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# Decolorization and COD reduction of dyeing wastewater from a cotton textile mill using thermolysis and coagulation

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**Abstract**

The decolorization and reduction of COD of dyeing wastewater from a cotton textile mill was conducted using catalytic thermal treatment (thermolysis) accompanied with/without coagulation. Thermolysis in presence of a homogeneous copper sulphate catalyst was found to be the most effective in comparison to other catalysts ($FeCl_3$, $FeSO_4$, CuO, ZnO and PAC) used. A maximum reduction of chemical oxygen demand (COD) and color of dyeing wastewater of 66.85% and 71.4%, respectively, was observed with a catalyst concentration of 5 kg/m$^3$ at pH 8. Commercial alum was found most effective coagulant among various coagulants (aluminum potassium sulphate, PAC, $FeCl_3$ and $FeSO_4$) tested during coagulation operations, resulting in 58.57% COD and 74% color reduction at pH 4 and coagulant dose of 5 kg/m$^3$. Coagulation of the clear fluid (supernatant) obtained after treatment by thermolysis at the conditions previously used resulted in an overall reduction of 89.91% COD and 94.4% color at pH 4 and a coagulant dose of 2 kg/m$^3$. The application of thermolysis followed by coagulation, thus, is the most effective treatment method in removing nearly 90% COD and 95% color at a lower dose of coagulant (2 kg/m$^3$). The sludge thus produced would contain lower inorganic mass coagulant and, therefore, less amount of inorganic sludge.

*Keywords:* Dyeing wastewater; COD removal; Color removal; Thermolysis; Coagulation

## 1. Introduction

Wastewater generated by different production steps of a cotton textile mill have high pH, temperature, detergents, oil, suspended and dissolved solids, toxic and non-biodegradable matter, color and alkalinity [1,2]. Dyes used in the cotton textile mills are characterized as per their application method into vat dye, reactive dye, disperse dye and cationic dye. Wastewater from fabric and yarn printing and dyeing pose serious environmental problems both because of their color and high COD [3–6]. Biological treatment process is generally efficient in BOD and suspended solids removal, however, it is considered unsatisfactory because of the low efficiency and low reaction rate of treatment. The coagulation process is widely employed for color removal. Adding a coagulant to the wastewater stream is costly and the sludge formed requires further treatment. The treatment of textile wastewater with ferrous sulphate and/or lime was proved to be very effective in removing color (70–90%) and COD (50–60%) [7–11]. Activated carbon adsorption has the associated cost and difficulty of the regeneration process and a high waste disposal cost. Advanced oxidation process like ozonation, UV and ozone/UV combined oxidation, photocatalysis, etc. are not economically feasible due to high consumption of energy and raw material. Fenton's oxidation and ozone process removed the COD in the range of 59% and 33%, while color removal was 89% and 91%, respectively. Advanced oxidation methods used before biological treatment increase the ratio of BOD/COD after ozonation and improved the biodegradability of toxic substances. However, the major disadvantage of using ozone is that it may form toxic byproducts even from

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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 ($kg/m^3$) |
| $C_w$ | catalyst mass loading ($kg/m^3$) |
| CCC | critical chemical concentration ($kg/m^3$) |
| COD | chemical oxygen demand ($kg/m^3$) |
| $COD_0$ | initial concentration of organic matter in the effluent expressed as COD ($kg/m^3$) |
| $e$ | Neper's number (2.7183) |
| $\Delta G$ | Gibbs free energy |
| $h$ | Plank's constant |
| $\Delta H$ | change of the enthalpy |
| $k_B$ | Boltzmann's constant |
| PCU | platinum cobalt unit (Pt–Co) |
| $R_m$ | filter medium resistance ($m^{-1}$) |
| $\Delta S$ | change in entropy for the active complex formation from the reactant. |
| $t$ | time (s) |
| $t_R$ | treatment time (h) |
| $T$ | absolute temperature (K) |
| $V_f$ | volumetric flow rate ($m^3/s$) |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | average cake resistance (m/kg) |
| $\theta$ | pre-heating time |
| $\mu$ | viscosity of the filtrate (Pa s) |
| $\chi$ | transmission coefficient (1.0 for mono-molecular reaction) |

biodegradable substances [12–17]. Wet air oxidation has been demonstrated to be a viable process for the treatment of desizing, scouring, dyeing and printing wastewater from the textile industry. Wet air oxidation requires high temperature (at 300 °C) and high pressure (over 10 MPa) [18–20]. Thermolysis is a chemical process by which a substance is decomposed into other substance by use of heat. Thermolysis is reported to have improved the biogasification of biomass due to breakdown of lower molecular weight compounds. During thermal treatment, a significant amount of COD reduction of about 63% was achieved in the author's laboratory for highly concentrated distillery/paper mill wastewater [21–26].

This study proposes the treatment of textile dyeing wastewater using the thermolysis and coagulation process. The effectiveness of the processes is measured by color and COD removal. The treatment of dyeing wastewater by catalytic thermolysis has been attempted in the presence of different catalysts. The effect of different parameters, such as initial pH ($pH_0$), chemical concentration (catalysts/coagulants) and temperature were also studied. The elemental analysis of the effluent and the precipitate as well as the thermogravimetric analysis (TGA) of the precipitate formed after the thermolysis was performed to understand its thermal degradation characteristics. In addition, the settle ability and filterability characteristics of the slurry obtained after treatment were also performed to see the optimum treatment conditions.

Table 1
Characteristics of dyeing wastewater

| S. no. | Parameters | Value |
|---|---|---|
| 1 | Total suspended solids | 152.1 |
| 2 | Total iron (as Fe) | 0.447 |
| 3 | Chlorides (as Cl) | 60 |
| 4 | BOD, 3 days at 20 °C | 1525 |
| 5 | Oil and grease | 62.4 |
| 6 | Sulphate (as $SO_4$) | 306.74 |
| 7 | Copper (as Cu) | 0.046 |
| 8 | Zinc (as Zn) | 0.048 |
| 9 | COD | 5744 |
| 10 | Color | 3840 (Pt–Co) |
| 11 | pH | 10.30 |

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

## 2. Materials and methods

### 2.1. Substrate

The dyeing wastewater samples were obtained from a textile mill located at Ghaziabad, UP, India. The original effluent has a COD of 5744 mg/l and color 3840 Pt–Co, containing reactive dyes. The effluent without any dilution was used for all treatment steps. The characteristics of the untreated dyeing wastewater are given in Table 1.

