

# Treatment of composite wastewater of a cotton textile mill by thermolysis and coagulation

Pradeep Kumar, B. Prasad, I.M. Mishra, Shri Chand\*

*Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India*

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## Abstract

Catalytic thermal treatment (thermolysis) accompanied with coagulation was used for the removal of COD and color of composite wastewater from a cotton textile mill.  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{CuO}$ ,  $\text{ZnO}$  and PAC were used as catalytic agents during thermolysis. Homogeneous copper sulphate at a mass loading of  $6 \text{ kg/m}^3$  was found to be the most active. Similarly during coagulation aluminum potassium sulphate [ $\text{KAl}(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$ ] at a coagulant concentration of  $5 \text{ kg/m}^3$  was found to be the best among the other coagulants tested, namely, commercial alum,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and PAC. During thermolysis, a reduction in COD and color of composite wastewater of about 77.9 and 92.85%, respectively, was observed at pH 12. Coagulation of fresh composite waste using aluminum potassium sulphate resulted in 88.62% COD reduction and 95.4% color reduction at pH 8. Coagulation of the supernatant obtained after treatment by catalytic thermolysis resulted in overall reduction of 97.3% COD and close to 100% color reductions at a lesser coagulant concentration of  $3 \text{ kg/m}^3$ .

The results reveal that the application of coagulation after thermolysis is most effective in removing nearly 100% of COD and color at a lower dose of coagulant. The sludge thus produced would contain lower inorganic mass coagulant and can be used as a solid fuel with high calorific value of about 16 MJ/kg, close to that of Indian coal.

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**Keywords:** Textile wastewater; Composite wastewater; COD reduction; Color reduction

## 1. Introduction

Textile industry is one of the largest industries in India and pointed attention is being directed towards pollution of water caused by the textile mills and dyestuff industries. Water pollution by the cotton textile mills is mainly attributable to the various waste streams coming out of the wet processing operations like desizing, scouring, bleaching, mercerizing, dyeing and printing. Usually each of these waste streams from the various units is merged into one common stream called composite effluent which is imparted necessary treatment before being discharged into the receiving body [1–5]. Textile processing employs a variety of chemicals depending on the nature of the raw material and product. Some of these chemicals are enzymes, detergents, dyes, acids, sodas and salts [6].

Many attempts have been made to treat textile wastewater using conventional wastewater treatment methods such as chemical coagulation, electrochemical oxidation, filtration and biological treatment [7–10]. Chemical coagulation is not effective for the removal of color. Activated carbon adsorption has the associated cost and difficulty of the regeneration process and a high waste disposal cost. Advanced oxidation processes such as ozonation, UV and ozone/UV combined oxidation, photo catalysis ( $\text{UV}/\text{TiO}_2$ ), Fenton reactive and ultrasonic oxidation are not economically feasible. Biological methods cannot be applied to most textile wastewaters due to the toxicity of most commercial dyes to the organisms used in the process [11–15].

Thermolysis with wet air oxidation or coagulation has been proposed in recent years in the author's laboratory as an effective method to treat various industrial wastewaters. Thermal pretreatment (thermolysis) is a chemical process by which a substance is decomposed into other substances by use of heat. A maximum reduction in COD and BOD observed for alcohol distillery effluent were 70 and 83%, respectively. For pulp and paper mill effluent, the COD and color reductions were 63.3 and 92.5%,

\* Corresponding author. Tel.: +91 1332 285217; fax: +91 1332 26535.  
E-mail address: [schanfch@iitr.ernet.in](mailto:schanfch@iitr.ernet.in) (S. Chand).

### Nomenclature

$A$	filtration area ( $m^2$ )
AGR	atmospheric pressure glass reactor
BOD	biochemical oxygen demand (mg/l)
$C$	concentration of slurry ( $kg/m^3$ )
$C_w$	catalyst mass loading ( $kg/m^3$ )
$C_0$	initial solids concentration ( $kg/m^3$ )
CC	coagulants concentration ( $kg/m^3$ )
CCC	critical chemical concentration ( $kg/m^3$ )
COD	chemical oxygen demand (mg/l)
$E$	activation energy (kJ/mol)
PCU	platinum cobalt unit
$R$	universal gas constant
$R_m$	filter medium resistance ( $m^{-1}$ )
RM	rapid mixing
SM	slow mixing
$\Delta S$	change in entropy (J/mol K)
$t_r$	treatment time (h)
$T$	temperature ( $^{\circ}C$ )
$v_f$	volumetric flow rate ( $m^3/s$ )

#### Greek symbols

$\alpha$	average cake resistance (m/kg)
$\mu$	viscosity of the filtrate (Pa s)

respectively [16–18], whereas for textile desizing wastewater the corresponding values were 71.6 and 87.2%, respectively [19]. The objective of this study is to investigate the effectiveness of thermolysis accompanied with coagulation with respect to the variations in parameters, such as, temperature, pH and catalysts/coagulant dose on the COD and color reduction efficiencies of the textile mill composite wastewater.

## 2. Materials and methods

### 2.1. Substrate

The effluent was obtained from a textile mill located in Ghaziabad, UP, India. The COD of the composite effluent was 1960 mg/l. To maintain the characteristics of composite effluent, the sample was stored at  $4^{\circ}C$  in a deep freezer.

For pretreatment step, the composite effluent was used without any dilution. The filtrate (having a reduced COD) obtained after pretreatment step was used for coagulation. The characteristics of the untreated composite wastewater are given in Table 1.

