

Combination of solar advanced oxidation processes and biological treatment strategy for the decolourization and degradation of pulp and paper mill wastewater

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ABSTRACT

This study is focused on the investigation of seven treatment strategies and the percentage reduction on COD and colour was evaluated and total time required for different treatment strategies were calculated. The results revealed that the COD and colour removal of 97% and 92%, respectively, was attained at 180 min of treatment for the coupled SPF-biological process, 97% and 90% of COD and colour removal was attained at 195 min of treatment for the coupled SPC-biological process whereas 98% and 95% of COD and colour removal at 95 min of treatment for the coupling of combined SPF-PC-biological process confirming the efficiency of the coupled process with a relatively shorter reaction time compared with the other processes. The values of the first order kinetics for the combined SPF-PC-biological process were 0.03 min^{-1} which is eight times greater than the biological process and 1.4 and 1.87 times faster than the coupled SPF-biological and SPC-biological process, respectively. The economic analysis of various AOPs and the relative cost of AOP–biological processes were discussed and the coupling of combined SPF-PC-biological process was found to be a technically and economically effective in treatment of pulp and paper mill wastewater to meet the effluent discharge standard.

Keywords: Advanced oxidation processes; Biodegradability; Coupled AOP and biological process; Economic assessment; Pulp and paper mill wastewater

1. Introduction

The pulp and paper industry is a very water-intensive industry and consumes about 100–250 m³ of freshwater per ton of paper produced [1]. About 175 m³ of wastewater is generated per ton of paper produced. The main source of wastewater comes from the pulping, bleaching and paper making processes [2]. Wastewater from pulp and paper industries contains high concentrations of organic matter, colour, phenolic compounds of high molecular weight, and other toxic substances that can cause significant damage to aquatic

environments [3]. The conventional biological treatments such as aerated lagoon or activated sludge are used for the treatment of pulp and paper mill wastewater. But their applicability is limited by a number of problems due to their incomplete degradation which generates potentially hazardous intermediates because the biologically treated wastewater does not eradicate the complex organics and presence of considerable amounts of recalcitrant organics after treatment contribute colour and substantial amount of COD [4]. Some economic and environmental friendly alternative to conventional methods have been developed known as advanced oxidation process [5].

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Advanced oxidation processes have recently emerged as a suitable technique to treat wastewaters capable of generating highly oxidizing radical species such as OH^\bullet oxidizing most recalcitrant organic compounds and completely mineralize them into CO_2 , H_2O and inorganic ions. Among AOPs, solar photo-Fenton (solar/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and solar photocatalysis (solar/ $\text{TiO}_2/\text{H}_2\text{O}_2$) have been considered to be the most promising tools in context to pollutants abatement [6]. The application of homogeneous Fenton's reagent is limited by the narrow pH. Solar photocatalytic oxidation using TiO_2 semiconductor is very efficient in wastewater treatment because of its high photocatalytic efficiency and chemical stability [7]. The disadvantage of this treatment process is that the conventional TiO_2 powder has low conversion efficiency. The combining of solar photo-Fenton and solar photocatalysis processes (solar/ $\text{Fe}^{2+}/\text{TiO}_2/\text{H}_2\text{O}_2$) is an attractive option which leads to maximum efficiency due to utilizing both the UV and visible region from solar radiation. The use of sunlight as source of irradiation to perform AOPs reduces operating costs and makes it more reasonable for commercial use as a water treatment technology [8]. Another attractive way of reducing costs is the coupling of AOPs with biological treatment in a combined technology.

The combination of AOPs with an inexpensive biological treatment, capable of reducing from the outset the biodegradable fraction, turns the overall process less expensive and, therefore, more economically attractive [9]. Sequencing batch biological reactor (SBR) is a wastewater treatment process based on the principles of the activated sludge process is typically used in combined systems due to its simplicity, flexibility of operation, small floor space requirements and good removal efficiency [10]. The SBR operation treatment cycle can be divided into the following five stages: filling, reaction, settling, decantation, and idle. All these stages occur in a single reactor. In addition, the hydraulic retention time (HRT) can be adjusted by varying the decanted volumes after a settling period [11]. There are several advantages of SBR over other reactors used in wastewater treatment and also the initial cost of this method is lesser compared with other treatment techniques [12].

The treatment of the wastewater by solar photo-Fenton, solar photocatalysis and combined solar photo-Fenton-photocatalysis was optimized as previously reported. The pretreatment of the wastewater was conducted under optimum conditions obtained from the previous experiments and the pretreated wastewater was subjected to biological treatment by SBR to make the wastewater consistent with the standard discharge limits. The objective of this study was to investigate the effectiveness of the coupled solar photo-Fenton followed by biological process (SPF-SBR), coupled solar photocatalysis followed by biological process (SPC-SBR) and the combined solar photo-Fenton-photocatalysis followed by biological process (SPF-PC-SBR) for the treatment of pulp and paper mill wastewater.

2. Materials and methods

2.1. Source and characterization of the wastewater

The wastewater samples used were obtained from the pulp and paper mill located near Erode, Tamil Nadu, India.

The raw wastewaters from various unit operations namely pulping, pulp washing, bleaching and paper making process are mixed together and the amount of wastewater discharged from the mill is 15,000 m^3/d . The samples were collected from the collection tank without modifications. The samples were transported to the laboratory in plastic cans and stored at 4°C . The physicochemical characteristics of the wastewater were analyzed as per standard methods [13] and it was determined as $\text{pH} = 6.99 \pm 0.1$, colour (at 465 nm) = 0.848 ± 0.100 , COD = $1,800 \pm 400$ mg/L, $\text{BOD}_5 = 400 \pm 50$ mg/L and $\text{BOD}_5/\text{COD} = 0.22 \pm 0.05$. The quantification of BOD_5/COD ratio was done to determine biodegradation potential and the value lower than 0.4 being considered as indicative of the presence of toxic or recalcitrant contaminants [14].