### 2.2. Chemicals

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

### 2.3. Analytical methods

The chemical oxygen demand (COD) of the effluent was estimated by the standard dichromator closed reflux method (APHA-1989) using a COD analyzer (Aqualytic, Germany). The color in Pt–Co unit was estimated using a color meter (Hanna HI93727, Hanna Instruments, Singapore) at 470 nm. The concentration of ions 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 μm filters. The pH was measured using a Thermo Orion, USA make pH meter. The treated wastewater samples were centrifuged (Model R24, Remi Instruments Pvt. Ltd., Mumbai, India) to obtain the supernatant and the precipitate [23,24].

### 2.4. Experimental procedure

#### 2.4.1. Catalytic thermal treatment (thermolysis)

The experimental studies at temperatures higher than ambient temperature were carried out in a 0.5 l three-necked glass reactor. Initially, the pH of the wastewater was adjusted by adding $H_2SO_4$ or ammonia solution and then the wastewater (300 ml) was shifted to the three-necked glass reactor. Thereafter, the catalyst/coagulant were added to the solution. The catalyst ($CuSO_4$, $FeCl_3$, $FeSO_4$, etc.) were used with a concentration range of 1–8 kg/m$^3$. The temperature of the reaction mixture was raised using a hot plate to the desired value by a PID temperature controller, which was fitted in one of the necks through the thermocouple. The raising of the temperature of the wastewater from ambient to 95 °C took about 30 min ($t_h$). A vertical water-cooled condenser was attached to the middle neck of the reactor to prevent any loss of vapour. The time taken to attain the desired temperature is the heating time, $t_h$. Further heating is done at the desired temperature and the time is measured by subtracting $t_h$ from the total time. Thus, $t_h$ is taken as zero for further heating. The reaction mixture was agitated using a magnetic stirrer. Initial experimental runs with different chemicals were conducted for 4 h at 95 °C and the reactor samples (5 ml) were taken at periodic intervals for the measurement of COD, color and pH. The samples were centrifuged to decant the supernatant. Except for initial runs, rest of the experiments, at temperatures higher than ambient temperature were carried out for 30 min reaction period, after attaining the desired temperature and then allowed to settle for 2 h. Then, the treated effluent including sludge was rapidly mixed and the slurry so formed was used to study the settling and filterability characteristics of the sludge. The effects of the reaction parameters, such as temperature, catalyst mass loading and reaction time were studied. The residue obtained after treatment using the best catalyst was assayed for its C, H, N, S and ash content.

#### 2.4.2. Jar test

A series of six graduated glass cylinders were used for the experiments. A 5 min rapid mixing (RM) at 80 rpm was followed by 30 min slow mixing (SM) at 40 rpm and 30 min settling. The objective of this experiment was to study the settling characteristics as well as estimation of COD and color in the final clear liquid.

## 3. Results and discussion

The effluent containing dyes when released into water bodies are visual even in small quantities due to their brilliance. As biological activities are incapable of removing dyes from effluent on a continuous basis, physicochemical methods have been suggested to be effective [25] only if the effluent volume is small. Adsorption and coagulation produce large quantity of residue. It is, therefore, desirable to use process which are cost effective as well as produce less inorganic sludge.

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

| pH | pH reduction after treatment with | | | | | | Without catalyst |
|---|---|---|---|---|---|---|---|
| | $CuSO_4$ | $FeSO_4\cdot16H_2O$ | $FeCl_3$ | CuO | ZnO | PAC | |
| 2 | 1.96 | 2.08 | 1.75 | 3.07 | 2.98 | 1.98 | 2.00 |
| 4 | 3.94 | 3.68 | 3.64 | 5.30 | 3.66 | 3.9 | 3.98 |
| 6 | 5.84 | 5.92 | 5.52 | 8.57 | 5.52 | 5.64 | 6.10 |
| 8 | 7.97 | 7.92 | 7.72 | 9.17 | 7.94 | 7.82 | 8.00 |
| 10 | 9.56 | 9.24 | 9.40 | 9.95 | 9.86 | 9.81 | 9.98 |
| 12 | 11.24 | 10.2 | 11.55 | 11.65 | 11.64 | 11.65 | 11.99 |

The experiments were planned to treat the undiluted dyestuff wastewater ($COD_0 = 5744$ mg/l) by catalytic thermal treatment followed by coagulation. During thermolysis the catalyst used were $CuSO_4$, $FeSO_4$, $FeCl_3$, CuO, ZnO and PAC whereas the coagulants used in the subsequent process include commercial alum, aluminum potassium sulphate, PAC, $FeCl_3$ and $FeSO_4$. The two processes (thermolysis and coagulation) were optimized with respect to the process parameters, such as pH, catalyst/coagulant concentration, etc.

### 3.1. Catalytic thermal treatment (thermolysis)

#### 3.1.1. Effect of pH

The experiments on the effect of $pH_0$ on COD and color reduction of dyeing wastewater were conducted at 95 °C for 4 h with a catalyst mass loading of 2 kg/m$^3$. The initial pH was varied during the experiments in the range of 2–12. After each experimentation, a portion of the treated effluent was taken out and centrifuged. The clear liquid was separated and its COD as well as color was measured. The results are shown in Fig. 1(a) and (b). Fig. 1(a) shows a slow increase in percent COD reduction initially from pH 2 to 4, which rises at a faster rate between pH 4 and 8. From pH 8 to 12 there has been almost no increase in COD reduction. This trend is uniformly followed by all the catalysts. $CuSO_4$ happens to be the best amongst the other catalysts showing a maximum percent COD reduction of about 52.16% at pH 8. The final pH after the treatment was also measured and a decrease in pH was observed in all the cases except the effluent treated by CuO. The results are presented in Table 2. The reasons for these phenomena may be attributed to the dissociation of sulphate/chlorides into corresponding ions and thereby forming $H_2SO_4$/HCl which are responsible for the reduction of the pH of the solution. Carboxylic acids may also have formed out of the degradation of high molecular weight hydrocarbons.