### 2.2. Chemicals

All of the chemicals used as coagulants/catalysts were of analytical reagent grade.  $CuSO_4 \cdot 5H_2O$  and  $CuO$  were procured from s.d. Fine Chemicals Ltd., Mumbai, India, whereas,  $ZnO$ ,  $FeCl_3$  and  $FeSO_4 \cdot 7H_2O$  were obtained from Qualigens Fine Chemicals, Mumbai, India. Ammonia solution and aluminum

Table 1  
Characteristics of composite wastewater

S. no.	Parameters	Value
1	Total dissolved solids	964.81
2	Total iron (as Fe)	1.81
3	Chlorides (as Cl)	650
4	BOD, 3 days at $20^{\circ}C$	420
5	Oil and grease	221.29
6	Sulphate (as $SO_4$ )	164.47
7	Copper (as Cu)	0.653
8	Manganese (as Mn)	0.46
9	Zinc (as Zn)	0.116
10	COD	1960
11	Color	2250 (PCU)
12	pH	7

All values except pH and color are in mg/l.

potassium sulphate [ $KAl(SO_4)_2 \cdot 16H_2O$ ] were procured from Ranbaxy Fine Chemicals Ltd., Mumbai and PAC was obtained from Vam Organics Ltd., Gajraula, UP, India.

### 2.3. Analytical methods

The COD value was assayed with an Aqualytic, Germany COD analyzer. The Standard Dichromator Closed Reflux Method (APHA-1989) was used. The color measurement followed the Pt–Co (Hazen) unit method. To determine the color in Pt–Co unit, a light of 470 nm was used in a Hanna HI93727 color meter (Hanna Instruments, Singapore). The concentration of Cu ion in the substrate (pretreated effluent) was measured by Avanta GBC, Australia atomic absorption spectrometer. Elemental analyzer model Vario EL III by Elementar, Germany, was used for elemental (C, H, N and S) analysis. The ash content (proximate analysis) was determined by Bureau of Indian Standards IS:1350 (Part-I)-1984. Thermal analysis (TGA/DTGA/DTA) of the wastewater and residue left after the thermolysis and coagulation was carried out using a TG analyzer (Pyris Diamond, Perkin-Elmer). Filtration for all the treated effluent was done using Millipore filtration assembly using  $0.45 \mu m$  filters [18–22]. The pH was measured using an Orion, U.S.A. make pH meter.

### 2.4. Experimental procedure

#### 2.4.1. Thermolysis (thermochemical pretreatment)

The thermolysis studies were conducted in a three-necked  $0.5 dm^3$  atmospheric pressure glass reactor (AGR). The glass reactor is equipped with a vertical condenser, heating mantle, magnetic stirrer and a sample withdrawal assembly. Digital temperature indicator-cum-controller was used to measure and control the temperature. The temperature of the reaction mixture during thermal pretreatment operations was maintained between 60 and  $95^{\circ}C$ . The amount of wastewater ( $COD_0 = 1960 mg/l$ ) taken in each run was 300 ml. The catalytic agents in desired concentration were used during the operation. Five milliliters of the sample was withdrawn at a definite interval of time and analyzed for its COD and color. The composite wastewater was preheated in the AGR from the ambient temperature ( $T_0$ ) to the

treatment temperature ( $T_R$ ). The preheating period ( $\theta$ ) 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  $T_0$ . The oven-dried residue was analyzed for its C, H, N, S and ash content. The initial pH of the wastewater was varied between 2 and 12 by using either 0.1N HCl or 0.1N NaOH.

### 2.4.2. Jar test

Jar-test experiments were conducted in a series of six graduated glass cylinders for 5 min rapid mixing (RM) at 80 rpm followed by 30 min slow mixing (SM) at 40 rpm and 30 min settling [23,24].

This experiment was aimed to study the settling characteristics as well as reduction in COD and color of the final effluent. Effect of initial pH on settling behavior was also studied.

## 3. Results and discussion

### 3.1. Thermolysis process

#### 3.1.1. Effect of pH

Fig. 1(a) shows the effect of initial pH at 25 °C on the COD and color reduction of composite wastewater by thermolysis using various catalysts, such as  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{CuO}$ ,  $\text{ZnO}$  and PAC (also without catalyst) at a mass loading of  $6 \text{ kg/m}^3$ . Different initial pH values maintained during the experiments were 2, 4, 6, 8, 10 and 12, and the reaction was conducted at 95 °C for 4 h. A portion of the resulting mixture after treatment was taken out and centrifuged for 10 min at a speed of 10,000 rpm. The supernatant was separated and its COD was measured. The figure shows an identical trend of increasing percent COD reduction with increase in the value of initial pH from 1 to 12 for all the catalysts. The reduction in COD was faster up to pH 8 in comparison to rate of reduction in the pH range 8–12. A maximum COD reduction of 77.9% was obtained using  $\text{CuSO}_4$  as catalyst at pH 12. The final pH after the treatment was also measured and a decrease in pH was observed in all the cases. The reduction in pH after the treatment has been shown in Table 2. The decrease in pH may be due to the dissociation into sulphate/chloride ions as the case may be and also the formation of lower carboxylic acids. The sulphate/chloride ions after combining with  $\text{H}^+$  ions present in wastewater form  $\text{H}_2\text{SO}_4/\text{HCl}$  which reduces the pH of the solution. The carboxylic acids are

