. It has been established that the photocatalytic degradation of paper mill wastewater is initiated by photoexcitation of the semiconductor to electron hole pair on the catalyst surface. The degradation of the aromatic part of the paper mill wastewater took a longer time for its removal. Initially the degradation is fast and at the end of the photocatalytic process the removal rate is slow. This is due to the formation of intermediate compounds in the wastewater.

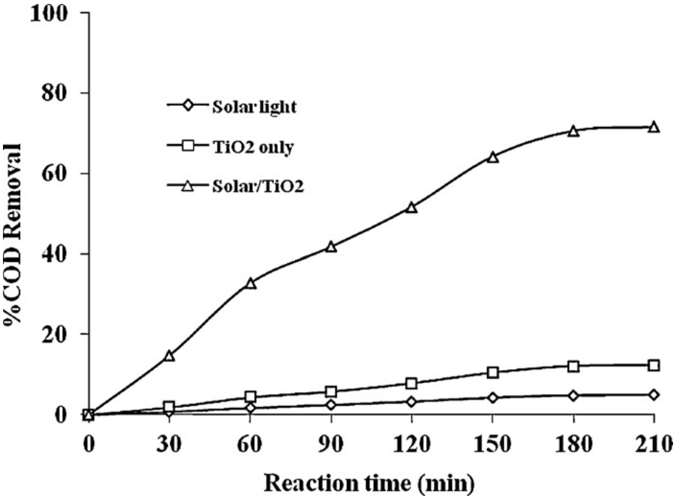

**Fig. 6.** %COD removal during the treatment of the wastewater by different oxidation processes against reaction time, with solar light only, with $TiO_2$ only and with solar/$TiO_2$ [$TiO_2$ = 0.75 g/L, pH = 6.5].

**Table 2**
Collective table for the experimental runs conditions and results in this study.

| Run no. | Catalyst loading (g/L) | pH | Solar radiation | $H_2O_2$ (ml/L) | $k_0$ ($min^{-1}$) | $\varphi_{180}$ (%) |
|---|---|---|---|---|---|---|
| 1 | 0 | 6.5 | + | 0 | 0.0003 | 4.7 |
| 2 | 0.75 | 6.5 | – | 0 | 0.0007 | 12 |
| 3 | 0.75 | 6.5 | + | 0 | 0.0066 | 70.5 |
| 4 | 0.25 | 6.5 | + | 0 | 0.0036 | 46.3 |
| 5 | 0.5 | 6.5 | + | 0 | 0.0043 | 55.1 |
| 6 | 1 | 6.5 | + | 0 | 0.0060 | 67.3 |
| 7 | 1.25 | 6.5 | + | 0 | 0.0049 | 57.5 |
| 8 | 1.5 | 6.5 | + | 0 | 0.0038 | 48.4 |
| 9 | 0.75 | 3 | + | 0 | 0.0032 | 43.1 |
| 10 | 0.75 | 5 | + | 0 | 0.0039 | 50.6 |
| 11 | 0.75 | 8 | + | 0 | 0.0068 | 72.1 |
| 12 | 0.75 | 10 | + | 0 | 0.0076 | 74.7 |
| 13 | 0.75 | 6.5 | + | 1 | 0.0073 | 73.9 |
| 14 | 0.75 | 6.5 | + | 2 | 0.0087 | 77.9 |
| 15 | 0.75 | 6.5 | + | 3 | 0.0065 | 68.0 |
| 16 | 0.75 | 6.5 | + | 4 | 0.0053 | 62.0 |

$k_0$ is the pseudo-first-order reaction rate constants in $min^{-1}$.
$\varphi_{180}$ is the efficiencies of %COD removals within 180 min reaction time.
+ means with or in the presence of.
– means without.

The competition of the intermediate compounds with the parent molecules in the photocatalytic degradation process slows down the rate. The removal of COD of the wastewater was analyzed at different reaction times and a pseudo-first-order kinetics was found in all cases. The obtained pseudo-first-order reaction rate constants ($k_0$) in $min^{-1}$ and the %COD removal at 180 min reaction time ($\varphi_{180}$) are shown in Table 2 (Runs 1–3).

