

Catalytic thermal treatment of desizing wastewaters

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Abstract

In the present study, catalytic thermal treatment (thermolysis) was investigated for the reduction of COD and color of the desizing wastewater under moderate temperature and atmospheric pressure conditions using various catalysts. The experimental runs were performed in a glass reactor equipped with a vertical condenser. The homogeneous copper sulfate catalyst was found to be the most active in comparison to other catalysts under similar operating conditions. A removal of about 71.6% chemical oxygen demand (COD) and 87.2% color of desizing wastewater was obtained with a catalyst concentration of 4 kg/m³ at pH 4. The initial pH value of the wastewater showed a pronounced effect on the precipitation process. During the thermolysis, copper gets leached to the aqueous phase, the residue obtained after the treatment is rich in copper and it can be blended with organic manure for use in agricultural fields. The thermogravimetric analysis showed that the thermal oxidation of the solid residue obtained after thermolysis gets oxidized at a higher temperature range than that of the residue obtained from the desizing wastewater. The results lead to the conclusion that thermochemical precipitation is a very fast (instantaneous) process and would need a very small reactor vessel in comparison to other processes.

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Keywords: Desizing wastewater; COD; Color

1. Introduction

Textile plants, particularly those involved in finishing processes, are major water consumers and the source of considerable pollution [1]. The textile mills can be classified into two major groups in India, viz., dry processing mills and woven fabric finishing mills. In the dry processing mills, mainly solid waste is generated due to rejects of cotton, whereas in the woven fabric finishing mills, desizing, scouring, bleaching, mercerising, dyeing and printing are the main processing stages. These stages consume approximately 2400–2700 m³ of raw water per tonne of finished product. In general, the wastewater from a typical cotton textile industry is characterized by high values of biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH and color [2–4].

In the sizing operation, the fibers are coated with a layer of sizing agents generally consisting of a mixture of polyvinyl alcohol (PVA), corn starch, carboxymethyl cellulose (CMC) and various surfactants. The sizing agents serve to smoothen and

strengthen the fibers, preventing them from being broken and getting entangled during the high-speed weaving process. After a weaving operation, the sizing agents are removed by washing with hot water. This washing step is called the desizing step in the industry. The hot wastewater generated in the desizing step is usually mixed with the wastewater streams emanating from other sources and sent to the wastewater treatment plant [5].

The desizing wastewater from natural fiber processing operations has COD of 10 000–20 000 mg/l and BOD of 5000–10 000 mg/l. Man made fiber desizing wastewater typically has high COD (10 000–40 000 mg/l), but a relatively small BOD (500–1000 mg/l). The high COD/BOD ratio makes wastewater refractory to biodegradation [6].

The Ministry of Environment and Forests (MOEF), Govt of India has prescribed wastewater discharge quality standards for surface waters: BOD 30 mg/l, pH 5.5–9, suspended solids (SS) 100 mg/l [7]. Therefore, the desizing wastewaters require adequate and sufficient treatment before being allowed to be discharged into surface waters.

Various treatment methods, viz., biological activated sludge process, activated carbon adsorption, chemical oxidation by ozone, or a combination of UV radiation and ozone and H₂O₂,

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Nomenclature

A	filtration area (m ²)
AGR	atmospheric pressure glass reactor
BOD	biochemical oxygen demand (kg/m ³)
C	concentration of slurry (kg/m ³)
COD	chemical oxygen demand (kg/m ³)
COD ₀	initial concentration of organic matter in the effluent expressed as COD (kg/m ³)
CCC	critical chemical concentration (kg/m ³)
C _w	catalyst mass loading (kg/m ³)
PCU	platinum cobalt unit
pH ₀	initial pH
pH _f	final pH
RM	rapid mixing
R _m	filter medium resistance (m ⁻¹)
SM	slow mixing
t	time (s)
t _r	treatment time (h)
T	temperature (°C)
v _f	volumetric flow rate (m ³ /s)

Greek symbols

α	average cake resistance (m/kg)
μ	viscosity of the filtrate (Pa s)
θ	preheating time

wet oxidation, etc. are being used. However, the treatment costs are very high. The application of membrane technologies in textile industries is not yet common. Focus of the attention is being paid on the recovery of sizing agents from the desizing effluents and on the recovery of indigo from the dyeing effluents by ultrafiltration, wet air oxidation [6,8,9], Fenton's process (using a mixture of hydrogen peroxide and ferrous sulfate) [5] and using nanofiltration membrane [10]. Recently our research group has suggested the possibility of using a thermal pretreatment step called thermolysis (uncatalytic and catalytic) to precipitate refractory organics and removal of color from high strength pulp and paper mill wastewaters [11], distillery spent wash [12], and biodigester effluent from the anaerobically treated distillery spent wash [13]. The pretreatment step can be followed by coagulation–flocculation–filtration, catalytic wet air oxidation or aerobic biological oxidation [14–18]. The chemical oxidation process is relatively simple to operate but is only cost-effective for effluents of low COD. It would become expensive to high COD wastewater such as that discharged from the desizing process [8]. The treatment conditions in the thermal pretreatment process employed in the present work use much lower temperature and pressure in comparison to wet air oxidation. Treatment of desizing wastewater through coagulation requires large amount of coagulant (which is not cost-effective) as well as produces huge amount of sludge. The thermal pretreatment step was found to have very high COD and color removal efficiencies (~63.3 and ~92.5%, respectively). In view of low cost of treatment, the thermal pretreatment step seems to be very