2.2. Chemical reagents

The experiments were performed using ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) reagent-grade hydrogen peroxide (H_2O_2) (30%, w/w) to obtain hydroxyl radical OH^\bullet . Sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used for the pH adjustment. The photocatalyst employed was commercial TiO_2 (P-25), supplied by Degussa (Germany). According to the manufacturer's specifications, P-25 has an elementary particle size of 30 nm, Brunauer, Emmett and Teller specific surface area of 50 m^2/g and crystalline mode comprising 80% anatase and 20% rutile. Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), mercuric sulphate (HgSO_4) and ferrous ammonium sulphate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) were used for COD analysis. Sodium sulphite (Na_2SO_3) was used to quench the reaction. All the reagents used in this experiment were of analytical grade and used without further purification.

2.3. Experimental procedure

2.3.1. AOP pretreatment

All photocatalytic experiments were carried out at Anna University Campus, Tirunelveli, India ($8^\circ44'\text{N } 77^\circ44'\text{E}$). The experiments were carried out in a solar photocatalytic plug flow baffle reactor. Experiments were conducted under solar illumination on clear sky days from January to April with the solar light intensity 103 ± 2 W/m^2 . Initially, the pH was adjusted using either sulphuric acid or sodium hydroxide at the beginning of the reaction. Then the required amount of ferrous sulphate and/or TiO_2 was added to the wastewater and mixed well to enhance the homogeneity of the wastewater during the reaction. The samples were taken from the solar photocatalytic plug flow baffle reactor at specific time intervals for COD and colour analysis. To the collected samples, quenching was done by adding sodium sulphite solution (2 mL) and then samples were filtered through filter paper (0.42 mm Millipore membrane) to remove the catalyst. The COD was determined using the dichromate closed reflux method according to the standard methods [13]. Biochemical oxygen demand (BOD_5) was determined at 20°C using the standard dilution technique according to the standard methods [13]. All the experiments were performed in triplicate.

2.3.2. Sequencing batch biological reactor treatment

After pretreatment by AOP, the effluent was collected for subsequent biological treatment. The biological treatment was carried out in SBR using a reactor made of plexiglass with a total volume of 7 L with operating volume of 5 L. The SBR was equipped with an air pump and air diffuser to keep dissolved oxygen above 3 mg/L. In the case of biological treatment alone, the SBR was operated with the HRT of 24 h for each sequential phase of 0.5 h feeding, 22 h aeration, 1 h for settle phase and 0.5 h for removal phase with sludge retention time of 15 d. The SVI value was in the range of 80–90 mL/g, indicating good sludge settleability.

2.3.3. Combination of AOPs with SBR treatments

For the coupled AOP-biological process, HRT 3.75 h was used and it was divided into five phases: filling (0.25 h), aeration (2 h), settling (1 h), decant (0.25 h) and idle (0.25 h). Pretreated wastewater was used to feed the SBR after pH adjustment to 7.0. The MLSS concentration after inoculation in the reactor was $4,000 \pm 1,000$ mg/L. Aeration and agitation of the reactor was ceased during the settle phase and sludge was allowed to settle under quiescent condition. The supernatant collected after settling was filtered through 0.45 μ m filter for measurement of COD and BOD₅. A schematic layout of the combined AOP-SBR process is shown in Fig. 1.

2.4. Treatments

The pulp and paper mill wastewater was treated by seven treatment strategies such as (i) solar photo-Fenton process (SPF); (ii) solar photocatalytic process (SPC); (iii) SBR treatment; (iv) combined SPF-PC process (SPF-PC); (v) SPF followed by biological process (SPF-SBR); (vi) SPC followed by biological process (SPC-SBR); (vii) SPF-PC followed by biological process (SPF-PC-SBR). In order to meet the stringent regulations, the Tamil Nadu Pollution Control Board (TNPCB) has directed the industries to implement zero discharge facilities and the high consumption of water by pulp and paper industries has necessitated the recycling

and reuse of processed water. As per the Minimum National Standards (MINAS) standards and TNPCB standards, the discharge limits of pulp and paper wastewater is COD = 100 mg/L, BOD₅ = 30 mg/L and TSS = 20 mg/L.

3. Results and discussion

3.1. Solar photo-Fenton process

The experiment was carried out previously by varying pH in the range of 2–6 and Fe²⁺ from 0 to 0.30 g/L and H₂O₂ from 0 to 5 mL/L. The highest COD and colour removal of 70% and 76%, respectively, was obtained at 60 min of treatment process under the optimum conditions viz. pH – 3, Fe²⁺ – 0.24 g/L and H₂O₂ – 4 mL/L. Therefore, the optimized values obtained from previous stages were used to gain the optimal contact time to meet the target COD. The influence of contact time on COD removal, colour removal, BOD₅ removal and BOD₅/COD ratio is shown in Fig. 2. The findings illustrated that an increase in contact time increased the removal efficiency and allowed the utilization of more solar energy to produce hydroxyl radicals from H₂O₂. At 15 min of contact time, the COD and colour removal was 41% and 32%, respectively, and the removal efficiency of COD and colour increased to 97% and 98% when the contact time was increased to 150 min which met the discharge limits as per the MINAS and TNPCB standards. Further increasing the contact time to 165 min, the complete COD and colour removal efficiencies (100%) were attained [15,16].