### 3.3. *Effect of catalyst loading*

The amount of catalyst is one of the main parameters for the degradation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum catalyst loading for efficient removal of COD of the wastewater. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process [33–35]. The effect of catalyst weight on the percentage removal of COD was investigated from 0.25 to 1.25 g/L of the catalyst at pH equals 6.5. The results are shown in Fig. 7. The results clearly show that the increase of catalyst weight from 0.25 to 0.75 g/L increases the %COD removal sharply from 46.3 to 70.5 at 180 min solar irradiation time. The minimum percentage COD degradation at lower $TiO_2$ loading can be attributed to the fact that more light is transmitted through the reactor and the transmitted light is not utilized in the photocatalytic reaction [36]. At 0.75 g/L of $TiO_2$, the percentage degradation of the wastewater increases this enhancement of removal rate is due to (i) the increase in the amount of catalyst weight which increases the number of organic pollutants adsorbed and (ii) the increase in the density of particles in the area of illumination.

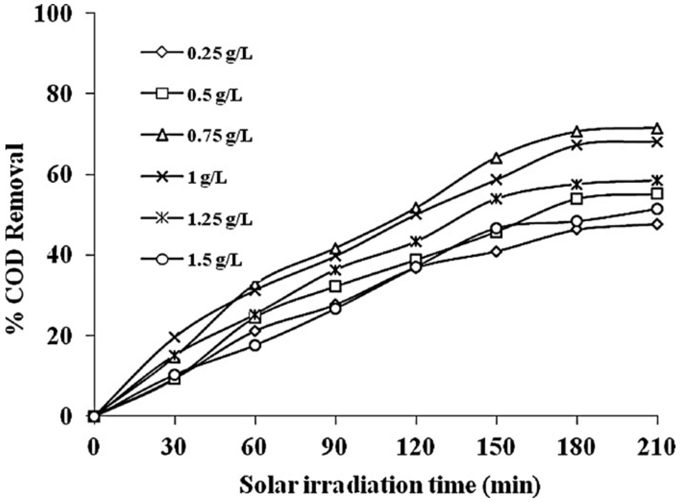

**Fig. 7.** %COD removal during the treatment of the wastewater by solar photocatalytic oxidation against solar irradiation time at different loading of $TiO_2$ [pH = 6.5].

But at concentrations more than 0.75–1 g/L the %COD removal is almost constant. This limiting value (0.75 g/L) may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration, aggregation of $TiO_2$ particles at high concentrations, causing a decrease in the number of active surface sites, and increase in opacity and high scattering of $TiO_2$ particles at high concentrations leading to a decrease in the passage of irradiation through the sample, hence the part of the catalyst surface become unavailable for photon absorption, and degradation rate decrease. Similar results have been reported in previous studies [37]. Thus, the decreased percentage degradation at higher catalyst loading (higher than 1.25 g/L $TiO_2$ in our study) may be due to deactivation of activated molecules by collision with ground state molecules. Shielding by $TiO_2$ may also take place (Eq. (6)):

$$TiO_2{}^{*} + TiO_2 \rightarrow TiO_2 + TiO_2{}^{\#} \tag{6}$$

where $TiO_2{}^{*}$ is the $TiO_2$ with active species adsorbed on its surface and $TiO_2{}^{\#}$ the deactivated form of $TiO_2$.

It should be pointed out that, the catalyst loading affects both the number of active sites on photocatalysts and the penetration of solar light through the suspension. Although, as the catalyst loading increases, the number of active sites increases but the penetration of solar light decreases due to shielding effect [38,39]. The photocatalytic degradation rate, which is influenced by both the number of active sites and the penetration of solar light, must therefore pass through a maximum at optimum catalyst loading. The similar results were observed previously by others [40–46]. It should also be noted that the optimum value of catalyst loading will strongly be dependent on the type and initial concentration of the pollutant and the operating conditions of the photoreactor [47]. So the optimum catalyst loading is different by varying the photocatalytic set-up and pollutant type and concentration. The optimum concentration of the catalyst for efficient solar photodegradation for the paper mill wastewater taken in this study is found to be 0.75 g/L. The pseudo-first-order reaction rate constants obtained for the solar photodegradation of the wastewater with the efficiencies of %COD

