

Treatment of bleaching effluent from the pulp and paper industry by photocatalytic oxidation

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ABSTRACT: We investigated the photocatalytic degradation of COD in bleach plant effluent in a low-cost, nonconcentrating shallow pond slurry reactor using artificial UV light. We studied the photocatalytic oxidative degradation using Degussa P25 titanium dioxide (TiO_2). Effects on degradation of catalyst loading, initial COD values, UV intensity, and aperture-to-volume ratio of the reactor were studied. Degradation rates were strongly influenced by some of these measures. Treatment efficiencies declined with a decrease in UV light intensity and increased with an increase in aperture-to-volume ratio. Results obtained in sunlight were similar to those obtained under artificial UV light in the laboratory.

Application: The information from this study will be helpful in deciding about the treatment system(s) for the bleach plant effluents, which contain many pollutants difficult to treat by conventional biological standards.

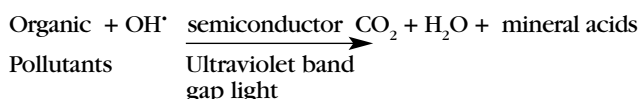
After each stage of bleaching or extraction in a bleached pulp mill, pulp is washed and the wash water is reused or sent to the sewer as effluent. The average volume of effluent generated from the bleach plant for a typical hardwood kraft pulp mill in India is 35-65 m^3/ton of pulp [1,2]. Several physical and chemical methods have been attempted for treatment of the organic matter in the effluent. Few methods have been shown to be technologically feasible and the costs for those that have been prohibitive. Conventional biological wastewater treatment is not effective in treating many of the bio-recalcitrant organic compounds that are measured as COD and color in bleach plant effluent.

Several recent developments in water decontamination processes provide new approaches to oxidizing bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade recalcitrant molecules into biodegradable compounds. They are called advanced oxidation processes (AOPs). Coburn et al. [3] and Prat et al. [4] studied the treatment of bleach plant effluents using hydrogen peroxide and UV radiation, which is one of the AOPs that uses spectra in the far-UV range. Semiconductor photocatalysis processes, using low energy UV light and titanium dioxide (TiO_2) as the catalyst, can completely mineralize organic pollutants. Photocatalytic treatment has received much attention in recent years [5-7]. For example, Boyd et al. [8] studied the degradation of paper mill wastewater using UV and TiO_2 .

In photocatalysis processes, photons with energy greater

than the bandgap of the semiconductor catalyst produce strong oxidizing electron holes at the semiconductor-liquid surface. At these holes, reactions with water result in oxidation of organic contaminants to CO_2 and simpler compounds. The most active photocatalyst for this application is the anatase form of TiO_2 , a photocatalyst that requires photons in the low energy UV radiation range. The energy needed to activate TiO_2 is 3.2 eV or more. Terrestrial solar radiation has sufficient energy in this range to make solar photocatalytic oxidation of wastewater feasible without transporting the waste to a radiation source.

In semiconductor photocatalysis process for water purification, pollutants are usually organic and therefore the overall process can be summarized by the following reaction equation:

