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Catalytic thermal treatment (thermolysis) process of tannery wastewater for the removal of chemical oxygen demand and color

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ABSTRACT

The aim of present research work is to treat the tannery wastewater (TWW) using catalytic thermal treatment process. The treatment of TWW was done on the basis of removal of COD and color in a batch system. All the experiments have been carried out in a batch system. Effect of various process parameters such as pH (2–9), thermolysis time (0–6 h), temperature (55°C–95°C), catalyst loading (C_w) (1–6 g/L), and two types of catalysts (copper sulfate and copper oxide) was studied on the removal efficiency of COD and color from wastewater. Copper sulfate was found to be a better catalyst as compared with copper oxide during thermolysis for TWW. The observed results exhibited that maximum COD removal of 71.36% and color removal of 77.56% were achieved using copper sulfate at the optimized conditions of pH of 4, catalyst loading of 4 g/L, temperature of 95°C, and thermolysis time of 6 h. Kinetic study followed the first order kinetics model and it was observed that the COD reduction was found to be two steps (fast and slow steps) mechanisms. The observed higher values of rate constant (k_1) showed that rate of reaction was fast in the first step of thermolysis. Initial pH played an important role in COD removal. The settling rate of the slurry was good and strongly affected by pH values. It has been observed that treated wastewater provided the best (fastest) filterability at the pH 12. The energy consumption was found to be 2,619 kWh/kg of COD removal under the optimized process conditions. Overall, it can be said that thermolysis process can be employed for the treatment of industrial wastewater.

Keywords: Tannery wastewater; Catalytic thermal treatment; COD; Color; Kinetics

1. Introduction

In recent years, discharge of wastewater from tannery industries into aquatic environment is the main environmental issue over the world [1]. The tanning process transforms raw hide and skins into stable and imputrescible substance known as leather, which is used for preparing numerous consumer products such as belt, purse, jacket, sport goods, etc. [2]. It comprises various mechanical and chemical processes to clean the raw hide/skin and eliminate the flesh and hair from the hide/skin, residual meat and also to improve its functional properties. These processes

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consume a large number of chemicals and huge amount of water, creating a large quantity of liquid wastewater, which is harmful to the water bodies. Almost 20–30 L of wastewater is discharged for 1 kg of skin/hide processed depending upon the raw materials and desired end products [3]. TWW is characterized by highly fluctuating pH conditions, strong color and high BOD, COD, because of wide range of contaminants such as protein, colloid, fats and tannins, debris of flesh and hair, dyes and toxic elements such as sulfide and chromium content [4–6]. However, the exact characteristics of TWW may vary considerably, depending on the hide/skin preservation process, nature of the raw materials used, processing volume and quantity of water utilized [7]. The dissolved compounds also cause the effluent to become highly toxic, mutagenic and carcinogenic. The wastewaters produced from tanneries are very complex due to the utilization of huge quantity and variety of chemicals in tannery processing. According to the Indian Standards Institution (ISI), New Delhi, India, 2000, the TWW should have COD < 250 mg/L, total suspended solids < 100 mg/L and BOD < 30 mg/L for discharge into surface waters [8]. The development of treatment methods for these wastewaters is extremely required for obtaining the desired standard of the treated wastewater.

In literature, there have been many studies reported for the treatment of TWW using various methods/processes such as sedimentation [9], coagulation-based process [10–14], biological process [15,16], adsorption [17–19], electrochemical treatment [20], advanced oxidation processes [4,21–23] and membrane filtration [24]. All these processes have their own limitations due to economical or sludge management. Currently, catalytic thermal treatment (CTT) has emerged as an advanced and novel process for the treatment of highly concentrated wastewater. CTT is a chemical process in which chemicals/metal salts react with complex molecules in the presence of heat converting them into other substances such as solid residue, smaller molecules, water and gas [25–28]. In recent years, it was successfully applied for the treatment of various industrial wastewaters, that is, dyeing wastewater [25–27], pulp and paper industries [28], petrochemical industries [29] and sugar industry wastewater [30] and distillery wastewater [31,32]. Kumar et al. [27] have investigated the COD and color removal from composite wastewater of a cotton textile industry using thermolysis. They have used various catalysts/chemicals in their study such as $FeCl_3$, $CuSO_4$, $FeSO_4$, CuO, PAC and ZnO. It was observed that maximum COD of 78% and color of 92.8% were removed using $CuSO_4$ (6 kg/m^3), temperature (95ºC) and pH (12). Garg et al. [28] reported that $CuSO_4$ among all the catalysts gave the highest removal efficiency of COD (63.3%) with a catalyst loading of C_w 5 kg/m^3 at pH of 5 from pulp and paper mill effluent. Chaudhari et al. [32] illustrated on the treatment of distillery wastewater using catalytic thermolysis at 80°C to 100°C using $CuSO_4$, CuO, MnO_2 and ZnO. They found that CuO was the best between various catalysts used in their study. Almost 47% COD and 68% color were reduced in case of distillery wastewater, whereas 78% color and 61% COD were removed from distillery bio-digester wastewater. Similar results were found in the study of Chaudhari et al. [31], showing a maximum of 60% COD reduction using catalyst (CuO) at a loading of 3 kg/m^3, pH 2 and temperature 140°C. It has been reported that metal oxides based on Cu, that is, CuO, $CuSO_4$ were found to be very effective in the CTT process for the industrial wastewater treatment [25,27,28,30–35]. Hence, the efficiency of two catalysts (CuO and $CuSO_4$) was studied in the present work and compared in order to choose the most effective catalyst in removing the COD and color from tannery effluent.

