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Treatment of pulp and paper mill wastewater by solar photo-Fenton process

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ABSTRACT

Solar photo-Fenton process is an attractive, alternative treatment technology among advanced oxidation processes for the treatment of wastewater containing recalcitrant compounds. The feasibility of solar photo-Fenton process for the treatment of pulp and paper mill wastewater was investigated in this study. The complete colour and chemical oxygen demand (COD) removal were obtained under optimal conditions, pH=4, Fe²⁺=1 g/L, H₂O₂=5 g/L and irradiation time=90 min. Also it enhances the biodegradability of wastewater and the biochemical oxygen demand (BOD₃)/COD ratio was found to increase from 0.028 to 0.83. The effluent's BOD and total suspended solids concentrations were found to be 0 and 30 mg/L, respectively, which meets the requirements of the discharge standard.

Keywords: Pulp and paper mill wastewater; Advanced oxidation process; Solar photo-Fenton; Biodegradability; Pilot-scale solar photo-Fenton reactor

1. Introduction

Pulp and paper industry discharges significantly large volumes of wastewater, containing recalcitrant and dissolved substances such as lignin. The volume of wastewater generated by pulping and bleaching operations is approximately in the range of 75–225 m³/ton of product [1]. The brown coloured raw wastewater is characterized by high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids and chlorinated compounds such as dioxins, furans and other halides. The release of coloured wastewater into the environment is a dramatic source of aesthetic pollution affecting human health. Slime

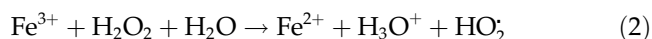
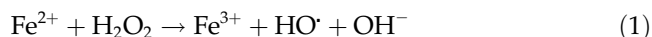
growth, scum formation, death of zooplankton and fish are some effects associated with wastewater discharge [2]. Many pulp and paper mills face a shortage of available water supply due to water scarcity. Thus, water consumption and consequent water production must be reduced. This necessitates the recycling of treated wastewater to reduce fresh water consumption [3]. In addition, the paper industry is likely to face more stringent regulations on the quality of effluents entering the receiving waters [4]. Conventional biological treatment processes are employed for the treatment of wastewater. Because of the presence of recalcitrant compounds in wastewater, the biological process is not effective. In addition, they generate a considerable amount of sludge which itself needs further treatment [1]. Also it has some drawbacks such

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as large area requirement, overall increase in cost, the requirement of additional carbon source, etc. [5]. Moreover, the intermediates produced during the degradation comprise the ability of biological treatment processes to completely mineralize in the wastewater. Therefore, the biological treatment techniques, if used alone have a serious limitation in treating wastewater containing non-biodegradable and toxic pollutants [6]. One interesting alternative that is gaining importance among the potential techniques is the advanced oxidation processes (AOP's) [7]. However, AOP's are expensive to operate compared with other conventional physicochemical or biological treatments but are able to increase the biodegradability of contaminants by converting these to smaller and more degradable intermediates. Thus, the use of AOP as a pre-treatment step prior to the biological process has to be considered to improve wastewater discharge quality.

AOPs are technologies employed to oxidize recalcitrant compounds that are difficult to degrade by biological methods. It involves the generation of hydroxyl radicals, a highly reactive species with the oxidation potential of 2.8V. These radicals are able to oxidize the recalcitrant compounds into inorganic substances such as CO₂ and H₂O under moderate temperature and pressure. AOPs involve Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H₂O₂ and O₃, TiO₂ photocatalysis and various combinations of these methods [8]. Among these processes, photo-Fenton process is one of the most important processes to generate hydroxyl radicals. The photo-Fenton process possesses several advantages of using iron as catalyst and H₂O₂ as oxidizing agent which is cheaper than other oxidants. It also increases the reaction rate and reduces the formation of sludge waste [9]. The photo-Fenton process can be carried out by either using UV lamp or solar radiation [10]. The cost of UV generation is high. Therefore, in a tropical country like India, receiving the highest level of global solar UV radiation, sunlight could be used as a potential and an economical light source. However, H₂O₂ has low molar extinction coefficient and partly absorbs UV above 320 nm, so photo-Fenton process can only use photons of wavelength up to 400 nm, which only represent minority of total solar radiation [10].

According to a simplified mechanism, Fe²⁺ is oxidized to Fe³⁺ and H₂O₂ is reduced to hydroxide anions and hydroxyl radicals explained by Eq. (1). Fe³⁺ can be reduced back to Fe²⁺ by H₂O₂ given by Eq. (2). This Fenton reaction can be accelerated by irradiation with UV-visible light improving degradation rate Eq. (3) [9].