When the initial effluent was heated without catalysts, under the identical conditions as mentioned above, the maximum COD reduction obtained at pH 8 was 12.6%. The $pH_0$ adjustment of the dyeing wastewater has been found to reduce the COD as well as color of the order of less than 10% mainly in the pH range of 8–12.

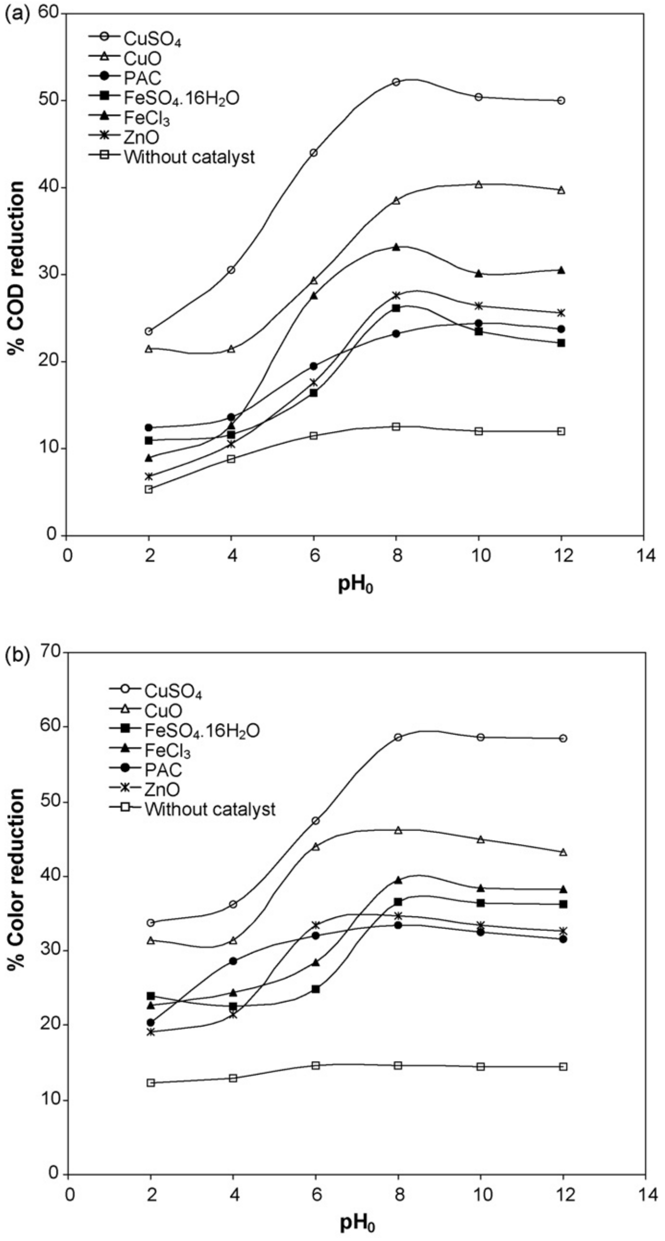

Fig. 1. (a) Effect of $pH_0$ on COD reduction of the dyeing wastewater by thermolysis. $COD_0 = 5744$ mg/l, $T_R = 95\,^{\circ}C$, $P$ = atmospheric, $t_r = 4$ h and $C_w = 2\,kg/m^3$. (b) Effect of $pH_0$ on color reduction of the dyeing wastewater by thermolysis. $COD_0 = 5744$ mg/l, $T_R = 95\,^{\circ}C$, $P$ = atmospheric, $t_r = 4$ h, $C_w = 2\,kg/m^3$ and color = 3840 Pt–Co.

The effect of $pH_0$ on percent color reduction of dyeing wastewater is shown in Fig. 1(b). A similar trend as noted in Fig. 1(a) has been observed with $CuSO_4$ giving the best color reduction of 58.71% at pH 8.

### 3.1.2. *Effect of catalyst mass loading*

Fig. 2 shows the effect of catalyst mass loading on COD as well as color reduction of dyeing wastewater during catalytic thermal treatment at 95 °C, pH 8 and 4 h duration. The percent reductions of COD and color increased with the increase in catalyst mass loading from 1 to 5 $kg/m^3$. With further increase in catalyst mass loading from 5 to 8 $kg/m^3$, there has been no increase in percent COD as well as color reduction. The catalyst concentration of 5 $kg/m^3$ may thus be considered as the optimum concentration at the given operating conditions. The maximum COD and color reduction obtained at 5 $kg/m^3$ catalyst concentration were 66.85% and 71.4%, respectively.

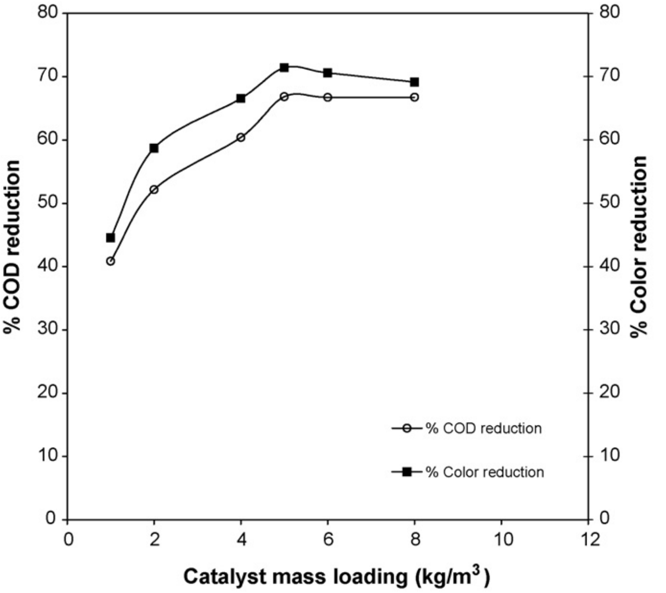

Fig. 2. Effect of catalyst (copper sulphate) concentration on COD and color reduction of the dyeing wastewater. $COD_0 = 5744$ mg/l, $t_r = 4$ h, $P$ = atmospheric, $pH_0$ 10 and color = 3840 Pt–Co.