To the best of our information, none of work was reported in literature for the CTT process of TWW. Therefore, the major objective of this study is to assess the efficacy of CTT process in terms of COD and color reduction from TWW, which is reported for the first time. The effect of different process factors such as pH, temperature, catalyst mass loading and thermolysis time was studied. Kinetic studies based on COD reduction were also examined. The characteristics of slurry obtained after treatment were also reported. The energy consumption analysis under the optimized conditions was done as well.

2. Materials and methods

2.1. Tannery wastewater (TWW)

TWW was taken from a tannery industry situated at Jazmau industrial area, Kanpur, India (details not given due to confidentiality issues). The TWW sample was previously treated using adsorption on tea waste, as reported in our previous study [17]. The wastewater was kept at 4°C in a freezer in the laboratory in order to prevent its quality from any variation. The chemical characteristics of pre-treated TWW are given in Table 1.

2.2. Chemicals

The AR grade chemicals were used in the present investigation for the experiments and analysis. Copper sulfate ($CuSO_4{\cdot}5H_2O$) and copper oxide (CuO) were purchased from Central Drug House (P) Ltd. (India) and used as catalyst in the CTT process. Chemicals, that is, mercuric sulfate, silver sulfate, sulfuric acid, potassium dichromate, ferrous ammonium sulfate, and ferroin indicator were used for the analysis of COD. All chemicals obtained from dealers were used for the experimentation without any extra purification.

2.3. Experimental details

Experiments were performed in a laboratory scale and the setup is shown in Fig. 1. This reactor consists of: (i) a 500-mL capacity three-necked glass reactor, (ii) the rotamantle with both heating and speed controlling device, (iii) a long vertical water cooler condenser was connected at the center of the atmospheric glass reactor to condense the vapors and recirculate into the glass reactor to avoid any loss of the vapor generated during the reaction, (iv) a mercury thermometer was inserted into the glass reactor to measure the reaction mixture temperature, (v) one neck of the glass reactor was used for sample withdrawal. In this work, all the experiments were performed with 300-mL sample of TWW. Effect of solution

Table 1
Chemical characteristics of the pre-treated tannery wastewater

Parameters	Values	Units
pH	3.9	–
Cr(VI)	14.88	mg/L
COD	2,140	mg/L
TDS	11,443.5	mg/L
TS	9,932.5	mg/L
Electrical conductivity	21.5	mS/cm
Turbidity	29.3	NTU

pH on the COD and color removal efficiency was studied over the range of 2.0–9.0. The solution pH was attuned using 0.1 N NaOH or 0.1 N HCl. The temperature of the reaction mixture was varied from 55°C to 95°C. The catalyst loading (C_w) was studied over the range from 1 to 6 g/L in order to optimize the catalyst mass loading. The reaction time was 6 h for all the experiments. The time taken (or heating time, t_h) for the raising temperature of the samples from ambient temperature to 95°C was almost 30 min. Further the time was measured by deducting heating time (t_h) from the total time. Therefore, t_h for starting experiments was considered as zero (0) for further heating. After the start of experiments, the wastewater samples were taken from the thermal reactor at a regular time interval and analyzed for its COD and color. All experiments were performed at least three times to get an average value. The experimental error was found to be within ±3%.

The % removal efficiency of COD and color was determined using Eq. (1):

$$\text{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i = initial concentration (mg/L) and C_f = final concentration (mg/L).

2.4. Analytical methods

The COD of the TWW was estimated by standard open reflux titrimetric method (APHA 1998) [36]. To determine the color removal efficiency, absorbance of the sample was measured using a UV-vis double beam spectrophotometer (Model: NSP 372) at 475 nm. The pH of the solution was measured using a pH meter (Hanna Instruments, USA). The wastewater samples obtained after treatment were centrifuged (Model R24, Remi Instruments Pvt. Ltd., Mumbai, India) to collect the supernatant and the precipitate.

3. Results and discussions

3.1. Effect of solution pH

The effect of solution pH over a range of 2–9 on the removal efficiency of COD and color was studied with copper sulfate ($CuSO_4 \cdot 5H_2O$) and copper oxide (CuO). The experiments were carried out at 95°C for 9 h with a catalyst mass loading of 4 g/L. The achieved results are

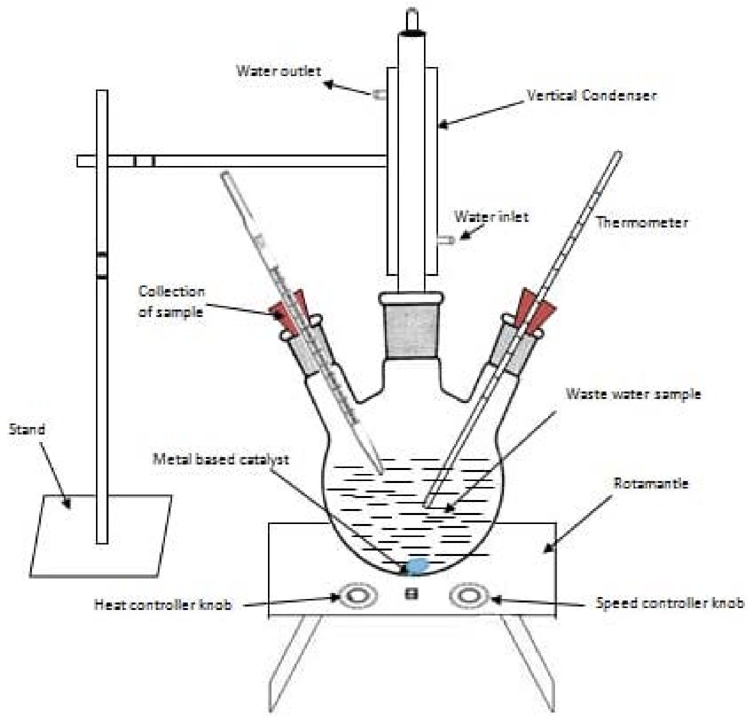

Fig. 1. Experimental setup of catalytic thermal process.

