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Synergistic photodegradation of pulp and paper mill wastewater by combined advanced oxidation process

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ABSTRACT

The photodegradation of pulp and paper mill wastewater via the combined advanced oxidation process (solar/Fe^{2+}/TiO_2/H_2O_2) has been investigated in a laboratory scale reactor. Central composite design (CCD) was used to evaluate the effect of four operational parameters,i.e., pH, Fe^{2+}, TiO_2 and H_2O_2, on the basis of chemical oxygen demand and colour removal and the optimum conditions were found to be at pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L and H_2O_2 = 1.80 mL/L. The experimental responses of 98% COD and colour removal were observed at 75 min of treatment, with a significant increase in biodegradability from 0.22 to 0.60 at 45 min of treatment. The combined process followed the first order reaction, with a reaction rate constant of 0.0537 min^{-1}, which was 2.70 times and 3.38 times more effective than the solar photo-Fenton and solar photocatalytic processes respectively. A synergetic effect of 1.50 and synergetic biodegradability of 0.80 were exhibited in the combined process. The results showed that the combined process were more economically feasible than the solar photo-Fenton and solar photocatalytic processes. Under optimum conditions, an overall treatment cost of 14 US$/$m^3$ of the combined process per day was calculated.

Keywords: Biodegradability; Combined advanced oxidation process; Pulp and paper mill wastewater; Response surface methodology; Synergetic effect

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1. Introduction

Pulp and paper industry consumes large quantities of fresh water. It is the third largest consumer of fresh water with consumption in the range 80–150 m^3/t of paper depending on the type of raw material being used [1]. In a pulp and paper industry, the most significant sources of pollutions during various processing stages are wood preparation, pulping, pulp washing, bleaching and paper making operations [2]. This wastewater, commonly called pulp and paper mill wastewater. Pulping is the major source of wastewaters in the manufacturing process. This process enables separation of cellulose fibres and removal of impurities. The pulping process employs three types of raw materials viz. hardwood, agro residues and recycled fibre waste paper. Kraft/sulphate process is the most widely used method of pulp production. In this process the wood chips are cooked at temperature of 165–170°C with sodium hydroxide (caustic soda) and sodium sulphide to separate lignin and wood resins from the pulp. The pulp is then washed and bleached, if necessary. About 97% of the chemicals are recovered and reused by operating in a closed loop system. Bleaching process is carried out to improve the brightness of the pulp [3]. Some of the bleaching agents used are chlorine, chlorinedioxide, hydrogen peroxide, caustic, oxygen, ozone, hypochlorite, sodiumbi-sulphite.

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Fugitive fibres, starch, hemi-cellulose and organic acids are the main source for organic pollution in wastewater. This results in a COD discharge in the range 25–125 kg/t of pulp. High BOD/COD concentration results in depletion of oxygen available to fauna and flora in the downstream of wastewater discharge [1]. Organochlorine compounds, such as, chlorinated derivatives of phenols, acids, dioxins, furans and other neutral compounds are generated, which is a cause for environmental concern [4]. In majority of the pulp and paper mills, all raw wastewaters from various unit operations are mixed together and treated using conventional activated sludge process which is not particularly efficient in removing recalcitrant compounds. Because of the ineffective removal of colour and toxicity from these wastewaters, the treated wastewater is generally not recycled back into the industrial process, and falls short of legal requirements governing discharge into natural waters [5]. The present environmental standards and discharge norms for Indian paper industry are pH = 5.5–9.0, BOD = 30 mg/L, COD = 250 mg/L, suspended solids = 100 mg/L and colour = 500 PCU [6]. In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt technologically advanced treatment systems.

Advanced oxidation processes (AOPs) are capable of generating hydroxyl radicals oxidizing most recalcitrant organic compounds and completely mineralize them into CO_2, H_2O and inorganic ions [7]. Among AOPs, solar photo-Fenton and solar photocatalysis are known for their effectiveness in treating complex organic pollutants. The formation of soluble iron-hydroxy and iron-organic acid complexes during the solar photo-Fenton increases the absorption wavelength towards the visible region (400 nm $< \lambda <$ 700 nm) as this process use the natural resource sunlight efficiently for the detoxification of highly polluted wastewaters with significantly lower costs [8,9]. The most important drawback is the acidic pH required for the solar photo-Fenton process.

Solar photocatalytic oxidation using TiO_2 semi conductor is very efficient in wastewater treatment because of its high efficiency in the degradation of various organic pollutants. The advantage of the TiO_2 catalyst is that it can often be recovered and reutilized for many cycles after treatment. The disadvantage of the catalyst is its sensitivity to fouling and slow reaction rate. Photocatalytic oxidation is highly efficient only under UV irradiation, using only 3–4% of the solar energy that reaches the earth [10]. To overcome the problems of each individual process, the solar photo-Fenton and solar photocatalytic processes are combined. The combining of the two processes is an attractive option because synergetic effects are likely to occur and it is possible to overcome the slow kinetics when using either the TiO_2 or Fenton process. Therefore, the combined process (solar/Fe^{2+}/TiO_2/H_2O_2) lead to maximum efficiency due to utilizing both the UV and visible region from solarradiation [11].

