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Comparative studies on TiO_2/ZnO photocatalyzed degradation of 4-chlorocatechol and bleach mill effluents

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ABSTRACT

The study presents a comparative account on TiO_2 and ZnO facilitated photocatalytic degradation of 4-chlorocatechol (4-CC) typically found in bleach mill effluents (BME). The effect of major process parameters such as catalyst dose, pH, oxidant concentration, and source of light (UV/solar) on degradation efficiency has been investigated. The degradation efficiency of 4-CC was assessed in terms of absorbance as a function of irradiation time. Of the two catalysts screened, ZnO has been observed to be a better catalyst over TiO_2. The maximum degradation of 99.2 and 91.6% was obtained with 1.5 g/L ZnO, at pH 8, after 2 h irradiation and with 2.5 g/L TiO_2, at free pH (6.5), 0.04 M NaOCl concentration after 6 h irradiation, respectively. Further, the kinetics of degradation process was found to follow pseudo-first-order reaction. The photocatalytic process was applied to treat actual BME and degradation of effluent, observed in terms of chemical oxygen demand reduction, was 36.5 and 39% with UV/TiO_2/NaOCl and UV/ZnO systems, respectively. A 10-fold dilution of effluent was, however, needed to make the effluent amenable to photocatalytic treatment. Degradation efficiency at optimized conditions under solar mode was almost the same as under UV irradiation, thus demonstrating the commercial viability of the process.

Keywords: Photocatalysis; Titanium dioxide; Zinc oxide; Sodium hypochlorite; COD; 4-Chlorocatechol; Bleach mill effluents

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1. Introduction

Organic compounds present in environment are of major concern due to their toxicity and nonbiodegradable nature. Production of 1 ton of pulp is reported to contribute 100 kg of color imparting substances and 2–4 kg of total organochlorines to the bleach plant effluents. The pulp bleaching effluents contain about 85% of low molecular weight organic compounds such as acidic, phenolic, and chlorinated organics [1]. Phenolic organics such as chlorophenols and chlorocatechols are dominantly present in wastewater generated from pulp and paper mills, tanning, petroleum refining, etc. [2]. Chlorocatechols are priority pollutants under United States Environmental Protection Agency due to their acute toxicity and recalcitrant nature. As a result of the presence of such compounds, bleach mill effluents (BME) are known to be biorecalcitrant and increasing concern has been expressed about their effective treatment and safe disposal in the environment. Different treatment technologies are applied for the removal of organic pollutants in industrial waste-

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waters. Amongst them, biological treatment methods are widely used despite obvious drawbacks such as the low reaction rate, difficult disposal of the activated sludge, and the narrow range of pH and temperature for efficient biological treatment [3–5].

As an effective alternative, advanced oxidation processes (AOPs) have been experimented extensively to accomplish complete degradation of organic pollutants. AOPs involve the production of strongly oxidizing agents mainly hydroxyl radical ($^{\bullet}OH$) that react rapidly and almost nonselectively with various inorganic and organic pollutants. Homogeneous oxidation systems carry out the degradation of pollutants using H_2O_2/UV, $H_2O_2/UV/O_3$, UV/O_3, and photoassisted fenton degradation techniques [6–9]. However, these oxidation techniques for the degradation of organics are both cost and energy intensive. The heterogeneous photocatalytic systems (UV/semiconductors) have been extensively studied due to their ability to photosensitize the wide range of organic substrates at ambient temperatures and pressures, without the production of harmful by-products and the use of solar irradiation. The photocatalytic degradation of several biorecalcitrant compounds like alkanolamines, phenols, aromatics, dyes, and pesticides have been successfully reported [10–13]. Titanium dioxide (TiO_2) is the most widely reported photocatalyst amongst various catalysts used for the degradation of organic pollutants [14]. The use of TiO_2 as photocatalyst for environmental cleanup has been of interest, because of its stability, nontoxicity, and cost effectiveness in addition to be activated under solar light [15].