shown in Figs. 2a and b. The maximum COD reduction of 71.36% and color reduction of 77.56% were achieved at pH of 4 with copper sulfate whereas, 61.47% COD and 70.74% color were removed at pH of 5 using copper oxide. The change in % of COD and color removal of TWW obtained with different catalysts may be because of combined effect of catalyst and the active functional groups present in wastewater, which react at definite pH, and the activity of the catalyst, which varied with solution pH [32]. It was observed that copper sulfate gave the higher COD and color removal efficiency from TWW as compared with that obtained in case of copper oxide. Hence, all the remaining experiments were investigated with copper sulfate at pH 4. The final solution pH was also checked after the treatment and a reduction in pH was found for all the cases. The decrease in pH may be due to the separation in to sulfate/chlorides ions and also due to the lower carboxylic acids formed. The sulfate/chloride ions after joining with H^+ ions decrease the pH of the solution [26].

3.2. Effect of temperature

As copper sulfate catalyst was found better compared with copper oxide, it was chosen for further studies. To examine the effect of temperature, tests were performed over the range of temperature 55°C–95°C at pH of 4, $CuSO_4{\cdot}5H_2O$ loading of 4 g/L and reaction time of 6 h. Fig. 3 clearly shows % removal of COD and color was enhanced as the temperature improved from 55°C to 95°C. The maximum COD and color reduction of 71.36%, 77.56%, respectively, were observed at 95°C{deleted}. Similar observations have been reported in literature by many authors [26,35,37]. Kumar et al. [37] have investigated the treatment of desizing wastewater using thermolysis process and reported that COD and color reduction were enhanced with an increase in the temperature. Almost 72% reduction in COD was found at the temperature of 95°C whereas almost 28% COD reduction was obtained at 60°C with 4 kg/m^3 $CuSO_4$ catalyst and pH of 4.

3.3. Effect of catalyst mass dosing

Catalyst mass loading is an important factor in treating the TWW. The effect of $CuSO_4$ mass dosing on the reduction of COD and color was carried out in the variation of 1–6 g/L at an optimum pH of 4 and temperature of 95°C with a reaction time of 6 h. The experimental results are depicted in Fig. 4. It has been seen that by increasing the catalyst mass loading, % reductions of color and COD increases with an increase up to 4 g/L while and while beyond a 4 g/L it drops. The highest COD and color reduction belonging to 4 g/L catalyst loading were

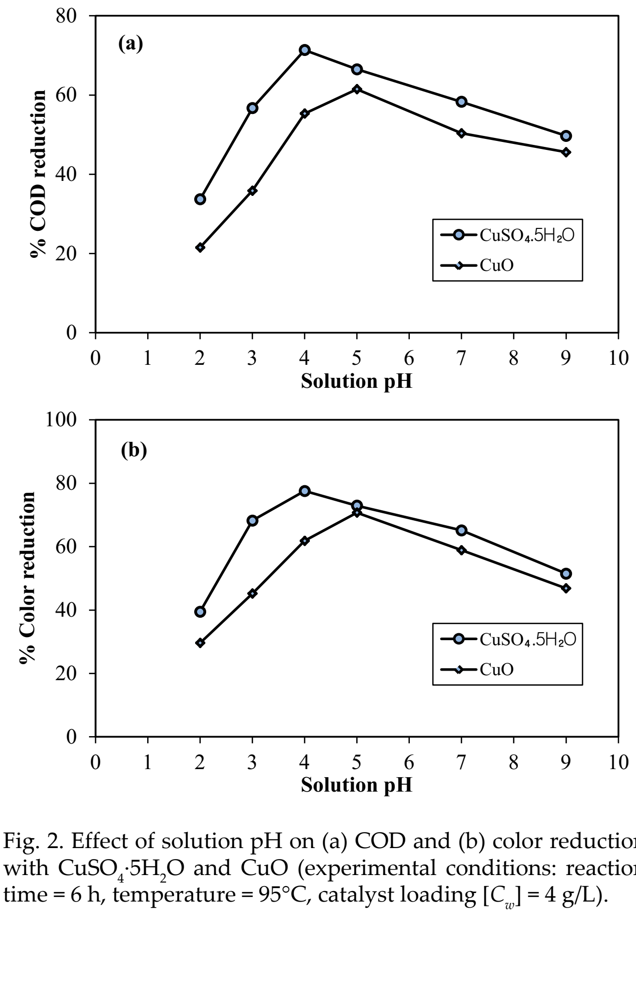

Fig. 2. Effect of solution pH on (a) COD and (b) color reduction with $CuSO_4{\cdot}5H_2O$ and CuO (experimental conditions: reaction time = 6 h, temperature = 95°C, catalyst loading [C_w] = 4 g/L).

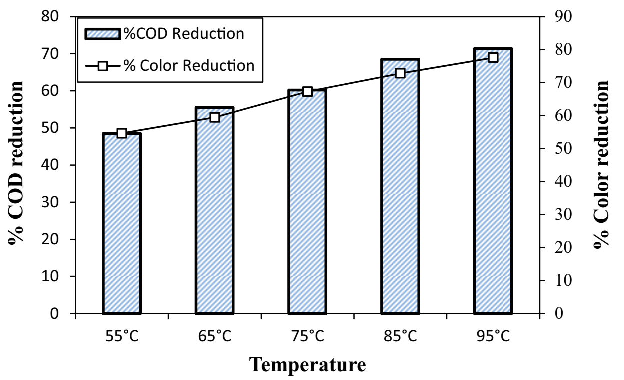

Fig. 3. Effect of reaction temperature on COD and color reduction (experimental conditions: reaction time = 6 h, solution pH = 4, catalyst [$CuSO_4{\cdot}5H_2O$] loading [C_w] = 4 g/L).