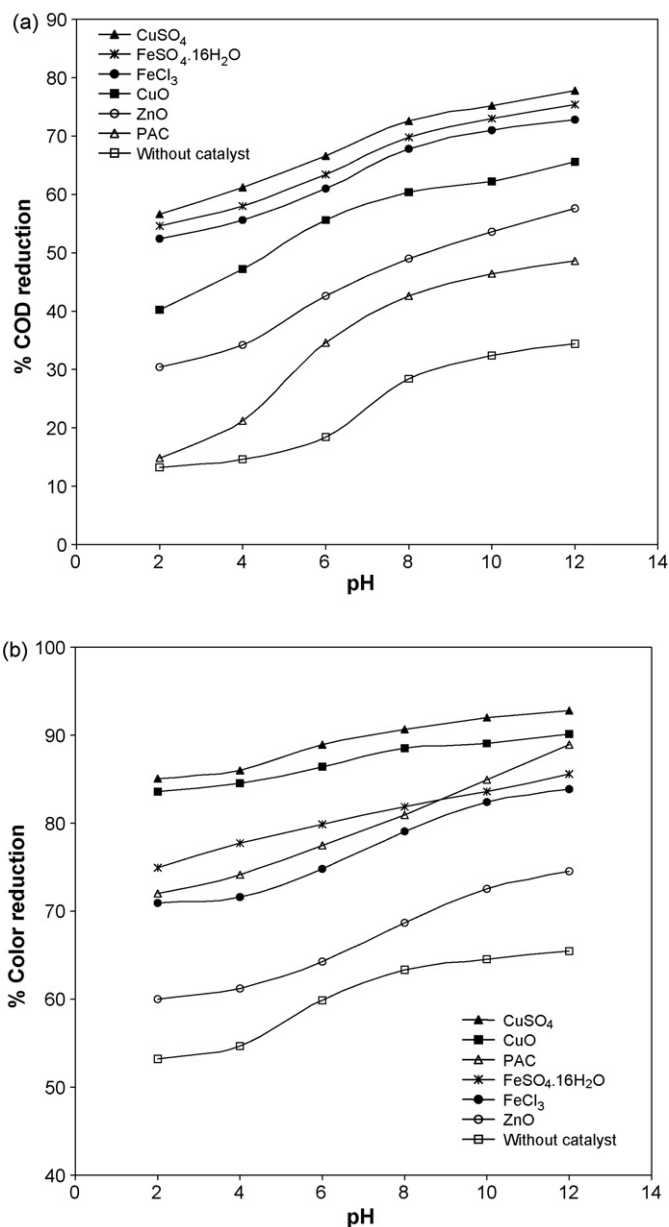


Fig. 1. (a) Effect of  $\text{pH}_0$  on COD reduction of the composite wastewater by thermolysis.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $T_R = 95^\circ\text{C}$ ,  $P = \text{atmospheric}$ ,  $t_r = 4 \text{ h}$  and  $C_w = 6 \text{ kg/m}^3$ . (b) Effect of  $\text{pH}_0$  on color reduction of the composite wastewater by thermolysis.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $T_R = 95^\circ\text{C}$ ,  $P = \text{atmospheric}$ ,  $t_r = 4 \text{ h}$  and  $C_w = 6 \text{ kg/m}^3$ .

Table 2  
Effect of catalyst on the reduction of pH after treatment of composite wastewater

pH	pH reduction after treatment with						pH reduction after treatment without catalyst
	$\text{CuSO}_4$	$\text{FeSO}_4 \cdot 16\text{H}_2\text{O}$	$\text{FeCl}_3$	$\text{CuO}$	$\text{ZnO}$	PAC	
2	1.95	1.65	1.85	1.13	1.72	1.62	1.98
4	3.65	2.94	3.14	3.36	3.75	3.83	3.95
6	5.42	5.92	5.64	5.86	5.57	5.62	5.90
8	8.54	7.95	7.62	7.73	7.54	7.86	7.98
10	9.02	9.12	9.24	9.92	9.64	9.57	9.99
12	10.96	10.54	10.74	10.54	11.64	11.52	11.85

formed out of the degradation of high molecular weight hydrocarbons. The initial pH adjustment of the composite waste has been found to reduce the COD of the solution. A value of pH 12 yielded in a precipitation of the solution (at room temperature) with about 22% COD reduction in supernatant. When the composite waste at pH 12 was thermally heated without any catalyst, the COD decrease observed was 34.5%. This clearly shows that the thermal pretreatment has better effect on precipitation than change in pH.

Fig. 1(b) shows the effect of different catalysts as well as initial pH on percent color reduction of composite wastewater. The reaction conditions were same as in the previous case. For all the catalysts the percent color reduction increases with increase in pH. The increase was fast initially whereas at pH 10 onwards, it was nearly constant. The reduction in COD without catalyst was much lower in comparison to the reduction using a catalyst.  $\text{CuSO}_4$  has been the best catalyst giving 92.85% color reduction at pH 12.

### 3.1.2. Effect of temperature

Fig. 2 shows the effect of treatment temperature on the COD and color reduction at pH 12. The concentration of catalyst used was  $2 \text{ kg/m}^3$  and temperature varied from 60 to  $95^\circ\text{C}$ . The increase in temperature does not increase the reduction in color appreciably. The reduction in COD, however, was found to increase with temperature, giving a maximum of 72.9% reduction at  $95^\circ\text{C}$ . The maximum color removal at these conditions was 85.54%.

### 3.1.3. Mass loading

The effect of catalyst mass loading on the COD as well as color reduction of composite wastewater (initial COD =  $1960 \text{ mg/l}$  and color 2250 Pt–Co) was observed during thermochemical pretreatment at  $95^\circ\text{C}$  and 4 h duration as shown

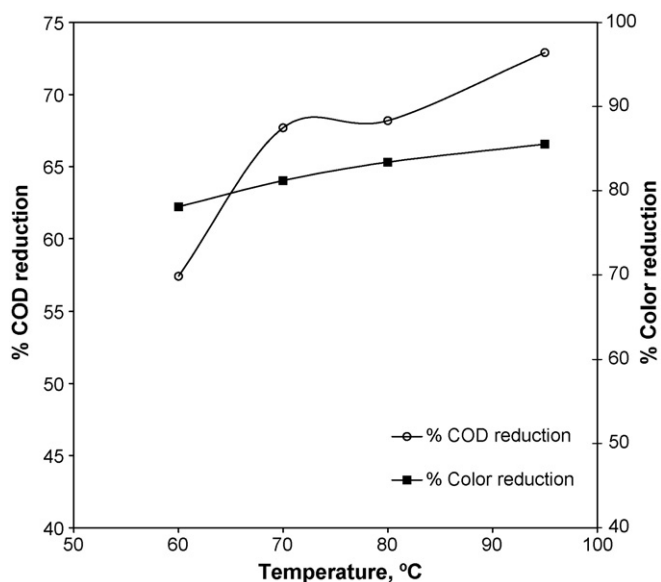


Fig. 2. Effect of temperature on COD and color reduction of the composite wastewater by catalytic thermolysis.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $t_r = 4 \text{ h}$ ,  $P = \text{atmospheric}$ ,  $\text{pH}_0 = 12$  and  $C_w = 2 \text{ kg/m}^3$ .

