OXIDATIVE TREATMENT BY HYDROGEN PEROXIDE FOR THE REMOVAL OF COD AND SULPHIDE FROM TANNERY LIMING WASTEWATER

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ABSTRACT
A simple oxidative treatment study using hydrogen peroxide solely was performed in batch mode for the removal of COD and sulphide from extremely polluted tannery liming effluent. This study investigated maximum COD removal of 92.71% with the optimum influencing parameters of oxidation processes as time (150 min.), temperature (35^0C to 40^0C), pH of the sample (7) and amount of H_2O_2 (2.5mL/100mL). The removal of BOD_5 was attained 82.33% in the above optimum experimental conditions. This study also explored that maximum sulphide removal efficiency of H_2O_2 was 99.09% from 4329 mg/L to 39.39 mg/L for 40 minutes of oxidation using 2.5mL of H_2O_2 per 100mL sample at 40^0C temperature where initial pH of wastewater was 8. Kinetics analysis based on Pseudo first and second order model revealed that the oxidation process for COD removal followed second order kinetics model. The obtained values of COD and BOD after the oxidative treatment were 2799.36 mg/L and 971.85mg/L respectively whereas the values of the raw effluent were accordingly 38400mg/L and 5500mg/L. This oxidative treatment technique would be able to contribute the reduction of environmental threats of tannery liming effluent as it could significantly reduce the COD loads and sulphides.

Keywords: Tannery wastewater; liming wastewater; COD; sulphide; oxidative treatment

INTRODUCTION
Tanneries convert raw hides and skins which are largely composed of the protein collagen into leather by several chemical and mechanical operations (Das et al., 2008; Covington, 2011). Liming is a tannery operation under the beam house sub-process where hides and skins are treated with milk of lime with the addition of sodium sulphide to remove keratinous matters, interfibrillary soluble proteins and natural fats and to bring the collagen to a proper condition for satisfactory tannage (Dutt, 1999). The immensely alkaline highly turbid foul smelling liming effluent is characterized by high concentration of sulphides and extreme level of suspended solids, BOD and COD creates severe health problems to the human, damages aquatic life and destroys oxygen dependent plants and microorganisms (UNIDO, 2003; Paredes and Banchon, 2015).
The low biodegradable complex natured tannery effluent creates not only unfavourable environmental outcome but also technological difficulties to treat it to discharge (Lofrano et al., 2013; Banuraman and Meikandaan, 2013). From this point of view a number of researches on oxidation and advanced oxidation processes (AOP) carried out for tannery wastewater treatment around the world with their effectiveness of the removal of sulphides and COD. The most commonly investigated oxidative treatment technologies for the conversion of COD and sulphides into stable inorganic compounds from tannery wastewater were UV, H_2O_2/UV, TiO_2/UV, O_3, O_3/UV, Fenton, Photo-Fenton, Electro oxidation, Electro-Fenton, Catalytic oxidation etc (Rameshraja & Suresh, 2011). Almost all the previous peroxide oxidation studies for tannery wastewater were done with the composite effluent using H_2O_2 along with different catalysts. Due to efficient performance of hydrogen peroxide as a strong oxidant the compatibility of this oxidative treatment has been investigated here for the removal of COD and sulphides from liming effluent.
The main objective of the study was to simple oxidation of segregated liming wastewater using only H_2O_2 for the removal of COD and to optimize the oxidation process parameters specific for liming

effluent. Evaluation of the removal efficiency of BOD was also aimed to the research. This study was also focused on the identification of the removal efficiency of sulphide by H_2O_2 through the oxidation process. Chemical kinetics study of H_2O_2 oxidation for COD removal was also a target of the research.

METHODOLOGY
Materials & Analytical methods
Liming wastewater for this study was collected from a tannery located at Nowapar in Jessore district. Collected samples were then characterized in the laboratory. Hydrogen peroxide used in this study was of commercial grade and purchased from a local scientific store in Khulna. In this study COD, BOD_5, TDS and TSS were measured by the methods 5220C, 5210B, 2540C and 2540D according to standard methods (APHA, 1997). Sulphide concentrations were measured using SLC 202 method (SLC, 1996). Other parameters were measured instrumentally. Examined parameters of the raw liming wastewater are represented in Table 1.