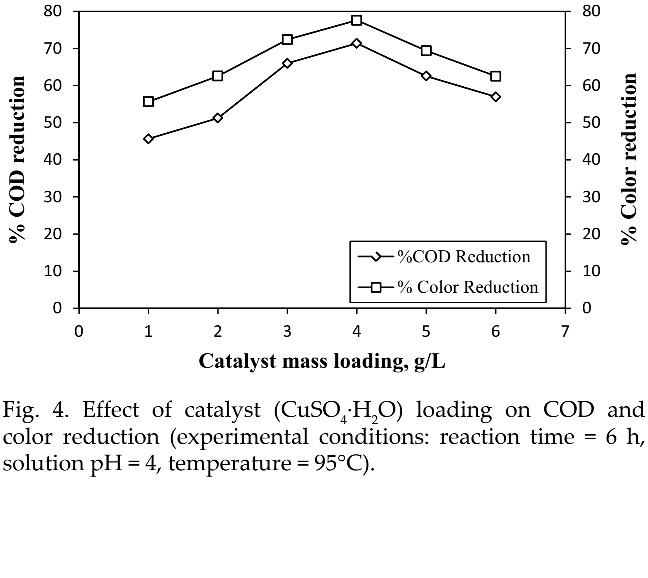

Fig. 4. Effect of catalyst ($CuSO_4{\cdot}H_2O$) loading on COD and color reduction (experimental conditions: reaction time = 6 h, solution pH = 4, temperature = 95°C).

71.36% and 77.56%, respectively. Moreover, as increasing the catalyst loading to 6 g/L, the COD 56.96% and color removal 62.53% were decreased. Therefore, optimum catalyst mass loading for treatment has been considered as 4 g/L. This may be attributed due to the generation of thermo-chemical precipitates. Similar results related to the effect of catalyst loading on the reduction of COD and colors from various industrial wastewaters are indicated in literature [25,29,34,35,37].

3.4. Effect of reaction time

Reaction time is also an important factor, which influences the thermal catalytic process. The effect of reaction time on the reduction efficiency of COD and color was conducted at optimum pH of 4, temperature of 95°C, and catalyst mass loading of 4 g/L. The effect of time was conducted from 0 to 6 h, the COD and color reduction are shown in Fig. 5. It has been found that the COD reduction was increased from 62.52% to 71.36% with an increase in time from 3 to 6 h whereas color reduction efficiency enhanced from 68.24% after 3 h up to 77.56% after 6 h in the presence of copper sulfate. The reduction in COD and color over the heating reaction time may be attributed to the fact that larger complex molecules are broken down into smaller molecules by thermal destruction and the generation of solid particles, which settled down [34]. Therefore, 6 h was chosen as an optimum reaction time for achieving the maximum removal efficiency of COD and color from TWW in the present work.

3.5. Kinetic study

The kinetic study of thermolysis process in the present study has been examined with different catalyst loading (1–4 g/L). During thermal catalysis process, two main mechanisms occur simultaneously. At the initial stage, both smaller and complex organic molecules are broken down thermally and chemically and undergo complexation. At the end, they transform into insoluble particles/molecules, which settle down in the thermal reactor [38]. In addition to this, larger complex molecules are broken down into the smaller soluble molecules.

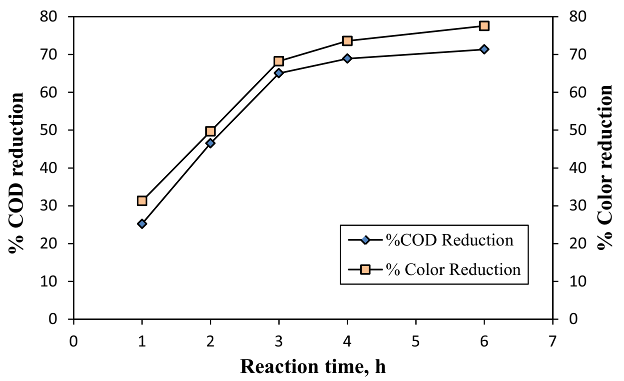

Fig. 5. Effect of reaction time on COD and color reduction (experimental conditions: reaction temperature = 95°C, solution pH = 4, catalyst [$CuSO_4 \cdot 5H_2O$] loading [C_w] = 4 g/L).

Thermal catalytic process can be written as follows:

$$\text{Complex organic molecules} \xrightarrow{\text{Catalyst} + H_2O + \text{heat}} \text{Solid residue} + \text{lower molecular weight organics} + H_2O + \text{gas} \quad (2)$$

The gas formation during the thermolysis is extremely less and can be disregarded. The kinetics of thermolysis can be written by a simple power law rate equation:

$$-\frac{dC_A}{dt} = k_n C_A^n C_w^m \quad (3)$$

where n and m are the order of reaction with respect to COD reduction and the catalyst loading, respectively, and k_n is the reaction rate constant.