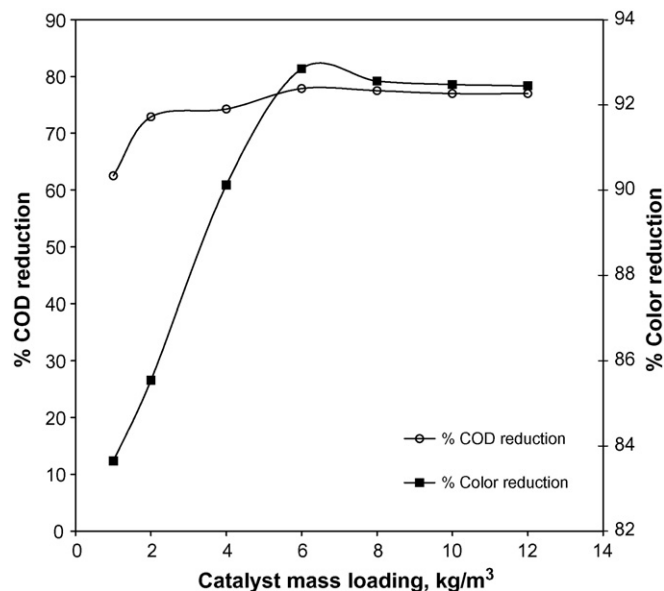


Fig. 3. Effect of catalyst (copper sulphate) concentration on COD and color reduction of the composite wastewater.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $t_r = 4 \text{ h}$ ,  $P = \text{atmospheric}$ ,  $\text{pH}_0 = 12$  and  $T_R = 95^\circ\text{C}$ .

in Fig. 3.  $\text{CuSO}_4$ , being the best among all the catalysts, was chosen for further studies. The catalyst mass loading was varied from 1 to  $12 \text{ kg/m}^3$  while the initial pH was adjusted at 12 for all the experimental runs. With  $1 \text{ kg/m}^3$  copper sulphate mass loading a 62.5% reduction in COD was observed which increased to 77.9% at catalyst mass loading  $6 \text{ kg/m}^3$ . Further increase in catalyst mass loading did not increase the COD reduction. The % color reduction under similar conditions increased from 83.65% at  $1 \text{ kg/m}^3$  to 92.85% at  $6 \text{ kg/m}^3$ .

### 3.1.4. TGA and DTA of sludge

The TGA, DTA and DTGA curves were obtained for the precipitated sludge at  $10^\circ\text{C}/\text{min}$  heating rate and  $200 \text{ ml/min}$  air flashing rate and are presented in Fig. 4(a). The nature of TGA trace shows dehydration and volatilization (removal of volatiles) of the sample up to a temperature of  $180^\circ\text{C}$  losing about 93.17% of its weight. Between 180 and  $240^\circ\text{C}$  the residue oxidizes losing about 20% of its original weight. The peak rate of weight loss at  $T_{\text{max}} = 227^\circ\text{C}$  is  $5 \text{ mg/min}$ . The oxidation is found uniform and exothermic with a heat evolution of  $889 \text{ MJ/kg}$ . The peak of exotherm being at a temperature of  $T_p = 242^\circ\text{C}$ . The oxidation of the residue seems to become slower between 240 and  $366^\circ\text{C}$ , losing weight of about 10% with a marginal heat of exothermic reaction of  $119 \text{ MJ/kg}$  at the peak temperature  $326^\circ\text{C}$ . The oxidation continued at very slow rate from 366 to  $990^\circ\text{C}$ , losing a maximum weight of only less than 7%, leaving the ash fraction of  $\sim 44.1\%$  as the residue.

Fig. 4(b) shows the TG, DTA and DTG traces of the composite wastewater under similar heating conditions. In contrast to the TGA behavior of the precipitate, the composite wastewater TG traces shows only about 0.62% decrease in weight up to  $82^\circ\text{C}$ . However, there has been a sudden drop in the weight of about 11% from 82 to  $117^\circ\text{C}$  on account of vaporization of volatiles and moisture.