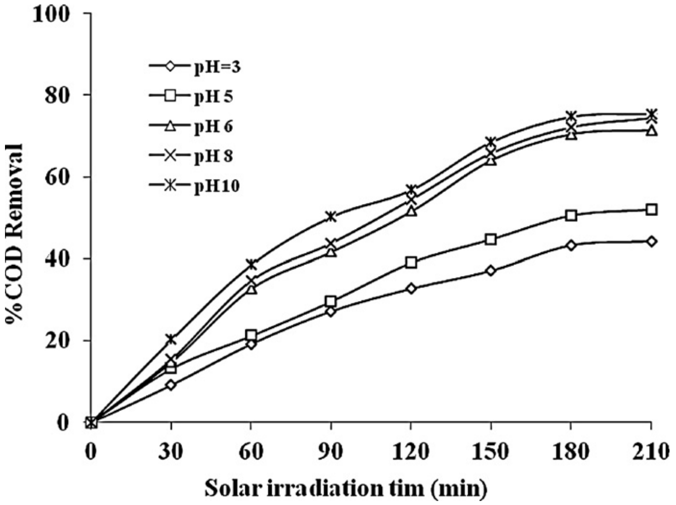

**Fig. 8.** %COD removal during the treatment of the wastewater by solar photocatalytic oxidation against solar irradiation time at different pH values [$TiO_2 = 0.75$ g/L].

removals within 180 min solar irradiation time at different $TiO_2$ loading (Runs 3–8) are listed in Table 2.

### 3.4. *Effect of pH*

The most important parameter that influences the photocatalytic degradation is the pH of the medium since the generation of hydroxyl radicals is a function of pH. Numerous experimental data have been published dealing with the effect of pH on photocatalytic degradation of various organic compounds [48]. The effects of pH from 3 to 10 on the photocatalytic degradation are shown in Fig. 8. In all the experiments pH was adjusted by adding appropriate amount of 0.02 N $H_2SO_4$ or 0.02 N NaOH solution.

Increase of pH of the wastewater from 3 to 10 increases the COD removal from 43.2 to 72.1% at 180 min solar irradiation time. The %COD removal was observed to be faster in alkaline pH than in acidic pH range. Similar observations have been reported earlier [49,50]. At acidic pH range the removal efficiency is low. This is due to two reasons: (i) at low pH value $TiO_2$ particle agglomeration reduces the adsorption as well as photon absorption [51]. (ii) The concentration of $H^+$ is in excess at low pH and $H^+$ ions interact with aromatic linkage of the organic pollutants present in paper mill wastewater decreasing the electron densities at the polycyclic groups. Consequently, the reactivity of hydroxyl radical by electrophilic mechanism decreases. An increase of pH from acidic to alkaline resulted in a significant reduction of adsorption. The point of zero charge (Pzc) for $TiO_2 \approx 6{:}8$ [52]. In acidic solution the pH is lower than Pzc and hence the $TiO_2$ surface is positively charged (Eq. (7)). In the basic solution the surface is negatively charged as given in Eq. (8).

Percentage removal of the COD increases with the increase in pH from 6.5 (the pH of the final effluent of the industry) to 10, the organic pollutants adsorption on the photocatalytic surface of $TiO_2$ decreases from pH 6.5 to 10. This indicates that the effect of dye adsorption on photocatalytic activity is limited. The photocatalytic degradation of the wastewater is mainly due to the hydroxyl radical attack on the organic molecules. The production of hydroxyl radical in the acidic medium is different from the basic medium.

