Treatment Of Pulp And Paper Mill Effluent Using Physico - Chemical Processes

Yadav B.R. & Garg A.

ABSTRACT

The present study was aimed to treat wastewater (pH = 7.23, chemical oxygen demand (COD) = 460 mg/l and total organic carbon (TOC) = 123 mg/l) from an agri-residue based pulp and paper mill using physico-chemical processes (such as coagulation and adsorption). For coagulation studies, $FeCl_3$ and alum were used, whereas adsorption was performed with activated carbon and 13 X molecular sieve zeolite. At an optimum $FeCl_3$ dose (= 200 mg/l) and solution pH of 5.0 (adjusted by CaO), a 65 % reductions in COD and TOC were found. An overall color removal of 97 % was also achieved under these conditions. These results were marginally better than those obtained when NaOH was used for pH adjustment (~ 3 % more COD and TOC reductions). Addition of alum showed lesser COD and TOC reductions (58 % and 51 % respectively) and same color removal to that obtained with $FeCl_3$. Treatment of the wastewater by adsorption using both the adsorbents were almost the same (at adsorbent dose = 500 mg/l and pH = 7.23; COD reduction = 58 % and TOC removal = 43 %). The detailed results obtained from characterization of sludge and settling are presented in the paper.

Introduction

Pulp and paper mills are one of the most water and energy intensive industries. During paper production, large amount of wastewater is generated that requires safe disposal. Typically in India, around 75% of the total freshwater supplied to pulp and paper industries emerge as wastewater[1]. In comparison to the other countries (like USA, UK), fresh water requirement in Indian pulp and paper industry is quite high (150-200 m^3/tonne of product). The effluent from pulp and paper industries if discharged without any treatment may cause slime growth, thermal impact, scum formation, color problem and deposition of toxic substances in natural water bodies[2]. The effluent from these industries may contain high levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and color producing compounds. However, the wastewater characteristics depend upon the type of unit process, raw material and management practices[2].

In view of low BOD_5/COD ratio of pulp and paper mill effluent, direct application of conventional biological processes is difficult. Therefore, chemical or physico-chemical processes are suggested as pretreatment steps so that the pre-treated wastewater could be treated easily by biological processes. In the present work, coagulation and adsorption processes are evaluated for treatment of the wastewater generated from a small scale agri-residue based pulp and paper mill.

Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Powai, Mumbai, -400076 INDIA

Previous studies have found copper, iron and aluminum salts as effective coagulants for pulp and paper mill effluent[3,4]. However, copper salts will be preferred only if chemical oxidative processes (such as wet oxidation) have to be employed as post treatment step. In these processes, copper ions act as an oxidation catalyst and helps in reducing the severity of oxidation conditions[5]. Afterwards, the toxic copper ions are separated from the treated effluent.

Aluminum and iron salts were used as coagulants for the removal of total carbon, color and turbidity from a mechanical pulping based pulp and paper mill effluent (total carbon of 1065 - 3560 mg/l)[6]. After the treatment, overall reductions of 88, 90 and 98 % in total carbon, color and turbidity, respectively were obtained.

In an another study, alum removed upto 88% color from a pulp and paper mill (using pine softwood as a raw material) effluent (COD = 260 mg/l, suspended solids = 10 mg/l, color = 1150 Pt-Co, pH = 6.0 to 8.0)[7]. Addition of clay improved the color efficiency and settling of sludge when used in conjunction with alum dose.

Srivastava et al.[8] performed pulp and paper mill (agri-residue based small paper mill) wastewater (pH = 5.61 - 9.30, COD = 1260 - 72000 mg/l) treatment in two steps: coagulation followed by adsorption. Polyaluminum chloride and bagasse fly ash (a waste material from sugar industries) were used as coagulant and adsorbent, respectively, in the two steps. The overall reductions in COD and color were in the range of 84 - 96 % and 91 - 98 %, respectively.

The coagulation process is generally governed by two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and capturing of colloids in an amorphous hydroxide precipitate (also called 'sweep flocculation'). The relative importance of these mechanisms is a function of pH and coagulant dose[9].

The aim of the present study was to determine the effectiveness of coagulation and adsorption processes for a mixed wastewater stream generated from a small scale pulp and paper mill (using agri-residue based raw materials). During coagulation process, the effect of NaOH and CaO (chemicals used for pH adjustment) on COD, TOC and color were observed. Adsorption studies were carried out with two adsorbents: activated carbon and 13X molecular sieve zeolite. The optimum pH and adsorbent dose determined for activated carbon and the results were compared with 13X molecular sieve zeolite under similar conditions. Apart from this, the settling time of the sludge in coagulated wastewater was also recorded. Besides, the sludge produced after coagulation process was quantified and characterized by conducting proximate and elemental analyses.