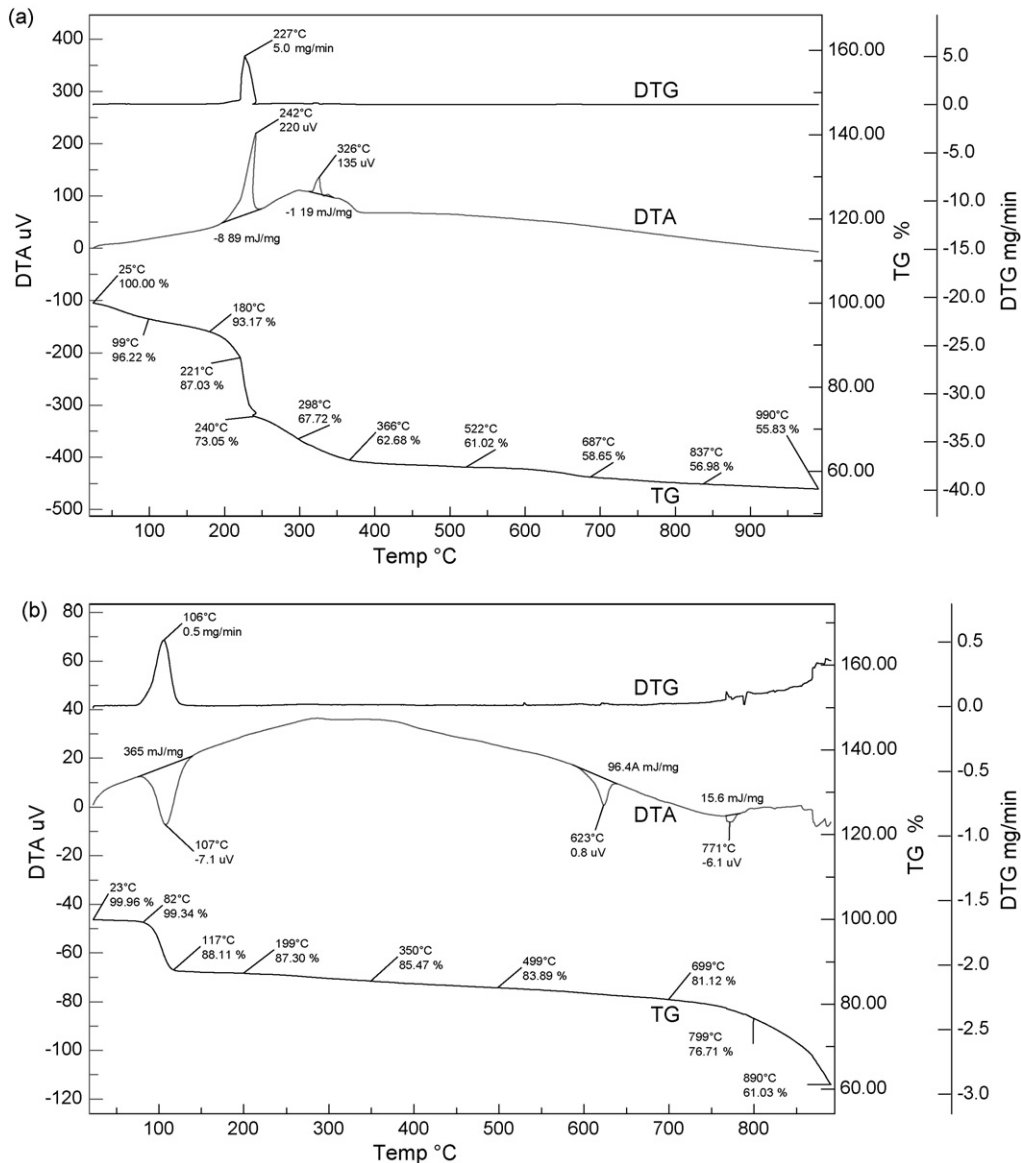


Fig. 4. (a) TGA–DTA of composite wastewater sludge. Sample weight: 10.89 g and atmosphere: air at 200 ml/min. (b) TGA–DTA of composite wastewater. Sample weight: 10.89 g and atmosphere: air at 200 ml/min.

The maximum rate of weight loss of 0.5 mg/min at 106 °C was observed with an endothermic heat requirement of 365 MJ/kg recorded at the peak temperature of 107 °C. The rate of weight loss from 117 °C onwards was extremely slow up to 699 °C losing weight of only 7%. Beyond 699 °C there has been a steady weight loss of about 20% up to 890 °C. The maximum rate of weight loss of about 0.35 mg/min was observed at around 870 °C. This might be due to the molecular level rearrangement.

The comparison of the thermal analysis of the two residues (precipitate as well as composite wastewater) shows that the precipitate obtained after thermolysis gets oxidized at a higher temperature range than that of the composite wastewater. This may be due to the presence of more stable compounds formed during thermolysis in presence of copper catalysts.

The thermal degradation data (TGA, DTA and DTGA) were analyzed using the kinetic models available in the literature [25–27]. The overall thermal degradation characteristics can be

represented by a one-way transport diffusion model assuming a first-order irreversible reaction of the organics in the precipitate. The reaction rate constant,  $k$ , through the use of the theory of the active complex [25,28] can be written as

$$k = \left( \frac{\chi e k_B T}{h} \right) \exp \left( \frac{\Delta S}{R} \right) \exp \left( -\frac{E}{RT} \right) \quad (1)$$

where  $\chi$  is the transmission coefficient (1.0 for mono molecular reaction),  $e$  the Neper's number (2.7183),  $k_B$  the Boltzmann's constant,  $h$  the Plank's constant,  $T$  the absolute temperature and  $\Delta S$  is the change in entropy for the active complex formation from the reactant. Eq. (1) may be modified with the help of Arrhenius equation to give

$$A = \left( \frac{\chi e k_B T}{h} \right) \exp \left( \frac{\Delta S}{R} \right) \quad (2)$$

Table 3

Kinetic parameters calculated for the solid residue left after treatment with copper sulphate from the one-way transport diffusion kinetics ( $D_1$ ) and Ginstling–Brounstein diffusion (GB) model

Parameters	Models	
	$D_1$	GB
$n$	1	1
$A$ ( $\text{min}^{-1}$ )	4.977	$6.89 \times 10^{-13}$
$E$ ( $\text{kJ mol}^{-1}$ )	120.28	120.84
$k$ ( $\text{min}^{-1}$ )	0.0128	0.0014
$\Delta S$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	-250.52	-250.79
$\Delta H$ ( $\text{kJ mol}^{-1}$ )	117.131	117.69
$\Delta G$ ( $\text{kJ mol}^{-1}$ )	212.017	212.688
$P_s$	$8.19 \times 10^{14}$	$7.92 \times 10^{14}$
$r^2$	1	0.892

or

$$\Delta S = R \left( \ln A - \frac{\ln \chi e k_B T}{h} \right) \quad (3)$$

The change of the enthalpy  $\Delta H$  and Gibbs free energy  $\Delta G$  for the active complex formation and  $\Delta S$  can be calculated at DTG peak temperature using the equations:

$$E = \Delta H + RT \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The DTG peak temperature characterizes the highest rate of the process and, therefore, is its most important parameter.

The steric factor for a particular temperature zone of degradation of the precipitate may be given by  $P = \exp(\Delta S/R)$  [25]. This factor allows estimating whether the degradation taking place in the selected zone is slow or fast. If value of  $P$  is closer to unity for the selected zone, than that for the other zone, it is inferred that the degradation in the selected zone is faster than that for the other zone. The best-fit values of the kinetic parameters from the one-way transport diffusion kinetics ( $D_1$ ) and Ginstling–Brounstein diffusion model [25,27] are given in Table 3.