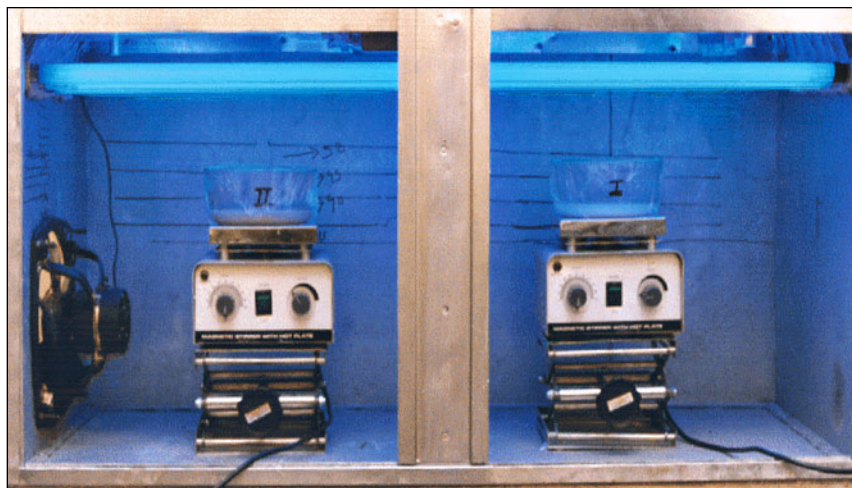


Application of photocatalysis for treating pulp and paper industry wastewaters has been explored, primarily in the treatment of bleach plant effluents [9-14]. Yeber et al. [9] observed approximately 50% degradation of both COD and toxicity with supported TiO_2 in wastewater from a bleached kraft pulp [9-11]. Balcioglu et al. observed that wastewaters treated by photocatalysis enhanced the biodegradability of remaining pollutants in bleach effluent and that photocatal-

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ysis was significantly more effective on pretreated wastewaters than on raw or untreated waters [12,13]. Although the strong potential of photocatalytic oxidation for wastewater treatment is widely recognized, commercial deployment efforts have not met with much success. This is due to the high operating cost of the photocatalytic oxidation process compared with biological treatment. Most of the reactor configurations are of the immersion type (with lamps immersed within the reactor), external type, (with lamps outside the reactor) or distributive type (with the light distributed from the source to the reactor by means such as reflectors or optical fibers). Because of their high cost, all of these reactor designs are limited to small-scale applications. Our work deals with degradation of effluent, at the laboratory scale, on a non-concentrating shallow pond slurry reactor, using UV intensity up to 50 Wm^{-2} . This is the intensity of UV light available in solar radiation, suggesting that this approach may have the potential for large scale applications.

There has been great interest in developing solar photocatalytic oxidation facilities for commercial application. In solar detoxification systems, reactor configurations that concentrate the solar radiation (concentrating reactors) and those that do not (nonconcentrating reactors) have been used. A disadvantage of concentrating reactors is that they cannot concentrate diffuse solar radiation, which can account for 50% or more of UV radiation during high humidity or partly cloudy conditions [15], while the nonconcentrating photoreactors use the direct and diffused components of UV radiation. Moreover, the prohibitive costs associated with solar concentrators limit their usefulness in industrial applications. Nonconcentrating reactors, however, can be simple in design and low cost. A number of different designs of nonconcentrating solar reactors have been proposed, including trickle-down flat plate



1. Laboratory apparatus for studying shallow-pond reactor treatment.

(16), pressurized flat plate (17), tubular flat plate (18) and shallow solar ponds (19). Flat plate reactors are most effective in applications where throughput is small, which is not the case for most pulp and paper mills. Since pulp and paper mills already use holding ponds for the microbiological treatment of wastewater, shallow solar ponds may be an option for the front or back end of a combined solar/microbiological treatment system for wastewater.

EXPERIMENTAL

Materials and equipment

The photocatalyst used in all the experiments was an anatase form of titanium dioxide powder, (Degussa P25 TiO_2 with a BET surface area of $50 \pm 15 \text{ m}^2\text{g}^{-1}$ and average particle size of 30 nm, procured from Degussa Co., Germany). Bleach plant effluents were obtained from pulp and paper mills. An Eppley UV radiometer (model no. 33013) was used for measuring the UV intensity. COD was determined by APHA standard method No. 5220 C. Samples were digested in a semi-automatic autoclave.

Photoreactor

Figure 1 is a diagram of the experimental, artificial-light irradiated, shallow-pond slurry reactor. The radiation

source consisted of a UV chamber, made of galvanized aluminum sheet, with dimensions of 4 ft x 2.5 ft x 2.5 ft. The chamber was fitted with eight 40W UV black fluorescent lamps (Philips), arranged in parallel on the top of the chamber. An exhaust fan was fitted on the sidewall of the chamber to maintain a constant temperature. The shallow effluent was contained in a cylindrical reactor made of borosil glass, 5 cm in diameter and 6 cm high, with a capacity of approximately 1000 mL. Radiation intensity was controlled by adjusting the distance of the reactor from the UV tubes. Using this method, the UV intensity in the reactor could be varied from 25 to 50 Wm^{-2} , corresponding to the average intensity of UV radiation in sunlight. The process was carried out in open atmosphere, with occasional oxygen purging to ensure that enough oxygen to guarantee the generation of adequate quantities of hydroxyl radicals was in solution.