Material And Methods: Wastewater and chemicals

The wastewater for the study was collected from an agri-residue based pulp and paper mill located in the state of Maharashtra, India. The paper mill uses jute rags and waste gunny bags as raw materials for pulping process and manufactures color tissue paper and news print paper as final products. The wastewater obtained from the mill was a mixture of all wastewater streams generating from different unit processes. The effluent was stored under 4°C temperature to maintain its original characteristics.

All the chemicals used in experimental runs were of analytical grade (A.R.) and purchased from Merck chemicals, Mumbai, India. 13X Zeolite based catalyst was purchased from Zeolite and Allied Products, Mumbai, India.

Coagulation process

Coagulation runs were carried out in a jar apparatus (Cintex Floculatior, Cintex Industrial Corporation, Mumbai) at ambient conditions. The unit was equipped with mechanical stirring device for six beakers. During the runs, 500 ml of wastewater was added to the glass beakers (capacity of each beaker = 1000 ml). In order to avoid effect of temperature on the coagulation process, the wastewater sample was removed from the refrigerator 2 h prior to each run so that the sample could achieve ambient temperature. Predetermined amount of alum or $FeCl_3$ was fed to the reactor in solution form (coagulant concentration in the solution = 100 g/l). pH of the wastewater was increased by adding NaOH (1 M)/CaO (1.78 M) solution in the runs carried out at pH higher than that of wastewater (achieved after addition of the coagulant), whereas 1.8 M H_2SO_4 was used to decrease the solution pH upto desired level (below the pH of wastewater).

The solution was then subjected to rapid mixing for 1 min (at a stirrer speed of 120 rpm) followed by a 15 min slow mixing (at 40 rpm). The flocs formed during slow mixing were allowed to settle for 45 min. After settling a small volume of supernatant was removed from the top and analyzed for pH, COD, TOC and color.

Adsorption process

The adsorption process was performed at ambient temperature in an orbital shaker cum incubator (supplied by Trishul Equipments, India). During the test, 50 ml of wastewater was added in five conical flasks (each one having a capacity of 100 ml). In each flask, different amounts activated carbon was added. After optimizing the adsorbent dose, pH of the wastewater was adjusted by adding 1 M NaOH or 1.8 M H_2SO_4 (whatever the case may be). The flasks were then shaked at 120 rpm for 1 h duration. The treated samples were filtered by passing through a Whatman filter paper (pore size 1.2 μm) and the filtrate was analyzed for different parameters (such as pH, COD and TOC).

Analytical methods

pH of the wastewater was measured using a digital pH meter (Polmon, LP-1395, India). COD was determined by standard closed reflux method using a COD reactor (Hach, DRB200 COD reactor, USA)[10]. TOC determination was done using a Shimadzu TOC analyzer (TOC-VCSH, Japan). The color of the untreated and treated wastewater was measured at 465 nm wavelength using a UV-visible spectrophotometer (Thermoelectron Corporation, GENESYS 20, USA). Total solids in the effluent were determined by drying the wastewater sample in an oven at 105-110 °C temperature till a constant mass was reached. To fractionate total solids, a wastewater sample was filtered through a Whatman filter paper of 1.2 μm pore size. For suspended solids, the residue left at the filter paper was dried in an oven at 105 - 110 °C for 24 h and the mass of residue retained on the filter paper was calculated. Other parameters like alkalinity, chloride and sulphate were determined using standard procedure[10]. Proximate analysis of the sludge sample was conducted as per standard method outlined in IS 1350 (1984)[11]. Elemental analysis was carried out in a CHNS analyzer (Flash EA1112 series, Therma Finnigan, Italy).

Results And Discussion : Wastewater characterization

The physical and chemical characteristics of the wastewater are presented in the Table 1. The wastewater was slightly alkaline (pH = 7.23) and pale yellow in color. COD of the wastewater was low (460 mg/l) since it was a mixture of various industrial streams generating from different unit operations. This value is still higher than 350 mg/l that is prescribed by CPCB for large scale pulp and paper mills[1]. BOD_5 and TOC of the effluent were 98 and 123 mg/l respectively. The effluent contained total solids (TS) concentration of 522 mg/l out of which around 85 % were total dissolved solids (TDS) and only 15 % were total suspended solids (TSS). Among other parameters, alkalinity, chlorides and sulphates were 170 mg/l as $CaCO_3$, 57.4 mg/l and 93.68 mg/l, respectively. The overall characteristics reveal that a low cost and simple treatment should be given to the wastewater before its final disposal.