In acidic medium photogenerated holes react with water molecule producing hydroxyl radical as given in Eq. (9). At alkaline pH the negative surface of the $TiO_2$ with $OH^-$ ions acts as an efficient trap for the photogenerated holes and produce hydroxyl radicals (Eq. (10)). At pH >$TiO_2$ zero charge (Pzc) the hydroxyl radical and $O_2{}^-$ radical can easily diffuse from the negative surface of $TiO_2$ into the bulk of reaction solution [53]. Hence hydroxyl radical is responsible for wastewater degradation. The pseudo-first-order reaction rate constants obtained for the solar photocatalytic degradation of the wastewater with the efficiencies of %COD removals within 180 min solar irradiation time at different pH values (Runs 3, 9–12) are reported in Table 2.

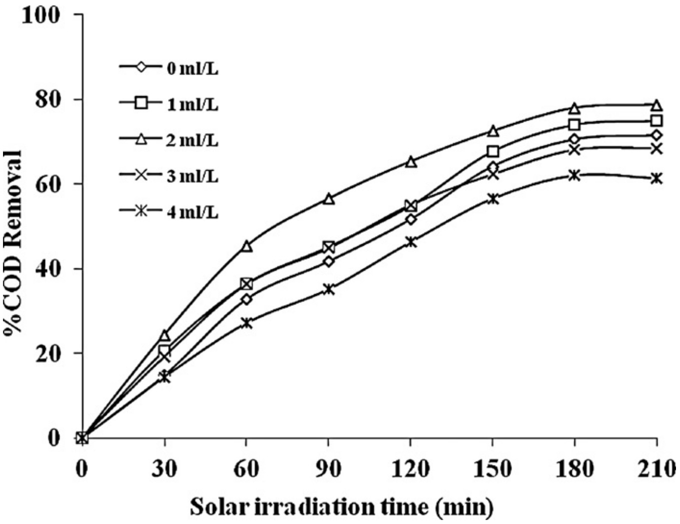

**Fig. 9.** %COD removal during the treatment of the wastewater by solar photocatalytic opxidation against solar irradiation time at different doses of hydrogen peroxide [$TiO_2 = 0.75$ g/L, pH = 6.5].

$$TiOH + H^+ \rightarrow TiOH_2{}^+ \qquad (7)$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \qquad (8)$$

$$H_2O + h^+_{vb} \leftrightarrow OH^{\bullet\bullet} + H^+ \qquad (9)$$

$$OH^-_{surface} + h^+_{vb} \leftrightarrow OH^{\bullet}{}_{surface} \qquad (10)$$

### 3.5. *Effect of $H_2O_2$ concentration*

The oxidizing agents have a great deal of influence on the photocatalytic degradation of the organic compounds. The effect of adding $H_2O_2$ on the photocatalytic oxidation of the paper mill wastewater was investigated. Fig. 9 illustrates the %COD removal against solar irradiation time for different initial concentration of $H_2O_2$. The experiment was conducted at the concentration range of 1–4 ml/L $H_2O_2$. The pseudo-first-order reaction rate constants obtained for the solar photocatalytic degradation of the wastewater with the efficiencies of %COD removals within 180 min solar irradiation time at different initial $H_2O_2$ concentrations (Runs 3, 13–16) are listed in Table 2. The experimental results revealed that hydrogen peroxide has a beneficial effect on the %COD removal of the paper mill wastewater. The %COD removal is found to increase with increase in $H_2O_2$ concentration, this is attributed that the reactive radical intermediate ($OH^{\bullet}$) formed from this oxidant by reactions with the photogenerated electrons can exert a dual function: as strong oxidant itself and as electron scavenger, thus inhibiting the electron–hole recombination at the semiconductor surface [54] according to Eqs. (11)–(13).

$H_2O_2$ is a powerful oxidant and electron acceptor so it can trap the electron of the electron–hole pair photogenerated in the reaction; therefore, inhibits the electron–hole recombination. Also, hydrogen peroxide under UV irradiation is split and produces hydroxyl radicals. So the number of hydroxyl radicals generated in the photoreaction is directly proportional to the hydrogen peroxide concentration [55,56].

It must be noted that the addition of peroxide increases the rate towards real reaction with adequate oxygen supply, because the solution phase may at times be oxygen starved as a result of either oxygen consumption or slow oxygen mass transfer.