The production of hydroxyl radicals are increased by the combination of TiO_2 photocatalysis and the Fenton system in the presence of sunlight under the neutral condition. In photocatalysis process, an electron is ejected from the valence band (VB) to the conduction band (CB) of the TiO_2 creating an h^+ hole in the VB using solar irradiation [Eq. (1)].

$$TiO_2 + h\nu \rightarrow TiO_2\,(e_{cb}^- + h_{vb}^+) \quad (1)$$

The generation of OH^- as shown in Eq. (2) and with reoxidation of Fe^{3+} by H_2O_2, the reduction through CB electron enables the catalytic cycle of Fe^{3+}/Fe^{2+}. The dual role of TiO_2 in the solar/Fe^{2+} system under neutral pH conditions, where Fe^{3+} adsorbed on the TiO_2 surface is reductively converted to ferrous ion (Fe^{2+}) by CB electron, with effective prevention of recombination of electron–hole pairs [Eq.(3)] [12].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \quad (2)$$

$$Fe^{3+} + TiO_2(e_{cb}^-) \rightarrow Fe^{2+} + TiO_2^- \text{ (photo-reduction)} \quad (3)$$

The production of H_2O_2 is maintained by the reaction of TiO_2 ejected electrons with dissolved oxygen through CB [Eqns. (4), (5)].

$$TiO_2(e_{cb}^-) + O_2 \rightarrow TiO_2 + O_2^- \text{ (photo-reduction)} \quad (4)$$

$$O_2^- + 2\,H^+ \rightarrow H_2O_2 \quad (5)$$

Second, VB holes more available for oxidation of adsorbed organic compounds, and adsorbed water molecules into $OH^{\cdot}$ generation [Eq. (6)].

$$TiO_2\,(h_{vb}^+) + H_2O \rightarrow TiO_2 + OH^{\cdot} + H^+ \text{ (photo-oxidation)} \quad (6)$$

The generated $OH^{\cdot}$ radicals oxidize the target organic compounds (RH), to produce H_2O and CO_2 shown in Eq. (7)

$$R\text{–}H + OH^{\cdot} \rightarrow \text{intermediates} \rightarrow H_2O + CO_2 \quad (7)$$

In this research, the laboratory study evaluates the effectiveness of the combined advanced oxidation process (solar/Fe^{2+}/TiO_2/H_2O_2) for treating pulp and paper mill wastewater. The response surface methodology (RSM) is used as a tool to study the influence of the various operational parameters, i.e., pH, Fe^{2+} dosage, TiO_2 dosage and H_2O_2 dosage, on the removal of COD and colour. The scope of the present paper is to study the reaction kinetics and to elucidate the synergetic effect on the rate of degradation and biodegradability for the combined process. Finally, the cost analysis was calculated to compare the economic feasibility among the solar photo-Fenton, solar photocatalytic and combined process.

2. Materials and methods

2.1. Source and characterization of the wastewater

The wastewater used was obtained from the pulp and paper mill industry located near Erode, Tamilnadu, India. All 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 treatment system consists of a plain sedimentation tank as a primary treatment and activated sludge process as a secondary treatment. The tests were performed with samples collected at the outlet of the plain sedimentation tank without modifications. The samples were collected in plastic cans that were transported to the laboratory and stored at 4°C. All samples were analysed to determine the physicochemical characteristics of the pulp and paper mill wastewater as per standard methods [13]. The physicochemical characteristics of the pulp and paper mill wastewater were pH = 6.99 ± 0.1, colour (at 465 nm) = 0.848 ± 0.100, COD = 1800 ± 400 mg/L, BOD = 400 ± 50 mg/L and BOD_5/COD = 0.22± 0.05.

2.2. Chemical reagents

The experiments were performed using ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$) reagent-grade hydrogen peroxide (H_2O_2) (30%, w/w, Merck) to obtain hydroxyl radical $OH^{\cdot}$. 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 (BET) specific surface area of 50 m^2/g and crystalline mode comprising 80% anatase and 20% rutile. Sodium thiosulphate ($Na_2S_2O_3$), potassium dichromate ($K_2Cr_2O_7$), mercuric sulphate ($HgSO_4$), and ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$) 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 as received without further purification.

2.3. Experimental

All photocatalytic experiments were carried out at Anna University Campus, Tirunelveli, India (8°44´N 77°44´E). The experiments were carried out in a bench scale solar photo-Fenton plug flow baffle reactor with a working volume of 5 L. The schematic diagram of photo-Fenton plug flow baffle reactor is shown in Fig. 1. The solar photo-Fenton plug flow baffle reactor is made of acrylic of size 0.45 m × 0.21 m × 0.08 m in the form of a pond divided with baffle plates at a spacing of 0.07 m. The irradiated surface area for the solar photo-Fenton plug flow baffle reactor is 0.09 m^2. The set up consists of a flow-through reactor placed on a platform under solar irradiation. The wastewater was continuously recycled with the help of a circulating pump. Air was supplied into the wastewater using aerators. Suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between pollutants and TiO_2. Experiments were conducted under solar illumination on sunny days between 12:00 pm and 1:00 pm from January to April. In all cases, 1 L of reaction mixture was irradiated. 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 stirred well to enhance the homogeneity of the wastewater during the reaction. Finally, hydrogen peroxide (H_2O_2) was added and irradiation was carried out in the open air using a pump for continuous aeration to provide oxygen and completely mix the reaction mixture. The samples were taken from the solar photo-Fenton reactor every 15 min for COD and colour analysis. Immediately after collecting samples, sodium sulphite solution (2 mL) was added to the samples to quench the oxidation reaction of H_2O_2 decomposition. The COD was measured by using the dichromate closed reflux method according to the standard method. Biochemical oxygen demand (BOD_5) was determined at 20ºC using the standard dilution technique according to [13].

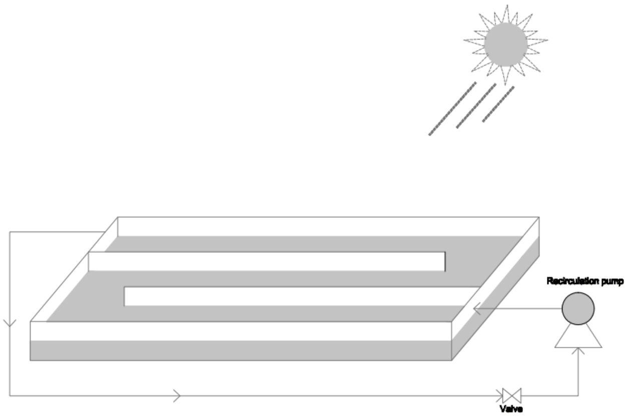

Fig. 1. Schematic diagram of solar photo-Fenton plug flow baffle reactor.