Experimental procedures
This oxidative treatment was done in batch process taking 100 mL of samples for each batch with continuous stirring in a magnetic stirrer at various experimental conditions. In the first part of the study different influencing parameters on COD removal by H_2O_2 oxidation was investigated and optimized. Dosage of hydrogen peroxide was investigated from 0.5mL to 3mL with a gradient of 0.5 mL where further increase of dosages were not tested due to avoid vigorous chemical reactions and accidental hazards. The effect of pH was checked and optimized from 7 to 11 by controlling with dilute nitric acid. Different temperatures (30^0C, 35^0C and 40^0C) were tested for getting most favourable one. Samples were withdrawn from all of the above mentioned experimental conditions at 30, 60, 90, 120, 150 and 180 minutes interval, filtered through 0.45μm filter paper, diluted to 100 times by distill

Table 1: Analysis of liming wastewater

Parameter	Values
pH	12.30
Turbidity (NTU)	7700
Salinity (ppt)	34.8
Conductivity (mS)	53.1
Sulfide(mg/L)	4329
TDS (mg/L)	34660
TSS (mg/L)	27900
Chloride (mg/L)	54.98
DO (mg/L)	0.01167
BOD_5 (mg/L)	5500
COD (mg/L)	38400
BOD_5/COD	0.143

water and immediately taken for COD determination. Based on the maximum COD removal efficiency (% of COD removal) operational parameters were optimized. The removal efficiency of BOD_5 was also investigated at the optimum experimental conditions of COD removal.

The evaluation of the removal efficiency of sulphides during oxidative treatment were done using six different dosages of H_2O_2 from 0.5mL to 3mL at different temperatures from 35^0C to 40^0C with the initial pH of the sample ranging from 7 to 11 for 10 to 60 minutes of oxidation.

RESULTS AND DISCUSSIONS

Removal of COD by H_2O_2 oxidation
Effect of amount of hydrogen peroxide on the removal efficiency of COD
The effect of hydrogen peroxide dosages on COD removal was investigated for six dosages from 0.5mL to 3.0mL at oxidation time from 30 minutes to 180 minutes while pH of wastewater was maintained at 7. The results represented in the [Fig. 1] revealed that in most of the cases with the increase of the amount of hydrogen peroxide and oxidation time the removal efficiency of COD increased. According to [Fig. 1] for all of the H_2O_2 dosages most of the COD degradation occurred in first 30 minutes of reaction where the greater value 56.25% and lower value 33.33% were observed for 2.5 mL and 0.5 mL of dosages. In each time interval starting from 0.5 mL to 1.5 mL the removal efficiency of COD increased significantly after that for 2.0 mL and 2.5 mL it raised slowly and reached to the maximum for 2.5 mL. Further increase of hydrogen peroxide dosage from 2.5 mL to 3.0 mL could not increase the process performance rather than the removal percentages of COD started to decrease. This inhibition effect may be due to the contribution of residual hydrogen peroxide to COD. In this experimental condition maximum removal of COD (92.71%) was achieved for 2.5 mL of H_2O_2 so, this dosage was selected as optimum and was taken in the following runs.
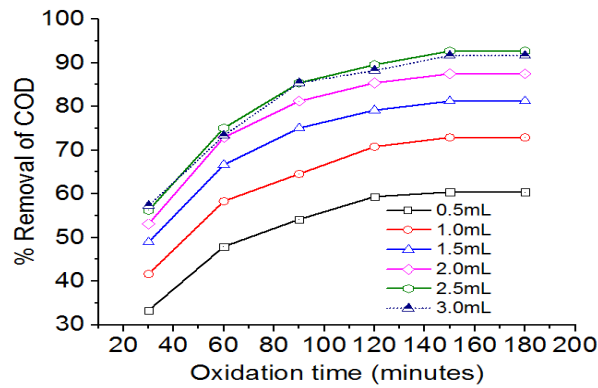
Fig. 1: Effect of Dosages of H_2O_2 on the removal efficiency of COD (pH = 7, Temperature = 35 °C)
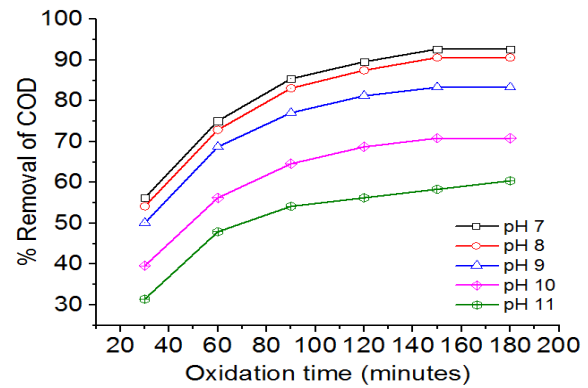
Fig. 2: Effect of pH on the removal efficiency of COD (Dosage of H_2O_2 = 2.5mL/100mL sample, Temperature = 35 °C)