### 3.1.3. *Effect of temperature*

The results are presented in Fig. 3. The percent reductions of COD and color increased as the temperature increased from 60 to 95 °C. The percent COD reduction (maximum) at 95 °C obtained was 66.85%, at which the percent color reduction was 71.4%.

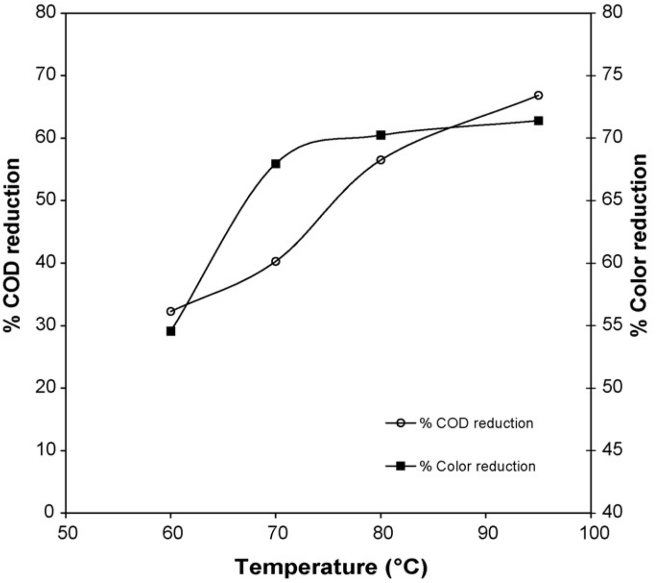

Fig. 3. Effect of temperature on COD and color reduction of the dyeing wastewater of catalytic thermolysis. $COD_0 = 5744$ mg/l, $t_r = 4$ h, $P$ = atmospheric, $pH_0$ 10, $C_w = 5\,kg/m^3$ and color = 3840 Pt–Co.

Since the experiment was conducted at atmospheric pressure (in a glass reactor under reflux), the reaction temperature was not exceeded beyond 95 °C.

Chen et al. (2003) observed similar phenomena where the reduction in COD was observed during the pre-heating period in absence of oxygen. Heating the reactor to the desired reaction temperature took 1–2 h time, when the textile mill wastewater was heated from 20 to 150 °C. The percent reduction of COD was found during this period to be much less than 1%. As the temperature increased, the COD reduction due to heating increased and reached to about 18% at 200 °C. The increase in COD reduction during heating was also observed for textile desizing wastewater by others [26,27]. The phenomena of reduction in COD during heating period, in the absence of oxygen, has been indicated to be caused by the loss of volatile organic compounds with continuous stirring as well as from thermal decomposition [28].

### 3.1.4. TGA and DTA of sludge

The thermal degradation data (TGA, DTA and DTGA) were analyzed using the kinetic models available in the literature [29–31]. The first order irreversible reaction rate constant, $k$, can be written as [32]:

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

Eq. (1) may be rewritten in the form:

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

or

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

The $\Delta H$, $\Delta G$ for the active complex formation and $\Delta S$ can be calculated at DTG peak temperature using the equations:

$$E = \Delta H + RT \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

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 $P = \exp(\Delta S/R)$ [29]. This factor allows to estimate 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 [29,31] are given in Table 3.

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 |
| $A$ (min$^{-1}$) | 1.525 | 0.180 |
| $E$ (kJ/mol) | 29.205 | 29.374 |
| $k$ (min$^{-1}$) | 0.077 | 0.009 |
| $\Delta S$ (J/(mol K)) | −264.60 | −264.90 |
| $\Delta H$ (kJ/mol) | 19.39 | 19.56 |
| $\Delta G$ (kJ/mol) | 331.66 | 332.18 |
| $P_s$ ($\times 10^{14}$) | 1.50 | 1.45 |
| $r^2$ | 1 | 0.614 |

Thermogravimetric analysis of sludge provides useful information on the kinds of materials present in it and their detection at various temperatures. To collect information on such materials, sludge sample was heated at a rate of 10 °C/min under purified air with a rate of 200 ml/min. The TGA profile presented in Fig. 4(a) shows the endothermic weight loss of 7.3% in the temperature range of 100–200 °C. This is possibly due to dehydration of sample along with the removal of organic volatiles. A weight loss of 24.98% occurs endothermically in the temperature range of 200–280 °C. The peak rate of weight loss at $T_{max} = 255$ °C is 0.5 mg/min. The endothermic weight loss with heat requirement of 526 MJ/kg suggests the involvement of energy in the oxidation of low C and H containing organic substance followed by their removal. As absorption of energy is relatively high, a partial oxidative decomposition of high concentration of dye may also be considered along with low hydrocarbons. The weight remains constant on further increment of temperature upto 417 °C and then a sharp weight loss of 5.23% in a very narrow temperature range of 417–420 °C with a peak rate of 2.4 mg/min occurs. This weight loss may possible be due to further decomposition of remainder of decomposed dye or decomposition of dye coordinated with metal ions present in the sludge. The complete decomposition of such metal coordinated dye occurs above 770 °C and continues till the formation of metal oxide at about 1000 °C. After thermolysis the dye coordinated with metal ions might have broken down into organics and metal ions. The organics part has been reduced as shown in the TGA curve between 200 and 700 °C in Fig. 4(a). The metal part got oxidized between 700 and 1000 °C (Fig. 4a). Since the oxidation of metal-to-metal oxides is neither an exothermic nor an endothermic process, no such peak, therefore, is found in Fig. 4(b). The existence of an endothermic peak between 700 and 1000 °C possibly indicates the heat requirement for the decomposition of dye (organics) coordinated with metal ions, which could not be decomposed earlier. The residue due to metal oxide obtained at this temperature is 8.5%.

