Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor

Anurag Garg*, I.M. Mishra, S. Chand

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

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ABSTRACT

The effectiveness of coagulation (using aluminium-based chemicals and ferrous sulfate) and acid precipitation (using H_2SO_4) processes for the pre-treatment of diluted black liquor obtained from a pulp and paper mill is reported. Commercial alum was found to be the most economical among all the aluminium and ferrous salts used as a coagulant. A maximum removal of chemical oxygen demand (COD) (*ca.* 63%) and colour reduction (*ca.* 90%) from the wastewater (COD = 7000 mg l^{-1}) at pH 5.0 was obtained with alum. During the acid precipitation process, at pH < 5.0, significant COD reductions (up to 64%) were observed. Solid residue obtained from the alum treatment at a temperature of 95 °C showed much better (3 times) settling rate than that for the residue obtained after treatment with the same coagulant at a temperature of 25 °C. The settling curves had three parts, namely, hindered, transition and compression zones. Tory plots were used to determine the critical height of suspension–supernatant interface that is used in the design of a clarifier–thickener unit. High heating values and large biomass fraction of the solid residues can encourage the fuel users to use this waste derived sludge as a potential renewable energy source.

1. Introduction

Increasing global pressure to improve the quality of the environment has necessitated the implementation of robust wastewater treatment strategies before the final disposal of wastewater into natural water streams or its recycle and reuse. The treated effluent should meet the water quality requirements for recycling in the water intensive processes so as to reduce the make-up water intake. Pulp and paper mill is one of the most water demanding industries which also generates a large quantity of wastewater (20–250 m^3/ton for an integrated paper mill having chemical recovery units) [1]. The wastewater from the pulp and paper mills contains high concentrations of lignocellulosic materials, phenolics and sulfur compounds [2–4]. The presence of suspended, colloidal and dissolved matter imparts high chemical oxygen demand (COD) and colour to the wastewater. The recovery of useful chemicals and energy is possible from wastewaters emanating from pulp and paper mills and distilleries [3,5,6] due to the presence of high organic and inorganic chemicals load.

Pulp and paper mill wastewater is not amenable to biological treatment due to low biochemical oxygen demand (BOD) to COD ratio (*ca.* 0.2) and the presence of persistent organic compounds [4,5]. Hence, a pre-treatment step is essential to eliminate the persistent constituents that may be toxic to micro-organisms, if biological treatment methods are to be used. The carbonaceous matter of the pre-treated effluent can be further oxidized using wet air oxidation (WAO) process at moderate operating conditions, since the requirements for temperature and pressure are reduced significantly due to the removal of biorefractory and recalcitrant degradable compounds during the pre-treatment step [4].

Several researchers have evaluated the efficacy of conventional coagulants (such as Al and Fe salts) for COD and colour removal from pulp and paper mill effluents [2,7–12]. Dilek and Gökçay [7] reported overall COD reductions of *ca.* 96%, 50% and 20% for the paper machine, alkali extraction and bleaching effluents, respectively and *ca.* 80% colour removal from the alkali extraction effluent using alum as a coagulant. Stephenson and Duff [8] made a comparative assessment of the efficacy of various iron and aluminium-based coagulants for the treatment of a mechanical pulping effluent (initial COD = 2520–7930 mg l^{-1}). Ferric chloride was found to be the best among all the coagulants showing 88 and 97% reductions in total carbon and colour, respectively. Sundin [9] reported the high efficiency of Na$^+$, Ca^{2+}, Mg^{2+}, Al^{3+}, Ca^{2+} and Mg^{2+} ions for lignin precipitation at 11 ≤ pH ≤ 13. Srivastava et al. [12] tested a hybrid process for the removal of COD and colour from the alkaline black liquor and acid wastewaters. The wastewaters were obtained from different sections of the small agri-based pulp and paper mills (with no chemical recovery units). The hybrid process

* Corresponding author. Present address: Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Mumbai, Maharashtra 400076, India. Tel.: +91 22 25767861; fax: +91 22 25764650.

E-mail addresses: a.garg@iitb.ac.in, agargdch@rediffmail.com (A. Garg).

Table 1
Major characteristics of black liquor.