Table 1
Characteristics of desizing wastewater

S. no.	Parameters	Value (mg/l)
1	Total suspended solids	56.7
2	Total iron (as Fe)	2.37
3	Chlorides (as Cl)	950
4	BOD, 3 days at 20 °C	3275
5	Oil and grease	145.9
6	Sulfate (as SO ₄)	520.94
7	Copper (as Cu)	0.038
8	Manganese (as Mn)	0.64
9	Zinc (as Zn)	0.364
10	COD	2884
11	Color	520 (PCU)

attractive. The present work deals with the thermal pretreatment followed by coagulation of desizing wastewaters.

2. Experimental section

2.1. Materials and methods

Textile desizing wastewater samples were taken from a textile mill located at Ghaziabad, U.P., India. This mill uses reactive dyes to color cotton fabric. The samples were stored in a refrigerator at 4 °C without adding any chemical. The characteristics of such a wastewater is given in Table 1.

All the chemicals used in the preparation of various coagulants/catalysts were of analytical reagent grade. CuSO₄·5H₂O and CuO were purchased from S.D. Fine Chemicals Ltd., Mumbai, India; FeSO₄·7H₂O from Qualigens Fine Chemicals, Mumbai, and Cu(NO₃)·3H₂O, Al₂(SO₄)₃·16H₂O from Himedia Laboratories (P) Ltd. and ZnO from E-Merck Pvt. Ltd., Mumbai. All these chemicals were used as procured. Zero-haze grade A (pore size 7–11 μm) filter papers were procured from S.D. Fine Chem. Ltd., Mumbai for filtration studies.

The thermolysis experiments were performed in a 0.5 dm³ atmospheric pressure glass reactor (AGR), equipped with a vertical condenser, heating mantle with magnetic stirrer, digital temperature indicator with controller and a sample withdrawal assembly.

2.2. Thermolysis

The initial pH (pH₀ 2–12), temperature (atmospheric to 95 °C) and catalyst mass loading (C_w = 2–8 kg/m³) were varied to study their effect on the COD and color removal efficiencies. The desizing wastewater was preheated in the AGR from the ambient temperature (T₀) to the treatment temperature (T_R). The preheating period (θ) varied with the T_R. Therefore, the time of start of treatment was considered as the “zero time” when the T_R was attained after the preheating of the wastewater from T₀. All the experimental runs in the AGR were carried out for a duration of 4 h. The pH₀ of the wastewater was varied between 2 and 12 by using either 0.1N HCl or 0.1N NaOH. The pH₀ was optimized through the AGR experiments to have maximum COD and color removal. The solid residue was dried in an oven at 105 °C until

its weight became constant. The filtration studies of the treated effluent were carried out on ordinary filter paper supported on a Büchner funnel. The oven dried residue was analyzed for its C, H, N, S and ash content [11].

2.3. Jar test

A series of jar test experiments were conducted on treated desizing wastewater using 5 min rapid mixing (RM) at 80 rpm, 30 min slow mixing (SM) at 40 rpm and 30 min settling in order to study the settling characteristics as well as reduction of COD and color in the final effluent (supernatant) [19].

2.3.1. Analytical

The COD of the sample was determined by the standard dichromate reflux method using a photometer and a digester (Aqualytic, Germany). The BOD of the samples was determined by incubating the seeded sample for 3 days at 27 °C following the method prescribed by the MOEF. The elemental (C, H, N and S) analysis was done using an elemental analyzer model Vario EL III (Elementar, Germany). The ash content was evaluated by combustion in a muffle furnace at 925 °C for 7 min. The amount of metal ions leached out in the solution and those fixed in the solid residue were determined by using an atomic absorption spectrometer (model Avanta; GBC, Australia). Thermal analysis (TGA/DTGA/DTA) of the wastewater and residue left after the treatment was carried out using a TG analyzer (Pyris Diamond, Perkin Elmer). Color of desizing waste water is determined by color meter (Hanna Instruments, Singapore).

3. Results and discussion

3.1. Effect of pH_0 and temperature

The effect of pH_0 on thermolysis of the desizing wastewater with and without catalyst/coagulant was studied in the AGR at atmospheric pressure and 95 °C. The results are shown in Fig. 1 as percent COD reduction in the final filtrate as a function of pH_0 , while keeping other parameters fixed. All the experiments were carried out for a treatment time $t_r = 4$ h, measured from zero time with the initial COD (COD_0) at 2884 mg/l and the catalyst/coagulant mass loading (C_w) at 4 kg/m³. The highest COD reduction of 71.6% with CuSO₄ was obtained at pH_0 4. This initial pH_0 was found to give highest COD reduction with ZnO and FeSO₄ as well. However, CuO showed maximum effectiveness at pH_0 12 and alum in the pH_0 range 6–8. It is also found that excepting CuSO₄, all other catalysts have only marginal effect on the COD reduction over that without any catalyst. The highest COD removal was not more than ~20% (using FeSO₄, which is much less than that for CuSO₄). In view of these results, further experiments on the effect of other parameters were performed with CuSO₄ at pH_0 4.