Although photodegradation of phenol and its derivatives has been widely reported [16], observations on the photodegradation of chlorocatechols are very limited. The TiO_2-mediated photocatalytic degradation of 4-chlorocatechol (4-CC) as a reaction intermediate formed during the degradation of 4-chlorophenol has been studied and the degradation pathway of 4-CC has been suggested [17]. As the chlorophenols and chlorocatechols are the major contributors toward biorecalcitrant organic pollutant in pulp and paper mill effluents, it becomes imperative to study the degradation of these compounds using heterogeneous photocatalysis. To the best of authors' knowledge, there are no reports dealing with the heterogeneous photocatalytic degradation of 4-CC using ZnO as a catalyst. In continuation of our earlier research findings on the photocatalytic degradation of phenol and its derivatives and catechol [18], an attempt has been made in the present paper to carry out photocatalytic degradation of 4-CC aqueous solution typically found in BME using both TiO_2 and ZnO under UV/solar light. Sodium hypochlorite has been used as an oxidant, which is widely employed in pulp bleaching. The effect of key operating parameters on degradation efficiency (i.e. catalyst dose, pH, and oxidant concentration) has been investigated. Having established optimal operating conditions, the applicability of the process to treat actual BME was tested.

2. Experimental details

2.1. Materials

Titania P-25 (surface area $50\,m^2/g$ and average particle size 30 nm) was obtained from Degussa, Germany and was used as received. ZnO ($5\,m^2/g$) was purchased from Merck, Germany. 4-CC was purchased from Aldrich, USA, which was used in the study. All the reagents were prepared in double-distilled water. pH of the solutions was adjusted with 1 M HCI or 1 M NaOH as required in the study. Sodium hypochlorite (4% available Cl_2, BDH Merck) was used as an oxidant. Reagents used for chemical oxygen demand (COD) determination were procured from S.D. Fine Chemicals, India. The composite samples of actual BME were collected from first alkaline extraction (E_1) stage of a bleaching sequence ($CE_{OP}HH$) of soda pulp, from an agro-based pulp and paper mill in Punjab province of India. The samples were stored and transported at 4°C.

2.2. Instrumentation

The UV reactor (rectangular) was made up of cast iron sheets with wooden roof equipped with seven UV tubes of 36 W (Philips) each having wavelength of 365 nm. The photocatalytic experiments were performed, in slurry mode, in specially designed double-walled reaction vessels (1,000 mL) having surface area of $0.025\,m^2$. Maximum UV intensity was found to be $25\,W\,m^{-2}$ at the middle of the UV reactor (measured with the help of radiometer) and all experiments were performed at this UV intensity. The photon flux was approximately 0.625 W. The solution was kept under constant stirring using magnetic stirrers and aeration was carried out with the help of conventional aerators. The ambient temperature of the reaction vessel and UV chamber was maintained at 30 ± 0.5°C by circulating the water in double-walled reaction vessels and providing air exhaust, respectively. For solar insolation experiments, the borosilicate glass reactors of diameter 0.18 m and 1,000 mL capacity, facilitated with ports at the top for sampling, gas purge, and gas outlet, were used. The solar experiments were performed in day time between 10.00 and 16.00 h in the month of April–May. The average intensity of sunlight in this region was 35 W/m^2 during the experiments. The degradation of 4-CC was measured by monitoring absorbance as a function of irradiation time using spectrophotometer (Hitachi V-500UV/VIS—Japan double beam spectrophotometer) at the wavelength (283 nm) associated with 4-CC. The degradation efficiency of BME was expressed with reference to the decrease in COD measured by closed reflux method (spectrophotometric) using standard protocols [19]. Simultaneously, the degradation of BME was also expressed with reference to the decrease in total organic carbon (TOC) measured by Hach DR 890 Colorimeter (Method No. 10,129; Hach, USA). pH of the wastewater was adjusted using Thermo Orion 920A digital pH meter.

2.3. Procedure

For the degradation studies, 100 mL of 4-CC (50 ppm) in aqueous solutions and 100 mL of BME were subjected to treatment under different experimental conditions (i) only UV, (ii) dark + TiO_2, (iii) UV + TiO_2, (iv) UV + TiO_2 + NaOCl and (i) only UV, (ii) dark + ZnO, (iii) UV + ZnO, (iv) UV + ZnO + NaOCl. For 4-CC, the experimental matrix was developed in order to optimize the photocatalytic process parameters such as dose of photocatalyst (1.0–3.0 g/L), initial pH of the solutions (2–12), and NaOCl concentration (0.02–0.06 M) under UV irradiation.