Effect of pH on the removal efficiency of COD

The experiments for the evaluation of the influence of pH on COD removal efficiency were done for different pH values (7, 8, 9, 10, and 11) at various reaction times from 30 minutes to 180 minutes. [Fig. 2] represents the experimental results from where it is seen that COD removal efficiency decreased with the increase of pH whereas for every pH values the efficiencies increased with times and reached maximum at 150 minutes of oxidation. It is also observed from [Fig. 2] that for each oxidation times the percentage removal of COD was higher for pH 7 that started to decrease slowly from pH 8 to 9 and significant decrease of the results were noticed for pH values 10 & 11. Various researches revealed that oxidation by H_2O_2 is a free radical based reaction and the formation of free radical is affected by pH values. This is may be the cause of the decrease of removal efficiency at higher pH values. The experimental data in the above mentioned figure illustrates that maximum 92.71 % of COD removal was obtained at pH 7 for 150 minutes of oxidation, for this reason pH 7 was taken as optimum for COD removal for this study.
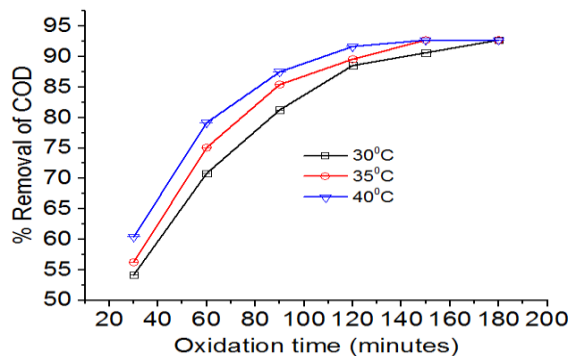

Fig. 3: Effect of Temperature on the removal efficiency of COD (Dosage of H_2O_2 = 2.5mL/100mL sample, pH = 7)
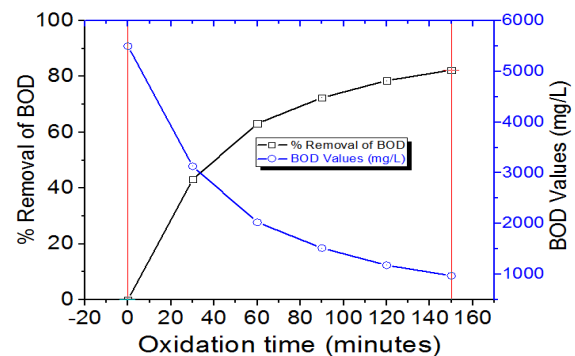
Fig. 4: Removal of BOD_5 during oxidation (Dosage of H_2O_2 = 2.5mL/100mL sample, pH = 7, Temperature = 35 °C)