The main purpose of this study is to evaluate the efficiency of solar photo-Fenton process for the treatment of pulp and paper mill wastewater by optimizing the parameters such as pH, initial ferrous sulphate concentration (Fe²⁺), initial hydrogen peroxide concentration (H₂O₂) and solar irradiation time. This work also evaluates the feasibility of enhancing the biodegradability thereby making the wastewater biocompatible and suitable for subsequent biological treatment.

2. Materials and methods

2.1. Pulp and paper mill wastewater

The wastewater used for the experiment was collected from the pulp and paper mill located at Cheranmahadevi, Tirunelveli District, India. These effluents were characterized with a high organic load of COD and low BOD. The characteristics of the wastewater found by standard methods (APHA 2005) [11] are listed in Table 1.

2.2. Chemicals

Hydrogen peroxide (30% w/w), ferrous sulphate (FeSO₄·7H₂O), sodium sulphite (Na₂SO₃), sulphuric acid (H₂SO₄) and sodium hydroxide (NaOH) (Merck) were used as received.

2.3. Solar photo-Fenton reactor

Laboratory scale solar photo-Fenton reactor was made of Plexiglas. The size of the reactor was 0.215 m × 0.215 m × 0.15 m. The irradiation surface area

Table 1
Characteristics of pulp and paper mill wastewater

S.No	Parameters	Values
1	pH	7.20
2	Colour	Brown
3	TSS (mg/L)	1,295
4	COD (mg/L)	2,133
5	BOD (mg/L)	60
6	BOD/COD ratio	0.028

and volume of the reactor were 0.0462 m^2 and 7 L , respectively.

2.4. Experimental procedure and analysis

All the experiments were carried out in Anna University Campus, Tirunelveli, India ($8^{\circ}44'\text{N } 77^{\circ}44'\text{E}$) and the photo-Fenton reactions were carried out in the laboratory scale solar photo-Fenton reactors with the working volume of 2 L . The reactor was exposed under strong solar irradiation during the months of January to April (UV intensity $32 \pm 2\text{ W/m}^2$). The tests were started at 12.00 noon and stopped at 1.00 pm. Initially, the pH of the wastewater was adjusted using sulphuric acid. Then the required amount of ferrous sulphate was added to the wastewater and stirred well to enhance the homogeneity of wastewater during the reaction. After that, hydrogen peroxide was added and the reactor with the mixture was exposed to solar light irradiation. The time at which hydrogen peroxide was added to the wastewater was considered as the beginning of the experiment. The sample was withdrawn from the reactor every five minutes once to analyse COD and the colour. Immediately after collecting the sample, about 0.5 mL of sodium sulphite solution per 10 mL of wastewater sample was added to quench the oxidation reaction for hydrogen peroxide decomposition and the pH was raised by adding sodium hydroxide for the iron salt precipitation.

The COD and BOD of the samples were carried out as per standard methods (APHA 2005). The colour of the treated sample was monitored at 475 nm in visible spectrophotometer (Cyber lab).

3. Results and discussion

3.1. Effect of pH

In order to investigate the effect of pH on colour and COD removal, the experiment was subjected to varying pH from 2 to 7. The percentage removal of colour and COD is depicted in Fig. 1. At pH 4, within 10 min of irradiation, about 99% of colour was observed to be removed. On the other hand, 96.5% COD removal was achieved in 1 h. Therefore the optimum pH is 4. This could be due to the formation of dominating species of $\text{Fe}(\text{OH})^+$ at acidic pH. $\text{Fe}(\text{OH})^+$ species is reported to have higher activity than the non-complex form of Fe^{2+} in Fenton's oxidation [12]. At pH lower than 4, the colour removal was observed to be less. This could be due to the fact that at low pH the hydrogen peroxide becomes stable probably because it solvates a proton to form an oxonium ion $(\text{H}_3\text{O})^+$. An oxonium ion makes H_2O_2 electrophilic, to