2.4. Central composite design

RSM is a statistical method that is useful for the optimization of chemical reactions to assess the relationship between dependent (response) and independent variables. It is used to verify the effects of different factors and their interactions in the process response within a certain range and with a minimum number of experiences [14]. This could remove the time consuming phase, which could not be achieved by using the conventional method (one-factor-at-a-time approach). The most popular RSM design is the central composite design (CCD). CCD's are designed to estimate the coefficients of a quadratic model.

All point descriptions will be in terms of coded values of the factors. CCD is an ideal design tool for sequential experimentation and allows for testing the lack of fit when an adequate number of experimental values are available [15]. After conducting the preliminary runs, the range of the parameters were fixed. To find the optimum conditions, this central composite design was applied to attain the interaction between dependent (response) and independent variables. In this study, four independent variables, i.e.,pH (3 to 11), Fe^{2+} (0 to 0.2 g/L), TiO_2 (0 to 0.25 g/L) and H_2O_2 (0 to 3.65 mL/L), were studied. Experimental data were analysed using the trial version of Design-Expert 8.0.7 software and fitted to a second order polynomial equation. Eq. (8) was used to attain the interaction between the dependent and independent variables.

$$Y = b_0 + \Sigma\, b_i X_i + \Sigma\, b_{ii} X_i^2 + \Sigma\, b_{ij} X_i X_j \qquad (8)$$

where Y is the predicted response, b_0 is the constant term, b_i is the linear regression coefficient, b_{ii} is the quadratic regression coefficient, b_{ij} is the interaction coefficient, and X_i and X_j are the input variables that influence the response (Y).The design consisted of 2^k factorial points augmented by 2^k axial points and a centre point, where k is the number of variables. A set of 30 experiments (= $2^k + 2k + 6$) was designed to optimize the condition for the COD and colour removal efficiencies of pulp and paper mill wastewater by using the combined advanced oxidation process. Six replications at the design centre point were utilized to provide information on the variation of the responses about the average and residual variance. Analysis of variance was used for graphical analyses of the data and also to determine the significance of the model and regression coefficients. The quality of the fit polynomial model was expressed by the coefficient of determination R^2.

3. Results and discussions

3.1.Design matrix fitting and statistical analysis

The following regression equations are the empirical models in terms of being coded for COD and colour removal.

$$\text{COD (\%)} = +\,96.42 - 0.93\,A + 4.78B - 2.49\,C - 1.72\,D - 0.80\,AB - 0.86AC - 0.55AD \qquad (9)$$

$$\text{Colour (\%)} = +\,96.50 - 5.92A + 4.53B - 3.75C + 1.55D + 1.38\,AB - 3.44\,AC + 1.38\,AD \qquad (10)$$

It can be seen from Eq. (9) that in the case of COD removal, the independent variables A, B, C, D and the interaction variables AB, AC, AD are significant model terms. Other model terms are not significant, as the probability value is larger than 0.05. Therefore, the insignificant model terms were eliminated in the equation. The lack of fit values 0.3066 and 0.1884 for COD and colour removal are not significant because the p-value > 0.05. For a model to be successfully used for prediction, the lack of fit should be insignificant and the response surfaces should be sufficiently explained by the regression equation. The degradation efficiency increases with increasing Fe^{2+}, as can be inferred by the positive linear coefficient. However an inhibitory effect is observed with the values of pH, TiO_2 and H_2O_2 based on the negative coefficients. Similarly, for colour removal, the test variables, i.e., A, B, C, D, AB, AC, AD, are the significant model terms and the remaining insignificant model terms were eliminated. The experimental data for both COD and colour removal were statistically analysed using analysis of variance; the results are shown in Table 1. Data given in the table demonstrate that the responses of COD and colour are highly significant, because the F-values for the models are 281.69 and 96.27, respectively. P-values were used to identify the significance of each variable, and the corresponding p-values are <0.0001; there was only a 0.01% chance of occurrence of the model F-value because of noise.

The predicted R^2 values of 0.9962 and 0.9890 for COD and colour removal, respectively, are in good agreement with the adjusted R^2 values. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study, the ratio of 55.954 indicates an adequate signal for COD removal, and 34.381, for colour removal. The degree of precision and reliability of the experimental values is indicated by the low value of the coefficient of variation (CV = 1.31% for COD and 3.02% for colour).

3.2. Influence of pH and Fe^{2+} concentration

To determine the effect of pH and Fe^{2+} dosage, the degradation and decolourization of pulp and paper mill wastewater was investigated by varying pH in the range from 3 to 11 and Fe^{2+} concentration of 0–0.20g/L. Three dimensional (3D) response surface plots for COD and colour removal are presented in Fig. 2a and 2b. Such plots present the function of two variables, maintaining all others at fixed levels. The figure depicts the effects of pH and Fe^{2+} concentration on the COD and colour removal efficiency at a TiO_2 concentration of 0.13 g/L and H_2O_2 dosage of 1.80 mL/L. As seen in the figure, the pH has a strong influence on the COD and colour removal. The degradation was observed to be faster when pH increased from acidic to neutral. At pH 7, the maximum COD and colour removal of 98% was obtained after one hour of solar irradiation. The iso-electric point of TiO_2 lies in pH less than 6.8. The wastewater at pH 7 renders TiO_2

Table 1
ANOVA results of the response surface quadratic model for COD and colour removal

	Source	Sum of squares	df	Mean squares	F value	p-value Prob> F
COD	Model	4079.03	14	291.36	281.69	< 0.0001
	Residual	5.29	10	0.53		
	Lack of fit	11.8781	10	1.19	1.63	0.3066
	Pure error	3.637	5	0.73		
	Cor total	4094.55	29			
Colour	Model	6733.66	14	480.98	96.27	< 0.0001
	Residual	74.95	15	5		
	Lack of fit	61.45	10	6.14	2.28	0.1884
	Pure error	13.5	5	2.7		
	Cor total	6808.61	29			