Effect of oxidation temperature on the removal efficiency of COD

[Fig. 3] shows the effect of temperature on COD removal efficiency. The graph is plotted by the data received from a series of experiments at different temperatures 30 °C, 35 °C (room temp.) and 40 °C. It is observed form the [Fig. 3] that the removal efficiency of COD increased with the increase of temperature as the removal efficiency of 54.16% was for first 30 minutes of oxidation at 30^0C which rose to 56.25% and 60.42% for 35^0C and 40^0C respectively and this increasing trend was also found in other reaction times. This increasing trend may results from the acceleration of free radical formation from H_2O_2 at higher temperatures that improves COD removal. The noticeable fact of the results was that maximum COD removal efficiency of 92.71% was not changed with the change of temperature. So, little influence of temperature was evaluated in this study and 35 °C to 40 °C was optimized for COD removal from liming wastewater.

Removal efficiency of BOD by H₂O₂ oxidation

The removal efficiency of BOD was measured for 30 to 150 minutes of oxidation with 100mL of sample at optimum experimental conditions of COD. The double Y axis plot of the results in the [Fig. 4] depicts the percentage removal of BOD with times along with the corresponding residual BOD values in mg/L. The figure shows that with times BOD removal efficiency increased. Almost half of the BOD degradation occurred in first 30 minutes of oxidation and maximum 82.33% removal was attained in 150 minutes with the residual value of 971.8mg/L.

Removal of Sulphides by H₂O₂ oxidation

Evaluation of the different influencing parameters on the removal of Sulphides during oxidation

[Fig. 5] represents the dependence of pH varied from 7 to 11 on sulphide removal during 40 minutes of oxidation at room temperature with 2.5mL H_2O_2. According to the figure higher pH values show lower removal efficiency of sulphides. Minimum residual sulphide concentration (117.32 mg/L) was attained at pH 8 and the values were very close for pH 7 (156.28 mg/L) and pH 9 (136.51 mg/L) whereas negative process performance was noticed for pH 10 &11.
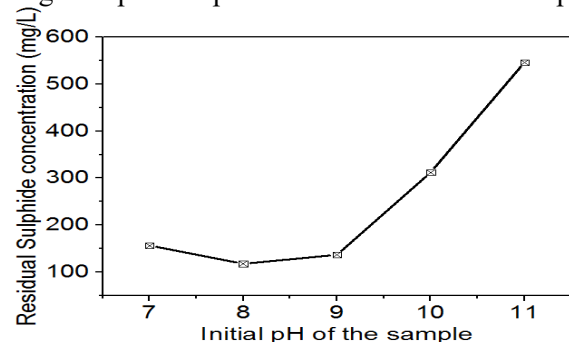

Fig. 5: Effect of pH on the removal of Sulphides (Dosage of H_2O_2 = 2.5mL/100mL sample, Temperature = 35 °C, Time = 40 minutes)
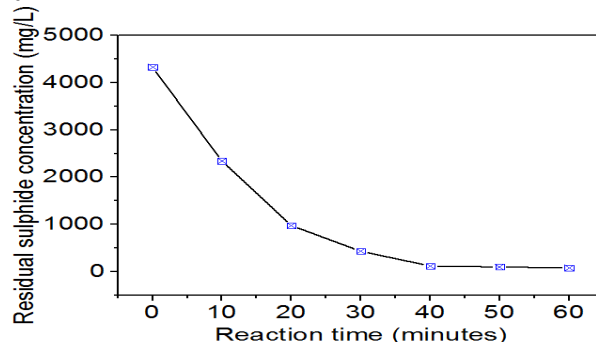
Fig. 6: Effect of Oxidation time on the removal of Sulphides (Dosage of H_2O_2 = 2.5mL/100mL sample, Temperature = 35 °C, pH = 8)

Behaviour of oxidation time on sulphide removal presented in [Fig. 6] tested for 10 to 60 minutes of oxidation at room temperature (35^0C) taking pH of the sample 8, dosage of H_2O_2 2.5mL. The figure shows that sulphides removed in an increasing trend with times and significant removal observed in 40 minutes of reaction where residual sulphide concentration was only 117.32 mg/L. In the additional reaction times sulphides removed slowly and reached to 77.92 mg/L of residual sulphides in further 20 minutes of oxidation.