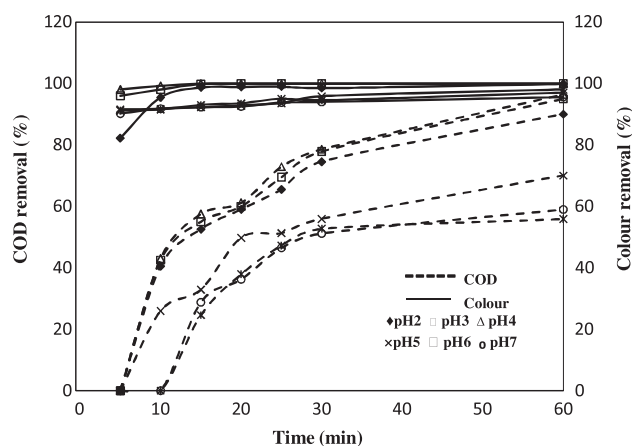


Fig. 1. Effect of pH on colour and COD removal ($\text{Fe}^{2+} = 1\text{ g/L}$, $\text{H}_2\text{O}_2 = 15\text{ g/L}$).

enhance its stability and apparently to reduce the substantial reactivity with ferrous ion [13]. However, the COD reduction increases rapidly as the pH increases from 2 to 4.

At a reaction higher than pH 5, a decrease in the COD removal was found. At pH 7, only 59% of COD was removed. This is because the ferrous catalyst was inactivated with the formation of ferric hydro complexes and also due to the decomposition of H_2O_2 . Also iron precipitates as hydroxide, which reduces the transmission of the radiation into the wastewater [7]. Chu et al. [14] reported that Fenton oxidation process could remove the pollutants from coking wastewater under acidic conditions. Similar results were also observed in the wastewater mineralization [15], treatment of olive mill wastewater [7], degradation of diisobutylphthalate [16], degradation of p-aminophenol, p-nitroaniline and acetanilide [17].

3.2. Effect of Fe^{2+} concentration

The effect of Fe^{2+} concentration on the colour and COD removal was evaluated by varying the concentration of Fe^{2+} in the range of $0\text{--}1.5\text{ g/L}$ with the H_2O_2 concentration of 15 g/L and the optimum pH 4. From the Fig. 2, it was observed that about 99% of colour was removed within 10 min and maximum COD reduction of about 95% occurred when the Fe^{2+} dosage was 1.0 g/L and therefore, it was taken as the optimum dosage. No significant removal of colour and COD were observed without the concentration of Fe^{2+} . The colour removal was faster in the early stage of the reaction than in the later stage, since ferrous ion catalyses H_2O_2 to form hydroxyl radical quickly in the initial stage of the reaction [10]. The degradation of COD increases as Fe^{2+} increases and it decreases

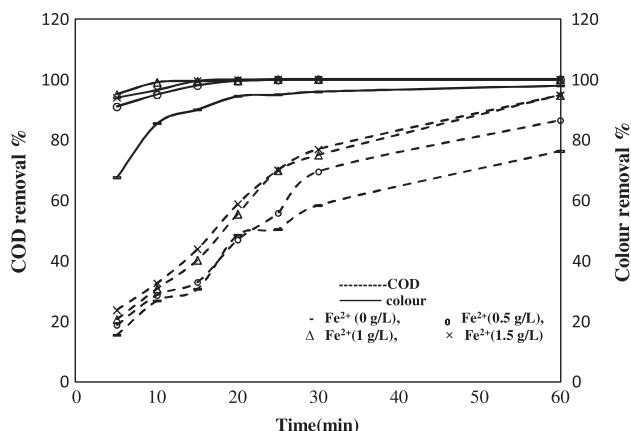
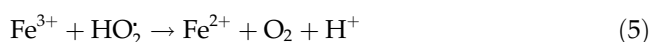
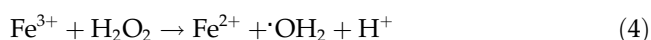


Fig. 2. Effect of Fe^{2+} on colour and COD removal (pH4, $\text{H}_2\text{O}_2 = 15 \text{ g/L}$).

after the optimum dosage of Fe^{2+} concentration. This is because the catalyst ferrous sulphate accelerates the decomposition of H_2O_2 . Further addition of iron becomes inefficient.

Tarek et al. [4] reported that photo-Fenton process was found to be the fastest one with respect to COD removal. The increase in colour and COD removal was due to the production of hydroxyl radicals. In the photo-Fenton process, the classical Fenton reaction is assisted by the photo reduction process which takes place in the near UV region and results in the regeneration of metal catalysts and production of hydroxyl radical [18]. The reproduced ferrous ions react with hydrogen peroxide to produce more hydroxyl radicals explained by the following equations Eqs. (4)–(6).