TABLE 1
Physical And Chemical Characteristics Of Pulp And Paper Mill Wastewater

S. No.	Parameter	Value (mg/l)
1.	pH*	7.23
2.	Color*	Pale yellow
3.	COD	460
4.	BOD_5	98
5.	TOC	123
6.	TS (Total solids)	522
7.	TDS (Total dissolved solids)	442
8.	TSS (Total suspended solids)	56
9.	Alkalinity**	170
10.	Chloride	57.4
11.	Sulfate	93.68

* All values are in mg/l except pH and color
** Alkalinity is expressed in mg/l as $CaCO_3$

Coagulation studies

As mentioned earlier coagulation

studies on the pulp and paper mill effluent were conducted using two conventional coagulants, namely alum and ferric chloride.

Using $FeCl_3$ as a coagulant

(a) Optimum coagulant dose

The effect of $FeCl_3$ dose on COD and color removals of wastewater was determined by performing runs at different coagulant concentrations varying from 50 to 500 mg/l (i.e. 50, 100, 200, 300, 400 and 500 mg/l). These doses were added to each of six beakers containing 500 ml of wastewater. During the runs, pH of the solution was maintained within 5.5 - 6 by using appropriate volume of 1 M NaOH solution. After adding different amounts of the coagulant, pH of the wastewater was found in the range of 2.66 6.22 (the lowest pH value for 500 mg/l coagulant dose and the highest value for 50 mg/l dose). Different concentrations of $FeCl_3$ (50, 100, 200, 300, 400 and 500 mg/l) were added to different beakers having 500 ml of wastewater. This can be seen from Figure 1 that a coagulant dose of 200 mg/l showed the maximum COD and color reductions from the effluent (58 % and 95 % respectively). Beyond this optimum dose, any addition of coagulant did not increase any further reductions in COD and TOC values, however the treated wastewater was found to be more colored at high coagulant dose. This may be attributed to the presence of more Fe^{3+} ions in the solution. It was also found that COD and color removals were insignificant at coagulant dose smaller than 200 mg/l (At $FeCl_3$ dose = 50 mg/l, final COD = 427 mg/l and color reduction = 10 %; At $FeCl_3$ dose = 100 mg/l, final COD = 395 mg/l and color reduction = 17 %).

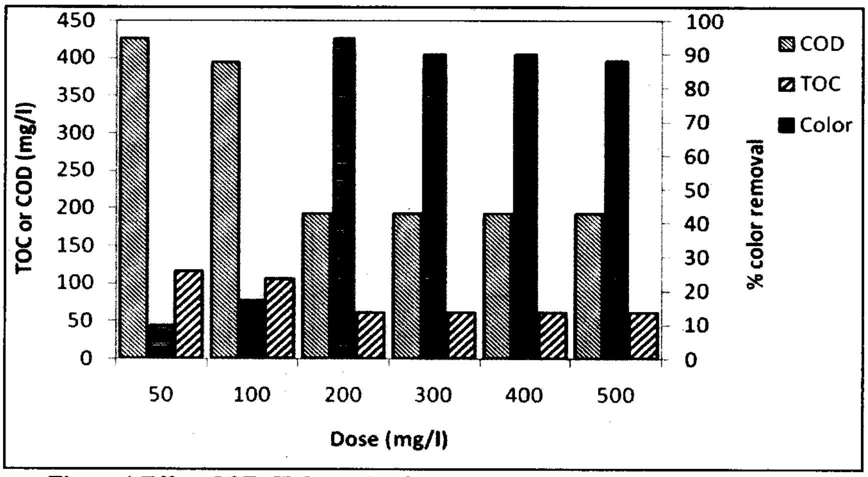

Figure 1 Effect Of $FeCl_3$ Dose On COD And TOC (Initial COD = 460 mg/l, TOC = 123 mg/l, pH = 7.23)

(b) pH optimization

To obtain the optimum pH, the coagulation studies were performed with $FeCl_3$ over a wide pH range of 4.23 - 9. In all the runs, $FeCl_3$ dose was maintained at 200 mg/l. The addition of metal coagulant reduced pH of the wastewater from 7.23 (original) to acidic region (i.e. pH = 4.23). The pH of the coagulant containing wastewater was increased by adding already prepared NaOH or CaO solutions. The amount of chemicals required to increase the pH upto certain levels are presented in Table 2. This can be seen that the much higher amount of CaO (almost twice or more than NaOH) was required to raise the pH. In both the cases, a pH value of 5.0 exhibited the best COD and color removal efficiencies (Figures 2 and 3). With NaOH, a final COD of the wastewater was reduced to 174 mg/l from an initial COD of 460 mg/l (total reduction = 62 %) whereas overall color reduction was around 98%.