Further, the BME sample was subjected to photocatalytic treatment under optimized conditions of 4-CC i.e. 2.5 g/L TiO_2 loading at pH 6.5, 0.04 M NaOCl and 1.5 g/L ZnO at pH 8. The aqueous suspension was magnetically stirred and subjected to irradiation under UV light/solar light for a period of 6 h. After regular time intervals of 2 h, aliquot was taken out with the help of a syringe and then filtered through a millipore syringe filter (0.45 μm). The degradation efficiency of 4-CC was studied in terms of changes in absorption spectra recorded at λ_{max} 283 nm. The degradation efficiency of BME was expressed with reference to the decrease in COD.

The percentage degradation was calculated as follows:

$$\% \text{ Degradation} = 100 \times \left[\frac{C_0 - C}{C_0}\right]$$

where C_0 is the initial concentration of solution and C is the concentration of solution after photoirradiation.

3. Results and discussion

3.1. Time dependent degradation of 4-CC

Fig. 1 shows the typical time dependent UV–Vis spectra of 4-CC in aqueous solution. The absorption peak was observed at 283 nm, which decreased gradually during photocatalysis employing TiO_2 indicating that the degradation of the organic compound was occurring.

3.2. Photolysis/photocatalytic degradation of 4-CC

100 mL of 4-CC (50 ppm) in aqueous solutions having free pH of 6.5 and catalyst dose of 2.5 g/L in case of TiO_2 and 1.5 g/L in case of ZnO were subjected to treatment under different experimental conditions as shown in Figs. 2(a) and 2(b), respectively. The irradiation in the absence of photocatalyst showed limited degradation of 4-CC (9.8%) in 6 h, whereas in the presence of UV and photocatalyst, 87.4% degradation was achieved in 6 h with TiO_2 and 98.6% degradation was achieved in only 2 h with ZnO. The weak disappearance of 4-CC in the absence of catalyst is assigned to the direct photolysis resulting in weak UV light absorption by the 4-CC. The results depict that heterogeneous photocatalytic treatment is more effective in the degradation of 4-CC as compared to photolysis. The results are in agreement with the previously reported observations on photolytic and photocatalytic degradation of azo dye [20]. When the adsorption studies of 4-CC (50 mg/L) were carried out with TiO_2 and ZnO in the dark, it was found that 37.1% of 4-CC was adsorbed on to TiO_2, whereas 39.4% 4-CC adsorption was observed with ZnO.

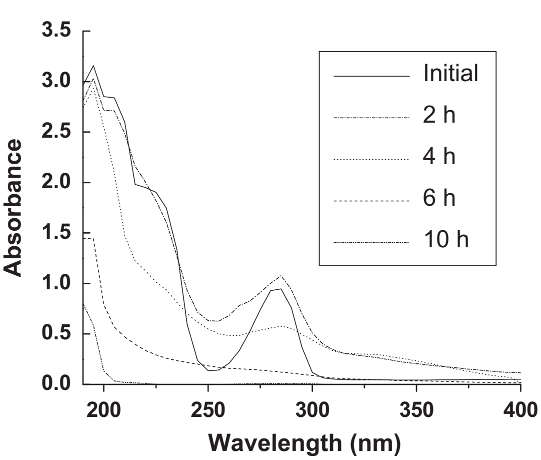

Fig. 1. Time dependent UV–Vis absorption spectra for 4-CC (50 ppm).

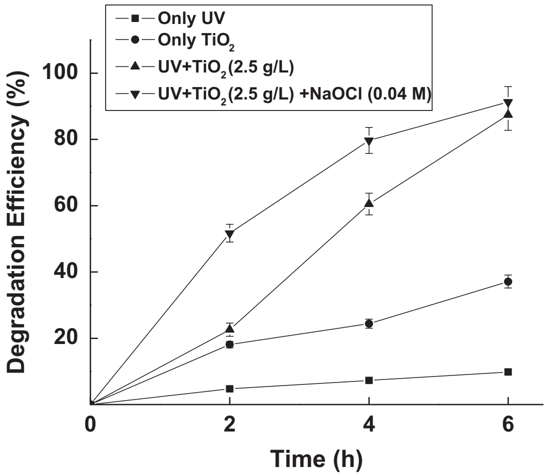

Fig. 2a. Effect of TiO_2 photocatalysis on degradation efficiency of 4-CC at free pH.