The biodegradability of raw wastewater was found to be 0.22 and this indicates the presence of non-biodegradable organic compounds. After the treatment by SPF, the biodegradability ratio increased and reached 0.4 at 60 min of solar irradiation which turned the wastewater biodegradable as reported before [17]. At this point, the wastewater was transferred to SBR for the biological degradation.

3.2. Solar photocatalytic process

The experiments were carried out previously by varying pH in the range of 2 to 10 and Fe²⁺ from 0 to 0.30 g/L and H₂O₂ from 0 to 5 mL/L. The highest COD and colour

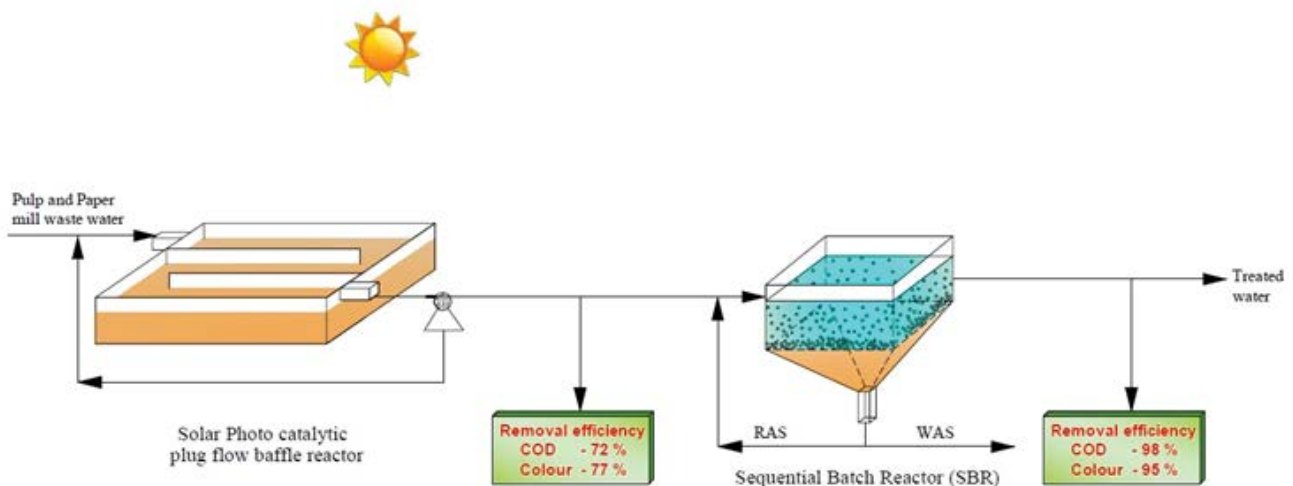


Fig. 1. Schematic layout of the combined AOP-SBR process.

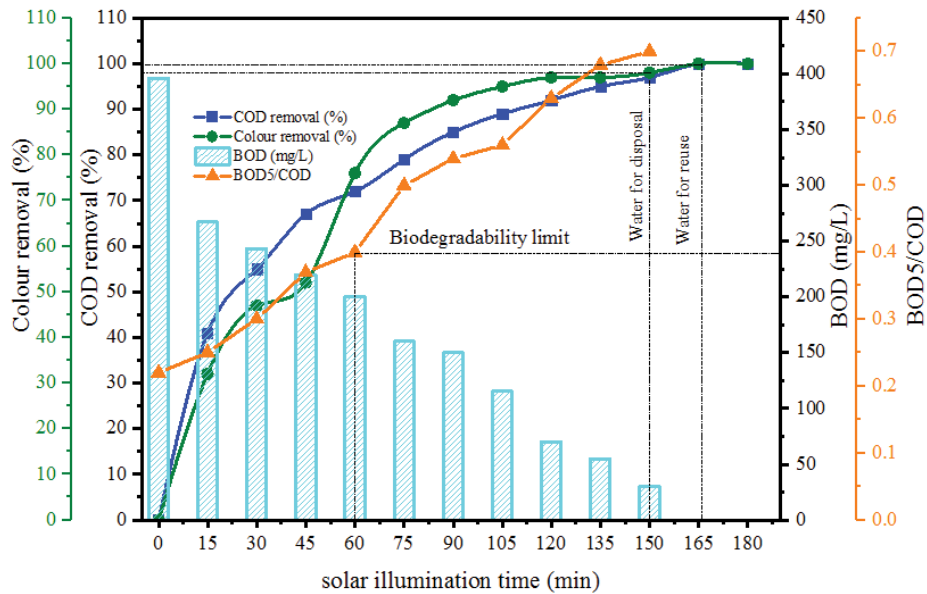


Fig. 2. Experimental steps for designing wastewater treatment by solar photo-Fenton process (pH = 3, Fe²⁺ = 0.24 g/L, H₂O₂ = 4 mL/L, solar intensity = 103 W/m²).

removal of 69% and 78%, respectively, was obtained at 60 min of treatment process under the optimum conditions viz. pH = 6, TiO₂ = 0.25 g/L, H₂O₂ = 3 mL/L. The effect of contact time was determined with the optimum conditions previously determined to meet the target COD. The influence of contact time between COD removal, colour removal, BOD₅ removal and BOD₅/COD ratio is shown in Fig. 3. It could be observed that longer the contact time greater the COD and colour removal. For 60 min of contact time, the COD and colour removal were 65% and 82%, respectively. Whereas for 165 min of contact time, the COD and colour

removal efficiency increased to 95% and 98%, respectively. The discharge standard was achieved at 180 min of contact time while the complete COD and colour removal efficiencies were attained at 195 min of contact time. In this process, the biodegradability limit was attained at contact time of 75 min. Therefore, this time was chosen as sufficient for the photo-biological step.