Similar results were observed in the photo-Fenton treatment of tannery wastewater [19] and pharmaceutical wastewater [20], in which the optimum dosage of FeSO_4 was 1 g/L. Kati et al. reported that about 82% of COD removal was obtained for the removal of recalcitrant contaminants from bleaching effluents with the optimum Fe^{2+} dosage as 1.4 g/L [21].

3.3. Effect of hydrogen peroxide

The removal of colour and degradation of COD was studied by varying the concentration of H_2O_2 in

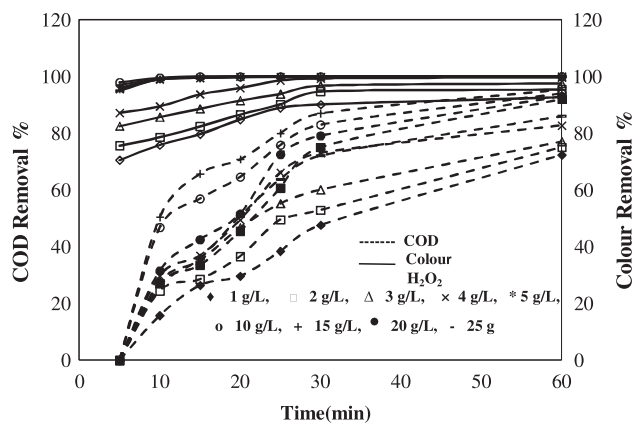
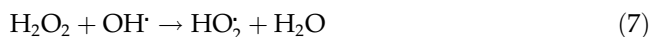


Fig. 3. Effect of H_2O_2 on colour and COD removal (pH4, $\text{Fe}^{2+} = 1 \text{ g/L}$).

the range of 0–25 g/L with the optimum value of pH4 and $\text{Fe}^{2+} = 1 \text{ g/L}$. From the Fig. 3, it was clear that increasing amount of H_2O_2 leads to greater COD and colour removal. The degradation increases as the H_2O_2 concentration increases until a critical concentration is achieved. Above this critical concentration, the removal of colour and the degradation of COD decrease as a result of the scavenging effect given by the Eqs. (7–9).



Also more H_2O_2 molecules are available for Fe^{2+} ions to react, which increase the number of $\text{OH} \cdot$ radicals [22]. The excess H_2O_2 reacts with the hydroxyl radicals earlier formed and hence acts as an inhibiting agent of degradation by consuming the hydroxyl radicals responsible for degrading the pollutant molecule [23]. It was also observed that the process was very fast in the beginning of the reaction and it might be due to the exhaustion of H_2O_2 [24]. There was a small difference between the COD removal with 5, 10 and 15 g/L of H_2O_2 dosage. Therefore, it was not worth taking of large amounts of H_2O_2 dosage for increasing degradation. Hence, lower dose of 5 g/L of H_2O_2 was taken as the optimum dosage in which 100% colour removal and 93% COD removal were achieved. Neval et al. [25] reported that solar photocatalysis is very efficient oxidation process to remove the colour from the textile dyestuff with a hydrogen peroxide concentration of 2.677 g/L. Similarly, photo-Fenton oxidation

process can effectively decolourize the C.I. Acid Blue 9 under the optimum conditions [26].

3.4. Effect of liquid depth

In order to find the light penetration depth and to fix the depth in the design of pilot plant reactor, different volumes of wastewater samples such as 1, 2, 3, 4, 5 and 6 L were taken with the corresponding depths of 1.15, 2.3, 4.6, 7.2, 9.7 and 12.2 cm. The percentage removal efficiencies of COD are determined. It was observed that 91% of COD removal was achieved at a depth of 2.3 cm of volume 2 L and 70% of COD was removed at a depth of 12.2 cm of volume 5 L. Thus, it is clear that the degradation of COD is more at shallow depth. Solar photo-Fenton process can take full advantage of photons to produce more hydroxyl radicals and it also makes use of UV and visible spectrum (200–800 nm) [10]. But for larger depths, only a certain portion of the wastewater will receive high intensity of sunlight. As the depth increases, light cannot penetrate deep into the reactor resulting in less production of hydroxyl radicals. A similar result has been observed in the photocatalytic detoxification method for zero effluent discharge in dairy industry. It was reported that the shallow solar pond having depth of 2 cm gives the best results compared to reactor having a depth of 4 cm [27].