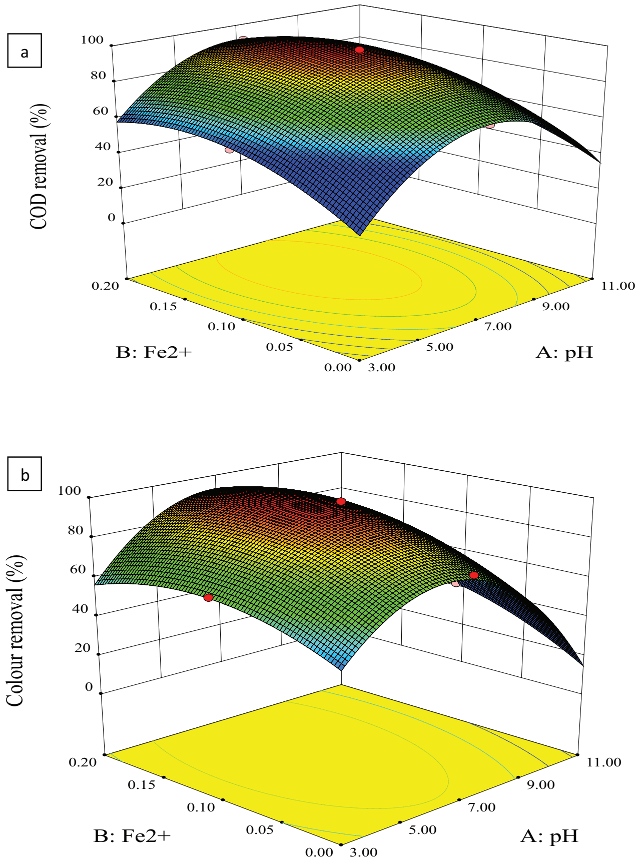

Fig. 2. (a) and (b) 3D surface plots showing the effects of mutual interactions between pH and Fe^{2+} on COD and colour removal efficiency (pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L, H_2O_2 = 1.80 mL/L).

powder surface a negative charge, resulting in negative zeta potentials values. The change of zeta potentials values with increase of Fe-content suggests that the isoelectric point of TiO_2 powder is changing with the increase of Fe concentration in it. Development of charge on TiO_2 powder surface in aqueous medium can be shown with Eqns. (11) and (12)

$$\text{Ti–OH} + \text{H+} \leftrightarrow \text{Ti–OH}_2^+ \quad (11)$$

$$\text{Ti–OH} + \text{–OH}^- \leftrightarrow \text{Ti–O}^- + H_2O \quad (12)$$

The surface of the TiO_2 powder exists in the form of TiOH groups. These hydroxyl groups dissociate into water and present to the particles a surface charge as shown in Eqns. (11) and (12). These equations further indicate that the wastewater pH also have a strong influence on the surface catalytic reactions of TiO_2 powders in aqueous medium. Since, these powders possess negative zeta potentials, it is expected that the reactions of organic molecules/reactants having positive charge would be higher on the surfaces of these Fe^{2+}/TiO_2 powders [16]. At neutral pH, the Fenton reaction, which occurred on the photoexcited TiO_2 surface produce a more reactive oxidant (e.g., $OH^{\bullet}$) than the Fe^{4+} species. As a result, the solar/$TiO_2/Fe^{2+}/H_2O_2$ system can improve the rate of contaminant oxidation by increased production of reactive oxidants as well as widen the range of degradable contaminants by further improvement in the reactivity of the oxidant produced from the Fenton reaction [12]. When pH greater than 7, the removal efficiency decreases because of the formation of $Fe(OH)_4$ ferric complexes with the generation of flakes and subsequent precipitation [17].

The Fe ions in TiO_2 can exist in three valence states; Fe^{2+} and Fe^{4+}, being relatively unstable, though Fe^{3+} have a half-filled d^5 orbital, which is known to be more stable. These ions trap photo-generated electrons and holes under the irradiation destroys the half filled electronic configuration; its stability decreases and the unstable ions Fe^{2+} and Fe^{4+} appear. The trapped electrons and holes can easily be transferred to the oxygen and OH^- group adsorbed on the catalyst surface. Then the Fe ions return to their original stable half-filled electron structure. This might promote charge transfer and efficient separation of electrons and holes [18]. The photocatalytic activity of Fe-doped TiO_2 is strongly dependent on the dopant concentration, since the Fe^{3+} ions can serve not only as mediators of the interfacial charge transfer but also as recombination centres [19].

It can be observed that 0.10 g/L Fe^{2+} concentration showed the highest photocatalytic activity and as the concentration of Fe^{2+} increased in TiO_2, the photocatalytic efficiency was gradually decreased. This is because the decomposition of hydroxyl radicals accelerated by the increase in Fe^{2+} catalyst. Further addition of iron becomes inefficient [20]. Thus a small amount of Fe^{2+} added to TiO_2 improves the degradation efficiency. But in the case of solar photo-Fenton process alone, the requirement of concentration of Fe^{2+} is more and also the process is efficient in acidic pH. This was clearly reported in the literature that 82% of COD was removed in the degradation of pulp and paper mill wastewater at a Fe^{2+} concentration of 1.4 g/L in 60 min of treatment [21]. Another author reported that the degradation of pulp and paper mill wastewater was maximum at a Fe^{2+} concentration of 0.20 g/L in 60 min of treatment [22]. Thus it is observed that the requirement of Fe^{2+} is reduced when it is added to TiO_2. In the combined process, the k values for each Fe^{2+} concentration were estimated from the slopes of straight line obtained by plotting Ln (C_0/C) vs. irradiation time as shown in Fig. 3. The order of rate constants was 0.10 g/LFe^{2+} (0.0600 min^{-1}) > 0.15 g/LFe^{2+} (0.0285 min^{-1}) >0.20g/LFe^{2+} (0.0239 min^{-1}) > 0.05 g/LFe^{2+} (0.0190 min^{-1}) > 0g/LFe^{2+} (0.0131 min^{-1}). When the Fe^{2+} concentration is too high, the recombination will compete with the redox processes because the distance between trap sites is shorter. These trapped e^- or h^+ might recombine before migrating to the surface, resulting in a lower photocatalytic activity, because all the reactions occur only on the surface.