Even though AOPs are highly efficient for the treatment of highly polluted wastewater; their operation is still quite expensive. The effective degradation of wastewater by AOP alone varied in the consumption of H₂O₂. It was observed

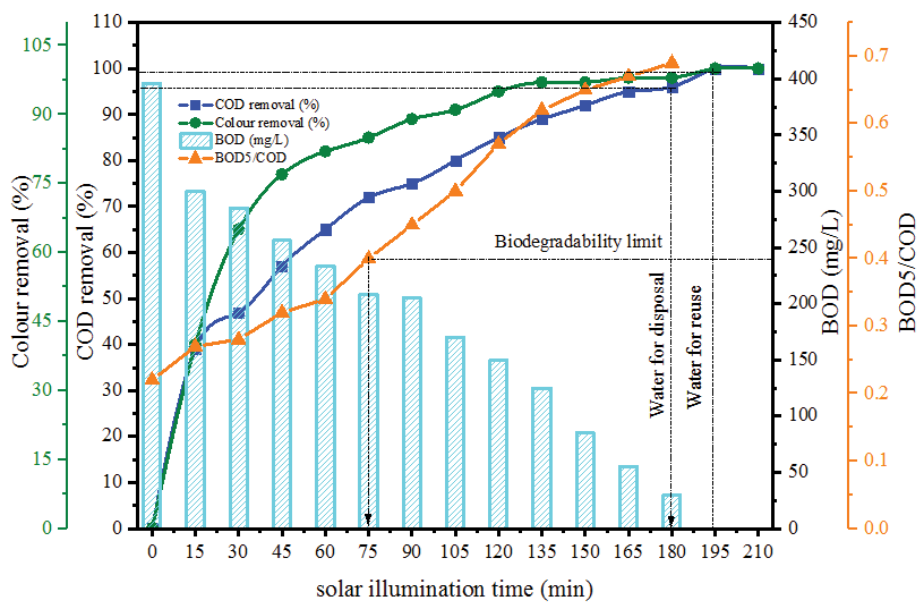


Fig. 3. Experimental steps for designing wastewater treatment by solar photocatalytic process (pH = 6, TiO₂ = 0.25 g/L, H₂O₂ = 3.00 mL/L, solar intensity = 103 W/m²).

that the oxidation of wastewater by single AOP is an uneconomical technology. Therefore, the advantage of coupling AOP with biological process was to reduce the treatment costs, particularly the hydrogen peroxide concentration used in the AOP. It is noteworthy that during the AOP pretreatment process, the reaction can be carried out at a low ferrous iron dosage resulting in the negligible amount of sludge generation. This can solve the problem of sludge disposal, thereby adding to the cost-effectiveness of the process.

3.3. Treatment of pulp and paper mill wastewater by biological process (SBR)

The SBR was operated for the treatment of pulp and paper mill wastewater under optimum conditions of the process variables. The removal performances of COD and colour were examined as depicted in Fig. 4. The SBR was operated with the influent COD concentration of 1,800 mg/L. The effluent COD concentration after SBR treatment was found to be 260 mg/L at 6 h of reaction time. It was observed that the COD removal percentage was increased from 2 to 6 h and afterwards with the gradual increase in COD removals up to 12 h. Increasing HRT from 12 to 24 h did not significantly improve the SBR performance. This indicates that most of the substrate degradation occurred during the first 6 h and a smaller portion was degraded in rest of the retention time.

According to Metcalf & Eddy [18], the biodegradable fraction of the COD can be divided into a slowly biodegradable fraction and a readily biodegradable fraction. This is because in SBR system, only biodegradable organic compounds were removed thereby the resulting wastewater contains most of the non-biodegradable organic compounds [19]. The fast biodegradable organic compounds include short chain volatile organic acids and more complex organic acids. Thus the findings from SBR suggest that the percentage removal of readily biodegradable organic compounds was attained at HRT as 6 h [20]. The COD removal efficiency was observed to be 85% while the removal efficiency of colour was found to be 57%. However, it is impossible to extend the aeration time limitless due to the increase of operating cost. Measurement of COD showed that the 12 h aeration time was able to achieve similar removal efficiencies as that of

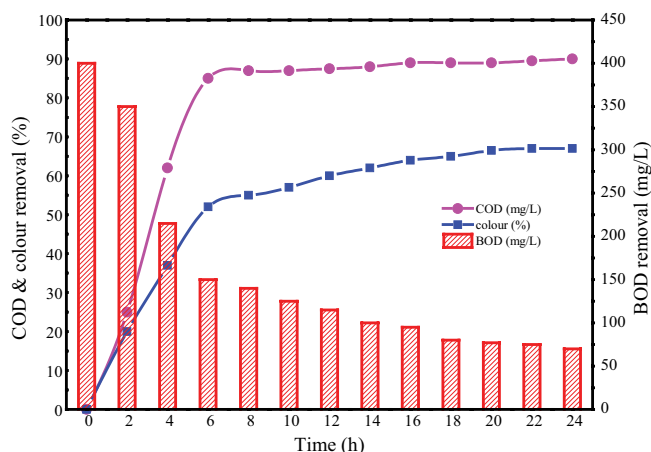


Fig. 4. Degradation of wastewater in SBR.

the 24 h cycle. Colour removal efficiency by the biological process alone was low because colour results from the presence of the lignin or polymerized tannins, compounds with high molecular weight, which are nontoxic but poorly biodegradable [21].