3.5. Effect of biodegradability

The pulp and paper mill wastewater is non-biodegradable in nature and they contain recalcitrant compounds. Enhancement of biodegradability was studied using solar photo-Fenton process. The biodegradability of the wastewater was evaluated by BOD/COD ratio. The results are shown in the Fig. 4.

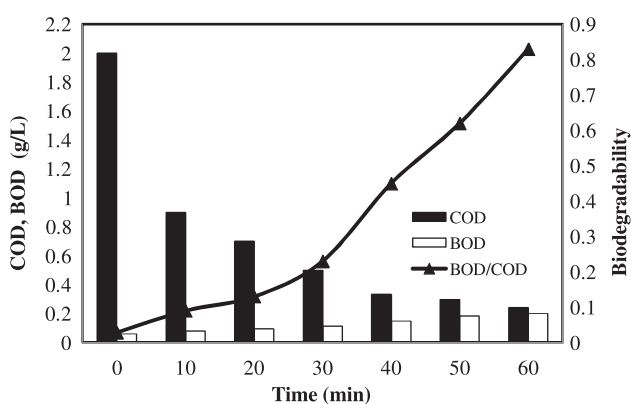


Fig. 4. Biodegradability of pulp and paper mill wastewater (pH 4, $\text{Fe}^{2+} = 1 \text{ g/L}$, $\text{H}_2\text{O}_2 = 5 \text{ g/L}$, irradiation time = 1 h).

Initially, the BOD/COD ratio of the untreated wastewater sample was 0.028. But after treating the wastewater by solar photo-Fenton process, the biodegradability was enhanced and it was observed that at 50 min, the BOD/COD ratio reached the value of 0.60. It indicates a readily biodegradable wastewater. The short oxidation time along with smaller initial peroxide concentration provides the highest biodegradability increase. Finally, it was observed after 60 min of irradiation time, the biodegradability was increased to 0.83. Enhancement in biodegradability suggests that further degradation could be achieved by coupling solar photo-Fenton and biological treatment processes, thereby reducing the cost of treatment [28].

3.6. Comparison of solar photo-Fenton and Fenton process

To compare the efficiencies of colour and COD removal, studies were conducted in five processes viz. Fenton, solar, solar/ H_2O_2 , solar/ Fe^{2+} and solar photo-Fenton. The COD removal and reaction rates for different treatment processes were found out. For solar reaction alone, there was no change in colour and COD removal. It was observed that in Fenton process, colour removal was about 40% and the COD removal was about 30% and the reaction kinetic constant was 0.008 min^{-1} . For solar/ Fe^{2+} , the COD reduction was 69.3% after one hour of irradiation time and the kinetic constant was 0.05 min^{-1} . For solar/ H_2O_2 , the COD reduction was about 25% after one hour of irradiation time and the rate constant was 0.011 min^{-1} . For solar photo-Fenton process, the COD reduction was 94% after one hour of irradiation time and rate constant was 0.21 min^{-1} . Comparing all the reactions, it was clear that the solar photo-Fenton processes are much faster than Fenton process. Table 2 shows the characteristics of pulp and paper mill wastewater after the treatment using solar photo-Fenton process. It is very clear from the table

Table 2
Characteristics of solar photo-Fenton treated wastewater

Parameters	Solar photo-Fenton treated wastewater		MINAS wastewater
	After 60 min	After 90 min	
pH	7.50	7.50	5.5–9.0
Colour	Colourless	Colourless	–
TSS (mg/L)	30	30	100
COD (mg/L)	126	0	350
BOD (mg/L)	100	0	30
BOD/COD ratio	0.83	–	–

that at 90 min of irradiation time, about 98% of total suspended solids and 100% of COD and BOD were removed which meets the required Minimal National Standards (MINAS).

3.8. Design of pilot plant reactor and cost analysis

The scale up of the solar photo-Fenton reactor is simple as there is no necessity of solar tracking system. The reactor is economical and the reactor does not require any aerator devices as there is absorption of oxygen from the atmosphere. The pilot plant reactor was designed to treat the pulp and paper mill wastewater with the flow rate of 1,500 m³/d. The reactor was designed for 100% colour removal and about 94% of COD removal. The average daily useful hours were found to be 6 h. The yearly average solar UV light intensity for the study location was estimated as 32 ± 2 W/m². In the performance studies, a kinetic model which accounts the effect of pollutant concentration, liquid volume, light intensity and area of solar irradiation was used to arrive at a lump

kinetic parameter (K_3) (Eq. (10)) as suggested by Sagawe and Bahnemann (1998) [29].

$$K_3 = \ln(C_0/C) \times Q / (q_{UV} \times A) \quad (10)$$

where K_3 = lump kinetic parameter representing the efficiency of the photocatalyst (m³/W.min)

C_0 = inlet concentration of COD (mg/L), C = outlet concentration of COD (mg/L), Q = volumetric flow rate (m³/min), q_{UV} = time averaged radiation density flux (W/m²), A = effect area of solar irradiation (m²), $K_3 = \ln(2,133/126) \times 0.0333 \times 10^{-3} / (32 \times 0.0462)$, $K_3 = 6.37 \times 10^{-5}$ m³/W min.