For constant and optimum catalyst loading, Eq. (3) can be further written as:

$$-\frac{dC_A}{dt} = kC_A^n \quad (4)$$

where

$$k = k_n C_w^m \quad (5)$$

In the present work, TWW comprises various organic matters characterized by chemical oxygen demand (COD). Thus C_A may be taken as the COD, and then Eq. (5) may be written as:

$$-\frac{d(\text{COD})}{dt} = k(\text{COD})^n \quad (6)$$

For zero order kinetics, Eq. (6) can be written in terms of COD as:

$$[\text{COD}] = kt \quad (7)$$

For first order kinetics, Eq. (6) can be written in terms of COD as:

$$\ln\frac{[\text{COD}]_0}{[\text{COD}]} = kt \quad (8)$$

The zero order kinetics was not fitted well into the experimental data as the R^2 value was found to be 0.8101 with catalyst loading of 4 g/L. However, the experimental data were found to be best fitted to the first order kinetics. Fig. 6 shows the plot of $\ln(\text{COD})_0/\text{COD}$ against time (t) with the experimental data. Fig. 6 depicts that the reduction in COD is fast for the initial period of reaction (0–180 min) and after that reaction becomes slow for the period (180–360 min). Hence, the reduction in COD is a two-step process in thermal catalytic process. Similar results were also reported in literature [31,32,38]. Therefore, two values of rate constants (k_1 and k_2) can be determined, where k_1 and k_2 are the rate constants for the fast step and slow step, respectively. The values of k_1, k_2, R^2 and the ratio of k_1/k_2 at different loadings have been

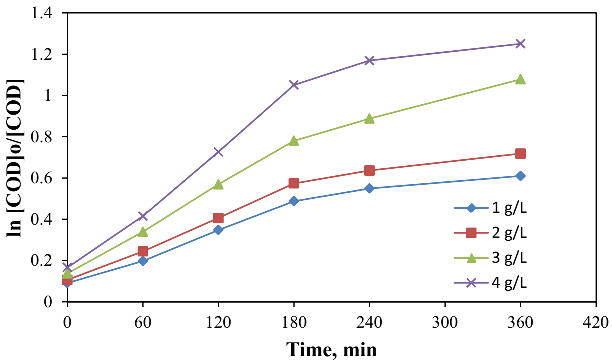

Fig. 6. First order kinetics plot of the tannery wastewater using thermal catalytic process (experimental conditions: reaction temperature = 95°C; time = 360 min; solution pH = 4; COD_0 = 2,140 mg/L; catalyst [$CuSO_4 \cdot 5H_2O$] loading [C_w] = 4 g/L).

summarized in Table 2. It was observed that the rate constant enhances with an increase in the catalyst loading for both steps. The values of k_2 are lower as compared with the values of k_1. The observed lower values of k_2 exhibited that the rate of reaction is slow in the second step during thermolysis. This may be due to the slow deactivation of catalyst by carbonaceous substance available in wastewater and resist to the subsequent reduction/degradation thereby slow reaction rate takes place [32,39]. Su et al. [39] have investigated the treatment of Cibacron blue in aqueous solution using catalytic thermolysis and reported that the first order kinetics model well fitted for thermolysis of dye wastewater.

3.6. Physico-chemical characteristics of solid and liquid

3.6.1. Settling characteristics

Settling process is used to separate the liquid and solid of slurry after the treatment process [27,28,33]. Hence, the obtained slurry after thermolysis process was subjected to sedimentation test. The settling of the wastewater strongly depends upon the solution pH. Therefore, the effect of solution pH on the settling characteristics of the precipitate acquired after thermolysis with copper sulfate was carried out. The sludge concentration at a time t was calculated by following formula:

$$C = \frac{C_0 (\text{total height})}{\text{height of suspension after time } t} \tag{9}$$

Settling characteristics were analyzed at different pH such as 3, 5, 7, 9 and 12 with temperature of 25°C, time of 6 h and catalyst loading of 4 g/L. For this purpose, the treated wastewater sample after the thermolysis was slowly mixed and collected in 100 mL measuring cylinder. The solid interfaces and supernatant are noted down at a regular period of time. The plot of height vs. time for settling sludge of treated wastewater at different pH has been shown in Fig. 7. It is observed that the settling rate was found to be higher in the case of pH 12 as compared with that obtained with others pH such as 3, 5, 7 and 9. The settling of copper sulfate treated wastewater at pH 9 was

Table 2
First order rate constant (k) for the first and second reaction steps of thermal catalytic process

Catalyst loading (g/L)	k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2	k_1/k_2
1	0.0023	0.9667	0.0007	0.9661	3.28
2	0.0027	0.9750	0.0007	0.9433	3.85
3	0.0043	0.9411	0.0009	0.9242	4.78
4	0.0050	0.9499	0.0010	0.9159	5.00

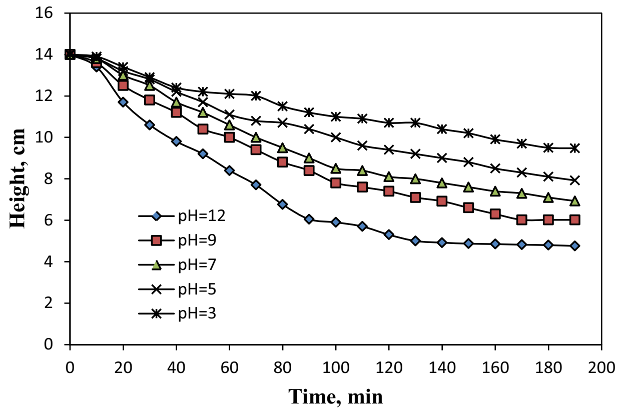

Fig. 7. Settling characteristics of tannery wastewater after thermal catalytic process at different pH (experimental conditions: reaction temperature = 25°C, time = 360 min, COD_0 = 2,140 mg/L, catalyst [$CuSO_4 \cdot 5H_2O$] loading [C_w] = 4 g/L).

found to be lesser with the 43% solid and 57% liquid interface within 190 min and thereafter it remained constant with time. Maximum 66% liquid and 34% solid interface were achieved after 190 min at pH of 12. It may be possible because of the greater size and more compact aggregated flocs [28]. It can be seen from Fig. 7 that settling rates after 190 min are in the order of pH 12 > pH 9 > pH 7 > pH 5 > pH 3. This study shows that it has very good settling characteristics thereby separating liquid and slurry and hence it may be feasible to design a continuous thickener. Richardson et al. [40] proposed a method to design a continuous thickener based on single batch sedimentation test appears to be the best suitable. Analysis of residue is summarized in Table 3.