3.4. Combined solar photo-Fenton-photocatalytic process (SPF-PC)

The experiments were carried out previously by varying pH in the range of 3–11 and Fe^{2+} from 0 to 0.30 g/L, TiO_2 from 0 to 0.25 g/L and H_2O_2 from 0 to 5 mL/L. The highest COD and colour removal of 70% and 76%, respectively, was obtained at 60 min of treatment process under the optimum conditions viz. pH – 7, Fe^{2+} – 0.10 g/L, TiO_2 – 0.13 g/L and H_2O_2 – 1.80 mL/L determined previously [22]. The optimized values obtained from previous stages were used to gain the optimal contact time to meet the target COD. The influence of contact time between COD removal, colour removal, BOD_5 removal and BOD_5/COD ratio is shown in Fig. 5. It could be observed that the increase in contact time increased the COD and colour removal. For 20 min of contact time, the COD and colour removal was 72% and 77%, respectively. Whereas for 75 min of contact time, the COD and colour removal efficiency increased to 97% and 96%, respectively, as per the discharge standard. The complete COD and colour removal efficiencies were attained at 90 min of contact time.

It was found that the initial biodegradability ratio of pulp and paper mill wastewater was increased steadily after pretreated by SPF-PC process. In this process, the biodegradability limit was attained at contact time of 20 min. Therefore, this time was chosen as sufficient for the photochemical pre-biological step.

3.5. Coupling of solar photo-Fenton followed by biological process (SPF-SBR)

The initial effluent concentration of COD of pulp and paper mill wastewater was 1,800 mg/L and BOD 396 mg/L. After pretreatment by SPF process, the effluent concentration of COD and BOD value reduced to 500 and 200 mg/L, respectively. The pretreated wastewater was then transferred to SBR for biological degradation with the BOD_5/COD ratio as 0.4. The degradation of wastewater in a coupled SPF followed by biological process is given in Fig. 6. The influence of the SPF-SBR process was undertaken and compared with the biological process. It was observed that the removal efficiency of COD, BOD and colour increased with the increase with the contact time. The overall organic removal efficiency confirmed 97% COD, 92% BOD and 92% of colour removal by the coupled SPF-SBR process at 180 min of treatment process (phototreatment time = 60 min, HRT in SBR = 120 min). The output of the result detailed that the efficiency of the coupled SPF-SBR process was higher relative to the biological process alone since in the coupled process, a significant portion of recalcitrant organic compounds is degraded chemically during pretreatment which converts the non-biodegradable compounds into more easily biodegradable organic compounds and is made biologically available to the following biological treatment [23]. The study by Elmolla and Chaudhuri [24] showed that the

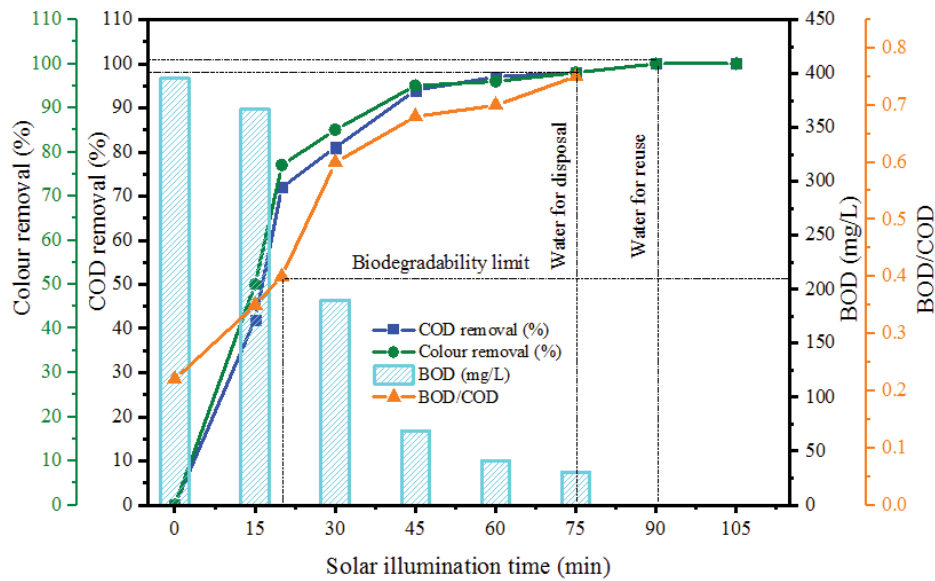


Fig. 5. Experimental steps for designing wastewater treatment by combined solar photo-Fenton and solar photocatalytic process ($\text{pH} = 7$, $\text{Fe}^{2+} = 0.10 \text{ g/L}$, $\text{TiO}_2 = 0.13 \text{ g/L}$, $\text{H}_2\text{O}_2 = 1.80 \text{ mL/L}$, solar intensity = 103 W/m^2).