3.3.Influence of pH and TiO_2 concentration

To determine the effect of pH and TiO_2 dosage, the degradation and decolourization of pulp and paper mill wastewater was investigated by varying pH in the range from 3 to 11 and TiO_2 of 0–0.25 g/L. Fig. 4(a) and (b)

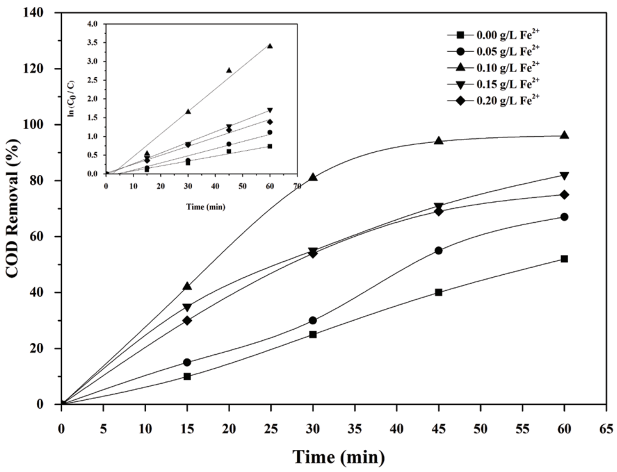

Fig. 3. Kinetic analysis for different Fe^{2+} concentrations based on COD removal.

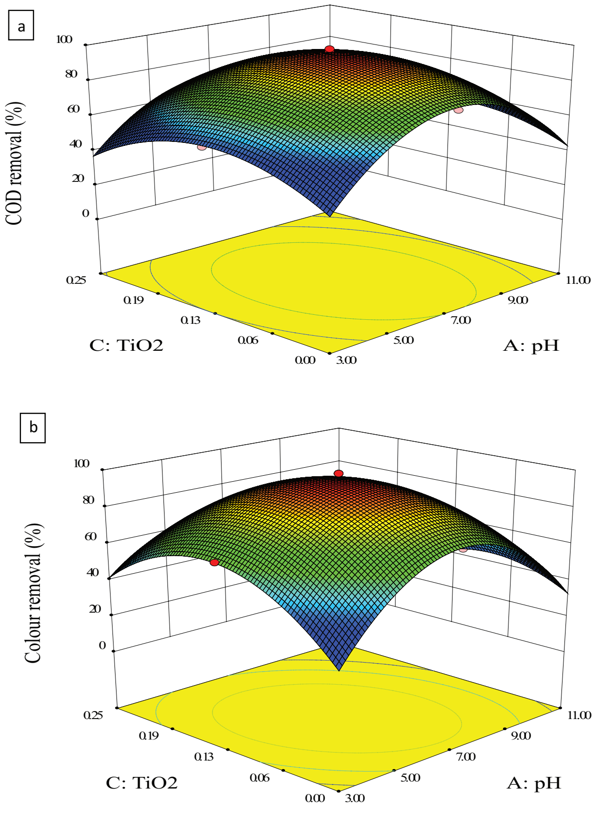

Fig. 4. (a) and (b) 3D surface plots showing the effects of mutual interactions between pH and TiO_2 on COD and colour removal efficiency (pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L, H_2O_2 = 1.80 mL/L).

demonstrate the influence of pH and TiO_2 on the COD and colour removal efficiency at a Fe^{2+} concentration of 0.10 g/L and H_2O_2 concentration of 1.80 mL/L. It can be observed that the degradation and decolourization efficiency increases with increasing pH and TiO_2 concentration. Atalkaline pH, hydroxyl radicals are easily generated by the oxidation of hydroxide ions on the TiO_2 surface [23]. The negative surface of TiO_2 with OH^- ions acts as an efficient trap for the photo generated holes and produces hydroxyl radicals. At pH > TiO_2 zero charge (Pzc) the hydroxyl radical and O_2^- radical can easily diffuse from the negative surface of TiO_2 into the bulk of reaction solution responsible for wastewater degradation. In the acidic pH range, the removal efficiency decreases due to the agglomeration of the TiO_2 particle which reduces the adsorption and the photon absorption [24]. When the concentration of TiO_2 increases from 0 to 0.25 g/L, the degradation also increases with an increase in TiO_2 concentration up to 0.13 g/L. Above 0.13 g/L, there is a slight decrease in the removal efficiency due to the growing turbidity of the suspension caused by the catalyst, which decreases the light penetration and high scattering of TiO_2 particles through the sample; hence, part of the catalyst surface becomes unavailable for photon absorption [25,26]. Thus in the combined process, the TiO_2 concentration is considerably reduced compared to solar photocatalytic process alone as the solar photocatalytic process requires a high concentration of TiO_2. It was reported that 71% of COD was removed at a TiO_2 concentration of 1 g/L at 12 h of reaction time [27]. Similarly, 81% of COD was removed by the solar photocatalytic degradation of pulp and paper mill wastewater at a TiO_2 concentration of 1 g/L [3].