3.6.2. Filterability

Since the treated wastewater after thermal catalytic process is to be separated from its residue and further the liquid wastewater is to be treated, it was required to test the gravity filtration characteristics of the sludge. To examine the gravity filtration characteristics of the sludge, the filtration experiments were conducted at ambient temperature using Whatman filter paper (No. 42) that was placed on a Büchner funnel. The filtration resistances for the filter media were determined by filtration equation [41]:

$$\frac{dt}{dV} = k_p V + \beta \tag{10}$$

Table 3
Analysis of residue obtained after thermal catalytic process at different pH

pH/parameters	Weight of residue (kg/m^3)	Color	Nature	Approximated drying period (h)
3	2.90	Blackish	Easily grindable	6
5	3.35	Light black	Easily grindable	6
7	3.65	Light black	Easily grindable	7
9	3.78	Light black	Easily grindable	7
12	3.88	Light black	Easily grindable	8

where

$$k_p = \frac{C\alpha\mu}{A^2(-\Delta P)} \quad (11)$$

and

$$\beta = \frac{\mu R_m}{A(-\Delta P)} \quad (12)$$

where t = filtration time (s), V = volume of the filtrate collected with respect to time (m^3), C = concentration of the solids in the sludge (kg/m^3), α = specific cake resistance (m/kg), μ = viscosity of the filtrate (Pa s), P = pressure drop across the filter is equal to ρgh (Pa), A = filtration area (m^2), and R_m = resistance of the filter medium (m^{-1}), k_p = slope of the graph of Eq. (10) (s/m^6), β = intercept of the graph of Eq. (10) (s/m^3).

The plot between dT/dV against volume (V) at different pH is shown in Fig. 8. The values of k_p and β were determined using the slope and intercept, respectively. The α and R_m values were calculated using Eqs. (11) and (12), respectively. The observed values of the filtration parameters are summarized in Table 4. The values of filter medium resistance (R_m) were observed as 1.79×10^9, 4.83×10^9, 8.88×10^9, 9.65×10^9, 13.53×10^9 (1/m) at pH 12, 9, 7, 5 and 3, respectively. Whereas specific cake resistance was 25.64×10^{10}, 29.74×10^{10}, 35.33×10^{10}, 59.99×10^{10} and 65.58×10^{10} (m/kg) at pH 12, 9, 7, 5 and 3, respectively. It has been observed that treated wastewater provided the best filterability at the pH values of 12. The values of specific cake resistance in the filtration studies using thermolysis process for different wastewater such as pulp and paper mill effluent [28], composite wastewater [27], sugar industry wastewater [30,34] and desizing wastewater [37] were reported in literature.

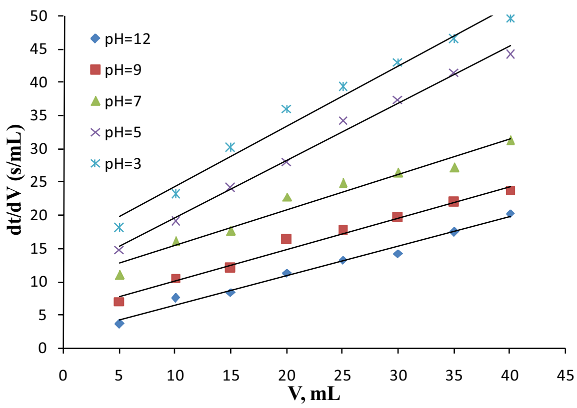

Fig. 8. Filterability characteristics of slurry at different pH.

3.7. Energy consumption analysis

Energy consumption analysis has a significant role in selecting the feasible process for the wastewater treatment. Therefore, the analysis of energy required to treat the effluent is essential so that to evaluate the efficacy of the process towards the treatment of wastewater. In this study, energy consumption analysis has been done under the optimum conditions, that is, temperature = 95°C, pH = 5, catalyst ($CuSO_4{\cdot}5H_2O$) loading (C_w) = 4 g/L) at which maximum 71.36% removal of COD (from 2,140 to 612.9 mg/L) was obtained. The energy consumed to remove 1 kg of COD during the thermolysis was calculated according to the following equation [42]:

$$\text{Energy consumption (kWh/kg of COD removed)} = \frac{P \cdot t}{\text{Treated volume (L)} \times \left(\text{COD}_i - \text{COD}_f\right)} \quad (13)$$

where P is the rated power (kW), t is the thermolysis time (h), COD_i and COD_f is the initial and final concentrations of COD (mg/L) and 0.3 is the treated volume of TWW (L). The energy consumption for 1 kg of COD removal was found to be 2,619 kWh/kg.