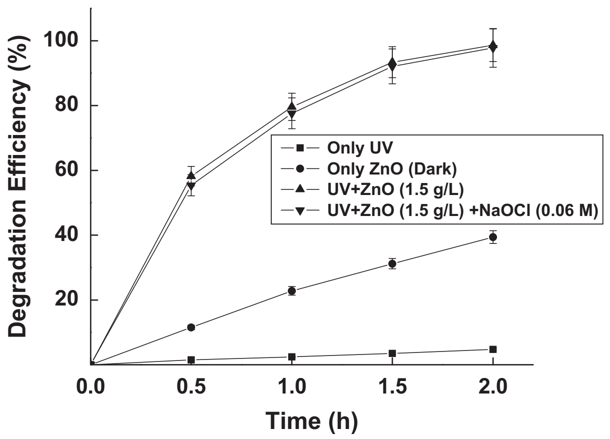

Fig. 2b. Effect of ZnO photocatalysis on degradation efficiency of 4-CC at free pH.

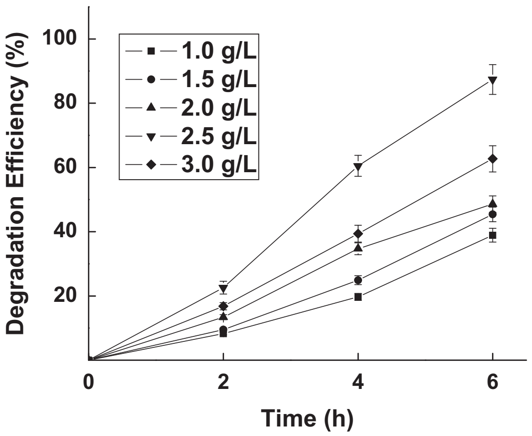

Fig. 3a. Effect of TiO_2 dose (free pH 6.5, 50 ppm 4-CC).

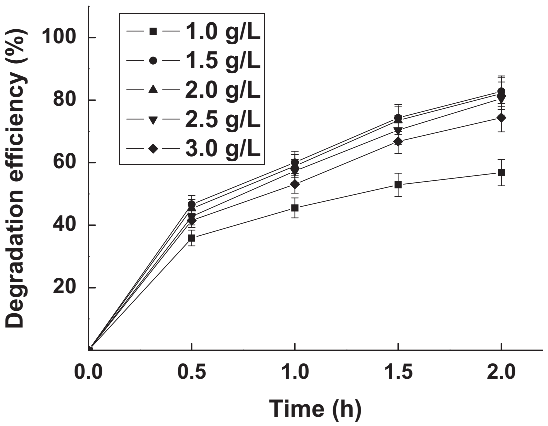

Fig. 3b. Effect of ZnO dose (free pH 6.5, 50 ppm 4-CC).

3.3. Degradation of 4-CC using TiO_2/ZnO as photocatalyst

The experiments were conducted to study the degradation of 4-CC employing TiO_2 and ZnO as catalyst under UV irradiation. The parameters considered were catalyst dose, pH, and oxidant concentration.

3.3.1. Effect of catalyst dose

Selection of optimum catalyst concentration is important in order to minimize excess of catalyst and to ensure total absorption of photons. Figs. 3(a) and 3 (b) show the effect of changing catalyst concentration of TiO_2 (a) and ZnO (b) from 1.0 to 3 g/L on degradation efficiency of 4-CC (50 ppm) at free pH (6.5) under UV irradiation up to 6 h. The extent of degradation was found to increase with increased TiO_2 and ZnO concentrations up to 2.5 and 1.5 g/L, respectively, which is presumably due to increase in the active sites for adsorption of the compound on the catalyst surface as well as the enhanced generation of free hydroxyl ($^{\bullet}OH$) radical, indicating a heterogeneous catalytic regime. However, further increase in concentration of catalyst dose decreased the percent degradation which may be due to increase in turbidity of the suspension and subsequent hindering of the UV light penetration [21,22]. Thus, 2.5 g/L TiO_2 and 1.5 g/L ZnO were selected as an optimum dose for further photocatalytic experiments.