### 3.1.5. Settling characteristics of the precipitate in the treated effluent

Several approximate methods have been reported for the calculation of the compression zone depth in continuous thickeners [29–32]. For various methods which have been suggested for calculating compression zone height in continuous thickeners from the batch sedimentation data [33–36], it is preferable to use the method proposed by Richardson et al. [29] to design a continuous thickener based on single batch sedimentation test.

In order to see the effect of pH on the settling characteristics of the precipitate obtained after treatment with  $\text{CuSO}_4$ , three different pH, i.e., pH 4, 6 and 10 were maintained in a 100 ml measuring cylinder. The settling rate was observed to be higher for pH 10 than that of pH 4, probably due to the bigger size and more compact aggregated flocs.

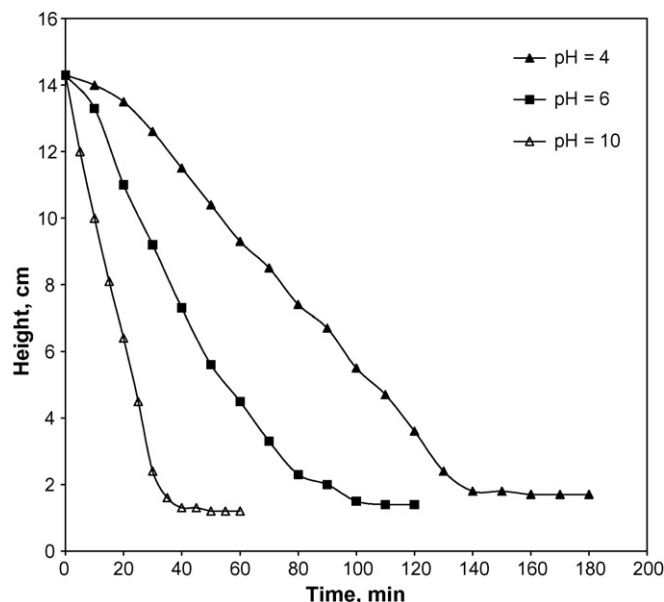


Fig. 5. Settling characteristics of composite wastewater after thermolysis using  $\text{CuSO}_4$  as catalyst.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $T = \text{ambient temperature}$ ,  $P = \text{atmospheric}$  and  $C_w = 5 \text{ kg/m}^3$ .

Fig. 5 shows the behavior of treated effluent during sedimentation.

The calculation of sedimentation velocity ( $u_c$ ), concentration  $C(t)$ , and the sedimentation flux were done using the Kynch theory [29]. The sedimentation velocity ( $u_c$ ) was found as the slope of the tangent at a given solids concentration,  $C$ . The concentration of sludge at a time  $t$  was determined using following relationship:

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

The concentration of the solids required in the underflow,  $C_u$ , for the effluents treated at pH 4, 6 and 10 were found to be 14, 17 and  $20 \text{ kg m}^{-3}$ , respectively. The maximum value of  $[\{(1/C) - (1/C_u)\}/u_c]$  was thus determined as  $0.078 \times 10^6$ ,  $0.183 \times 10^5$  and  $0.08 \times 10^5$  at pH 4, 6 and 10, respectively. Using these values, the area of the sedimentation tank for any effluent flow rate can, thus, be calculated as

$$A = \frac{v_f C_0 [(1/C) - (1/C_u)]}{u_c}$$

The settling of the effluent treated at a higher pH is faster than that treated at a lower pH. Thus an increase in the treatment temperature will bring down substantially the area of the sedimentation tank. From Fig. 5, it can also be seen that the settling rate is very fast during the zone settling region at pH 10. The settling rate becomes very slow, as the solids settling enter compression region. It is also seen that the compression region for the pH 10 settled sludge is much denser (more than twice) than that for the pH 4 settled sludge.

### 3.1.6. Filterability

The gravity filtration characteristics of the slurry were carried out at room temperature on an ordinary filter paper sup-

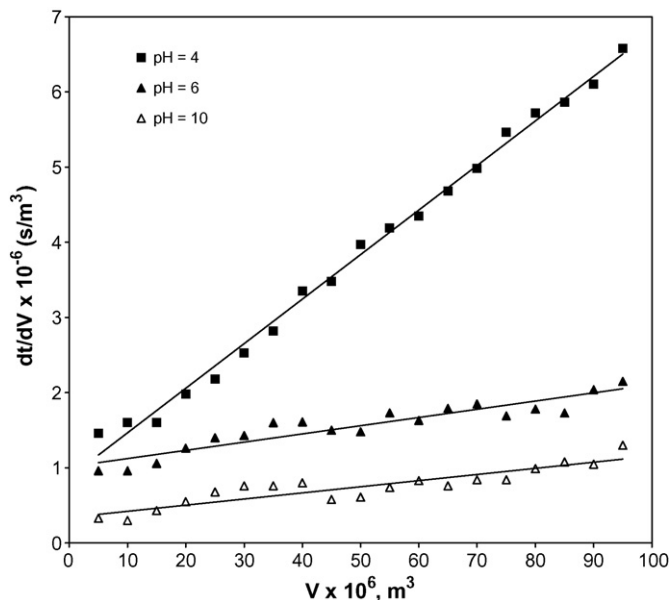


Fig. 6. Effect of  $pH_0$  on the filterability of the composite wastewater after thermolysis using  $CuSO_4$  as catalyst.  $COD_0 = 1960 \text{ mg/l}$ ,  $T = \text{ambient temperature}$ ,  $P = \text{atmospheric}$  and  $C_w = 5 \text{ kg/m}^3$ .

ported on a Büchner funnel, under constant pressure filtration.