One practical problem in using $TiO_2$ as photocatalysts in photocatalytic reactions is the undesired electron–hole recombination, which in the absence of proper electron acceptor or donor, is extremely efficient and thus represents the major energy-wasting step, thereby limiting the achievable quantum yield [57,46]. One strategy to inhibit electron–hole recombination is to add irreversible electron acceptors to the reaction system, such as $H_2O_2$. The experimental results indicated that the optimal dosage of $H_2O_2$ was at 2 ml/L, at which the %COD removal of the paper mill wastewater on the $TiO_2$ attained the height with 77.9%. At higher dosage of $H_2O_2$ beyond the optimum, the degradation efficiency of the wastewater decreased. This is because the very reactive radicals $OH^\bullet$ and valence band holes could be consumed by $H_2O_2$ itself as given in Eqs. (14)–(16) [58]. At the same time, radical–radical recombination as a competitive reaction must be taken into account, as described in Equation (17) [51].

$$H_2O_2 + O_2{}^{\bullet -} \rightarrow OH^\bullet + OH^- + O_2 \qquad (11)$$

$$H_2O_2 + h\gamma \rightarrow 2OH^\bullet \qquad (12)$$

$$H_2O_2 + e_{cb}{}^- \rightarrow OH^\bullet + OH^- \qquad (13)$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O^\bullet + H_2O \qquad (14)$$

$$OH^\bullet + H_2O^\bullet \rightarrow O_2 + H_2O \qquad (15)$$

$$TiO_2(h_{vb})^+ + H_2O_2 \rightarrow TiO_2 + O_2 + H^+ \qquad (16)$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \qquad (17)$$

As both $OH^\bullet$ and $h_{vb}{}^+$ are strong oxidants for organic pollutants, the photocatalytic degradation of the par mill wastewater will be inhibited in the condition of excess of $H_2O_2$. Furthermore, $H_2O_2$ can be adsorbed onto $TiO_2$ particles to modify their surfaces and subsequently decrease its catalytic activity.

### *3.6. Effect of solar photocatalytic treatment on the biodegradability and TSS removal*

The experimental results show that the biodegradability of the paper mill wastewater was enhanced by using the solar photocatalytic oxidation, converting the non-biodegradable organic substrates into more biodegradable compounds. The ratio of $BOD_5$/COD increased from 0.16 to 0.35 at optimum loading of $TiO_2$ of 0.75 g/L. When 2 ml/L of $H_2O_2$ was added, the $BOD_5$/COD ratio was increased to 0.4 proving the use of solar photocatalytic oxidation as a pretreatment step.

The experimental analysis of the treated paper mill wastewater by the solar photocatalytic oxidation exhibited also efficiency in the removal in the TSS of the wastewater to 80.4% at optimum $TiO_2$ loading of 0.75 g/L and pH equals 6.5. Addition of 2 ml/L $H_2O_2$ increased the removal of TSS to 86.5%.

## 4. Conclusions

The solar photocatalytic degradation of wastewater from paper mill industry was studied using synthesized nano $TiO_2$. The conclusions drawn from this study can be summarized as follows:

(i) The photocatalytic degradation obeys pseudo-first-order kinetics. The rate of degradation with synthesized $TiO_2$ increase with the increase of catalyst loading till definite amount up to 0.75 g/L. The optimum pH value was 6.5 the same pH of the effluent and near the point of zero charge (Pzc) for $TiO_2 \approx 6{:}8$. Within 180 min solar irradiation time, 70.5% COD removal of the wastewater was achieved at 0.75 g/L $TiO_2$ and pH equals 6.5.

(ii) The solar photocatalytic oxidation efficiency increased also with the addition of $H_2O_2$ up to a dose of 2 ml/L, since it plays as electron acceptor.

(iii) The higher solar photocatalytic activity of synthesized $TiO_2$ can be attributed to the nano-size, crystal structure (anatase), crystallinity, large amount surface hydroxyl groups and decreased band-gap energy of the catalyst which enhances the solar energy absorption.