Experimental procedure

In a typical experiment, effluent was diluted in a ratio of 1:3. The TiO_2 catalyst, at a loading of 2.0 g L^{-1} was dispersed in a 200 mL solution. In experiments described below, this loading was determined to be the optimum amount of catalyst to be used. This suspension was

then irradiated under UV light and stirred magnetically at a constant temperature of 30°C throughout the reaction. An aliquot of 10 mL was taken from the reactor at regular intervals and filtered through a 0.45 μm millipore filter disc. The filtrate was analyzed for COD. Except when a specific parameter was changed to study its effect, all the experiments were carried out under an intensity of 35 Wm^{-2} , an aperture to volume ratio (A/V) of 1.14 $\text{cm}^2 \text{mL}^{-1}$ in the reactor, and a catalyst loading of 2.0 g L^{-1} .

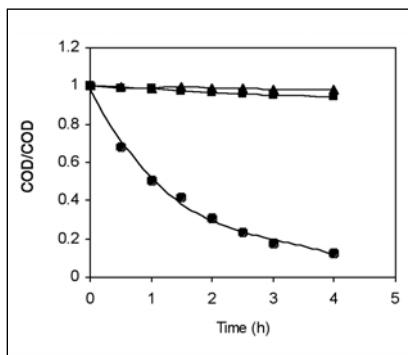
RESULTS AND DISCUSSION

Degradation of effluent

Figure 2 shows the removal of COD from an initial value of 320.14 mg L^{-1} using 2 g L^{-1} of photocatalyst at an intensity of 35 W m^{-2} . We observed that 88.6 % of COD removal takes place in 4 hours. In the blank experiments, there was no observable COD removal when the irradiation was carried out in the absence of TiO_2 . In case of the nonirradiated suspension, there was only a 6% removal of COD, which was attributed to adsorption onto TiO_2 particles.

Effect of catalyst (TiO_2) concentration

The variation in the rate of effluent degradation was determined by varying the amount of TiO_2 in the range of 0.5 to 3.0 g L^{-1} and irradiating for 4.5 hours. **Figure 3** shows that as TiO_2 concentration increases from 0 g L^{-1} to 2.0 g L^{-1} , the removal of COD increases in response. However, light penetration into the reaction slurry decreases as the TiO_2 concentration increases. At some TiO_2 concentrations, the reduced penetration of light into the reaction slurry cancels out the benefits of higher amounts of TiO_2 . In our case the optimum TiO_2 concentration was found to be 2.0 g L^{-1} and this concentration was used for all subsequent tests. This has been observed and reported in the literature [20,21].

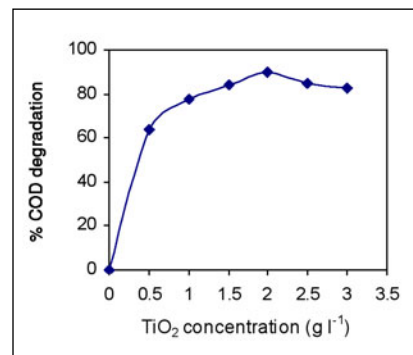


2. Photocatalytic degradation of effluent.

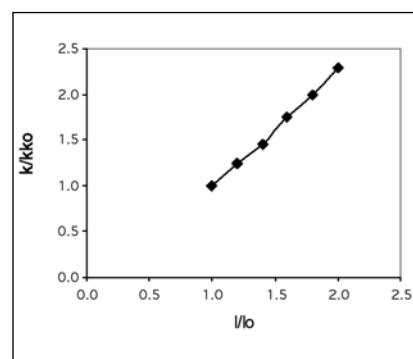
(Δ) only UV, ($\blacksquare$) only TiO_2 , ($\bullet$) TiO_2 and light at 35 Wm^{-2} intensity