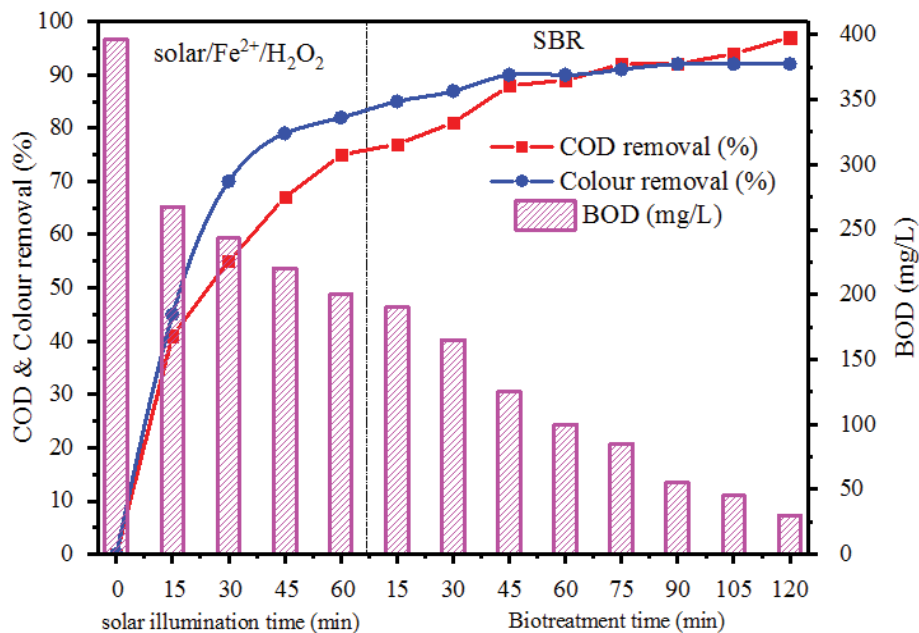


Fig. 6. Degradation of wastewater in a combined solar photo-Fenton and SBR.

combined Fenton-SBR process achieved the COD removal of 89% with the Fenton reaction of 120 min and SBR with the HRT of 12 h. Vidal et al. [23] treated the tannery wastewater by sequential AOP-biological treatment which increased the overall COD removal up to 96%, compared with 60% without pretreatment.

3.6. Coupling of solar photocatalysis followed by biological process (SPC-SBR)

The pretreatment of wastewater was carried out with the optimum conditions obtained previously to determine

the enhancement in biodegradability. It was observed that the biodegradability ratio of pulp and paper mill wastewater was increased steadily when pretreated by SPC process and when it reached 0.4, the pretreatment was stopped at this oxidation time corresponding to the BOD_5/COD ratio. After pretreatment by SPC process, the effluent concentration of COD was decreased from 1,800 to 545 mg/L and with this concentration of COD; the pretreated wastewater was subjected to biological degradation. The degradation of wastewater in a coupled solar photocatalysis followed by biological process is given in Fig. 7. The overall organic removal efficiency confirmed 97% COD, 92% BOD and

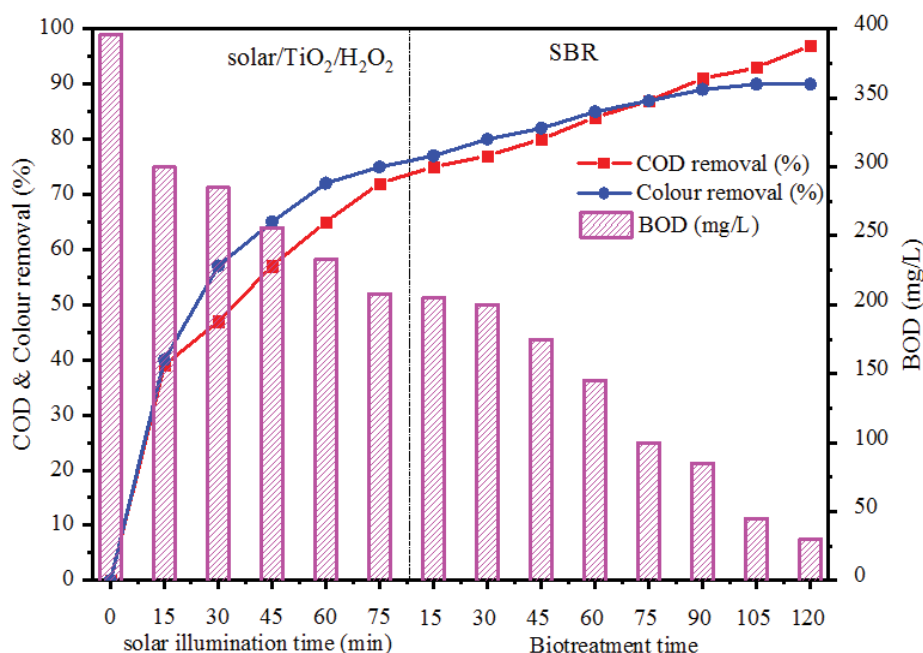


Fig. 7. Degradation of wastewater in a combined solar photocatalytic and SBR.

90% of colour removal by the coupled SPC-SBR process at 195 min of treatment process (phototreatment time = 75 min, HRT in SBR = 120 min). The efficiency of this coupled process was observed to be greater than the biological process alone with the three fold reduction in treatment time. In a literature, a study reported by Zapata et al. [25], the efficiency of the combined photo-Fenton/bio system in terms of mineralization was found to be 94%, of which 35.5% corresponds to the AOP and 58.5% to the aerobic biological treatment.