On the other hand, CaO solution showed marginally better COD removal efficiency (final COD = 161 mg/l, total reduction = 65 %) at a

TABLE - 2
Quantity Of Chemical Required To Adjusts The pH For $FeCl_3$ (Coagulant Dose = 200 mg/l)

S. No.	pH after adjustment	NaOH (mg/l)	CaO (mg/l)
1.	4.23	0	0
2.	5	40	100
3.	6	80	150
4.	7	120	250
5.	8	140	300
6.	9	160	400

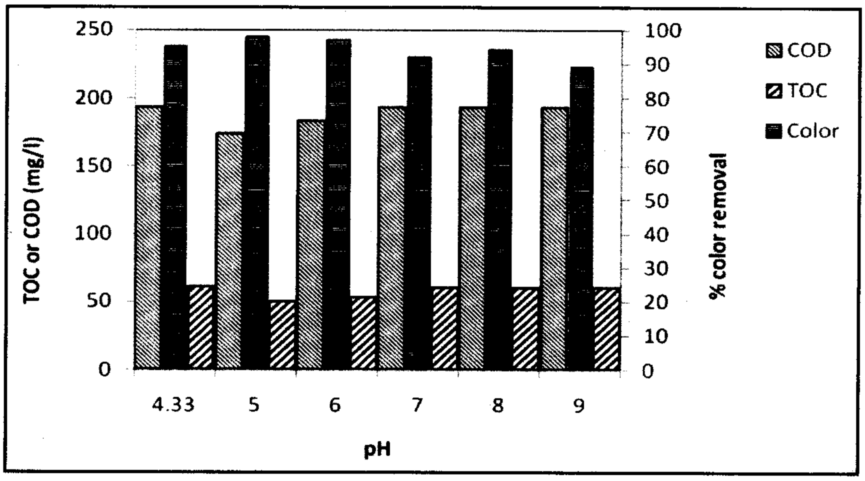

Figure 2 Effect of pH On COD And TOC With $FeCl_3$ (pH Adjusted By NaOH) (Initial COD = 460 mg/l, TOC = 123 mg/l, Coagulant Dose = 200 mg/l)

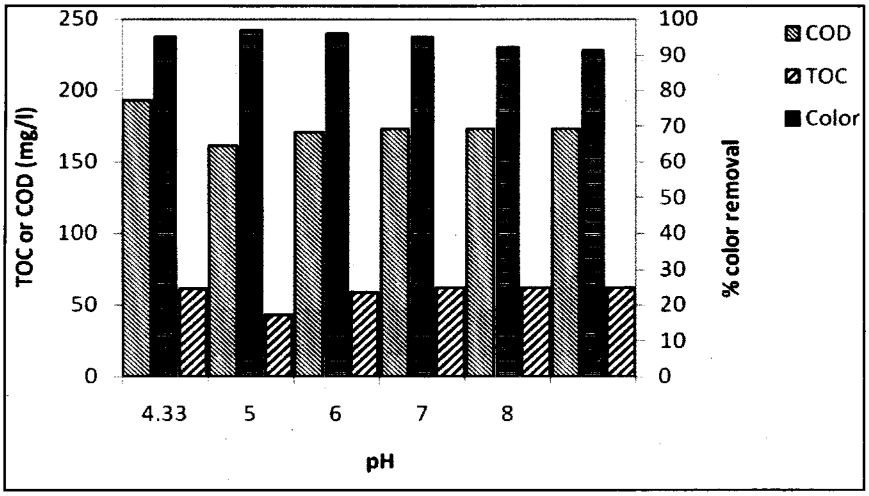

Figure 3 Effect Of pH On COD And TOC With $FeCl_3$ (pH Adjusted By CaO) (Initial COD = 460 mg/l, TOC = 123 mg/l, Coagulant Dose = 200 mg/l)

solution pH of 5.0 though the overall color removal was the same, i.e., 98 %. However, higher CaO dose was required to achieve only 3 % more COD reduction than that obtained with NaOH. Moreover, CaO is 1.46 times more expensive than NaOH (costs of NaOH and CaO are Rs. 324/kg and Rs. 474/kg of the respective chemicals). It can be seen from Table 2, that CaO requirements are 2.5 times higher than NaOH to adjust a pH to 5.0. As a result, the cost of pH adjustment with CaO will be 3.65 times more than NaOH to achieve almost the same COD reduction (62 - 65 %) for the pulp and paper mill wastewater (Cost with NaOH = Rs. 12.96/ m^3 and CaO = Rs. 47.4/ m^3 of the wastewater). Hence, NaOH was chosen for pH adjustment in all subsequent runs.