Effect of UV intensity

The amount of degradation depends on the radiation intensity. Various researchers have found that the reaction rate increases with the square root of intensity at high levels, but changes to a first-order relationship at lower levels of illumination [22-24]. The transition point between these regimes varies between different types of photosystems. In the degradation of 3-CP in TiO_2 aqueous suspensions, the initial degradation rate was reported to be proportional to radiant flux for values smaller than 200 Wm^{-2} , while above this value, it was proportional to its square root [24]. The initial degradation rate of 4-CP against the radiant flux was also investigated in the range of 20-500 Wm^{-2} [22] where a similar rate shift from first order to half-order in intensity was observed. The degradation studies of effluent were done below 50 Wm^{-2} , hence the dependence of rate constant on intensity was of first order. The work was done below 50 Wm^{-2} as the intensity available in the solar energy is 50 Wm^{-2} or less. To study the effect of intensity, the aperture to volume (A/V) ratio was kept constant at 1.14 $\text{cm}^2 \text{mL}^{-1}$ and the intensity was varied from 25 to 50 Wm^{-2} . The value of degradation rate constant increases from 0.3868 to 0.8834 h^{-1} as intensity increases from 25 to 50 Wm^{-2} . **Figure 4** shows the relation between reaction



3. Effect of TiO_2 concentration on COD degradation of the effluent.



4. Rate of constant variation with intensity for degradation of effluent.

rate constant k and intensity for constant A/V ratio. The intensity of solar UV radiation varies throughout the year, therefore the experimentally determined reaction rate constant k_0 must be adjusted for the actual UV intensity. The variation in reaction rate constant with intensity of incident light depends on the type of reactor used. This is shown in the following equations.

For a shallow-pond solar reactor, the intensity dependence of the reaction rate constant is shown in

$$k / k_0 = m [I (A/V) / I_0 (A/V)_0]^n$$

where “m” and “n” are the empirical constants whose values, for some systems, have been reported by Wyness et al. [22], and “ k_0 ” is the reference rate constant corresponding to reference intensity I_0 . Hence, the rate constant “k” is dependent on intensity when the aper-

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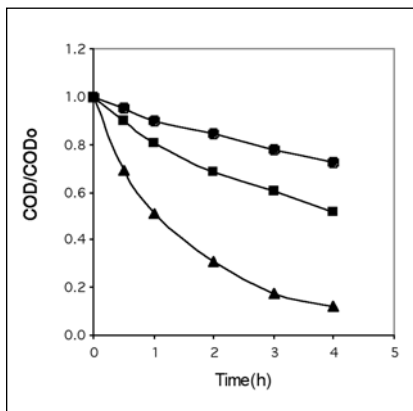
ture to volume ratio (A/V) is kept constant as shown in the equation

$$k / k_0 = m [I / I_0]^n \text{ (A/V ratio constant)}$$

The value of "n" is 1.1779 and of "m" is 0.036 for degradation of effluent obtained by plotting k/k_0 vs. I/I_0 (Fig. 4). These values are quite comparable to the values reported in the literature for degradation of 4-chlorophenol in shallow pond reactor [19].

Effect of initial substrate concentration

It is important to study the effect of initial COD on the rate of degradation. The initial COD of the effluent was around 945 mg L⁻¹. It was diluted in the ratio of 1:3 for all the experiments. To study the effect of initial COD concentration on degradation rate, the effluent was diluted in different ratios. We observed that the degradation rate decreased with increases in initial COD (Fig. 5). When the initial concentration increases, more molecules are adsorbed on the surface of the catalyst. Hence, the penetration of light on the surface of the catalyst decreases and the relative amount of reactive oxidizing species on the surface of the catalyst does not increase as the intensity and time of illumination remain constant, thus de-



5. Effect of initial concentration on degradation of effluent
(●) 945 mg L⁻¹; (■) 630 mg L⁻¹;
(▲) 315 mg L⁻¹

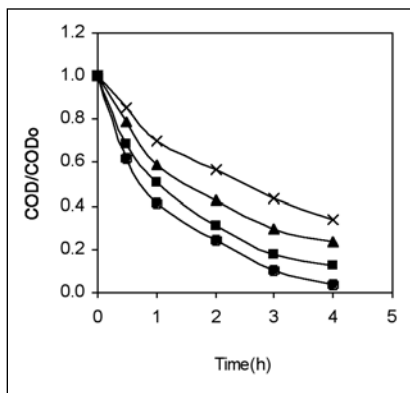


Fig. 6. Concentration vs time profiles at different A/V ratio
(●) 2.27 cm² ml⁻¹; (■) 1.14 cm² ml⁻¹;
(▲) 0.76 cm² ml⁻¹;
(x) 0.57 cm² ml⁻¹

creasing the degradation rate. Our observations are in agreement with those reported in the literature [20,25,28].