3.7. Coupling of combined solar photo-Fenton and photocatalytic with biological process (SPF-PC-SBR)

The pretreatment of wastewater was carried out with the optimum conditions obtained previously to determine the enhancement in biodegradability. The biodegradability ratio of pulp and paper mill wastewater was increased steadily when pretreated by SPF-PC process. It was observed that the concentration of COD of the wastewater decreased from 1,800 to 600 mg/L after pretreatment by SPF-PC process and with this COD concentration, the pretreated wastewater was subjected to biological degradation. The degradation of wastewater in coupling of combined solar photo-Fenton-photocatalytic followed by SBR is given in Fig. 8. The degradation of wastewater increased with the increase in contact time during the biological oxidation. The results obtained showed that the highest removal efficiency for the coupled system overcomes the limitations in the degradation efficiencies obtained during the individual implementation of combined SPF-PC pretreatment and biological activity [26]. The output of the result detailed that the overall organic removal efficiency confirmed 98% COD, 92% BOD and 95% of colour removal at 95 min of treatment process (phototreatment time = 20 min, HRT in SBR = 75 min). These results are

as high as reported by other researchers working on coupled AOP-biological process. Li et al. [27] evaluated the performance of coupled AOP-biological system for the degradation of Cibacron Yellow LS-R commercial dye. The coupled system completed the dye degradation in 34 h, reaching a mineralization level of 70%, measured as COD. Guzmán et al. [28] studied the degradation of citrus wastewater by the combined solar photo-Fenton and sequential batch reactor. The results showed degradation yields up to 93% of the initial DOC removal without producing undesired side effects, using an HRT of 1.59 d.

3.8. Kinetics

The kinetics for the treatment of pulp and paper mill wastewater was studied to evaluate the treatment method. The kinetic rate constant for the AOP and SBR processes was estimated by drawing a plot of $\ln(C/C_0)$ vs. time under optimum conditions. The straight line obtained indicates that the reaction followed the pseudo-first order reaction with high value of coefficient R^2 . The higher the degradation rate constant, the higher or faster is the rate of degradation. The reaction rate constant and half life time are given in Table 1.

The SBR process followed the pseudo-first order kinetics and the biokinetic rate constant was found to be 0.0035 min^{-1} . This was compared with the biokinetics of coupled AOP-SBR process. It was observed that after pretreatment by SPF process, SPC process and combined SPF-PC process, the order of kinetic rate constant was found to be combined SPF-PC followed by SBR (0.037 min^{-1}) > solar photo-Fenton followed by SBR (0.02 min^{-1}) > solar photocatalysis followed by SBR (0.016 min^{-1}) > SBR (0.0035 min^{-1}).

The half-life time of various treatment strategies was calculated. The half-life time is the time required to decrease the concentration of the reactant to half of the initial value [29].

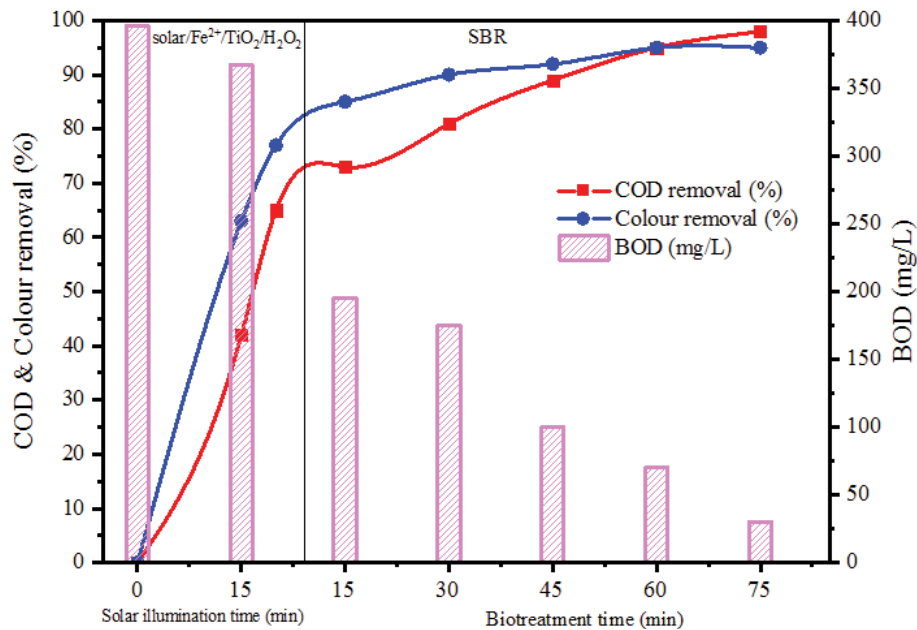


Fig. 8. Degradation of wastewater in a combined solar photo-Fenton and photocatalytic with SBR.

Table 1
Reaction rate constant and half life time of various treatment strategies

S. no	Treatment strategies	Initial COD (mg/L)	Final COD (mg/L)	Kinetic constants (min ⁻¹)	Half life time (t _{1/2}) min		
1	Solar photo-Fenton	1,800	45	0.0199	34.82		
2	Solar photocatalytic	1,800	45	0.0159	43.58		
3	Combined solar photo-Fenton and photocatalytic	1,800	45	0.0537	12.9		
				Pretreatment	Biological	Pretreatment	Biological
4	Coupled solar photo-Fenton and biological	1,800	45	0.018	0.021	38.5	33
5	Coupled solar photocatalytic and biological	1,800	45	0.013	0.016	53.3	43.3
6	Coupled solar photo-Fenton and Solar photocatalytic and biological	1,800	45	0.04	0.03	17.32	23.1
7	Biological process	1,800	150		0.0035		198

The degradation half-life times ($t_{1/2}$) are calculated by the equation as follows:

$$t_{1/2} = \frac{0.693}{k}$$

It was observed from the table that the half-life time of the combined SPF-PC process was less among AOPs and also among the coupled AOP-biological processes, half-life time was less for the coupling of combined SPF-PC with biological process. The higher the kinetic rate constant, lesser is the half-life time.