Using alum as coagulant

(a) Optimum coagulant dose:

To find the best alum dose, coagulation studies were carried out for alum doses ranging from 100 mg/l to 600 mg/l. The six beakers were charged with different amounts of the coagulants (100, 200, 300, 400, 500 and 600 mg/l) in 500 ml wastewater. The addition of coagulant reduced the pH of solution in the range of 4.32 - 6.67 from an initial value of 7.23. The maximum pH drop was observed for the highest alum dose and vice-versa. Before rapid mixing, pH of the wastewater samples was adjusted within the range of 5.5 - 6 by adding NaOH solution. With alum dose of 300 mg/l, the maximum reductions in COD, TOC and color of 56 %, 47 % and 97 %, respectively were obtained (Figure 4). At higher coagulant doses, no further improvement in any of the three parameters could be seen. Below the optimum coagulant dose, only marginal reductions in COD, TOC and color were obtained. A coagulant dose of 100 mg/l reduced the COD to around 430 mg/l from an initial value of 460 mg/l whereas only 30 % color could be removed. From Figures (2 and 4), it can be suggested that less amount of $FeCl_3$ is required for better COD reduction than alum. \

(b) pH optimization

For alum, pH optimization studies were conducted over a pH range of 4 - 9. The optimum coagulant dose of 300 mg/l was used in all the runs. Addition of alum to the wastewater reduced initial pH of the wastewater from 7.23 to 5.47. To adjust the experimental pH lower than 5.47, H_2SO_4 solution (1.8 M) was added, whereas a basic solution of NaOH (1 M strength) was used for adjusting higher pH values. A pH value of 5.0 again showed the best COD and color removal efficiencies. At this pH, COD of the wastewater was reduced to 190 mg/l from 460 mg/l (~ 58 % reduction) whereas a color reduction of 98 % was achieved (Figure 5).

The results show that alum dose

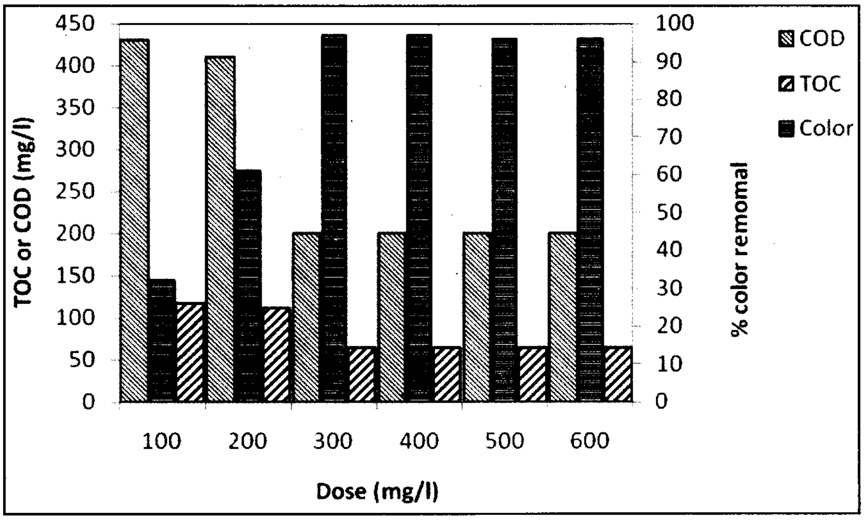

Figure 4 Effect Of Alum Dose On COD And TOC (Initial COD = 460 mg/l, TOC = 123 mg/l, pH = 7.23)

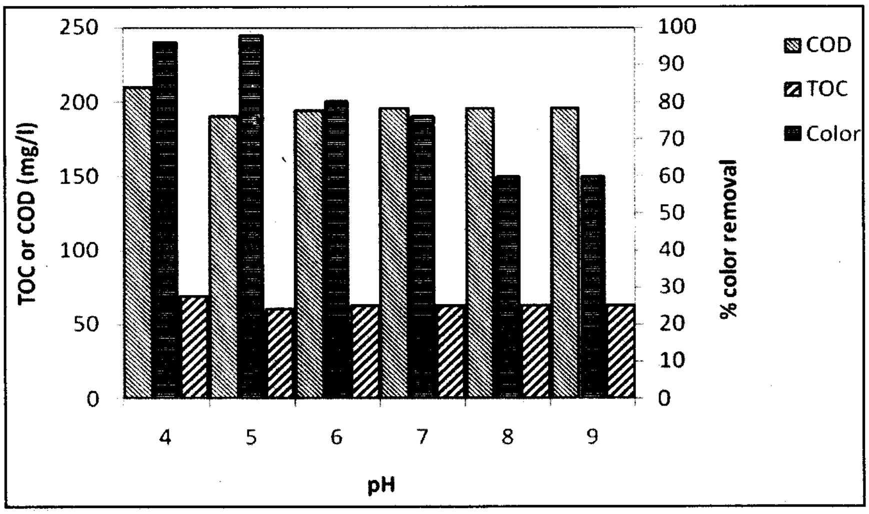

Figure 5 Effect Of pH On COD And TOC With Alum (Initial COD = 460 mg/l, TOC = 123 mg/l, Coagulant Dose = 300 mg/l)