The thermo-chemical precipitation (or thermolysis) undergoes complex reactions over the reaction time, thereby affecting the pH of the reactor mass. The compounds probably undergo hydrolysis to a limited extent with the formation of small amounts of lower carboxylic acids. This leads to the change

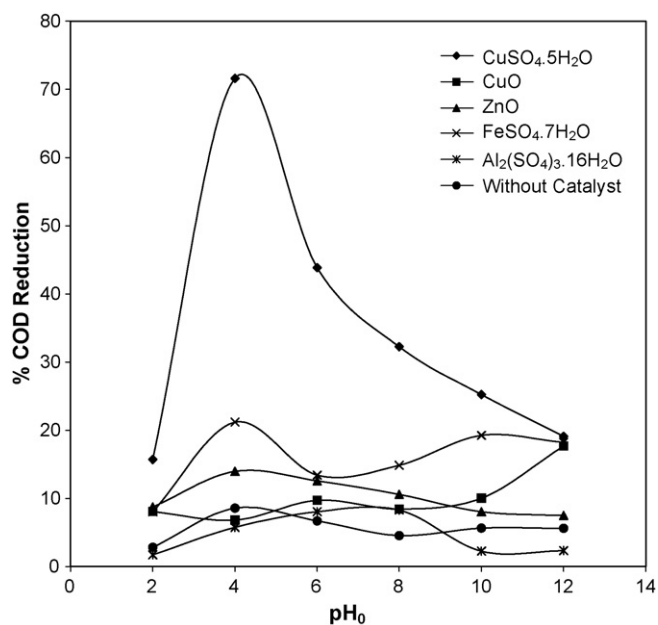


Fig. 1. Effect of pH_0 on COD reduction of the desizing wastewater by thermolysis. $COD_0 = 2884$ mg/l, $T_R = 95$ °C, $P =$ atmospheric pressure, $t_r = 4$ h, $C_w = 4$ kg/m³.

in the pH. Complexation of the organics with CuSO₄ making them insoluble and thereby precipitating the organics seems to play a major role in COD reduction.

It was also found that the preheating period up to 95 °C is sufficient for effecting the COD removal of 71.6% and no further increase in COD removal is observed even when the reactor is maintained at this temperature for further 4 h. The COD reduction during preheating to 60, 70, 80 and 95 °C was 27.8, 38.5, 49.7 and 71.63%, respectively (Fig. 2). This leads to the conclusion that the thermochemical precipitation is a very

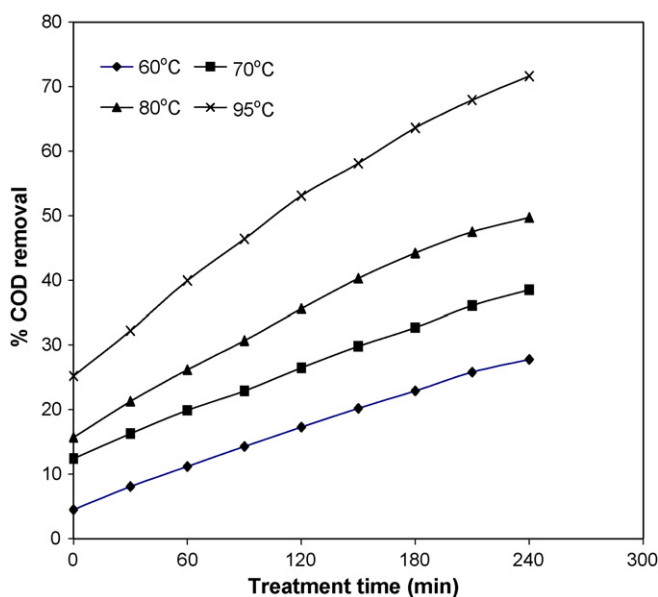


Fig. 2. Effect of temperature on COD reduction of the desizing wastewater of catalytic thermolysis. $COD_0 = 2884$ mg/l, $t_r = 4$ h, $P =$ atmospheric pressure, $pH_0 = 4$, $C_w = 4$ kg/m³.

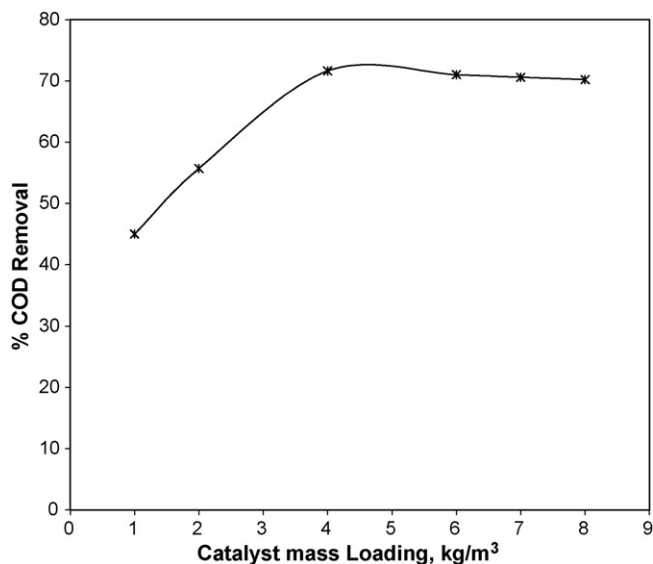


Fig. 3. Effect of catalyst (copper sulfate) concentration on COD reduction of the desizing wastewater. $COD_0 = 2884 \text{ mg/l}$, $t_r = 4 \text{ h}$, $P = \text{atmospheric pressure}$, $pH_0 = 4$, $T_R = 95^\circ \text{C}$.