Effect of A/V ratio of the reactor

The ratio of area to volume (A/V) is critical for the shallow pond reactor as the photocatalytic oxidation reaction depends on area available for the irradiation of light. More area and less depth enhance the rate of degradation as the penetration of UV rays into the solution increases. Hence, the degradation rate increases with increasing aperture to volume ratio of the shallow pond type reactor as shown in Figure 6. Klausner et al [29] have also reported that the rate of degradation of 4-Chlorophenol in shallow pond reactor depends on aperture to volume ratio (A/V).

The results of degradation under sunlight, observed to have an intensity of 35 W/m², were comparable with those under UV radiation of same intensity in the laboratory, as shown in Figure 7. This shows that this process can be used in open atmosphere.

CONCLUSION

Photocatalytic treatment using TiO₂ and UV light in a shallow pond type reactor can efficiently remove COD. The investigations demonstrate the impor-

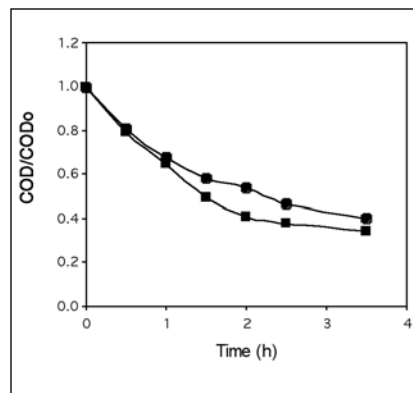


Fig. 7 Concentration vs time profile for degradation of effluent (●) under sunlight and (■) in the lab at 35 Wm⁻²

tance of choosing the optimum degradation parameters to obtain high degradation rates. Experiments revealed that the rate of degradation increases as UV intensity increases, aperture to volume ratio increases and initial concentration of COD decreases. Experiments carried out in sunlight gave results comparable to those obtained in laboratory conditions.

Received: August 12, 2005
Accepted: October 20, 2006

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INSIGHTS FROM THE AUTHORS

Bleach plant effluent contains recalcitrant compounds resulting from the use of chlorine and chlorine-based chemicals in bleaching. Conventional chemical and biological processes are not very effective in degrading these compounds. On the basis of encouraging results from photo-catalytic treatment of synthetic effluents containing dyes and some organochlorine compounds, we decided to study the photo-catalytic process for treating bleach plant effluents containing recalcitrant compounds.

Before starting this research, we had studied the photo-catalytic degradation of a few compounds such as chlorophenols and chlorocatechols in synthetic effluents, but not much study has been done on the degradation of real bleach plant effluent by this method. In addition, we have used a low-cost shallow pond-type reactor, which can handle a larger quantity of effluent, compared other types of reactors used by various investigators for different compounds.

We encountered no major difficulties in this research. There was a minor problem in maintaining the temperature inside the UV chamber in the laboratory, but this was solved by installing a small air-circulating fan inside the chamber.



Bajpai



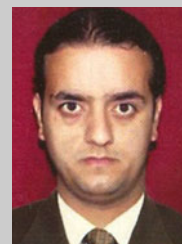
Toor



Jotshi



Singh



Verma

Our research showed that efficient degradation of pulp and paper mill effluent containing recalcitrant compounds is possible by this method. Experiments under solar radiation yielded results comparable to those obtained in laboratory conditions under UV lamps, which shows that this process can be applied on an industrial scale and its cost may not be prohibitive.

Since pulp and paper mills already use holding ponds for microbiological treatment of wastewater, large-scale shallow pond reactors for solar detoxification may be an option on the front or back end of a combined solar/microbiological treatment system for wastewater. We plan to optimize the process further using solar radiation only and scaling up the process, and then to try it in a pulp mill.

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