Fig. 4(b) shows the thermogravimetric trace of the dyeing wastewater was done after drying the wastewater at 45 °C for 36 h in an oven. The TGA curve shows only about 3.86% decrease in weight upto 110 °C from 110 to 791 °C and there has been very little weight drop of 11.57%, which has been gradual all along. From 791 °C onwards and upto 933 °C, a percent weight loss of the order of 65.84% at a rate of 1.0 mg/min (at 907 °C), was recorded. This is the maximum weight loss

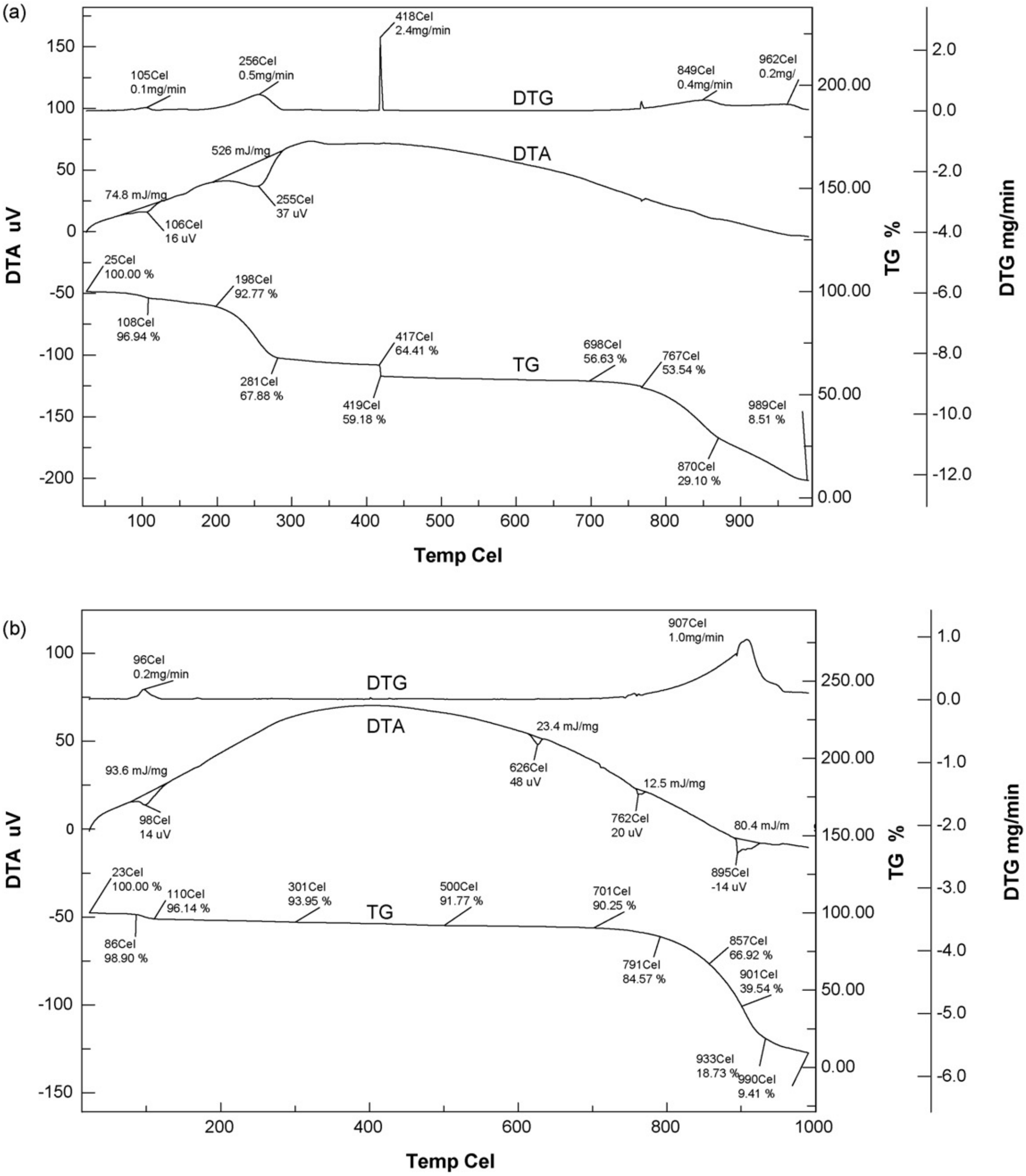

Fig. 4. (a) TGA–DTA of dyeing residue. Sample weight, 10.36 mg; atmosphere, air at 200 ml/min. (b) TGA–DTA of dyeing wastewater. Sample weight, 10.26 mg; atmosphere, air at 200 ml/min.

observed during the entire process. This may once again be attributed to the oxidation of metal ions coordinated to dye present in the dyeing wastewater.

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

A faster settling of the treated effluent is desirable. The settling characteristics are strongly affected by the treatment parameters [33–36]. Various methods have been suggested for calculating compression zone height in continuous thickeners from the batch sedimentation data [36–40]. The method proposed by Richardson et al. [33] to design a continuous thickener based on single batch sedimentation test seems to be the most appropriate. The settling of an effluent is strongly influenced by its pH.

In order to see the effect of pH on the settling characteristics of the precipitate obtained after thermolysis using $CuSO_4$ as catalyst, three different pH, i.e., pH 6, 8 and 10 were maintained in a 100 ml measuring cylinder. The settling rate was observed to be higher for pH 6 than that of pH 10. This may probably be due to the bigger size and more compact aggregated flocs. 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 [33]. The sedimentation velocity ($u_c$) was found as the slope

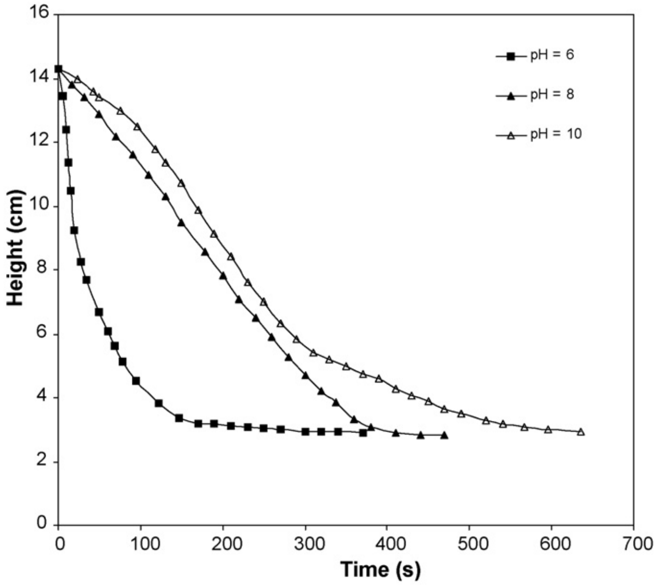

Fig. 5. Settling characteristics of sludge in the treated effluent at ambient temperature using $CuSO_4$ as catalyst. $COD_0 = 5744$ mg/l, $P$ = atmospheric and $C_w = 5\ kg/m^3$.