(iv) Photocatalytic oxidation of the paper mill wastewater reduced the total suspended solids from the initial effluent with 80.4%.

(v) Solar photocatalytic oxidation of the paper mill wastewater enhanced the biodegradability of the wastewater since the $BOD_5$/COD increased from 0.16 to 0.35 proving that the solar photocatalytic oxidation may be used as an efficient pre-treatment step to biological post-treatment of paper mill effluents.

## References

[1] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater—a review, Sci. Total Environ. 333 (2004) 37–58.

[2] G. Thompson, J. Swain, M. Kay, C.F. Forster, The treatment of pulp and paper mill effluent: a review, Bioresour. Technol. 77 (2001) 275–286.

[3] H. Lachheb, F. Puzenat, A. Houas, M. Ksibi, F. Elaloui, C. Guillard, J. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, Appl. Catal. B: Environ. 39 (2002) 75.

[4] G. Sivalingam, K. Nagaveni, M. Hegde, G. Madras, Photocatalytic degradation of various dyes by combustion synthesized nano anatase $TiO_2$, Appl. Catal. B: Environ. 45 (2003) 23–38.

[5] M. Stylidi, D. Kondarides, X. Verykios, Pathways of solar light-induced photocatalytic degradation of azo-dyes in aqueous $TiO_2$ suspensions, Appl. Catal. B: Environ. 40 (2003) 271–286.

[6] J. Herrmann, C. Guillard, J. Disdier, C. Lehaut, S. Malato, J. Blanco, New industrial titania photocatalysts for the solar detoxification of water containing various pollutants, Appl. Catal. B: Environ. 35 (2002) 281–294.

[7] A. Yawalkar, D. Bhatkhande, D. Pangarkar, A. Beenackers, Solar assisted photocatalytic and photochemical degradation of phenol, J. Chem. Technol. Biotechnol. 76 (2001) 363–370.

[8] W. Kuo, P. Ho, Solar photocatalytic decolorization of methylene blue in water, Chemosphere 45 (2001) 77–83.

[9] D. Robert, S. Malato, Solar photocatalysis: a clean water process for water detoxification, Sci. Total Environ. 291 (1–3) (2002) 85–97.

[10] D. Bhatkhande, V. Pangarkar, A. Beenackers, Photocatalytic degradation of nitrobenzene using $TiO_2$: chemical effects, Water Res. 376 (2003) 1223–1230.

[11] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and $TiO_2$ assisted degradation of textile dye reactive blue 4, Chemosphere 46 (2002) 1173–1181.

[12] S. Sakthivel, B. Neppolian, M. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and $TiO_2$, Sol. Energy Mater. Sol. Cells 77 (2003) 65–82.

[13] A. Machado, A. Furuyama, S. Falone, R. Ruggiero, P. da Silva, A. Castellan, Photocatalytic degradation of lignin and lignin models, using titanium dioxide: the role of the hydroxyl radical, Chemosphere 40 (2000) 115–124.

[14] M. Ksibi, S. Ben Amor, S. Cherif, E. Elaloui, A. Houas, M. Elaloui, Photodegradation of lignin from black liquor using a UV/$TiO_2$ system, J. Photochem. Photobiol. A: Chem. 154 (2003) 211–218.

[15] M. Yeber, J. Rodríguez, J. Baeza, J. Freer, C. Zaror, N. Durán, H. Mansilla, Toxicity abatement and biodegradability enhancement of pulp mill bleaching effluent by advanced chemical oxidation, Water Sci. Technol. 40 (1999) 337–342.

[16] G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, Singlet oxygen degradation of lignin: a GC–MS study on the residual products of the singlet oxygen degradation of a steam exploded lignin from beech, J. Photochem. Photobiol. A: Chem. 128 (1999) 139–143.

[17] X. Deng, Y. Yue, Z. Gao, Gas-phase photo-oxidation of organic compounds over nanosized $TiO_2$ photocatalysts by various preparations, Appl. Catal. B: Environ. 39 (2002) 135–147.

[18] G. Montes-Hernandez, S. Rihs, A simplified method to estimate kinetic and thermodynamic parameters on the solid–liquid separation of pollutants, J. Colloid Interface Sci. 299 (2006) 49–55.