Parameter	Value
COD	700 000 mg l^{-1}
BOD	140 000 mg l^{-1}
pH	11.2
Total solids	724 000 mg l^{-1}
Colour	Dark brown

comprised coagulation (with polyaluminium chloride (PAC)) followed by adsorption (using bagasse fly ash as the absorbent). At an optimum pH ≈ 3 and PAC dosage of 3 kg m^{-3}, 80% COD and 90% colour removals were obtained in the first step. However, overall reductions in the two parameters could be increased to 87% and 95%, respectively, after the two-step treatment. Garg et al. [5] have used copper sulfate as a catalyst/coagulant for the pre-treatment of diluted black liquor. The characteristics of this diluted black liquor (COD = 7000 mg l^{-1}) corresponded with that of the wastewater obtained from an integrated pulp and paper mill with chemical recovery units. A COD reduction of *ca.* 61% was obtained at a catalyst concentration of 5 g l^{-1} and the initial solution pH of 8.0. The supernatant was treated further by using catalytic WAO at moderate operating conditions [4].

Alum has been found to be a very effective coagulant for treating wastewaters [6,13,14]. Use of sulfuric acid in conjunction with coagulants like alum and lime may reduce the quantity of coagulants required for the precipitation. Addition of an acid with a coagulant has been found to be very effective in the removal of COD and suspended solids from laundry wastewater [15]. Extraction of the lignin from pulp mill effluent by acidification process has also been reported in the past [16–20]. Lowering of the pH is carried out by introducing CO_2 gas and mineral acids (e.g. H_2SO_4) to the wastewater. It has been reported that the separation of 1 ton of lignin requires 275 kg CO_2 and 100 kg H_2SO_4 [18]. The profitability of the process depends on the cost of CO_2 and H_2SO_4. However, CO_2 produces more problems than H_2SO_4 during filtration stage [16].

The present study was aimed to assess the feasibility of coagulation (using aluminium and iron salts) and acid precipitation processes in the pre-treatment step of diluted black liquor by evaluating the overall COD and colour reduction, settling characteristics of the slurry produced after the coagulation/acid precipitation performed under different conditions and the energy recovery potential from the precipitated sludge.

2. Experimental and analytical methods

2.1. Materials

Concentrated black liquor (COD ≈ 700 000 mg l^{-1}) was obtained from a local pulp and paper mill using kraft pulping process and stored at 10 °C to preserve its original characteristics. Black liquor in a pulp and paper mill is concentrated for firing in the recovery furnace to recover chemicals. The major characteristics of concentrated black liquor are presented in Table 1. For preparing synthetic wastewater of desired strength, this concentrated black liquor was diluted with the required amount of tap water. In order to perform comparative study, a number of researchers have used synthetic wastewater by diluting the concentrated black liquor stock from the recovery system of an integrated pulp and paper mill, as the substrate simulates the original pulp and paper mill effluent [3–5,21]. It is easier to use concentrated black liquor for preparing synthetic wastewater rather than using fresh black liquor or wastewater from a pulp and paper mill owing to collection problems. In the current study, the wastewaters having COD values of 7000 mg l^{-1} and

14 500 mg l^{-1} were subjected to coagulation tests. In the majority of runs, lower COD value was used, whereas the higher one was used only for the optimization of solution pH.

Commercial alum was purchased from local market. Analytical reagent grade ammonium alum and aluminium sulfate were purchased from E. Merck (India), Mumbai and Reidel (India) Chemicals, respectively, whereas ferrous sulfate was obtained from Qualigens Fine Chemicals, Mumbai (India). H_2SO_4 was purchased from S.D. Fine Chemicals Ltd, Mumbai.

2.2. Experimental procedure

The experimental runs were performed in a three-necked glass reactor (GR) having a capacity of 500 ml. A vertical glass condenser was attached to the central neck of the reactor to prevent any loss of vapour to the atmosphere during the coagulation/acid precipitation at temperatures higher than ambient temperature. Thermo-well fitted to one of the side necks was used to monitor the temperature of the mixture during the run. The third neck was kept closed using a glass stopper and used only for the withdrawal of samples during experimental run. The original pH of the wastewater was adjusted to the initial desired value by adding H_2SO_4 before transferring the wastewater to the GR. A pre-determined dose of coagulant was added to the reactor. The experimental runs were performed at temperatures ranging from ambient to 95 °C (i.e. 25, 40, 60, 70, 80 and 95 °C). The reactor contents were heated on a hot plate to achieve the desired temperature. The hot plate was equipped with a proportional integral derivative (PID) temperature controller that was connected with a thermocouple (placed in the thermo-well). It took about 30 min to attain the wastewater temperature from ambient to 95 °C. The time at which reaction mixture attained the desired temperature was taken as 'zero time' and at this point, the agitation of the wastewater–coagulant mixture was started with a magnetic stirrer. It must, however, be stated that during the heating of the reaction mixture up to the desired temperature, coagulation–flocculation did take place and COD got removed. Rapid agitation of the reaction mixture for 5 min was followed by slow agitation for 30 min. The mixture was then allowed to cool for 1 h. The supernatant was used for the determination of the COD and colour of the treated sample. The final pH of the solution after the reaction was also recorded. The cooled reaction mixture was again stirred for uniformity and the slurry so formed was used to study the settling characteristics of the flocs/solids. The settling study was conducted in a 100-ml graduated cylinder. Effect of temperature (during coagulation process) on the settling characteristics was observed and critical solid concentration was calculated using sedimentation data.