The lump kinetic parameter was found to be 6.37×10^{-5} m³/W min.

Scaling up of the reactor and area of pilot-scale reactor are given by the Eqs. (11) and (12), respectively.

$$(K_3)_{\text{bench-scale reactor}} = (K_3)_{\text{pilot-scale reactor}} \quad (11)$$

Table 3

Cost analysis for the treatment of pulp and paper mill wastewater by solar photo-Fenton process

Sl No	Parameters	Values
(a)	Common input data	
	Yearly working days	365 days
	Availability factor	80%
	Average useful hours	6 h
	Effective yearly operating hours	1,752 h
	UV global radiation (average at operating hours)	32 W/m ²
	Total collector area	1,445 m ²
	Cost of Fe ²⁺	Rs.590/kg
	Cost of H ₂ O ₂	Rs.440/kg
	Cost of solar photo-Fenton reactor civil works	Rs.2,500/m ²
(b)	Cost estimation	
(i)	<i>Direct cost</i>	
	Total reactor cost (1,445 m ² × 2,500)	Rs.3,612,500
	Piping and tanks (8% of reactor cost)	Rs.289,000
	Auxiliary equipment and controls (10% of reactor cost)	Rs.361,250
	Others (15% of reactor cost)	Rs.541,875
	Total direct cost (TDC)	Rs.4,804,625
(ii)	<i>Indirect cost</i>	
	Contingencies (12% of TDC)	Rs.576,555
	Spare parts (1% of TDC)	Rs.48,046
	Total Capital Required (TCR)	Rs.624,601
(iii)	<i>Annual cost</i>	
	Capital (13% of TCR)	Rs.81,198
	Consumables (Fe ²⁺ , H ₂ O ₂)	Rs.5,201 × 10 ⁶
	Operation and maintenance (5% of TCR)	Rs.31,230
	Total annual cost	Rs.52,014 × 10 ⁵
	Treatment cost	Rs.9,500/m ³

Area of pilot-scale reactor

$$= \ln(C_0/C) \times Q_{\text{pilot-scale reactor}} / (q_{UV}) \\ \times (K_3)_{\text{bench-scale reactor}}$$

Area of pilot-scale reactor

$$= \ln(2,133/126) \times 1.0417 / (32 \times 6.3721 \times 10^{-5})$$

Area of pilot-scale reactor = 1,445m²

Assume the depth of the reactor including free board = 0.15 m.

The size of the solar photo-Fenton reactor = 54 m × 27 m × 0.15 m.

The cost estimation for the treatment of pulp and paper mill wastewater by solar photo-Fenton process is shown in the Table 3. The cost of construction of solar photo-Fenton reactor is found to be approximately Rs.2,500/m² and the treatment cost of pulp and paper mill wastewater is found to be Rs.9,500/m³.

4. Conclusions

In this study, it has been found that solar photo-Fenton oxidation is an appropriate process for the treatment of pulp and paper mill wastewater. The optimum pH for colour and COD removal was found to be 4. The maximum colour and COD removal were achieved at 1 g/L of Fe²⁺ dosage. The decrease in the removal efficiencies at high Fe²⁺ concentrations was due to the colour resurgence caused by Fe²⁺ intermediate. At H₂O₂ dosage of 5 g/L, over 100% colour and 93% COD removal were obtained. The degradation of COD decreased with the increase in liquid depth. The degradation rate of solar photo-Fenton process was faster than Fenton process. Solar photo-Fenton process enhances the biodegradability of pulp and paper mill wastewater. The BOD₃/COD increased from 0.028 to 0.83 at 60 min. Thus, there is a possibility of coupling the solar photo-Fenton process with the biological treatment thereby the cost of the treatment can be reduced. At optimal conditions complete removal of colour and COD were achieved at 90 min of irradiation time.

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