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 6, 8 and 10 were found to be 29 kg/m$^3$ in each case. The maximum value of $[\{(1/C) - (1/C_u)\}/u_c]$ were thus determined as $0.136 \times 10^3$, $0.039 \times 10^4$ and $0.044 \times 10^4$ at pH 6, 8 and 10, respectively. Using these values, the area of the sedimentation tank for any effluent flow rate can thus be calculated as

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

From Fig. 5, it can also be seen that the settling rate is very fast during the zone settling region at pH 6. The settling rate becomes very slow, as the solids settling enter compression region. It is also seen that the compression region for the pH 6 settled sludge is much denser than that for the pH 10 settled sludge.

### 3.1.6. Filterability

Filtration is one of the steps used to clarify the treated effluent. The filterability studies are important to decide upon the optimal treatment process parameters which could produce a treated effluent with flocs having faster filtration.

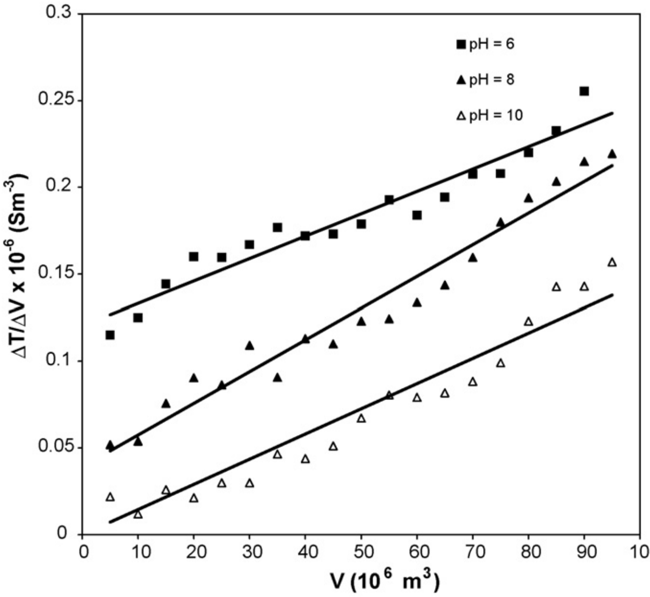

Fig. 6. Filterability characteristics of sludge in the treated effluent at ambient temperature using $CuSO_4$ as catalyst. $COD_0 = 5744$ mg/l, $P$ = atmospheric and $C_w = 5\ kg/m^3$.

The gravity filtration of the slurry was carried out at room temperature on an ordinary filter paper supported on a Büchner funnel, under constant pressure filtration. 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. It is evident that the filterability of the treated effluent gets improved with an increase in the $pH_0$. 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 [40]:

$$\frac{dt}{dV} = k_p V + \beta \tag{6}$$

where

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

and

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

where $k_p$ (slope) and $\beta$ (intercept) are determined by the plot of Eq. (6) as shown in Fig. 6. The 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 ($pH_0$)[a]

| $pH_0$ | $k_p$ ($\times 10^{-10}$ s/m$^6$) | $\beta$ ($\times 10^{-6}$ s/m$^3$) | $C$ (kg/m$^3$) | $\mu$ ($\times 10^3$ PaS) | $\alpha$ ($\times 10^{-10}$ m/kg) | $R_m$ ($\times 10^{-8}$ m$^{-1}$) |
|---|---|---|---|---|---|---|
| 6 | 0.125 | 0.12 | 6.34 | 1.96 | 0.058 | 0.563 |
| 8 | 0.178 | 0.04 | 6.96 | 1.987 | 0.075 | 0.185 |
| 10 | 0.138 | 0.00 | 6.10 | 1.951 | 0.067 | 0.000 |

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

Table 5
Elemental analysis of dyeing wastewater and precipitate formed as a result of thermal pretreatment with $CuSO_4$

| | Material | | | |
|---|---|---|---|---|
| | C (%) | H (%) | N (%) | S (%) |
| Dyeing wastewater | 0.114 | 17.57 | 0.00 | 0.00 |
| Precipitate | 3.083 | 3.287 | 0.00 | 0.00 |
| Supernatant | 1.53 | 0.05 | 0.00 | 0.00 |
| Indian coal | 4.887 | 5.01 | 0.80 | 1.70 |

Typical values of specific cake resistance ($\alpha$) for different kind of sludges are given by Barnes et al. [41] for pulp and paper mill effluent by Garg et al. [23] and for alcohol distillery waste by Lele et al. [42].

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

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

The C, H, N, S and proximate analyzes of the settled precipitate and the dyeing wastewater, respectively are presented in Tables 5 and 6. The elemental analysis shows that there is an increase in carbon and hydrogen composition in the precipitate.

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 a considerably lower ash content in the precipitate than that in the dyeing wastewater and a considerably higher fixed carbon content in the precipitate than that in the dyeing wastewater.