fast (instantaneous) process and would need a very small reactor vessel in comparison to those for other catalysts/adsorbents.

3.2. Effect of copper sulfate mass loading

The effect of copper sulfate mass loading on the COD reduction of the wastewater was observed at a temperature of 95°C . The copper sulfate mass loading was varied from 1 to 8 kg/m^3 , while the initial pH of the desizing wastewater was kept 4 for all the experimental runs. With 1 kg/m^3 copper sulfate mass loading, only 44.96% reduction was observed. The solid precipitate was also observed in a very small quantity. The color also got converted into sea green after the completion of the reaction. However, at a mass loading of 2 kg/m^3 , a COD reduction of 55.7% was obtained with a small amount of precipitated solid residue. With an increase in the mass loading to 4 kg/m^3 , a maximum of 71.63% COD reduction was obtained, as shown in Fig. 3. This catalyst mass loading is termed as the critical chemical concentration (CCC) at which the precipitation just starts. Beyond 4 kg/m^3 chemical mass loading, no increase in the COD reduction was observed. The final pH of the treated wastewater increases from its initial value. In some catalysts, the final pH of the treated wastewater decreased from its initial value. This trend may be attributed to the enhanced formation of SO_4^{2-} ions and/or the formation of carboxylic acids [11]. As the initial COD of the wastewater increases, comparatively larger chemical mass loading is required for optimum COD reduction. It is also found that the efficiency of COD reduction due to thermochemical precipitation increases as the initial COD of the effluent increases with optimum chemical mass loading.

3.3. Effect of pH on the color removal

The effect of initial pH on the color removal for a treated desizing wastewater having an initial COD value of 2884 mg/l

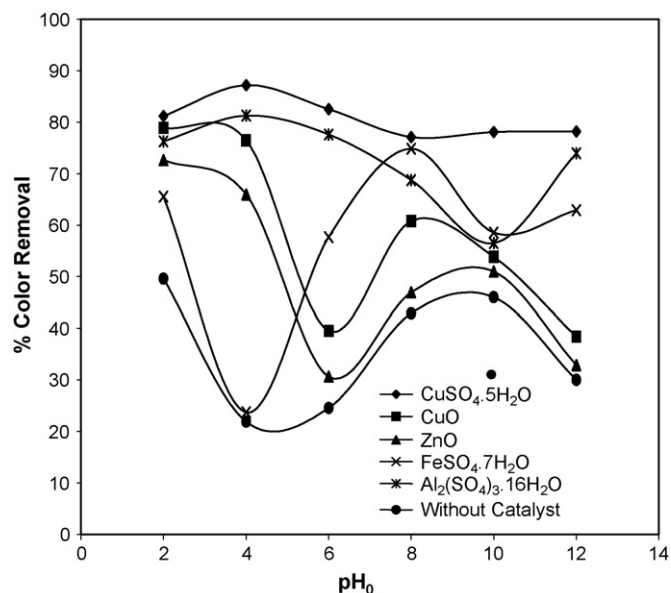


Fig. 4. Effect of pH_0 on color removal of the desizing wastewater by using thermolysis. Color = 520 PCU, $t_r = 4 \text{ h}$, $P = \text{atmospheric pressure}$, $pH_0 = 4$, $T_R = 95^\circ \text{C}$.

is shown in Fig. 4. A maximum color removal of 87.2% was obtained at pH 4 and a minimum color removal of 78.18% was found at pH 12 using copper sulfate as catalyst. It may be due to the increased concentration of copper ion present in the supernatant, thus affecting lower adsorption of color on the precipitate. Several researchers have reported a color removal of the order of 70–100% using different coagulants [20–22] and at varying operating conditions. Kang et al. reported 90% color removal at an optimum pH of 4 using Fenton process [23].