3.3.2. Effect of medium pH

It is well known that pH can affect the mechanism and routes of degradation. The TiO_2 point of zero charge (pzc) is between pH 5.6 and 6.4 [8]. Hence, depending on the pH, the catalyst surface will be either charged positively (for $\mathrm{pH} < \mathrm{pzc}$), negatively (for $\mathrm{pH} > \mathrm{pzc}$), or remain neutral (for $\mathrm{pH} \approx \mathrm{pzc}$). This characteristic significantly affects the adsorption and desorption properties of TiO_2. In addition, the structure of the pollutants is also influenced by change in pH. For example, 4-CC has a $pK_a = 6.5$ and can be charged either positively or negatively on basis of the pH. To sum up, it seems clear that the interaction and affinity between both species will be different relying on the pH. To study this aspect in our system, degradation studies were conducted in non-buffering conditions with different initial pH values ranging from 2 to 12, at an optimum catalyst dose (2.5 g/L TiO_2 and 1.5 g/L ZnO) under UV irradiation. Observations indicated pronounced influence of pH on the degradation of 4-CC. The maximum photodegradation of 87.4% could be achieved with TiO_2 (2.5 g/L) at free pH of 6.5 (Fig. 4(a)), which is expectedly due to the more adsorption of organic compound in this pH range. Degradation was observed to be minimum at pH 2, the reason may be external addition of chlorides ions for pH adjustments which may be responsible for interferences in photo catalysis. The near-complete photodegradation (98.6%) was obtained with ZnO (1.5 g/L) at pH 8 as depicted in Fig. 4(b). This behavior is attributed to the fact that variation in pH entails an alteration in the properties of semiconductor-liquid interface, mainly related to acid base equilibrium of the adsorbed hydroxyl group. The formation of hydroxyl radical from OH^- is favored at high pH. This observation is further supported by earlier report on photocatalytic degradation of lignin using TiO_2 and ZnO semiconductors, wherein maximum photocatalytic degradation of lignin was attained at pH value of 11 using ZnO [23].

3.3.3. *Effect of addition of oxidant*

Addition of sodium hypochlorite as an oxidant along with TiO_2 (2.5 g/L) at free pH of 6.5 was observed to improve the rate of photocatalytic degradation of 4-CC. The observations presented in Fig. 5 indicated that the addition of oxidant in the concentration range of 0.02–0.06 M enhanced the rate constant or alternatively, reduces the time required to achieve same degree of degradation up to 0.04 M NaOCl. Maximum degradation of 91.6% was noted in the presence of 0.04 M NaOCl. A reason for this could be the availability of hypochlorite ion (OCl^-), which is unstable and ultimately degrades to chloride and chlorate ions resulting in oxidation of more organic matter. Our earlier research findings also depict the enhanced degradation of BME in the presence of NaOCl [24]. Further increase in the concentration of NaOCl may be contributing toward the slight increase in COD value due to more consumption of potassium dichromate by hypochlorite ion, so degradation decreases with 0.06 M NaOCl. Blank experiments were conducted by irradiating the aqueous solution of organic compound in the absence of photocatalyst using optimum concentration of oxidant and no observable loss of the compound was noticed during irradiation. Similar trend was also reported during photodegradation of chlorophenols by using UV/TiO_2 in presence of inorganic oxidant perchlorate [25]. The presence of oxidant (sodium hypochlorite) along with ZnO (1.5 g/L) at pH 8 did not result in increase in the degradation efficiency of 4-CC.

3.3.4. *Effect of light source*

In order to reduce the operating cost of the process, further investigations were carried out using

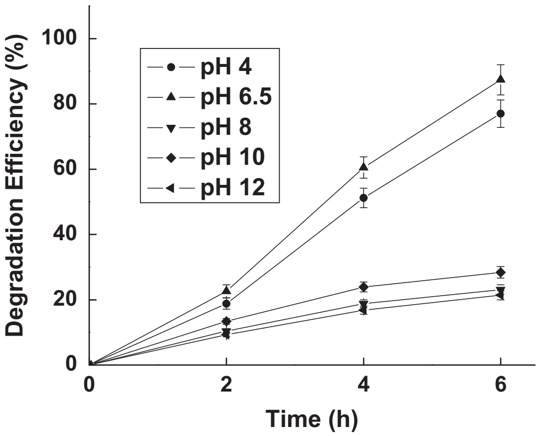

Fig. 4a. Effect of medium pH (2.5 g/L TiO_2).