Apart from this, the metal ion concentration in the supernatant and the sludge was also examined. The solid residue obtained after the treatment was subjected to thermal analysis to determine its high heating value (HHV).

2.3. Analytical methods

COD of the effluent was determined by using standard dichromate open reflux method [22]. Colour of the untreated and treated wastewater was measured at a wavelength of 363 nm using an UV/VIS spectrophotometer (Model Lambda 35, PerkinElmer, Switzerland). The concentration of metal ions in the wastewater and the sludge was determined using an atomic absorption spectrophotometer (Model Avanta, GBC, Australia).

The proximate analysis of the sludge was carried out as per procedure laid down in IS: 1350 (Part-I)-1984 [23]. Elemental analysis for C, H, N and S was performed using a CHNS analyzer (Elementar Vario EL III, Elementar Analysensysteme, Germany). The HHV of the

precipitated dried sludge was determined by preparing a suitable pellet and combusting it in a standard adiabatic bomb calorimeter [24].

3. Theory

3.1. Mechanism of coagulation

The separation of organic compounds from the wastewater in the presence of conventional aluminium- and iron-based coagulants can be brought about by the destabilization of colloids and suspended matters [8,25]. Two mechanisms are suggested for the destabilization: charge neutralization and sweep flocculation. It is recognized that the precipitation of organic pollutants takes place due to 'sweep flocculation' in which enmeshment and adsorption of suspended impurities in the cationic metal hydroxides occur [25]. Formation of metal hydroxides results because of the hydrolyzing of metal salts or coagulants in the wastewater. Al and Fe salts form monomeric and polymeric hydrate species on dissolving in wastewater [6,8,25]. These anionic polymers are amorphous and hydrophobic in nature. The particulate organic and inorganic compounds form large and amorphous flocs primarily due to adsorption and bridging enmeshment [26]. The dissolved organics generally get precipitated by adsorption onto the metal hydroxide coagulant surface [8]. The pH of the wastewater has a strong effect on the removal of COD and colour. Each coagulant has its own optimum pH range. Alum is generally more effective in a pH range of 4.5–7.0 for highly alkaline wastewaters such as pulp and paper mills, whereas $FeSO_4$ is effective in the pH range of 4–7 [15]. The optimum pH range, however, is also affected by the composition of the wastewater. This may change with the presence of specific chemicals/compounds.

Addition of mineral acid to the wastewater reduces the COD by 30–70% due to the precipitation of lignin [20]. Lowering of pH causes the agglomeration of lignin molecules resulting in their eventual precipitation [18].

3.2. Settling curves

Determination of the settling characteristics of flocculated mixture is of immense importance since it affects the decontamination of wastewater [14] and the economics of the treatment. Good settling parameters exhibit high level of purification. It has been reported that the intermittent settling of concentrated flocculated suspensions takes place in three zones, namely, hindered settling zone or uniform zone, transition zone and compression zone [5,14,27]. Hindered settling zone is characterized by rapid settling of suspended and colloidal matters present in the wastewater, whereas the settled mass is consolidated in the compression zone and attains the ultimate sludge height. These two zones are separated by a transition zone, where the flocs start coming closer due to increased concentration of settleable components.