3.4. Analysis of precipitated sludge and the supernatant left after the precipitation

Using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the chemical agent for the precipitation of dissolved solids, certain amount of Cu^{2+} ions also

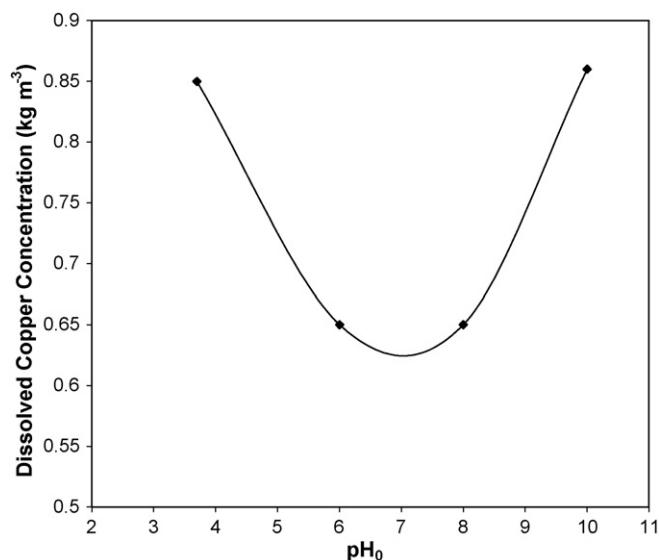


Fig. 5. Copper concentration in filtrate as a function of initial pH (initial CuSO_4 concentration = 4 kg/m^3).

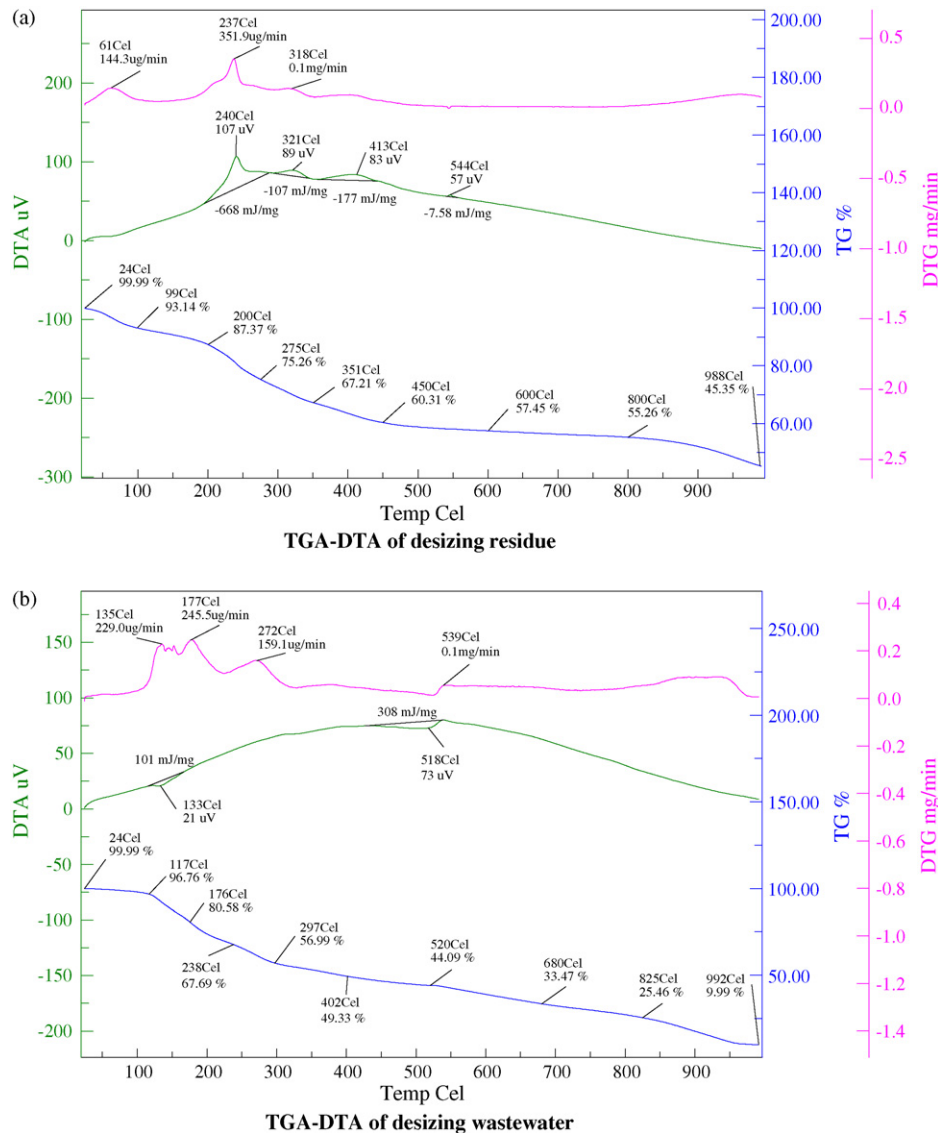


Fig. 6. (a) TGA–DTA of desizing residue. (b) TGA–DTA of desizing wastewater.

remain in the solution or filtrate (supernatant). The amount of Cu^{2+} ions in the solutions varies with the pH of the solution, as shown in Fig. 5. The initial Cu^{2+} concentration added to the desizing wastewater was 1.107 kg/m^3 (corresponding to 4 kg/m^3 of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The pH of the thermally pretreated solution was 3.7. In a study, a small amount (50 ml) of the solution was taken and the pH were adjusted to values 6.0, 8.0 and 10.0. The solutions were allowed to remain for 2 h and then filtered, and the Cu^{2+} ion concentration in the filtrate was measured. The copper concentration was found to be almost the same at pH 6.0 and 8.0 (at around 0.65 kg/m^3) but at pH 3.7 and 10.0 the majority of the copper remain in the solution (0.85 and 0.86 kg/m^3 , respectively). The presence of Cu^{2+} ions in the solution imparts toxicity to it. However, for the situation where the supernatant is to be taken for catalytic wet oxidation/coagulation (secondary treatment), Cu^{2+} ion concentration in the supernatant may serve as the catalyst/coagulant [11,24].