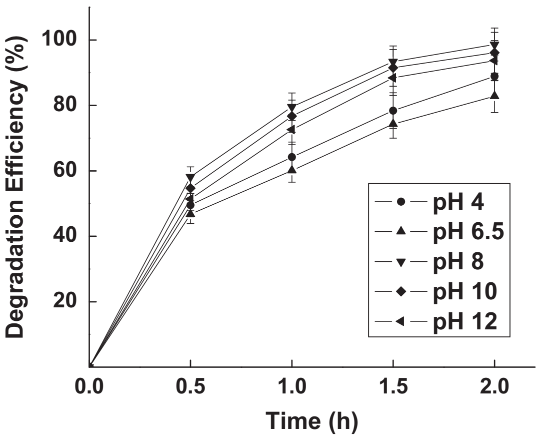

Fig. 4b. Effect of medium pH (1.5 g/L ZnO).

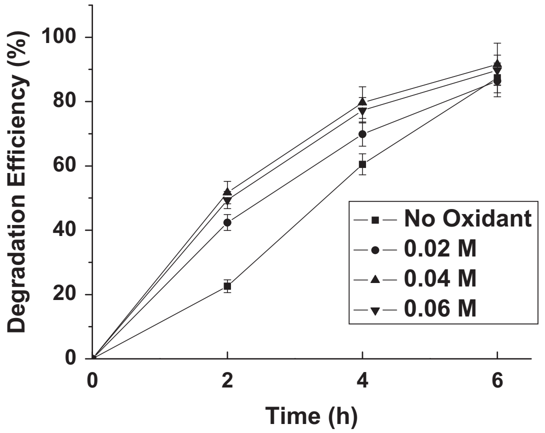

Fig. 5. Effect of oxidant concentration (2.5 g/L TiO_2 at free pH).

solar light rather than UV irradiation. The aqueous suspensions of 4-CC (50 ppm) were exposed to UV and solar light under optimized conditions (2.5 g/L TiO_2, pH 6.5 in the presence of 0.04 M NaOCl and 1.5 g/L ZnO, pH 8). The respective percent degradation was found to be 92.7 and 99.1% in solar light as compared to 91.3 and 98.6% in UV light (Figs. 6(a) and 6(b)). The percentage degradation with solar light was in close proximity to UV light which is due to their ability to absorb part of the visible light [26]. The adsorption of chemical molecule on the catalyst surface results in excited states caused due to visible illumination and these excited states facilitate transfer electrons to the conduction band of TiO_2 particles. The results indicate efficient use of solar light for the photocatalytic degradation of 4-CC.

3.4. Kinetics of degradation

In order to study the kinetics of 4-CC degradation, we have tried to determine the order of kinetics and the apparent rate constant of the 4-CC degradation.

$$\mathrm{HO}_{\mathrm{ads}^{\cdot}} + \text{4-CC} \rightarrow \text{Intermediates}_{\mathrm{ads}} \rightarrow \text{Intermediates}_{\mathrm{free}} \tag{1}$$

$$\mathrm{HO}_{\mathrm{ads}^{\cdot}} + \text{Intermediates} \rightarrow \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{Cl}^- \tag{2}$$

If we presume that the reaction (1) is of a first order relating to 4-CC concentration, keeping the hydroxyl radicals concentration constant, the degradation rate r would be governed by the following equation:

$$r = d[\text{4-CC}]/\mathrm{d}t = K_{(\text{4-CC})}[\mathrm{HO}_{\mathrm{ads}^{\cdot}}]^{\alpha}[\text{4-CC}] = K_{\mathrm{app}(\text{4-CC})}\,[\text{4-CC}] \tag{3}$$

where α is the reaction order relating to the adsorbed hydroxyl radicals concentration, $K_{(\text{4-CC})}$ is the real rate constant, and $K_{\mathrm{app}(\text{4-CC})}$ is the apparent rate constant of the 4-CC degradation. The above equation can further be solved as follows:

$$\ln[\text{4-CC}]_0/[\text{4-CC}] = K_{\mathrm{app}(\text{4-CC})}t \tag{4}$$

where $[\text{4-CC}]_0$ and [4-CC] are, respectively, the 4-CC concentration at time 0 and t.