The change in the hydrostatic head was assumed to be negligible. The filtrate volume obtained as a function of time was observed and a plot between  $\Delta t/\Delta V$  and  $V$  was drawn for the effluents treated at different pH. The plot in Fig. 6 shows a linear relationship. Thus, it is clear that the filterability of the treated effluent gets improved with an increase in the initial pH. pH 10 seems to offer least resistance to filtration. The filtration resistances for the filter media as well as the filter cake were obtained using the filtration equation [36]:

$$\frac{dt}{dV} = k_p V + \beta \quad (6)$$

where

$$k_p = \frac{C\alpha\mu}{A^2(-\Delta p)} \quad (7)$$

and

$$\beta = \frac{\mu R_m}{A(-\Delta p)} \quad (8)$$

where  $k_p$  (slope) and  $\beta$  (intercept) were determined by the plot of Eq. (6) as shown in Fig. 6. These values of  $\alpha$  and  $R_m$  were calculated from  $k_p$  and  $\beta$  and are presented in Table 4.

Table 4  
Filterability of the slurry: effect of the initial pH ( $pH_0$ )<sup>a</sup>

$pH_0$	$k_p (\times 10^{-12} \text{ s/m}^6)$	$\beta (\times 10^{-6} \text{ s/m}^3)$	$C (\text{kg/m}^3)$	$\mu (\times 10^3 \text{ Pa s})$	$\alpha (\times 10^{-10} \text{ m/kg})$	$R_m (\times 10^{-8} \text{ m}^{-1})$
4	0.5	0.9	1.65	1.83	10.67	4.53
6	0.12	1.0	1.61	1.85	2.36	4.98
10	0.71	0.4	1.69	1.80	1.34	2.04

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

Table 5

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

Material	C (%)	H (%)	N (%)	S (%)	Heating value of residue (MJ/kg)
Composite wastewater	10.65	3.013	0.00	7.094	7.2
Precipitate	14.32	0.28	0.00	5.045	16.0
Supernatant	2.975	0.169	0.00	4.887	–
Indian coal	4.887	5.01	0.80	1.70	20.90

Table 6

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

Material	Ash (%)	Volatile matter (%)	Fixed carbon (%)
Composite wastewater	46.0	37.0	5.0
Precipitate	41.6	43.6	9.2

Typical values of specific cake resistance for different sludge's are given by Barnes et al. [38]. Pulp and paper mill effluent characteristics are given by Garg et al. [17], whereas alcohol distillery waste characteristics are presented by Lele et al. [37].

The reported values for other effluents are higher than those shown in Table 4 for textile mill effluent. The difference can be ascribed to several factors like treatment conditions, morphological and floc characteristics of the sludge, which may be different for the textile mill effluent.

### 3.1.7. Elemental and compositional characterization of the sludge and composite wastewater

The C, H, N, S and proximate analyses of the settled precipitate and the composite wastewater, respectively, are presented in Tables 5 and 6. The heating values of the precipitate and the composite wastewater are also given and compared with those of Indian coal. The elemental analysis shows that there are enhancements in carbon and hydrogen composition in the precipitate and that its heating value compares well with that of Indian coal.

The carbonaceous load of the treated wastewater after filtration has gone down considerably as the supernatant is much leaner in carbon and hydrogen composition. The proximate analysis, as shown in Table 6, indicates considerably lower ash content in the precipitate than that in the composite wastewater and considerably higher fixed carbon content in the precipitate than that in the composite wastewater.

## 4. Coagulation

### 4.1. Combined effect of catalytic thermal pretreatment followed by coagulation

Fig. 7(a) and (b) shows COD as well as color reduction, respectively, during coagulation of the fresh composite wastewater. The coagulants used include aluminum potassium sulphate, commercial alum,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and PAC. A general trend of increase in COD reduction with increase in pH (from 2 to 12) was observed. The major increase was from pH 4 to 10. PAC and  $\text{FeSO}_4$ , however, did not follow this trend. The curve

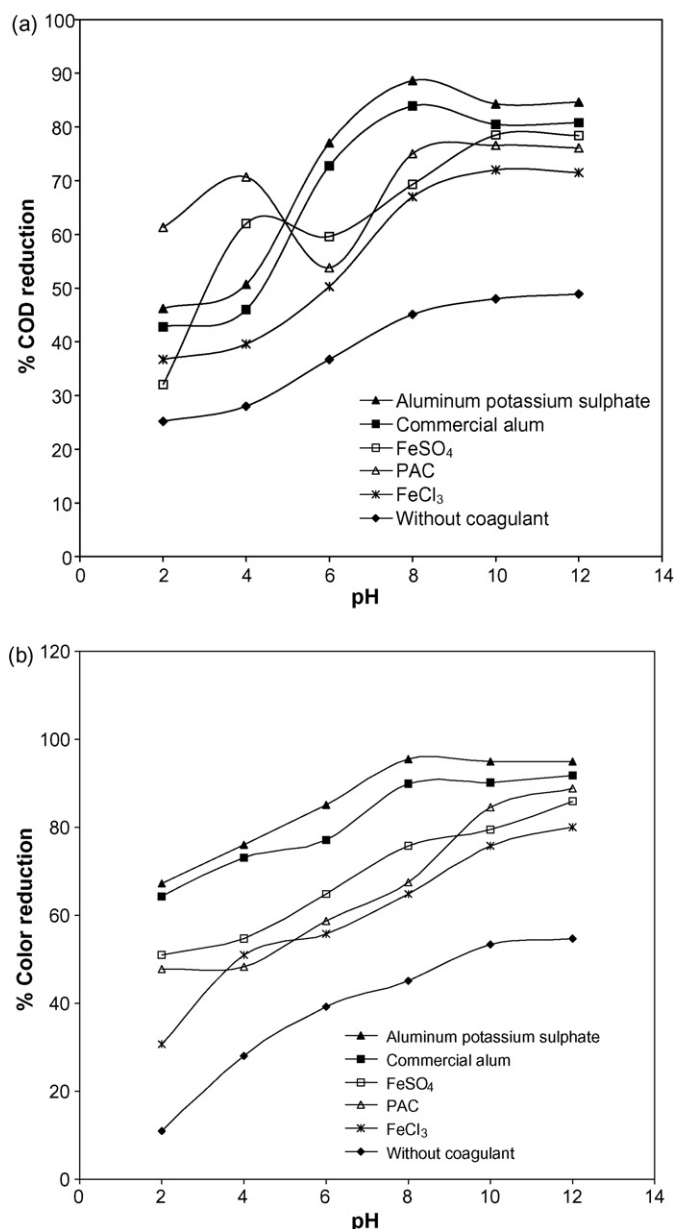


Fig. 7. (a) Effect of  $\text{pH}_0$  on COD reduction of the composite wastewater by using different coagulants.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $t_r = 1 \text{ h}$ ,  $P = \text{atmospheric}$  and  $C_w = 5 \text{ kg/m}^3$ . (b) Effect of  $\text{pH}_0$  on color reduction of the composite wastewater by using different coagulants.  $\text{COD}_0 = 1960 \text{ mg/l}$ ,  $t_r = 1 \text{ h}$ ,  $P = \text{atmospheric}$  and  $C_w = 5 \text{ kg/m}^3$ .