3.4. Influence of H_2O_2

To determine the effect of H_2O_2 dosage, the degradation and decolourization of pulp and paper mill wastewater was investigated by varying the H_2O_2 concentration from 0 to 3.65 mL/L. Fig. 5a and 5b demonstrate the influence of pH and H_2O_2 concentration on the COD and colour removal efficiency at a Fe^{2+} dosage of 0.10 g/L and TiO_2 concentration of 0.13 g/L. The figure illustrates that the degradation increases with increasing H_2O_2 concentration. At pH 7, the maximum COD and colour removal of 98% was obtained at a H_2O_2 concentration of 1.80 mL/L after one hour of solar irradiation. This is because H_2O_2 could increase the degradation by providing additional hydroxyl radicals through the trapping of photogenerated electrons. Additionally, the self-decomposition by illumination would produce hydroxyl radicals [28]. The decrease in degradation at acidic pH is due to the increase in the hydroxyl radical scavenging effect which inhibits the reaction between H_2O_2 and Fe^{2+} [29]. When the concentration of H_2O_2 increases, the degradation also increases upto 1.80 mL/L. Above 1.80 mL/L, there is a scavenging of radicals and the formation of less reactive hydroperoxyl radicals as given in Eq. (13) and Eq. (14). The excess H_2O_2 may act as a hole and react with TiO_2 to form peroxo compounds which are also detrimental to the photocatalytic action. The concentration of H_2O_2 in the combined process is considerably less compared to individual solar photo-Fenton and solar photocatalytic process. It was reported in the literature that 4 mL/L of H_2O_2 was needed for 65% decolourisation of pulp and paper mill wastewater using solar photo-Fenton process [30] and 3 mL/L of H_2O_2 was required to remove 57.9% of COD in the pulp and paper mill wastewater [31]. Thus in

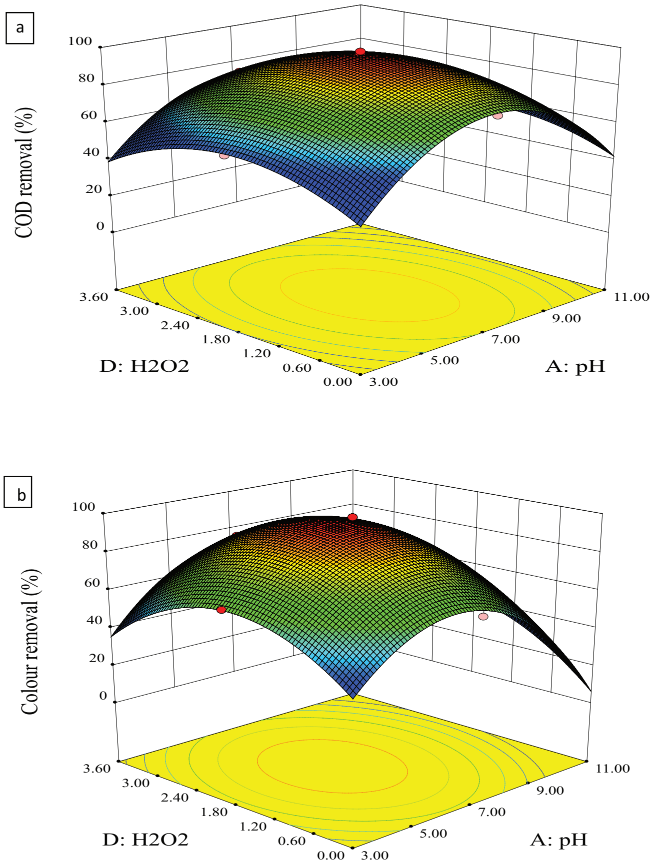

Fig. 5. (a) and (b) 3D surface plots showing the effects of mutual interactions between pH and H_2O_2 on COD and colour removal efficiency (pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L, H_2O_2 = 1.80 mL/L).

this study, the concentration of Fe^{2+}, TiO_2 and H_2O_2 were less and also the efficiency of the process was enhanced within short reaction time.

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \tag{13}$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \tag{14}$$

3.5. Response optimization and confirmation

In the present study, the desired goals in terms of COD and colour removal efficiencies were defined as “maximize” to achieve highest treatment performance while the process variables pH, Fe^{2+}, TiO_2 and H_2O_2 were selected to be in the range. Table 2 shows the optimum conditions for the predicted and the experimental values of COD and colour removal for the combined process. The corresponding experimental values for the degradation of pulp and paper mill wastewater for the combined process under the optimum conditions were found to be 96% and 95.75% for COD and colour removal, respectively,being in good agreement with the values predicted using the Central Composite Design.

3.6. Reaction kinetics

The kinetics of the combined advanced oxidation process (solar/Fe^{2+}/TiO_2/H_2O_2), solar photo-Fenton (solar/Fe^{2+}/H_2O_2) and solar photocatalysis (solar/TiO_2/H_2O_2) for the removal of COD are evaluated. To achieve the correct design of a reactor, it is very important to determine the kinetic coefficients involved in a reaction [32]. For practical applications, the kinetic reaction under different conditions is required. The first order kinetic expression is given by Eq. (15)

$$\ln C_0/C = kt \tag{15}$$

where C_0, C, t and k are the initial COD, final COD, degradation time (min) and the global reaction apparent rate constant (min^{-1}), respectively. The COD and colour removal for the different processes are shown in Fig. 6. These results revealed that COD and color removals of pulp and paper mill wastewater follow the below mentioned order: solar/TiO_2/Fe^{2+}/H_2O_2 > solar/Fe^{2+}/H_2O_2 > solar/TiO_2/H_2O_2. The degradation rate constant, k (min^{-1}) has been chosen as the basic kinetic parameter to compare the different systems and therefore enables determination of the photocatalytic activity; it is given in Fig. 7. The experimental data appears to fit the linear kinetic equation, and consequently, the degradation efficiency follows the first order kinetics. The order of rate constants was solar/TiO_2/Fe^{2+}/H_2O_2 (0.0537 min^{-1}) > solar/Fe^{2+}/H_2O_2 (0.0199 min^{-1}) > solar/TiO_2/H_2O_2 (0.0159 min^{-1}). A significant enhancement of the degradation efficiency was observed during the application of the combined solar/Fe^{2+}/TiO_2/H_2O_2 process. Eq. (16) was used to evaluate the synergetic effect on the rate of degradation [33].