[19] S. Sakthivel, M. Shankar, M. Palanichamy, B. Arabindoo, V. Murugesan, Photocatalytic decomposition of leather dye. Comparative study of $TiO_2$ supported on alumina and glass beads, J. Photochem. Photobiol. A: Chem. 148 (2002) 153–159.

[20] M. Pera-Titus, V. Garcĭa-Molina, M.A. Banos, J. Jiménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[21] J. Theurich, M. Lindner, D. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: a kinetic and mechanistic study, Langmuir 12 (1996) 6368–6376.

[22] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-plant scale: an overview, Appl. Catal. B: Environ. 37 (2002) 1–15.

[23] W. Gernjak, M. Maldonado, S. Malato, J. Aceres, T. Krutzler, Pilot-plant treatment of olive mill wastewater (OMW) by solar $TiO_2$ photocatalysis and solar photo-Fenton, Solar Energy 77 (2004) 567–572.

[24] D. Bahnemann, Photocatalytic water treatment: solar energy applications, Solar Energy 77 (2004) 445–459.

[25] A. Chan, C. Chan, J. Barford, J. Porter, Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing wastewater, Water Res. 37 (2003) 1125–1135.

[26] A.M. Fathy, J.Y. Farah, M.Y. Ghaly, Effect of catalyst type and dose on solar photocatalytic oxidation for the degradation of zenafix yellow reactive dye aqueous solution, Afinidad 63 (524) (2006) 308–314.

[27] A. Mills, R. Davis, D. Worsley, Water purification by semiconductor photocatalysis, Chem. Soc. Rev. 22 (1993) 417–434.

[28] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.

[29] Standard Methods for the Examination of Water and Wastewater, 20th ed., AWWA, Washington, DC, 1998.

[30] A. Linsebigler, L. Lu, G. Yates, Photocatalysis on $TiO_2$ surfaces: principles, mechanisms, and selected results, Chem. Rev. 95 (1995) 735–738.

[31] K. Mogyorosi, I. Dekany, H. Fendler, Preparation and characterization of clay mineral intercalated titanium dioxide nanoparticles, Langmuir 19 (2003) 2938–2946.

[32] M. Andersson, L. Österlund, S. Ljungstrom, A. Palmqvist, Preparation of nanosize anatase and rutile $TiO_2$ by hydrothermal treatment of microemulsions and their activity for photocatalytic wet oxidation of phenol, J. Phys. Chem. B 106 (2002) 10674–10679.

[33] M. Addamo, V. Augugliaro, A.D. Paola, E. Garcia-Lopez, V. Loddo, G. Marci, R. Molinari, L. Palmisano, M. Schiavello, Preparation, characterization, and photoactivity of polycrystalline nanostructured $TiO_2$ catalysts, J. Phys. Chem. B 108 (2004) 3303–3310.

[34] N. San, A. Hatipoğlu, G. Koctürk, Z. Cinar, Prediction of primary intermediates and the photodegradation kinetics of 3-aminophenol in aqueous $TiO_2$ suspensions, J. Photochem. Photobiol. A: Chem. 139 (2001) 225–232.

[35] A. Gouvea, F. Wypych, S. Moraes, N. Duran, N. Nagata, P. Peralta-Zamora, Semiconductor assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433–440.

[36] M. Saquib, M. Muneer, Photocatalytic degradation of the textile dye, alizarin red S, in aqueous suspension of titanium dioxide, Adv. Color Sci. Technol. 5 (2002) 71–78.

[37] U Stafford, K.A. Gary, P.V. Kamat, Photocatalytic degradation of 4-chlorophenol: the effects of varying $TiO_2$ concentration and light wavelength, J. Catal. 167 (1997) 25–32.

[38] R. Terazian, N. Serpone, Heterogeneous photocatalysed oxidation of creosote components: mineralization of xylenols by illuminated $TiO_2$ in oxygenated aqueous media, J. Photochem. Photobiol. A: Chem. 89 (1995) 163–175.