Amount of H_2O_2 was identified to affect significantly on sulphide removal has been illustrated in [Fig. 7]. It is seen from the figure that starting from 0.5mL to 2mL of oxidant sulphides removed sharply compared to the subsequent dosages. As in the figure for the first 1mL of H_2O_2 residual sulphide concentration was 780.08 mg/L whereas for 2mL and 3mL of oxidant the values were 195.24 mg/L and 77.92 mg/L respectively indicating the removal of 584.84 mg/L of sulphides for additional 1mL (from 1 to 2 mL) and only 117.32 mg/L of sulphides for final 1mL (from 2 to 3 mL). [Fig. 8] shows the positive influence of the increase of temperature on sulphides removal. Minimum residual sulphide concentration 39.39 mg/L which is the notification of maximum removal efficiency was attained by oxidation at 40 °C.
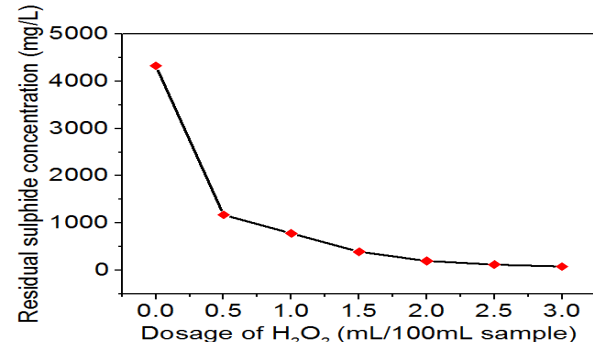

Fig. 7: Effect of dosages of H_2O_2 time on the removal of Sulphides (Time = 40 min., Temperature = 35 °C, pH = 8)
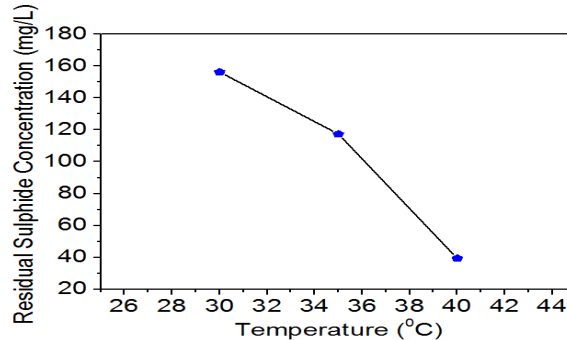
Fig. 8: Effect of Temperature time on the removal of Sulphides (Dosage of H_2O_2 = 2.5mL/100mL sample, Time = 40 min., pH = 8)

Kinetics analysis for COD removal in the oxidative treatment

In this research both first and second order kinetics model has been studied. Equation [1] represents first order kinetic model (Panizza & Cerisola, 2001) whereas according to (Haddad et al., 2014) second order kinetic analysis can be done by Eq. (2).

$$\ln \frac{C_0}{C_t} = k_1 t \qquad (1), \qquad\qquad \frac{1}{C_t} - \frac{1}{C_0} = k_2 t \qquad (2)$$

Where, C_0, C_t, k_1 and k_2 are COD concentration of raw sample (mg/L), COD concentration with times, first order rate constant (min^{-1}) and second order rate constant $(L.mg^{-1}.min^{-1})$ of the kinetics model respectively.