## 3.2. Coagulation

The combined thermolysis/coagulation treatment process was performed in two successive steps where thermolysis was followed by coagulation. The thermolysis and coagulation studies were also conducted independently on fresh samples. The chemical coagulation using various coagulants such as commercial alum, aluminum potassium sulphate, PAC, $FeCl_3$ and $FeSO_4$ were studied as a function of initial pH ($pH_0$). The results are presented in Figs. 7 and 8 as COD and color reductions, respectively. It can be seen that the (maximum) COD and color reductions of 34.57% and 60.33%, respectively, were obtained using commercial alum as coagulant at pH 4 and a coagulant concentration of 3 kg/m$^3$. The effect of pH on the dye reduction could be explained by the combined effect of (i) the ionization of amino, hydroxy and sulpho groups in the dye molecules which increases with pH in acidic range, (ii) the decrease in the concentration of dissolved hydrolysis products [43] and (iii) Al-based coagulants show better results than that of Fe-based coagulants. This may be attributed to dominance of compounds having positive charge. $Fe^{3+}$ has more coordination than $Al^{3+}$ due to the presence of unfilled d-orbitals. The cationic compounds of the hydrolyzed dyes act as a good reagents and electron acceptors from $Al^{3+}$. PAC is found to be active at pH 10. The multivalent Al cations of PAC coordinate with the anions present in the effluent and result in complexation. The gel structure of the

Table 6
Proximate analysis (moisture-free basis) of dyeing wastewater and precipitate formed as a result of thermal pretreatment with $CuSO_4$

| Material | Ash (%) | Volatile matter (%) | Fixed carbon (%) |
|---|---|---|---|
| Dyeing wastewater | 91.1 | 5.74 | 0.09 |
| Precipitate | 47.0 | 31.0 | 10.0 |

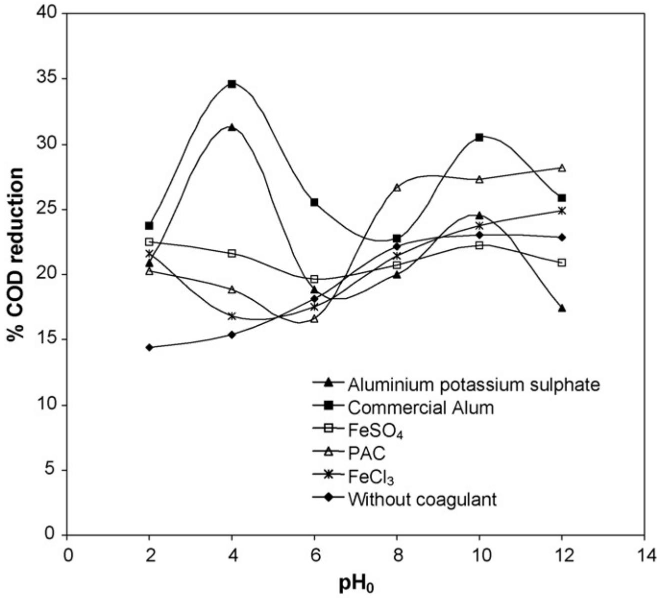

Fig. 7. Effect of $pH_0$ on COD reduction of the dyeing wastewater by using different coagulants. $COD_0 = 5744$ mg/l, $t_r = 1$ h, $P$ = atmospheric and $C_w = 5$ kg/m$^3$.

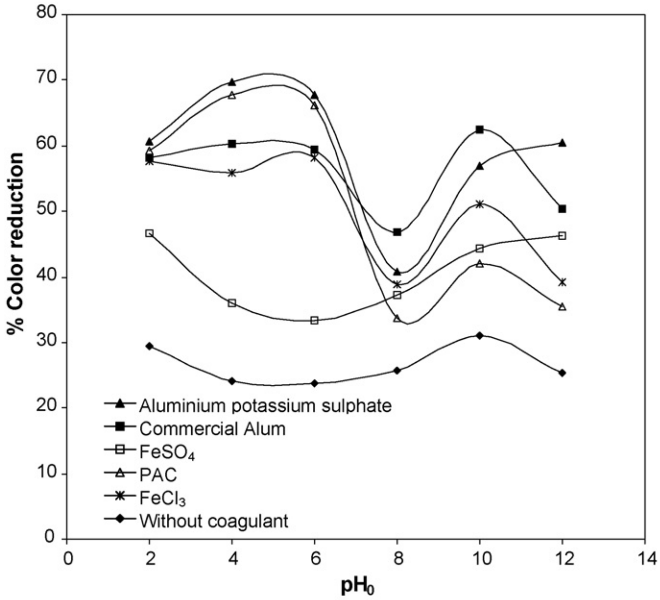

Fig. 8. Effect of $pH_0$ on color reduction of the dyeing wastewater by using different coagulants. $COD_0 = 5744$ mg/l, $t_r = 1$ h, $P$ = atmospheric, $C_w = 5$ kg/m$^3$ and color = 3840 Pt–Co.

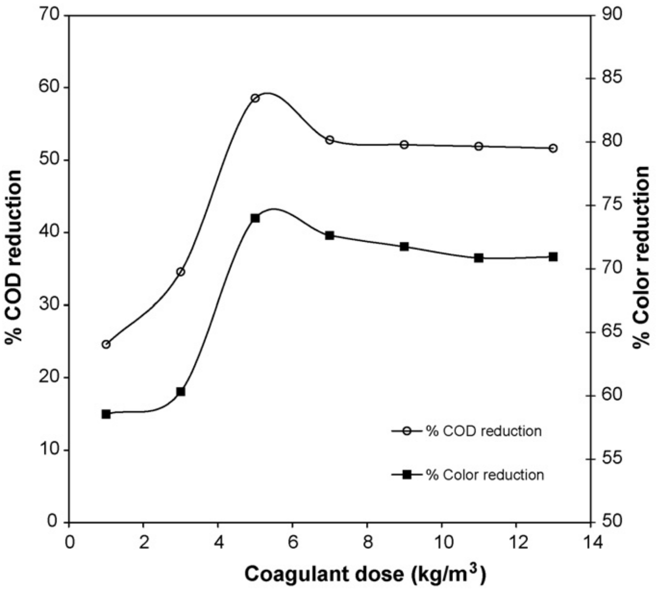

Fig. 9. Effect of coagulant (commercial alum) concentration on COD and color reduction of the dyeing wastewater. $COD_0 = 5744$ mg/l, $t_r = 1$ h, $P$ = atmospheric, $pH_0$ 4 and color = 3840 Pt–Co.