Moreover, a significant enhancement of the degradation rate was observed during application of the combined SPF-PC process. The reaction rate for the combined SPF-PC process was found to be 2.69 times faster than SPF process and 3.37 times faster than SPC process. The values of correlation coefficients indicate that the pseudo-first order

reaction is more suitable for the combined SPF-PC than the other two processes. Also, the synergetic effect between the SPF and SPC process was quantified by the rate constants and it was found to be 1.50. Thus the outcome of the experimental results revealed that the combination of SPF-PC process was found to be more efficient than the individual process with less consumption of chemical reagents and short reaction time. Therefore, a feasible option is the partial oxidation of recalcitrant pollutants in AOPs and the subsequent treatment in a biological process. This exploits the advantages of both processes by choosing the reaction time as short as possible to achieve partial oxidation and to guarantee the economic feasibility of the AOP pretreatment [30].

3.9. Comparative study of economic assessment

In a view of a wastewater treatment system, it is necessary to assess the economic feasibility of the various treatment

strategies. The economic assessment was evaluated by considering the following parameters: reagents consumption based on solar irradiation, labour and investment costs. The radiation energy and the chemical reagent costs are the main factors that influence the treatment process. In this study, only the chemical reagents were considered for the cost estimation. The use of abundant solar light reduced the costs of the AOPs. The cost estimation was done for a flow rate of 15,000 m³/d. The estimated annual cost of treatment for the individual AOP and the coupled AOP and biological process are depicted in Fig. 9. The cost of treatment of wastewater was found to be Rs. 1,887/m³, Rs. 1,652/m³ and Rs. 990/m³ for the SPF, SPC and SPF-PC process, respectively. The cost of treatment of wastewater by the coupled AOP-biological process was estimated and it was determined as Rs. 926/m³, Rs. 707/m³ and Rs. 423/m³ for the SPF-SBR, SPC-SBR and SPF-PC-SBR process, respectively. It was observed that the calculated treatment cost in the combined SPF-PC process was lower than the individual process due to highly reduced reaction time. The results revealed that the treatment costs of combined SPF-PC process was 1.14 and 1.90 times less than that of SPF and SPC process. Compared with the treatment costs of AOPs alone, the treatment costs of coupling of combined SPF-PC-biological process was 2.34 times less than that of combined SPF-PC process.

The main advantage of the application of coupled SPF-biological process was the efficient COD and colour removal with the possible reduction in treatment time without affecting the efficiency of the SPF process with less reagent consumption and consequently cost reduction [21]. Thus from the above discussions, the combined SPF-PC process showed better results operating at an optimal pH of 7 thereby it overcomes the drawbacks of the individual process because no pH adjustment is necessary for the degradation of pulp and paper mill wastewater. Biological treatment as a single process could achieve an acceptable reduction in 12 h whereas there was a significant reduction in detention time in the coupled AOP-biological process which is considered

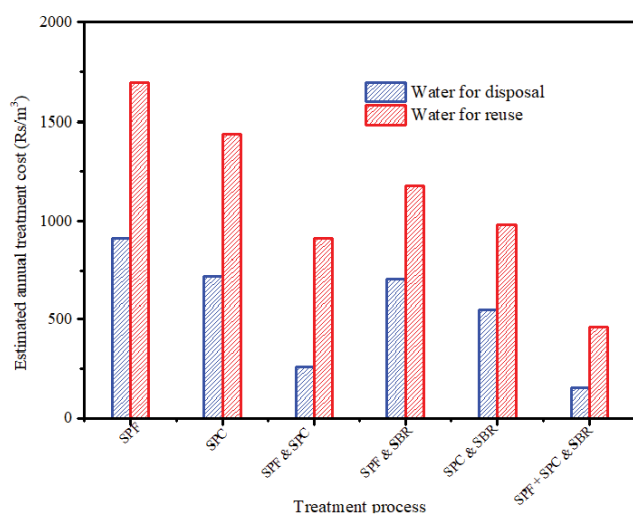


Fig. 9. Summary of estimated annual treatment cost of various treatment strategies.

to be more cost-effective because shorter HRT decreases the installation cost. Thus the retention time was reduced to more than half of that needed for the biological treatment alone [31]. Thus the coupling of combined SPF-PC with biological process resulted in reduction of total costs avoiding unnecessary expenditure on chemicals which represents the most economically feasible process reducing the potential health and environmental risks by providing treated wastewater for reuse purposes.

4. Conclusion

The pretreatment by solar photo-Fenton, solar photocatalysis and combined solar photo-Fenton and photocatalytic process showed to be successful approach for the biological treatment of pulp and paper mill wastewater. The pretreatment by solar photo-Fenton, solar photocatalysis and combined solar photo-Fenton and photocatalytic process enhanced the biodegradability from 0.22 to 0.4 in 60, 75 and 20 min of phototreatment, respectively. Thus the phototreatment processes led to the COD removal resulting in a biodegradability enhancement being possible to couple with a further biological treatment, achieving a final wastewater quality in agreement with discharge limits into receiving water bodies. The degradation of pulp and paper mill wastewater by various treatment strategies accorded well with the pseudo-first order reaction kinetics. After pretreatment by SPF process, SPC process and combined SPF-PC process, the biokinetic rate constant was found to be more for the combined SPF-PC-biological process and gave better results relative to the other treatment strategies and was considered economically feasible, able to achieve up to 98% COD and 95% colour removal with a total cost of 4.5 US\$/m³ of treated water. Thus the economic evaluation showed a marked increase in removal efficiency resulting in reduction in reagent costs and reaction time.

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