In this study kinetics analysis for COD removal was done for 30 minutes to 180 minutes of oxidation at temperature of 35 °C and 40 °C with the other previously optimized parameters. Based on the Eq. (1) and Eq. (2) data of $\ln (C_0/C_t)$ vs. t and $(1/C_t – 1/C_0)$ vs. t were plotted for the study of Pseudo first order and second order reaction kinetics respectively. The linear plot of the kinetics model are shown in the [Fig. 09] and [Fig. 10].
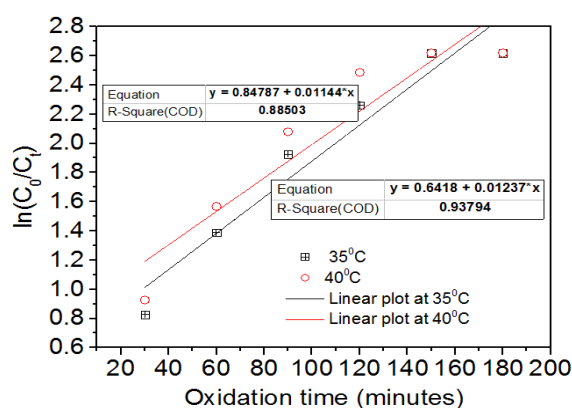

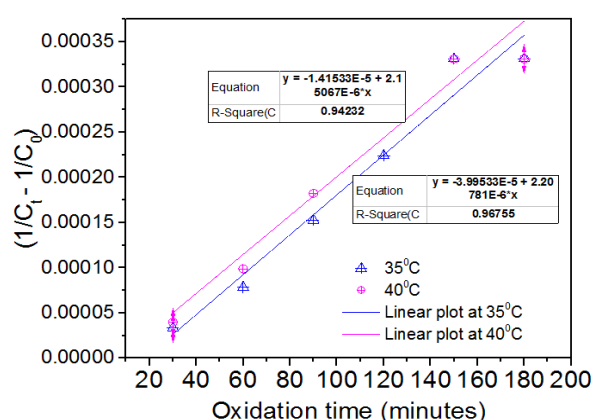Fig. 9: Kinetic plots of first order model

Fig. 10: Kinetic plots of second order model

From the equation of the straight lines of the kinetic plots rate constants k_1, k_2 and half times of first and second order reactions were calculated and the values are showed in Table 2. The data of kinetics study in the Table 2. Shows that reaction rate constants k_1 and k_2 decreased with the increase of temperature but the values were very close for each model that signifies little impact of temperature on the COD removal by H_2O_2 oxidation. Lower half times for second order model 11.78min at 35 °C and 12.11min at 40 °C supported the experimental results. In addition the greater values of coefficient of determination (R^2) 0.968 at 35 °C and 0.942 at 40 °C of the second order model than first order model (0.938 at 35 °C and 0.885 at 40 °C) are the indication of the better fit of the experimental data in the second order model. From the above explanation it can be concluded that the Removal of COD from tannery liming wastewater by H_2O_2 oxidation was a Pseudo second order reaction.

Table 2: The values of R^2, rate constant and halftimes for first and second order model

	Temperature (^0C)							
	35^{0}C				40^{0}C			
	R^2	k_1 (min^{-1})	k_2 $(L.mg^{-1}.min^{-1})$	$t_{1/2}$ (min.)	R^2	k_1 (min^{-1})	k_2 $L.mg^{-1}.min^{-1}$	$t_{1/2}$ min.
First order model	0.938	0.012	-	57.75	0.885	0.011	-	63
Second order model	0.968	-	$2.21*10^{-6}$	11.78	0.942	-	$2.15*10^{-6}$	12.11

CONCLUSIONS

In this batch oxidative treatment study H_2O_2 was found as an effective oxidant for the removal of COD and sulphides from tannery liming wastewater. Oxidation occurred effectively at neutral pH and additional amount of H_2O_2 over optimum dosage was observed negative impact on COD removal while a little influence of the increase of the reaction temperature provided with the benefit of the greater

degradation of COD at initial reaction times was noticed. The evaluation of the influencing parameter on sulphide removal revealed that the removal efficiency increased with the increase of temperature and the amount of oxidant and H_2O_2 was detected to work better at neutral to slightly alkaline pH range whereas most of the sulphide removal was noticed at 40 minutes of oxidation. Kinetics analysis of this study showed that the oxidative treatment could better be explained by Pseudo second order model.

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