4. Conclusions

The treatment of TWW in terms of COD and color reduction was investigated using CTT. It was found that the removal efficiency of treatment was dependent upon the process parameters. Copper sulfate ($CuSO_4{\cdot}5H_2O$) was found to be the best catalyst during thermolysis. The observed results of maximum 71.36% COD and 77.56% color reductions were found at pH of 4, temperature of 95°C, catalyst mass loading ($CuSO_4{\cdot}5H_2O$) of 4 g/L and thermolysis time of 6 h. The first order kinetics model signifies better the experimental data obtained as compared with the zero-order kinetics model. The kinetics of thermolysis is of TWW indicated two steps mechanism, that is, the

Table 4
Filterability of slurry of tannery wastewater after catalytic thermal treatment

Initial pH	$k_p \times 10^{-12}$ (s/m^6)	$\beta \times 10^{-6}$ (s/m^3)	C (kg/m^3)	$\alpha \times 10^{-10}$ (m/kg)	$R_m \times 10^{-9}$ (1/m)
12	0.442	2.0209	9.72	25.64	1.79
9	0.472	5.4439	8.95	29.74	4.83
7	0.537	10.018	8.57	35.33	8.88
5	0.866	10.884	8.14	59.99	9.65
3	0.906	15.261	7.79	65.58	13.53

first step and second step (first step was faster as compared with second step). Both steps obey the first order kinetics model in terms of COD. The settling rate and filterability studies of the slurry were found to be strongly affected by initial pH values. Maximum 66% liquid and 34% solid interface were achieved after 190 min at pH of 12. The obtained power consumption for thermolysis process was found to be 2,619 kWh/kg of COD. From the experimental results, it can be said that thermolysis process may be used as pretreatment steps to the biological methods for the treatment of industrial wastewater.

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References

[1] H. Dargo, A. Ayalew, Tannery waste water treatment: a review, Int. J. Emerging Trends Sci. Technol., 1 (2014) 1488–1494.
[2] S. Dixit, A. Yadav, P.D. Dwivedi, M. Das, Toxic hazards of leather industry and technologies to combat threat: a review, J. Cleaner Prod., 87 (2015) 39–49.
[3] T. Verma, P.W. Ramteke, S.K. Garg, Quality assessment of treated tannery wastewater with special emphasis on pathogenic *E. coli* detection through serotyping, Environ. Monit. Assess., 145 (2008) 243–249.
[4] S. Saxena, S. Rajoriya, V.K. Saharan, S. George, An advanced pretreatment strategy involving hydrodynamic and acoustic cavitation along with alum coagulation for the mineralization and biodegradability enhancement of tannery waste effluent, Ultrason. Sonochem., 44 (2018) 299–309.
[5] G. Saxena, R. Chandra, R.N. Bharagava, Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants, Rev. Environ. Contam. Toxicol., 240 (2016) 31–69.
[6] A. Mannucci, G. Munz, G. Mori, C. Lubello, Anaerobic treatment of vegetable tannery wastewaters: a review, Desalination, 264 (2010) 1–8.
[7] P.C. Caliari, M.J. Pacheco, L. Ciríaco, A. Lopes, Tannery wastewater: organic load and sulfide removal dynamics by electrochemical oxidation at different anode materials, Environ. Technol. Innovation, 14 (2019) 100345.
[8] Indian Standards Institution (ISI), Guide for Treatment and Disposal of Effluents of Tanning Industry, New Delhi, India, 2000.
[9] Z. Song, C.J. Williamsm, R.G.J. Edyvean, Sedimentation of tannery wastewater, Water Res., 34 (2000) 2171–2176.
[10] K.M. Nazmul Islam, K. Misbahuzzaman, A.K. Majumder, M. Chakrabarty, Efficiency of different coagulants combination for the treatment of tannery effluents: a case study of Bangladesh, Afr. J. Environ. Sci. Technol., 5 (2011) 409–419.
[11] M. Chowdhury, M.G. Mostafa, T.K. Biswas, A. K. Saha, Treatment of leather industrial effluents by filtration and coagulation processes, Water Res. Ind., 3 (2013) 11–22.
[12] I. Ahmed, M. Habib, U. Habib, A. Hai, A.U. Khan, Analysis and Treatment of Tannery Waste Water by using Combined Filtration and Coagulation Treatment Process, Proceedings of the Pakistan Academy of Sciences: B. Life and Environmental Science, Vol. 53, 2016, pp. 179–183.
[13] M.A. El-Khateeb, E.H.A. Nashy, Abdel-Aziz A. Nayl, Combining chemical coagulation process and innovative aerobic reactor for the treatment of De-Hairing wastewater, Waste Biomass Valorization, (2020) https://doi.org/10.1007/s12649-020-01204-0.
[14] M.A. El-Khateeb, El-Shahat H.A. Nashy, N.A. Abdel Ghany, Ahmed M. Awad, Environmental impact elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation, Desal. Water Treat., 65 (2017) 147–152.
[15] M.A. El-Sheikh, H.I. Saleh, J.R. Flora, M.R. AbdEl-Ghany, Biological tannery wastewater treatment using two stage UASB reactors, Desalination, 276 (2011) 253–259.
[16] R. Baccar, P. Blánquez, J. Bouzid, M. Feki, H. Attiya, M. Sarrà, Decolorization of a tannery dye: from fungal screening to bioreactor application, Biochem. Eng. J., 56 (2011) 184–189.
[17] M. Nigam, S. Rajoriya, S.R. Singh, P. Kumar, Adsorption of Cr (VI) ion from tannery wastewater on tea waste: kinetics, equilibrium and thermodynamics studies, J. Environ. Chem. Eng., 7 (2019) 103188.
[18] T. Khan, M.H. Isa, M.R.U. Mustafa, H. Yeek-Chia, L. Baloo, T.S.B. Abd Manana, Cr(VI) adsorption from aqueous solution by an agricultural waste based carbon, RSC Adv., 6 (2016) 56365–56374.
[19] K.K. Garg, P. Rawat, B. Prasad, Removal of Cr (VI) and COD from electroplating wastewater by corncob based activated carbon, Int. J. Water Wastewater Treat., 1 (2015) 2381–5299.
[20] C.R. Costa, C.M.R. Botta, E.L.G. Espindola, P. Olivi, Electrochemical treatment of tannery wastewater using DSA® electrodes, J. Hazard. Mater., 153 (2008) 616–627.
[21] T.S. Natarajan, K. Natarajan, H.C. Bajaj, R.J. Tayade, Study on identification of leather industry wastewater constituents and its photocatalytic treatment, Int. J. Environ. Sci. Technol., 10 (2013) 855–864.
[22] G. Lofranoa, S. Meriça, M. Inglese, A. Nikolaouc, V. Belgiorno, Fenton oxidation treatment of tannery wastewater and tanning agents: synthetic tannin and nonylphenol ethoxylate based degreasing agent, Desal. Water Treat., 23 (2010) 173–180.
[23] V. Preethi, K.S.P. Kalyani, K. Iyappan, C. Srinivasakannan, N. Balasubramaniam, N. Vedaraman, Ozonation of tannery effluent for removal of cod and color, J. Hazard. Mater., 166 (2009) 150–154.
[24] H.I. Abdel-Shafy, M.A. El-Khateeb, M.S.M. Mansour, Treatment of leather industrial wastewater via combined advanced oxidation and membrane filtration, Water Sci. Technol., 74 (2016) 586–594.
[25] P. Kumar, R. Agnihotri, M.K. Mondal, Catalytic treatment of synthetic dye wastewater: COD and color reduction, J. Environ. Chem. Eng., 1 (2013) 440–447.
[26] P. Kumar, B. Prasad, I.M. Mishra, S. Chand, Decolorization and COD reduction of dyeing wastewater from a cotton textile