The value of apparent rate constants of 4-CC degradation has been shown in Table 1, which was determined from the slope of straight line obtained. The

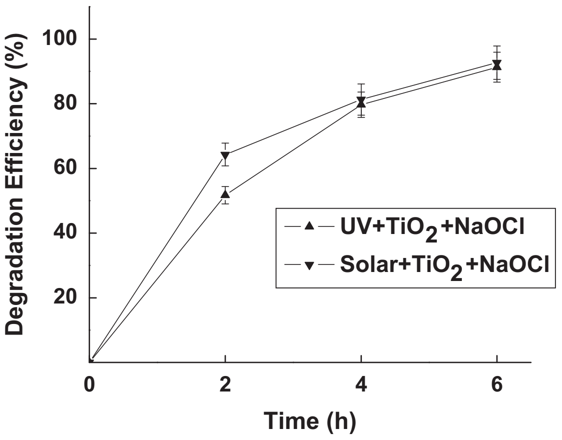

Fig. 6a. Effect of UV/solar light under optimized conditions in case of TiO_2.

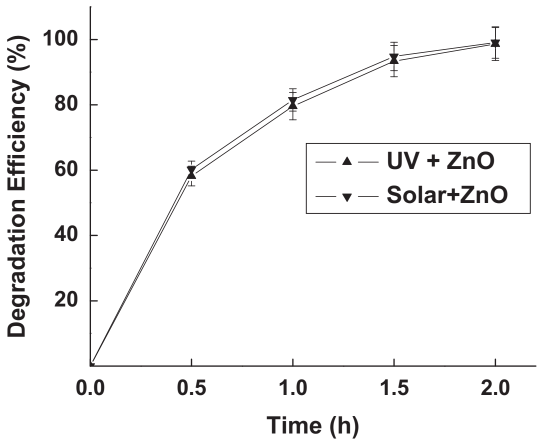

Fig. 6b. Effect of UV/solar light under optimized conditions in case of ZnO.

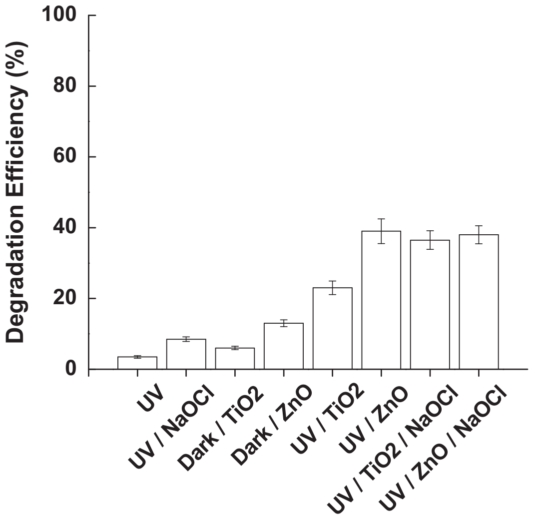

Fig. 7a. Degradation of BME under different photocatalytic systems.

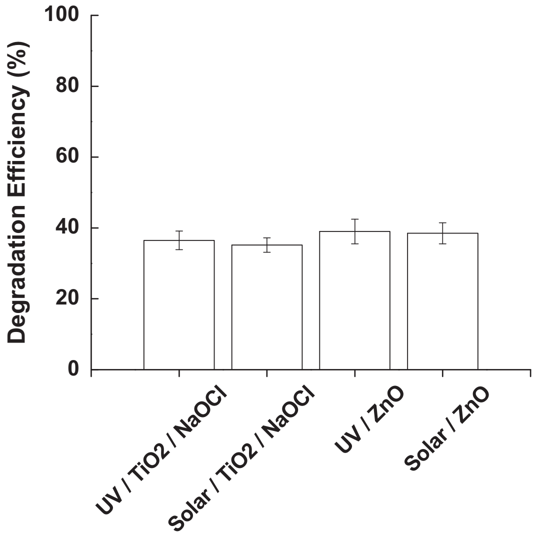

Fig. 7b. Degradation of BME under solar mode.

Table 1
Apparent first-order rate constants and linear regression coefficiants of 4-CC

Catalyst	$K_{\mathrm{app(4\text{-}CC)}}$ (h^{-1})	r^2
ZnO	1.036	0.975
TiO_2	0.689	0.923

results reveal that the 4-CC degradation was more with ZnO as compared to TiO_2. Moreover, the degradation of 4-CC is in agreement with a pseudo first-order kinetics of Langmuir–Hinshelwood model.