[39] M. Goncalves, A. Oliveira-Compos, E. Pinto, P. Plasencia, M. Queiroz, Photochemical treatment of solutions of azo dyes containing $TiO_2$, Chemosphere 39 (1999) 781–786.

[40] O. Kartal, M. Erol, H. Oguz, Photocatalytic destruction of phenol by $TiO_2$ powders, Chem. Eng. Technol. 24 (2001) 645–649.

[41] N. Sobana, M. Swaminathan, The effect of operational parameters on the photocatalytic degradation of acid red 18 by ZnO, Sep. Purif. Technol. 56 (2007) 101–107.

[42] N. Daneshvar, S. Aber, M. Seyed Dorraji, A. Khataee, M. Rasoulifard, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light, Sep. Purif. Technol. 58 (2007) 91–98.

[43] M. Saquiba, M. Tariqa, M. Faisala, M. Muneer, Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide, Desalination 219 (2008) 301–311.

[44] L. Chen, C. Huang, F. Tsai, Characterization and photocatalytic activity of $K^+$-doped $TiO_2$ photo catalysts, J. Mol. Catal. A: Chem. 265 (2007) 133–140.

[45] M. Huang, C. Xu, Z. Wu, Y. Huang, J. Lin, J. Wu, Photocatalytic decolorization of methyl orange solution by Pt modified $TiO_2$ loaded on natural zeolite, Dyes Pigments 77 (2008) 327–334.

[46] J. Sun, L. Qiao, S. Sun, G. Wang, Photocatalytic degradation of Orange G on nitrogen-doped $TiO_2$ catalysts under visible light and sunlight irradiation, J. Hazard. Mater. 155 (2008) 312–319.

[47] S. Liu, J. Yang, J. Choy, Microporous $SiO_2$–$TiO_2$ nanosols pillared montmorillonite for photocatalytic decomposition of methyl orange, J. Photochem. Photobiol. A: Chem. 179 (2006) 75–80.

[48] P. Gogate, A. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[49] D. Bahnemann, Photocatalytic detoxification of polluted waters, in: P. Boule (Ed.), The Handbook of Environmental Chemistry, Springer, Heidelberg, 1999, pp. 285–351.

[50] I. Konstantinou, T. Albanis, $TiO_2$-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[51] H. Chang, T. Tsung, H. Lin, C. Lin, Photocatalytic activity of $TiO_2$ nanoparticle fluid prepared by combined ASNSS, China Particuol. 2 (2004) 171–173.

[52] I. Alaton, I. Balcioglu, D. Bahnemann, Advanced oxidation of a reactive dye bath effluent: comparison of $O_3$, $H_2O_2$/UV-C and $TiO_2$/UV-A processes, Water Res. 36 (2002) 1143–1154.

[53] H. Zhan, H. Tian, Photocatalytic degradation of acid azo dyes in $TiO_2$ colloidal suspension. III. Spectral characterization of excited state, Dyes Pigments 37 (1998) 249–254.

[54] O. Carp, C. Huisman, A. Reller, Photoinduced reactivity of titanium oxide photoinduced reactivity of titanium oxide, Solid State Chem. 32 (2004) 33–177.

[55] N. Mahmoodi, M. Arami, L. Yousefi, T. Salman, Chem. Eng. J. 112 (2005) 191–196.

[56] N. Mahmoodi, M. Arami, N. Limaee, N. Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized $TiO_2$ photocatalytic reactor, J. Colloid Interface Sci. 295 (2006) 159–164.

[57] J. Sun, X. Wang, J. Sun, R. Sun, S. Sun, L. Qiao, Photocatalytic degradation and kinetics of Orange G using nano-sized Sn(IV)/$TiO_2$/AC photocatalyst, J. Mol. Catal. A: Chem. 260 (2006) 241–246.

[58] H. Coleman, V. Vimonses, G. Leslie, R. Amal, Degradation of 1,4-dioxane in water using $TiO_2$ based photocatalytic and $H_2O_2$/UV processes, J. Hazard. Mater. 146 (2007) 496–501.