PAC also enmeshes the organics present in dyeing waste. Thus, the complexation followed by precipitation and the capture of organic in the gel are responsible for both COD and color reduction by PAC as compared to those obtained with $FeSO_4$ and $FeCl_3$. Figs. 7 and 8 reveal that the optimum $pH_0$ for COD and color reduction for all the five coagulants are different. Some are better active in acidic medium whereas the other are active in alkaline medium. The reduction of dissolved organics during coagulation with metal salts at different pH values follow two different mechanisms. At low pH the effluent containing anionic organic molecules coordinate with metal cation and form insoluble metal complexes at higher pH (alkaline range). The organics are adsorbed on to pre-form flocs of metal hydroxides and get precipitated. The combined effect of two mechanisms is that the reduction of dissolved organics with different functional groups can occur at different pH. The maximum COD and color removal may thus occur at a pH where the combined effect of both the mechanisms is high.

### 3.2.1. *Effect of coagulant doses*

During coagulation, the effluent is gently mixed which initiates floc formation, complexation and adsorption of organics resulting in precipitate formation and settling down of insoluble solids. In order to determine the optimum coagulant dose of the best coagulant (commercial alum) from amongst the various coagulant used, the effect of coagulant dose (1–13 $kg/m^3$) at optimum pH 4 was studied. The results are shown in Fig. 9 as percent COD as well as color reduction. It is clear that the reduction in both color and COD increases as the dose is increased from 1 to 5 $kg/m^3$, giving a maximum COD reduction of 58.57% and a color reduction of 74%. With further increase in coagulant dose, the percent reduction in COD and color do not change substantially. Thus, a coagulant dose of 5 $kg/m^3$ is assumed to be an optimum value under the prevailing treatment conditions. In coagulation process, color degradation is observed after effective COD reduction. Some metal complexes may be formed during coagulation [44]. The assay of commercial alum used for coagulation experiments show a (maximum) concentration of aluminum (as Al) of 16,289 ppm, followed by potassium content (as K) of 42 ppm, hydrogen (as $H_2$) of 0.49% and sulphur (as S) of 2.33%.

It has been seen that the addition of coagulants reduces the pH of the effluent. The pH reduction was found to be high with $FeSO_4$ and $FeCl_3$. This indicates that if Fe-based coagulants are used, higher amount of alkali is required to be added to neutralize the effluent during disposal. This further indicates that commercial alum is better from the point of view of post-coagulation treatments.

### 3.2.2. *Thermolysis accompanied with coagulation*

The treatments carried out using thermolysis show a maximum of COD and color reduction of 66.85% and 71.4% at pH 8 with catalyst concentration of 5 $kg/m^3$ using $CuSO_4$, whereas maximum COD and color reduction during coagulation using commercial alum were 58.57% and 74%, respectively at a coagulant dose of 5 $kg/m^3$ at pH 4. In order to see the effect of the combined treatment by thermolysis as well as coagulation, the thermolysis studies were conducted as before and the supernatant obtained was subsequently treated with the coagulant at optimized conditions mentioned above (except the coagulant concentration 2 $kg/m^3$). An overall reduction of COD and color of 89.91% and 94.4%, respectively as shown in Fig. 10, were obtained. The results thus indicate that the combined treatment of thermolysis followed by coagulation is the most effective process for reduction of COD as well as color at a lower coagulant concentration which would lead to lesser production of inorganic sludge and thereby reducing the sludge disposal problem.

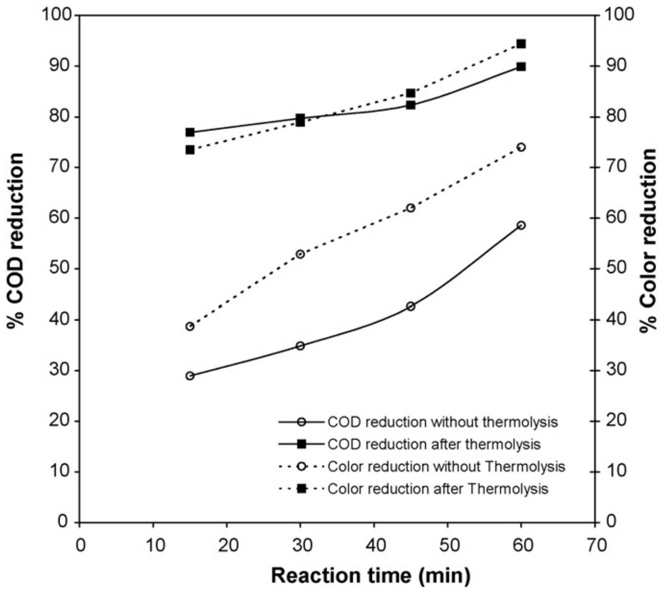

Fig. 10. Reduction of COD and color with time by coagulation. Coagulant = commercial alum, $pH_0$ 4, $T_R = 18\,^{\circ}C$ and $C_w = 2\,kg/m^3$.

## 4. Conclusion

The treatment of dyeing wastewater of a cotton textile mill for the reduction of COD and color was carried out using catalytic thermal treatment (thermolysis) with/without coagulation. During thermolysis of the fresh effluent, copper sulphate was found to be the best catalyst giving 66.85% COD as well as 71.4% color reduction, respectively, with a catalyst concentration of 5 kg/m$^3$ at pH 8 and 95 °C temperature. The settle ability as well as filterability of the slurry obtained are strongly influenced by pH. The slurry obtained after catalytic thermolysis at pH 6 settled much faster than the one obtained at pH 10. During treatment by coagulation process, commercial alum is found to be the best coagulant among the other coagulants tested, resulting in 58.57% COD and 74% color reduction, respectively, at pH 4 and a coagulant concentration of 5 kg/m$^3$. Coagulation of the supernatant obtained after catalytic thermolysis at above-mentioned operating conditions (except at a lower coagulant concentration of 2 kg/m$^3$) resulted in overall reduction of about 89.91% COD and 94.4% color.

Thermolysis followed by coagulation is, therefore, the most effective process in removing COD as well as color at a lower dose of coagulant. The sludge thus produced would contain lower inorganic mass coagulant and, therefore, less amount of sludge containing dye coordinated metal ions has to be disposed.

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