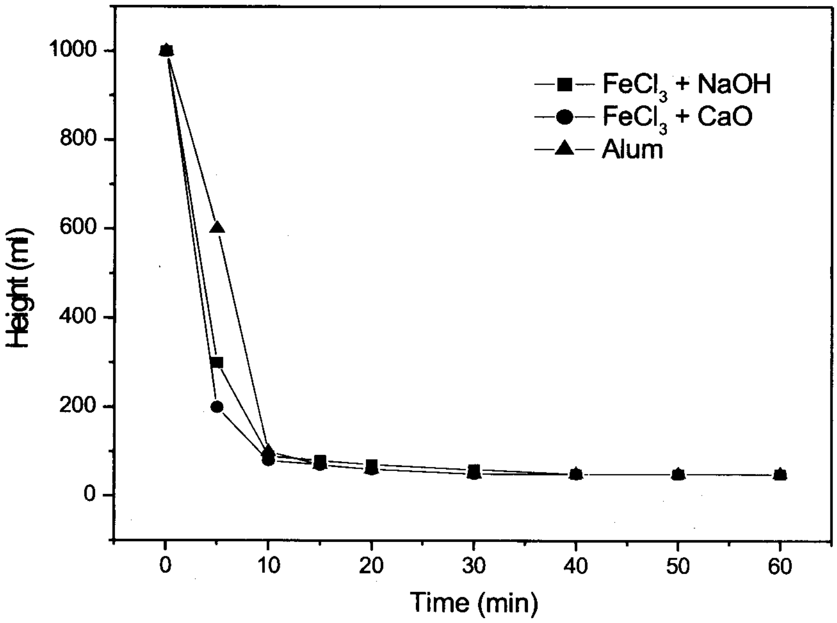

Figure 6 Settling Characteristics Of Floc For $FeCl_3$ And Alum

requirements were 1.5 times higher than $FeCl_3$ for achieving same color removal. Moreover, COD reduction was slightly lower with alum than that obtained with $FeCl_3$ and also $FeCl_3$ is less expensive than alum (costs of $FeCl_3$ and alum are Rs. 350/kg and Rs. 370/kg of the chemical, respectively). This can be calculated that use of alum will cause 1.6 times more cost than the treatment performed with $FeCl_3$. For $FeCl_3$, only Rs. 70/- per m^3 of the wastewater (used in present study) will be spent on the coagulant for the COD removal of 62% from the pulp and paper mill effluent. This figure will be increased to Rs. 111/- per m^3 of the pulp and paper mill effluent for lower COD reduction (i.e., 58%) if alum is used as coagulant. Hence, this can be deduced that ($FeCl_3$ + NaOH) combination is the best among all tested ones in the present research study.

Settling characteristics

The settling characteristics of the sludge in the wastewater treated under optimized conditions with both the coagulants were observed. After transferring the treated sample in to a measuring cylinder (1 L capacity), it was gently mixed to protect the flocs formed during coagulation process. For settling curves, the sludge blanket height with (Figure 6) time was recorded. This can be seen that the solids in $FeCl_3$ treated water settled at slightly faster rate compared to that found in alum treated wastewater during first 5 min or so. Though after 10 min rapid settling, the height of the interface was the same for all three combinations. Beyond this rapid settling zone almost no settling was occurred.

Adsorption

In adsorption process, powdered activated carbon and 13X molecular sieve zeolite were used as adsorbents for treatment of the wastewater. The optimum pH and adsorbent dose were obtained for activated carbon and the results were compared with 13X zeolite. In order to optimize pH, 500 mg/l (in solid form) of activated carbon was added to 50 ml wastewater in 5 flasks. The pH of sample was adjusted in range of 5 9 by adding acidic or basic solution. The mixture was shaked in an orbital shaker at 120 rpm for 1 h to ensure proper contact between pollutants and adsorbent. The treated water was then filtered and analyzed for COD and TOC. The maximum COD reduction of around 62 % (final COD = 170 mg/l from an initial value of 460 mg/l) was obtained at a pH of 5.0 whereas TOC was reduced to 58 mg/l from an initial value of 123 mg/l (~ 53 % reduction) (Figure 7). According to the trend, COD and TOC reductions were lower at higher pH values, but overall difference in COD and TOC at pH 5.0 and 7.23 (original) was not very significant (At pH = 7.23, final COD = 189 mg/l and TOC = 69 mg/l). Therefore, the adsorbent dose was obtained at original pH of the wastewater (i.e. 7.23) so that the additional cost of H_2SO_4 (required to reduce the pH) could be saved.