showing COD reduction without any coagulant, however, shows 48.9% reduction only. By pH adjustment, the decrease in COD at alkaline condition is much higher than those in the acidic condition.

A similar trend with color reduction was also obtained in both the cases. Aluminum potassium sulphate was best coagulant giving 84–88% COD reduction and about 95% color reduction at pH 8.

The effect of coagulants concentration (CC) on COD and color reduction of the composite waste at pH 8 were studied. For a number of coagulants, pH 8 happens to be the optimum pH for both COD and color reduction. The results show a sharp increase in percent reductions with increase in coagulant dose from 1 to  $5 \text{ kg/m}^3$ . Beyond this, there was almost no change. Coagulant dose  $5 \text{ kg/m}^3$  may thus be called as critical coagulant concentration (CCC). At coagulant dose  $5 \text{ kg/m}^3$  and  $\text{pH}_0 8$ , the maximum COD and color reduction were 88.62 and 95.4%, respectively.

In another series of runs, coagulation (using aluminum potassium sulphate) was carried out to the supernatant obtained from the catalytic thermal pretreatment (using  $\text{CuSO}_4$ ). Fig. 8 depicts % COD and color reductions and compares the results of coagulation with/without thermal pretreatment. Coagulation has significant effect on further increasing the percent COD and color reductions when it is applied after thermolysis. An increase in COD reduction of about 20% (from 78.15 to 97.3%) is achieved when coagulation is applied to the thermally pretreated effluent. A similar result on the color reduction indicates about 12.5% (from 87.59 to 100%) increase. The results thus show that the thermolysis (using  $\text{CuSO}_4$ ) followed by coagulation (using aluminum potassium sulphate) is the most effective method of treatment of composite wastewater of a cotton textile mill giving close to 100% reduction of COD as well as color.

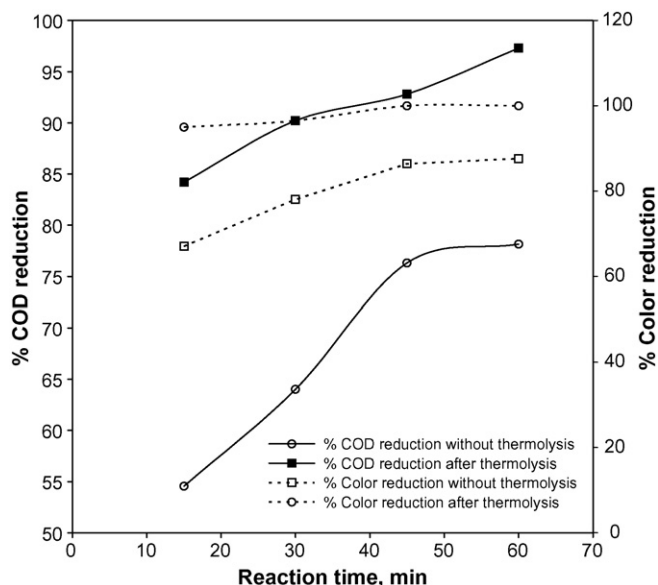


Fig. 8. Reduction of COD and color with time by coagulation (coagulant = aluminum potassium sulphate,  $\text{pH}_0 8$ ,  $T = 18^\circ \text{C}$ ,  $C_w = 3 \text{ kg/m}^3$ ).



## 5. Conclusions

The present study deals with the treatment of textile mill effluent using catalytic thermal treatment (thermolysis) followed by coagulation. The thermolysis process was carried out in presence of several catalysts:  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{CuO}$ ,  $\text{ZnO}$  and PAC. Among these copper sulphate was found to be the best giving about 77.9% COD as well as 92.85% color reduction, respectively, at a catalyst concentration of  $6 \text{ kg/m}^3$ , pH 12 and  $95^\circ\text{C}$ . The settling rate of the slurry was also observed and was found to be strongly influenced by treatment pH. The slurry obtained after treatment by thermolysis at pH 10 settled much faster in comparison to slurries obtained at other pH. The filterability of the treated effluent is also strongly dependant on the initial pH. pH 10 was adjudged to be the best in giving highest filtration rate. During coagulation aluminum potassium sulphate is found to be the best among other coagulants (commercial alum,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and PAC) used resulting in 88.62% COD reduction and 95.4% color reduction, respectively, at pH 8 and a coagulant concentration of  $5 \text{ kg/m}^3$ . Coagulation applied to clear fluid (supernatant) obtained after catalytic thermal treatment (at above mentioned operating conditions except at a lower coagulant concentration of  $3 \text{ kg/m}^3$ ) resulted in overall reduction of 97.3% COD and close to 100% of color.

During catalytic thermal treatment using copper sulphate as catalyst, the copper gets leached out and the residue obtained is rich in copper. This residue can be blended with organic manure to be used in agriculture.

Thermolysis followed by coagulation has been found to be the most effective in removing almost 100% COD as well as color at a lower dose ( $3 \text{ kg/m}^3$ ) of coagulant. The sludge thus produced would contain lower inorganic mass coagulant and also can be used as a solid fuel with high calorific value of about  $16 \text{ MJ/kg}$ , close to that of Indian coal.

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