$$\text{Synergetic effect} = \frac{k_{\left(\text{solar}/\text{TiO}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2\right)}}{k_{\left(\text{solar}/\text{TiO}_2/\text{H}_2\text{O}_2\right)} + k_{\left(\text{solar}/\text{Fe}^{2+}/\text{H}_2\text{O}_2\right)}} = 1.50 \tag{16}$$

The main role of a chemical pre-treatment, such as AOPs, is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of degradation should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating costs. Therefore, and with the aim to identify the best possible combination point between the chemical and biological treatment steps, biodegradability analysis must be performed. Biodegradability index (BI) is expressed as the ratio of BOD_5:COD and is a parameter for evaluating biodegradability (amenability to biological treatment) of a wastewater. This parameter is generally referred as BI with reference to suitability of wastewater for biological treatment. For good biodegradability of any wastewater, a minimum BOD_5:COD ratio (BI) of 0.6 is considered to be ideal, for coupling with aerobic treatment. In the present study, the combined processes have lead to an enhancement of BI under optimal experimental conditions. The values of BOD and BI are shown in Fig. 8. It was observed that there is three fold increases in the ratio after 45 min treatment. The results indicated that the combined processes could break down or rearrange molecular structures of organic matters and convert the non-biodegradable organics to more

Table 2
The predicted and experimental values of COD and colour removal for the optimum conditions at 1 h of treatment

pH	Fe^{2+} (g/L)	TiO_2 (g/L)	H_2O_2 (mL/L)	COD removal (%)	Colour removal (%)
Predicted value					
7	0.10	0.13	1.80	98.00	98.00
Experimental value					
7	0.10	0.13	1.80	96.00	95.75
Error (%) [(Actual value–predicted value)/(Actual value)] x 100				2.08	2.35

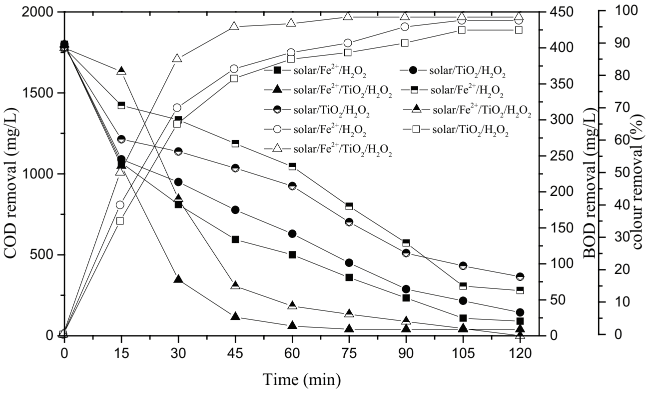

Fig. 6. Percentage COD and colour removal of pulp and paper mill wastewater under optimum conditions (solar/Fe^{2+}/H_2O_2, pH = 6, Fe^{2+} = 0.24 g/L, H_2O_2 = 3.99 mL/L), (solar/TiO_2/H_2O_2, pH = 2.81, TiO_2 = 0.25 g/L, H_2O_2 = 3.00 mL/L), (solar/Fe^{2+}/TiO_2/H_2O_2, pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L, H_2O_2 = 1.80 mL/L), open symbols – colour removal, closed symbols – COD removal, partial open symbols – BOD removal.

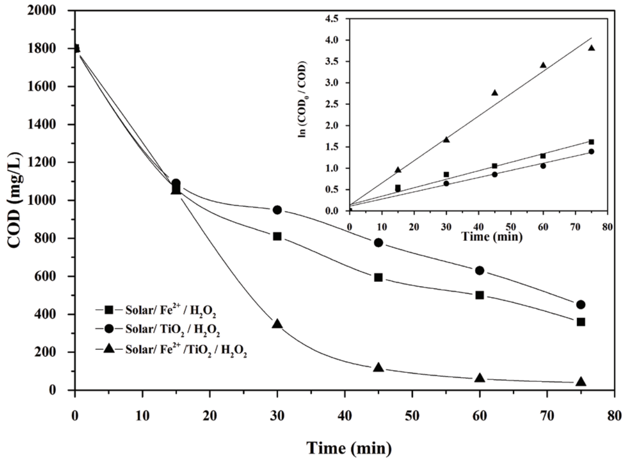

Fig. 7. Kinetic analysis for different treatment systems based on COD removal.

biodegradable forms. The COD and BOD5 of the treated wastewater after 75 min of treatment were reduced to 40 mg/L and 30 mg/L. Behavior of the integration of combined AOPs and biological treatment processes is defined Eq. (17) by a new parameter to depict the biodegradability enhancement.

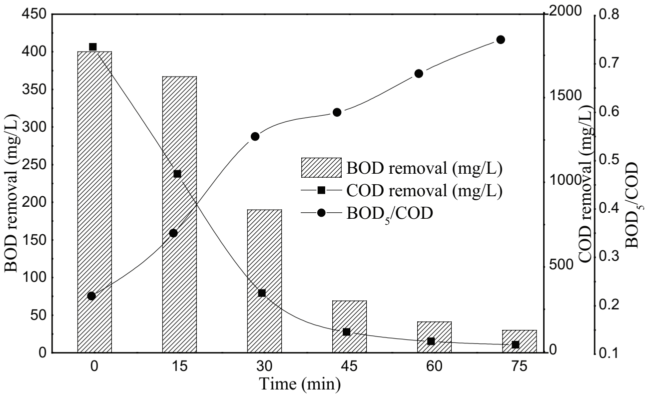

Fig. 8. BOD values and biodegradability index for the combined process under optimized conditions (pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L and H_2O_2 = 1.80 mL/L).

$$\text{Synergetic biodegradability enhancement} = \frac{\text{Biodegradability enhancement by combined process}}{\text{Total biodegradability enhancement by individual processes}} \quad (17)$$

This equation shows the amount of additional BOD produced by combined process. The synergetic biodegradability enhancement effect of this combined homogeneous and heterogeneous advanced oxidation process is based on the BOD_5:COD ratio. The ratio was 0.30, 0.45 and 0.60 for solar/TiO_2/H_2O_2 process, solar/Fe^{2+}/H_2O_2 process and solar/TiO_2/Fe^{2+}/H_2O_2 process, respectively. Based on the ratio, the synergetic biodegradability enhancement effect of the combined process was 0.8.