The effect of adsorbent (activated carbon) dose on COD and TOC of the wastewater is illustrated in Figure 8. As expected, an increase in adsorbent dose showed more COD and TOC reductions. However, beyond 1000 mg/l activated carbon, the reduction in two parameters was insignificant. At an adsorbent dose of 1000 mg/l, the improvement in COD and TOC reductions was marginal than with 500 mg/l dose (at 500 mg/l adsorbent dose, final COD = 189 and at 1000 mg/l adsorption dose, final COD = 168 mg/l). Therefore, an adsorbent dose of 500 mg/l was considered as optimum quantity.

At a solution pH of 7.23, a 500 mg/l 13X zeolite dose reduced COD and TOC values to 185 mg/l and 67 mg/l, respectively. These values are analogous to that obtained with activated carbon. However, future studies may be aimed for optimizing operating conditions for 13X molecular sieve zeolite.

Sludge characteristics

Solids quantity in treated wastewater

Total solids concentration in the treated wastewater was determined using the same procedure as adopted for untreated effluent. In the treated wastewater with ($FeCl_3$ + NaOH), TS concentration was found to be 686 mg/l. Out of which, 264 mg/l solids were in suspended form. TS concentrations in the wastewater samples treated with ($FeCl_3$ + CaO) and (alum + NaOH) were 666 mg/l and 748 mg/l, respectively. Higher sludge formation in alum treated wastewater was expected due to the addition of high coagulant dose.

Proximate and elemental analyses

The waste sludge obtained after treatment with ($FeCl_3$ + NaOH) was characterized using proximate and elemental analyses. The proximate analysis of the sludge sample was performed to determine moisture content (on wet basis), volatile matter, fixed solids and ash content (on dry basis).

The moisture content in the fresh sludge was determined by drying the sludge sample in an oven at 100 105 °C temperature till the sample attained a constant weight. From the analysis, it was found that the fresh wet sludge contained a solids concentration of 0.3 % (by weight).

The oven dried sludge was used to

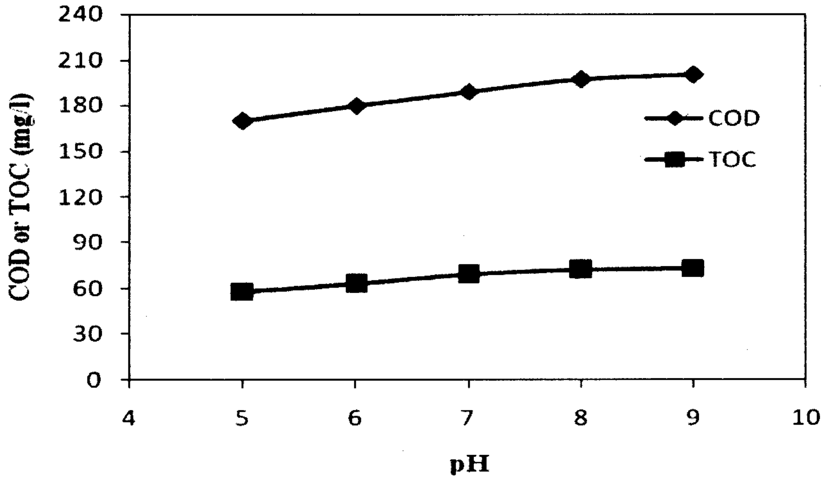

Figure 7 Effect Of pH On COD And TOC With Activated Carbon (Initial COD = 460 mg/l, TOC = 123 mg/l, Adsorbent Dose = 500 mg/l)