mill using thermolysis and coagulation, J. Hazard. Mater., 153 (2008) 635–645.
[27] P. Kumar, B. Prasad, I.M. Mishra, S. Chand, Treatment of composite wastewater of a cotton textile mill by thermolysis and coagulation, J. Hazard. Mater., 151 (2008) 770–779.
[28] A. Garg, I.M. Mishra, S. Chand, Thermochemical precipitation as a pretreatment step for the chemical oxygen demand and color removal from pulp and papermill effluent, Ind. Eng. Chem. Res., 44 (2005) 2016–2026.
[29] S. Verma, B. Prasad, I.M. Mishra, Thermochemical treatment (thermolysis) of petrochemical wastewater: COD removal mechanism and floc formation, Ind. Eng. Chem. Res., 50 (2011) 5352–5359.
[30] O.P. Sahu, P.K. Chaudhari, Removal of color and chemical oxygen demand from sugar industry wastewater using thermolysis processes, Desal. Water Treat., 56 (2015) 1758–1767.
[31] P.K. Chaudhari, I.M. Mishra, S. Chand, Effluent treatment for alcohol distillery: catalytic thermal pretreatment (catalytic thermolysis) with energy recovery, Chem. Eng. J., 136 (2008) 14–24.
[32] P.K. Chaudhari, R. Singh, I.M. Mishra, S. Chand, Kinetics of catalytic treatment pretreatment(catalytic thermolysis) of distillery wastewater and biodigester effluent of alcohol production plant at atmospheric pressure, Int. J. Chem. React. Eng., 8 (2010) 1–22.
[33] A.K. Prajapati, P.K. Chaudhari, B. Mazumdar, R. Choudhary, Catalytic thermal treatment (catalytic thermolysis) of a rice grain-based biodigester effluent of an alcohol distillery, plant, Environ. Technol., 20 (2015) 2548–2555.
[34] O. Sahu, Catalytic thermal pre-treatments of sugar industry wastewater with metal oxides: thermal treatment, Exp. Thermal Fluid Sci., 85 (2017) 379–387.
[35] D. Sharma, A.K. Prajapati, R. Chaudhari, R.K. Kaushal, D. Pal, A.N. Sawarkar, Preparation and characterization of CuO catalyst for the thermolysis treatment of distillery wastewater, Environ. Technol., 39 (2018) 2604–2612.
[36] APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water Pollution Control Federation), Standard Methods for the Examination of Water and Wastewater, 20th ed., Washington, DC, 1998.
[37] P. Kumar, B. Prasad, I.M. Mishra, S. Chand, Catalytic thermal treatment of desizing wastewaters, J. Hazard. Mater., 149 (2007) 26–34.
[38] M. Nigam, S. Rajoriya, S.R. Singh, P. Kumar, Thermal catalytic treatment (thermolysis): an effective process for the removal of COD and color from industrial wastewater, J. Environ. Treat. Technol., 8 (2020) 818–826.
[39] C.X.H. Su, T.T. Teng, Y.S. Wong, N. Morad, M. Rafatullah, Catalytic thermolysis in treating Cibacron Blue in aqueous solution: kinetics and degradation pathway, Chemosphere, 146 (2016) 503–510.
[40] J.F. Richardson, J.H. Harker, J.R. Backhurst, Coulson and Richardson's Chemical Engineering, Particle Technology & Separation Processes, Vol. 2, 5th ed., Elsevier, a division of Reed Elsevier India Pvt. Ltd., 2003.
[41] W.L. MaCabe, J.C. Smith, P. Harriot, Unit Operations of Chemical Engineering, 6th ed., McGraw-Hill, New York, 2001.
[42] P. Vijayalakshmi, G. BhaskarRaju, A. Gnanamani, Advanced oxidation and electrooxidation as tertiary treatment techniques to improve the purity of tannery wastewater, Ind. Eng. Chem. Res., 50 (2011) 10194–10200.