It is suggested that in alkaline environment, copper sulfate gets hydrolyzed and forms copper hydroxides, which are insol-

uble in water. The hydroxide is somewhat amphoteric, dissolving in excess sodium hydroxide solution to form trihydroxycuprate $[\text{Cu}(\text{OH})_3]$ and tetrahydroxycuprate $[\text{Cu}(\text{OH})_4]$. Thus, in a basic environment, the majority of copper is present in precipitated hydroxide form and very little copper is present in a soluble form.

3.5. TGA–DTA of the sludge obtained after thermolysis

Fig. 6(a) shows the thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) curves for the precipitated sludge at $10^\circ \text{C min}^{-1}$ heating rate with 200 ml/min air flushing rate. The nature of the TGA trace shows dehydration and volatilization (removal or volatiles) of the sample and other components up to a temperature of 193°C , losing about 88.11% of its weight. In this regime, the precipitate is unstable. Between 193 and 464°C , the precipitate oxidizes, losing about 28% of its original weight. The peak rate of weight loss of $351.9 \mu\text{g/min}$ is at a tempera-

ture $T_{\max} = 237^{\circ}\text{C}$. The oxidation is found to be uniform and exothermic with a heat evolution of 1.77 MJ/kg, the peak of the exotherm being at a temperature of $T_p = 241^{\circ}\text{C}$. The oxidation seems to be completed at 464°C , and the traces of TG, DTG and DTA reflect this fact. It is found that the organics of the precipitate get oxidized catalytically, leaving the ash fraction ($\sim 45.2\%$) as the residue.

Fig. 6(b) shows the TG, DTG and DTA behaviours of the desizing wastewater under similar linear heating and air flushing rate condition. In contrast to the TGA trace of the precipitate, the desizing TG trace shows only about 3% decrease in weight up to 117°C , beyond which a gradual decrease in residual sample weight up to a temperature of 297°C , shedding about 56% of the sample weight. Thereafter, the weight loss rate is extremely slow, and up to 680°C , the weight loss is only 23.52%. This shows that the desizing wastewater sample loses moisture at an almost steady rate up to 117°C along with volatilization of light volatiles up to 297°C , and thereafter the sample becomes dry and stable. At 520°C , the oxidation of the dry sample started, and the sample lost weight ($\sim 10.62\%$ weight loss) over a temperature range of $520\text{--}680^{\circ}\text{C}$ (a temperature span of 160°C). The maximum weight loss rate was $245\ \mu\text{g}/\text{min}$ at T_{\max} of 177°C followed by $159\ \mu\text{g}/\text{min}$ and $0.1\ \text{mg}/\text{min}$ at 272 and 539°C , respectively (see DTGA trace). The peak temperature for the exothermic reaction as exemplified by the DTA curve was at $T_p = 518^{\circ}\text{C}$ with heat releases of 3.08 MJ/kg. Beyond 680°C , the weight loss is steady but very slow, giving off $\sim 8\%$ weight from 680 to 825°C and 15.47% weight loss observed between 825 and 992°C (over a temperature increase of 167°C).

A comparison of Fig. 6a and b brings out clearly the fact that the residue obtained after thermolysis gets oxidized at a higher temperature range than that of the desizing wastewater. This may be due to the presence of more stable compounds formed during thermolysis in presence of copper catalyst.

3.6. Settling characteristics of the precipitate in the treated effluent

The settling characteristics of the precipitate of the effluent after treatment with CuSO_4 at three different pH at ambient temperature 20°C was observed in a 100 ml measuring cylinder. This was done to see the effects of the pH on the settling characteristic of the precipitate. The settling rate was observed to be higher for pH 8 than that of pH 12, probably due to the bigger size and more compact aggregated flocs. Fig. 7 shows the behaviour of treated effluent during sedimentation.

Although the average driving forces in batch and continuous sedimentation operations are different and the batch driving

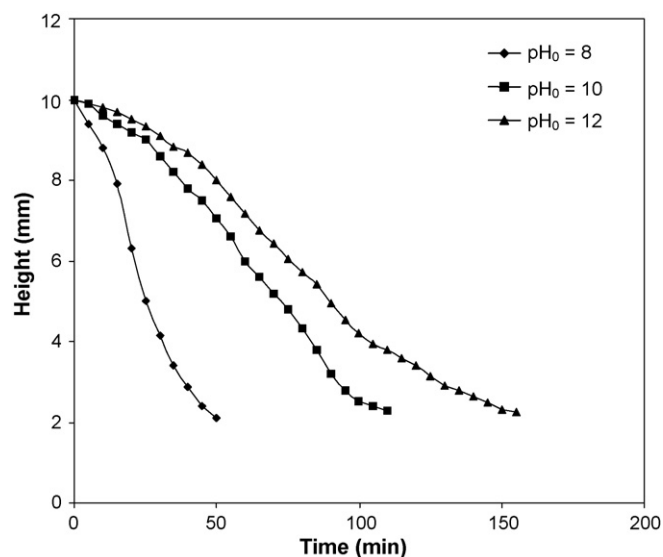


Fig. 7. Settling characteristics of sludge in the treated effluent at pH 8, 10 and 12 using CuSO_4 conditions. COD = 2884 mg/l.