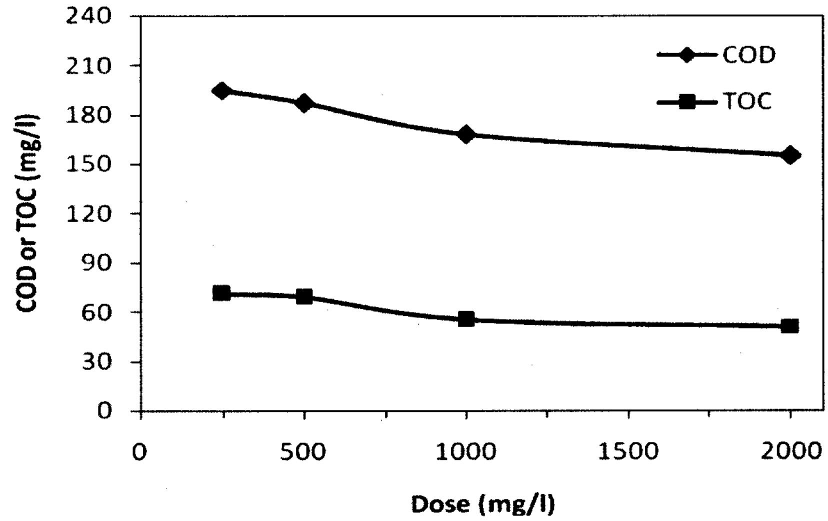

Figure 8 Effect Of Alum Dose On COD And TOC (Initail COD = 460 mg/l, TOC = 123 mg/l, pH = 7.23)

measure volatile matters, ash content and fixed solids in the waste residue. The sludge had 44.44 % volatile solids, 58.81 % ash and 4.78 % fixed carbon. Moderate volatility will prevent the formation of excessive soot during elevated temperature applications. High ash content may be a major concern for the facilities using this sludge as a fuel. For àssessing the possibility of using ash in other activities (such as aggregates in construction activities) complete characterization of the ash sample is required. The elemental analysis demonstrated the presence of low C (~ 20 %) and H (= 0.28 %) in the dry sludge. Other elements such as N and S were found to be 3.38 and 6.86 %, respectively. High N and S contents may be a concern for industries utilizing this material as mono fuel or co-fuel in their processes[3]. The presence of these compounds can enhance the emissions of SO_2 and NO_x (depending upon the operating temperature). This may necessitate the installation of scrubbers for the removal of acidic gases. Since these gases have corrosion potential, the thermal facilities will need to take appropriate steps to avoid this problem.

Conclusions:

Several conclusions can be drawn from the study. Since pulp and paper mill effluent had low COD and TOC (460 mg/l and 123 mg/l, respectively), coagulation and adsorption can be effective treatment processes for such wastewater. $FeCl_3$ and alum exhibited similar COD and color removal efficiencies (COD reduction = 58 62 % and color reduction = 98 %) at pH of 5.0 and optimum coagulant dose. After the treatment with alum, larger amount of sludge is produced due to higher dose for the same removal efficiency. For pH adjustment NaOH was preferred over CaO due to much lower requirements. Settling of the sludge was found to be very good for the treated wastewater at optimum conditions. Adsorption with activated carbon and 13 X zeolite showed similar COD reduction as that obtained from coagulation process, but required high adsorbent dose. Sludge obtained after the treatment can be characterized as a material having low carbon and hydrogen but high sulfur and ash content.

Further studies can be aimed for the treatment of pulp and paper mill wastewater with low cost adsorbents and coagulants. Complete sludge characterization must be done for suggesting its final disposal method.

Acknowledgement:

The authors acknowledge Department of Science and Technology (DST), New Delhi for their financial support through the project funded under "SERC Fast Track Scheme". We are also thankful to Sophisticated Analytical Instrument Facility (SAIF), IIT Bombay for their support in analyzing the samples.

Literature Cited:

1 CPCB (Central Pollution Control Board), "Development of Guidelines for Water Conservation in Pulp and Paper Sector", 2006.
2 Pokhrel, D. and Viraraghavan, T., *Sci Total Environ* **333** (2004)37-58.
3 Garg, A., Mishra, I.M.and Chand, S., *Ind. Eng. Chem. Res.* **44** (2005)2016-2026.
4 Garg, A., Mishra, I.M. and Chand, S., *Clean* **38(1)** (2010)27-34.
5 Garg, A., Mishra, I.M.and Chand, S., *Chemosphere* **66** (2007)1799-1805.
6 Stephenson, R.J. and Duff, S.J.B., *Water Res* **30(4)** (1996) 781-792.
7 Dilek, F.B. and Bese, S., *Water SA* **27(3)** (2001)361-366.
8 Srivastava, V.C., Mall, I.D. and Mishra, I.M., *Colloids and Surfaces A: Physicochem. Eng. Aspects* **260** (2005)1728.
9 Metcalf, and Eddy, "Wastewater Engineering, Treatment and Reuse", Tata McGraw-Hill 4th Ed. 2003.
10 APHA (American Public Health Association), "Standard Method for the Examination of Water and Wastewater", 20th Ed. 2005.
11 IS: 1350 (Part I) 1984, "Indian Standard Methods of Test for Coal and Coke", 1984.