3.5. Application of photocatalytic treatment to actual bleaching effluent

In a final series of experiments, the photocatalytic process was applied for the treatment of actual soda BME from agro residue-based pulp and paper mill, and the results are summarized in Fig. 7(a). BME was subjected to photocatalytic treatment in different degradation systems: in the dark or under light (UV), in presence or absence of NaOCl, variation of photocatalyst, and all possible combination of these systems (UV, UV/NaOCl, dark/TiO_2, dark/ZnO, UV/TiO_2, UV/ZnO, UV/TiO_2/NaOCl, and UV/ZnO/NaOCl). The concentrations of TiO_2, ZnO, and NaOCl were kept same as that of optimum conditions obtained in degradation of 4-CC i.e. 2.5 g/L TiO_2 loading at pH 6.5, 0.04 M NaOCl and 1.5 g/L ZnO at pH 8. A preliminary blank experiment was performed in UV with effluent having initial COD of 2240.3 (±20.7) mg/L without catalyst yielding only about 3.5% degradation after 6 h. However, when the same run was performed in the presence of TiO_2 and ZnO, degradation increased to 23 and 39%, respectively, after 6 h of reaction. In the presence of NaOCl (UV/NaOCl), only an insignificant effect on the degradation of effluent was observed. This poor degradation (8.5%) may be due to the weak photolysis of NaOCl. In the absence of light (dark/TiO_2 and dark/ZnO system), less degradation of 6 and 13% of effluent has been observed due to absence of electron-hole generation. The systems UV/TiO_2/NaOCl and UV/ZnO/NaOCl lead to 36.5 and 38% degradation of effluent after 6 h of irradiation

Table 2
Characteristics of BME before and after solar photocatalytic treatment

S. no.	Parameter	Before treatment	After treatment (solar/TiO_2/NaOCl)	After treatment (solar/ZnO)
1.	pH ($n = 11$)	8.2 (±0.01)	7.8 (±0.01)	7.4 (±0.01)
2.	Temperature (°C)	34	32	32
3.	BOD_5 ($mg\,L^{-1}$) ($n = 5$)	1,386 (±11)	–	–
4.	COD ($mg\,L^{-1}$) ($n = 19$)	2240.3 (±20.7)	1451.7 (±28.4)	1377.7 (± 25.7)
5.	TOC ($mg\,L^{-1}$) ($n = 16$)	560 (±24)	368 (±24.9)	346 (±18.5)

exposure. Hence, the addition of oxidant is effective in increasing the degradation efficiency in case of TiO_2. Moreover, ZnO appears to be better photocatalyst than TiO_2 as depicted in Fig. 7(a). Table 2 shows effluent characteristics before and after treatment showing that degradation of effluent progressively occurred.

From Figs. 4(b), 5 and 7(a), it is clear that degradation of the 4-CC is much higher than that for the actual bleaching effluent, which may be possibly due to the fact that the actual effluent also contains several other organics that compete with 4-CC for radicals and other reactive moieties and this is consistent with the fact that the COD content of actual effluent is as much as about eight times that of the 4-CC solution. Decreasing organic load of the effluent facilitates degradation; for instance, 90% degradation was achieved with UV/ZnO system after 6 h with the 10% effluent (initial COD = 220 mg/L). Similar studies have been reported on the degradation of pulp mill effluents by advanced oxidation treatment [27,28].

Fig. 7b shows the degradation of effluent in the presence of solar light and degradation efficiency in the presence solar mode were found to be almost same as compared to UV light. Similar observations have also been reported by other researchers, wherein solar light was observably effective over UV in degradation of pulp and paper mill effluent [29,30].

4. Conclusion

The conclusions drawn from this study include:

(1) ZnO proved to be a better photocatalyst than Degussa P-25 TiO_2 for the degradation of 4-CC.
(2) Addition of sodium hypochlorite (0.04 M) enhances considerably treatment efficiency (91.6%) in case of TiO_2.
(3) The photodegradation increases with increase in catalyst dose up to an optimum loading.
(4) The percentage degradation was facilitated with ZnO at pH 8.
(5) Solar light was found to be efficient in the degradation of 4-CC when compared to UV.
(6) The photocatalytic degradation reaction follows pseudo-first-order kinetics of Langmuir–Hinshelwood model.
(7) The applicability of the proposed process to treat actual BME depends strongly on the effluent's composition and concentration. The systems solar/TiO_2/NaOCl and solar/ZnO lead to 35.2 and 38.5% degradation of effluent. The effluent needs to be separated from its solid content and then diluted several times prior to photocatalytic treatment in order to achieve practically significant treatment efficiencies. This implies that photocatalysis may be part of a process train for the effective treatment of this type of industrial effluents.

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