force varies with time, approximate methods are available for the calculations of the compression zone depth in continuous thickeners [25–27]. Although a number of papers have appeared in the literature on the subject of calculating compression zone height in continuous thickeners from the batch sedimentation data [28–32], it is still preferable to use the method proposed by Richardson et al. [28] to design a continuous thickener based on single batch sedimentation test. The method of Richardson et al. [25] gives a conservative estimate with an inherently high safety limit due to the changing nature of the flocs and their settling and compression characteristics.

The parameters such as sedimentation velocity (u_c), concentration $C(t)$, and the sedimentation flux were calculated. The sedimentation velocity was found as the slope of the tangent at a given solid concentration C . The concentration of sludge at a time t was determined by using the following formula $C = C_0$ (total height)/(height of suspension after time t). The area of the sedimentation tank for any effluent flow rate can thus be calculated as

$$A = v_f C_0 \frac{1/C - 1/C_u}{u_c}$$

where v_f is the volumetric flow rate of the effluent (m^3/s), C_0 the initial solid concentration (kg/m^3) and C_u is the concentration of solids required in the underflow.

Table 2

Elemental analysis of desizing wastewater and precipitate formed as a result of thermal pretreatment with CuSO_4

Material	C (%)	H (%)	N (%)	S (%)	Heating value of solids (MJ/kg)
Desizing wastewater	17.10	3.14	0.85	0.80	4.3
Precipitate	22.21	3.59	0.98	1.76	8.5
Supernatant	3.46	1.21	0.00	0.86	–
Indian coal	50.00	5.01	0.80	1.70	20.90

Table 3
Proximate analysis (moisture-free basis) of desizing wastewater and precipitate formed as a result of thermal pretreatment with CuSO_4

Material	Ash (%)	Volatile matter (%)	Fixed carbon (%)
Desizing wastewater	25.3	47.0	7.5
Precipitate	26.4	38.2	29.44

3.7. Characterization of the sludge and desizing wastewater

Tables 2 and 3 show the results of the C, H, N, S and proximate analysis of the settled precipitate and the desizing waste respectively. The heating values of the precipitate and the desizing wastewater are also given. The elemental analysis shows that there are enhancements in carbon, nitrogen, hydrogen and sulfur composition in the precipitate, with substantially high heating value of the dried precipitate (8.5 MJ/kg). The increase in the content of C, H, N and S in the dried precipitate may be attributed to the reduced mass of the waste as well as the contribution of the catalyst. The proximate analysis, as shown in the Table 3 indicates a considerable amount of ash content in the precipitate.

3.8. Filterability study

Because of the treated effluent is to be separated from its residue and the liquid effluent is to be treated further, it was necessary to test the gravity filtration characteristics of the slurry at ambient temperature on an ordinary filter paper supported on a Büchner funnel. The ceramic Büchner funnel diameter was 0.15 m. The change in the hydrostatic head was assumed negligible, and the gravity filtration was considered as constant pressure filtration. The filtrate volume with time were observed, and a plot between $\Delta t/\Delta V$ and V was drawn for the effluents treated at different pH. The filtration resistances for the filter media as well as the filter cake were obtained using the filtration equation [27]:

$$\frac{dt}{dV} = k_p V + \beta \quad (1)$$

where

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

Table 4
Filterability of the slurry: effect of the initial pH (pH_0)^a

pH_0	$k_p (\times 10^{-12} \text{ s/m}^6)$	$\beta (\times 10^{-6} \text{ s/m}^3)$	$C (\text{kg/m}^3)$	$\mu (\times 10^3 \text{ Pa s})$	$\alpha (\times 10^{-10} \text{ m/kg})$	$R_m (\times 10^{-8} \text{ m}^{-1})$
2	0.2	0.6	0.3666	0.9639	331.74	5.738
4	0.3284	1.0513	0.4666	0.9315	442.87	10.404
6	0.8349	3.1733	1.5	0.9829	331.925	29.764
8	0.9491	4.6067	4.333	1.0126	125.83	41.941
10	1.0954	6.5467	4.4	1.0842	134.59	55.667
12	1.1577	10.507	4.6	1.132	130.316	85.569

^a $A = 6.358 \times 10^{-3} \text{ m}^2$.