3.7. Reusability, recyclability of catalyst

The reusability, recyclability of catalyst was investigated for the degradation of pulp and paper mill wastewater. The floc/coagulant was allowed to settle for 30 min before the supernatant was drained. Next the new wastewater without iron was poured into the reactor where sulphuric acid was added to both dissolve the iron sludge and set the pH. Then the combined advanced oxidation process was applied once more. The results of the experimental studies are depicted in Fig. 9. It was observed that the removal efficiency was above 90% for the first five consecutive trials and it gradually decreases. Hence, the catalyst could be recycled for at least five trials. The activity reduction may be due to conglomeration of the catalyst and the adsorption of contaminant on reactive sites on the catalyst surface and loss of some catalyst during the separation through settling [34,35].

3.8. Economic assessment

In this study, the efficiency of the combined process (solar/Fe^{2+}/TiO_2/H_2O_2) and their synergetic effect are determined; however, it is also necessary to assess the economic feasibility of the combined process. An economic assessment was assessed considering the following parameters: reagents consumption based on solar irradiation, labour and investment costs. The estimated annual treatment costsare given in Table 3. The cost estimation was done for a flow rate of 15,000 m^3/d. The solar photo-Fenton process and solar photocatalytic processes individually have high operation costs; by combining these two processes, the operation cost and reaction time are reduced. The combined process is estimated to be lower than alternative technologies, such as incineration or wet oxidation, and higher than air stripping, adsorption or membrane separation technologies, but with the important advantage that the combined processes constitute a real treatment process; the others are only contaminant separation technologies. In this study, the estimated treatment cost was 26 US$/$m^3$ for the solar photo-Fenton process, 22 US$/$m^3$ for the solar photocatalytic process and 14 US$/$m^3$ for the combined processes. From the estimated treatment costs, it is evident that the combined treatment processes represent the most economically feasible, reducing the potential health and environmental risks by providing treated wastewater for reuse purposes.

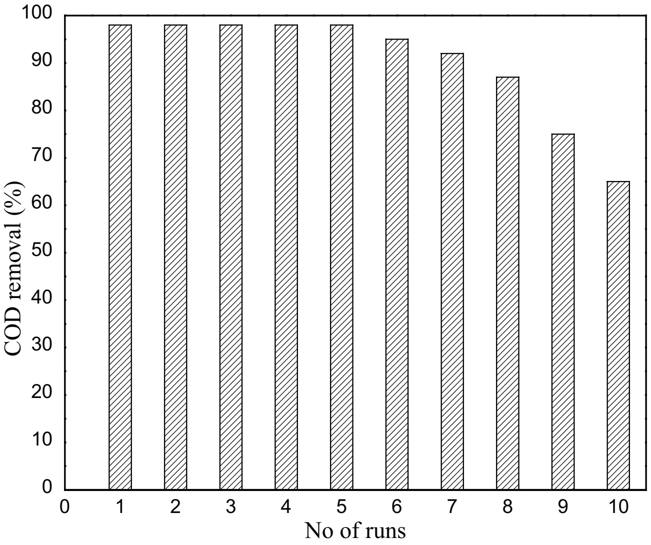

Fig. 9. Effect of catalyst reuse (pH = 7, Fe^{2+} = 0.10 g/L, TiO_2 = 0.13 g/L and H_2O_2 = 1.80 mL/L).

4. Conclusion

This study demonstrated that the combined advanced oxidation processes synergistically accelerated oxidative degradation of organic compounds at neutral pH. The photodegradation of pulp and paper mill wastewater was modelled and optimized with the central composite design. The combined process was more efficient than the individual processes achieving a very high reduction (98%) of COD and colour. The combination approaches were found to be synergistic and followed pseudo-first order kinetics. It was noticed that the main operating cost comes from the reagent's consumption, compared with the costs of other design parameters,while the electricity requirement was found to be insignificant because a natural resource, i.e., solar irradiation,was used. The combined process has less operating cost than the individual processes. Thus, the combined process is cost effective, environmentally friendly and can be considered as a complementary process to improve the quality of the final wastewater for internal recycling and reuse.

Table 3
Estimated annual treatment cost (US$)

			Treatment processes		
			Solar/Fe^{2+}/H_2O_2	Solar/TiO_2/H_2O_2	Solar/Fe^{2+}/TiO_2/ H_2O_2
A	Facility cost		1122786	1122786	1122786
B	Project contingency	15% of A	168418	168418	168418
C	Engineering and set up	50% (A + B)	645602	645602	645602
D	Spare parts	0.5% (A + B)	6456	6456	6456
E	Total installed cost	A + B + C + D	1943262	1943262	1943262
F	Personnel cost	0.25 man year	4022	4022	4022
G	Maintenance material cost	2% (A + B)	25824	25824	25824
H	Electricity	5 KW/h (1752 h)	39420	39420	39420
I	Chemical		141540930	156802743	74214468
J	Total operating cost	F + G + H + I	141207409	121467578	72794835
K	Annual levelized cost	E × FCR + J	141534266	121794435	73121692
L	Annual treatment cost	K/(15000 × 365)	26	22	14

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