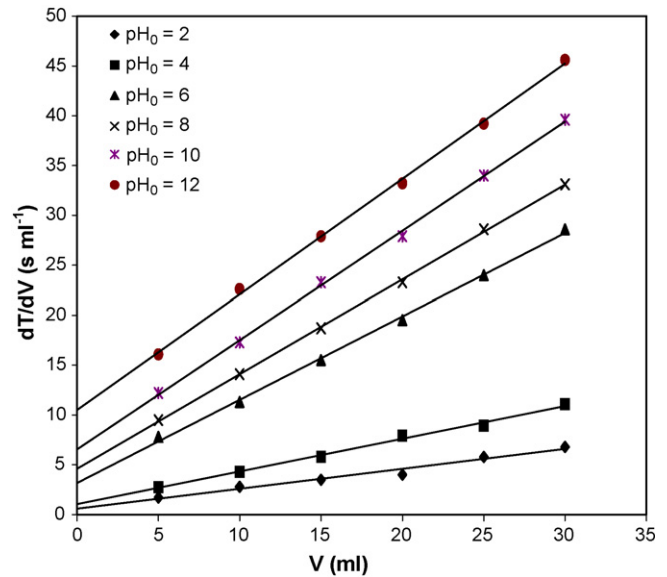


Fig. 8. Effect of pH_0 on the filterability of the desizing wastewater after thermolysis. $T_R = 95^\circ\text{C}$, $P =$ atmospheric pressure, $\text{COD}_0 = 2884 \text{ mg/l}$, $C_w = 4 \text{ kg/m}^3$.

and

$$\beta = \frac{\mu R_m}{A(-\Delta p)} \quad (3)$$

A plot of Eq. (1) for the experimental data is presented in Fig. 8 from which the values of k_p (slope) and β (intercept) were determined. The value of α and R_m were calculated from k_p and β and are presented in Table 4.

The viscosity of the filtrate was determined at room temperature (18°C) using an Ostwald capillary viscometer. It is observed that pH_0 has a pronounced impact on the filterability of the slurry.

3.9. Variation in final pH after treatment

The final pH values after the thermolysis were also observed. A minor shift in the pH was observed, which varied from about 3.0 to 5.0 from the initial pH_0 4 as depicted in Fig. 9. This adjustment in pH may be due to the dissociation of various catalysts into respective ions, which thereby combined with H^+ ions in the water to form H_2SO_4 etc. The formation of carboxylic acids is also feasible due to decomposition of bigger organic molecules. The net effect, thus, was observed to be getting an acidic final effluent.

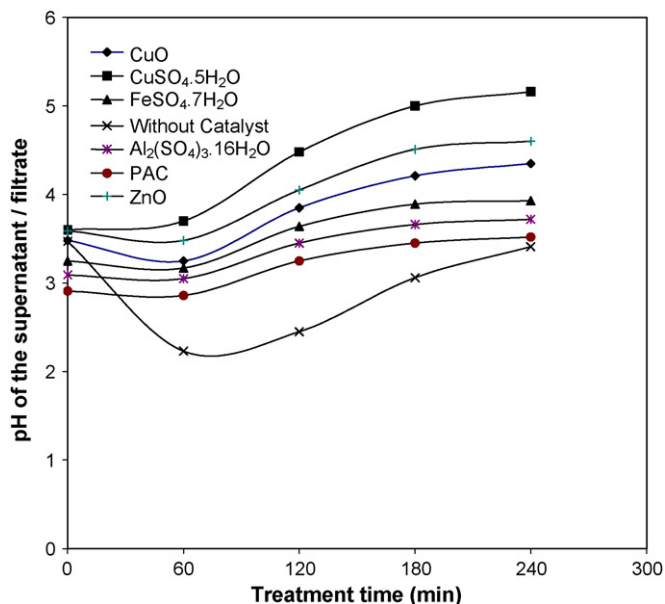


Fig. 9. Variation in supernatant pH with time during thermolysis with different chemicals. $\text{pH}_0 = 4$, $T_R = 95^\circ\text{C}$, $P = \text{atmospheric pressure}$, $\text{COD}_0 = 2884 \text{ mg/l}$, $C_w = 4 \text{ kg/m}^3$.

4. Conclusion

Thermolysis (thermal pretreatment) experiments at moderate temperatures (60–95 °C) and atmospheric pressure in the presence of a CuSO_4 catalyst showed that the desizing wastewater from a textile mill can be pretreated to reduce its COD and color. A maximum removal of about 71.6% of COD and 87.2% of color was achieved with a catalyst concentration of 4 kg/m^3 at 95°C and initial pH 4. The results on the effect of variation of catalyst mass loading revealed that 4 kg/m^3 is the critical chemical concentration. The settling rate of the treated effluent is strongly affected by pH of the effluent before treatment.

The initial pH (pH_0) of the effluent plays an important role in thermolysis with $\text{pH}_0 = 4$ showing most favourable treatment condition. The final pH of the treated effluent slightly increases above its pH_0 .

COD reduction is accompanied with the formation of a settleable solid residue, which is enriched in carbon. The elemental analysis of the desizing wastewater, filtrate and sludge shows carbon, hydrogen and sulfur enrichment in the sludge in relation to desizing wastewater itself.

The settling and filtration characteristics of the treated effluent improve with the increase in the treatment pH. The residual copper concentration in the filtrate after the thermolysis can be utilized as a catalyst in the secondary treatment, e.g., in coagulation/wet oxidation. Copper in the filtrate can also be reduced by pH adjustment. The sludge obtained after thermolysis has high heating value and can be used as a fuel.

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