4. Results and discussion

4.1. Effect of different coagulants

The effect of different aluminium compounds and ferrous sulfate as coagulants on COD reduction of synthetic pulp and paper mill effluent (initial COD $(COD_i) = 7000\,mg\,l^{-1}$) was observed. Aluminium-based coagulants that were used in the treatment included commercial alum, aluminium sulfate and ammonium alum. The treatment was performed at 95 °C and atmospheric pressure (i.e. 0.1 MPa). The pH_i of the wastewater was adjusted to 8.0 and the coagulant concentration added to the wastewater was

$5\,g\,l^{-1}$. Under these conditions, all Al-based coagulants exhibited same COD reduction of the order of 61%. The COD of the supernatant (filtrate) got reduced to $2700\,mg\,l^{-1}$ from $7000\,mg\,l^{-1}$. The efficiency of $FeSO_4$ in removing COD was found to be marginally lower (ca. 60%) in comparison to all other coagulants. The pH of the wastewater was reduced to 4.5–5.0 (from an initial value of 8.0) after the addition of coagulants. The major mechanism seems to be the sweep coagulation since large amount of coagulant was used ($5\,g\,l^{-1}$). The presence of high concentration of cationic ions results in the formation of metal hydroxides and subsequent enmeshment and/or adsorption of compounds present in the wastewater.

Since commercial alum is available at a very low price (ca. INR $160\,kg^{-1}$) in the market, it was chosen for the study. The comparative cost of treatment with different coagulants compared to commercial alum (INR $186\,kg^{-1}$ COD removal) was found to be as follows: ferrous sulfate = INR $335\,kg^{-1}$ COD removal, aluminium sulfate = INR $419\,kg^{-1}$ COD removal, ammonium alum = INR $651\,kg^{-1}$ COD removal.

Ferrous sulfate, aluminium sulfate and ammonium alum are 1.8, 2.25 and 3.5 times more expensive than commercial alum. The cost of the reaction increased in the same proportion since the quantity of the chemicals added to the wastewater was the same. While using aluminium-based coagulants, the residual aluminium in the supernatant is found to be in the range of 35–40% of the total Al added to the wastewater (Table 2). For ferrous sulfate, ~87% of the total Fe added to the effluent remains in the supernatant. The remaining Al and Fe were ended up in the sludge.

4.2. Effect of temperature on the COD removal of paper mill effluent

The COD reduction of the effluent at different temperatures (from 25 °C to 95 °C) was determined using commercial alum (coagulant mass loading = $5\,g\,l^{-1}$) as the coagulant. The initial pH of the wastewater was adjusted to 8.0 for all the runs. An increase in temperature did not result in any improvement in the COD removal. The COD removal was found to be constant at ca. 61%. However, the settling characteristics of the sludge were found to improve considerably with increase in reaction temperature. Higher viscosity of the liquid at lower temperature leads to poor rapid mixing conditions resulting in slower settling [25]. This aspect is discussed later in detail (Section 4.5).

4.3. pH optimization with alum and H_2SO_4

Effect of pH on the COD reduction of synthetic pulp and paper mill wastewater (initial COD = $14\,500\,mg\,l^{-1}$) was evaluated over a wide range of pH under ambient temperature, and atmospheric pressure. Commercial alum was used as a coagulant whereas 10% (by volume) H_2SO_4 solution was used to reduce the pH of the wastewater to the desired level. pH of the wastewater mixture was reduced from $pH_i = 10.5$ to 0.5 (highly acidic). Alum was used as the coagulant in those experimental runs that were conducted between pH 4.0 and 10.5. After addition of the coagulant, the final pH values of wastewaters were in the range of 3.9–8.95 (for $pH_i = 4.0$, final pH 3.9 and for $pH_i = 10.5$, final pH = 8.95). Acid precipitation runs were taken in the pH range of 0.5–5.0. Alum was not added to the reactants for experimental runs in this pH range. The results obtained from the experimental runs are illustrated in Fig. 1.

It can be seen that a decrease in pH from 10.5 to 7.0 increases the COD removal in the presence of alum. With Al coagulant dose of $3\,g\,l^{-1}$, the COD of the treated wastewater was reduced to $13\,500\,mg\,l^{-1}$ and $11\,500\,mg\,l^{-1}$ at pH 10.5 and 7.0, respectively from an initial COD load of $14\,500\,mg\,l^{-1}$. While reducing pH from 7.0 to 6.0, the COD removal decreased abruptly resulting in a sharp

Table 2
Concentration of different ions in the supernatant and the sludge after thermal pre-treatment.

S. no.	Compound	Original concentration ($g\,l^{-1}$)	Concentration in the supernatant		Concentration in the sludge	
			($g\,l^{-1}$)	% of original	($g\,l^{-1}$)	% fixation of cation in the sludge
1.	Commercial alum	Al = 0.306	0.120	39.22	0.186	60.78
2.	Ammonium alum	Al = 0.298	0.104	34.90	0.194	65.10
3.	Aluminium sulfate	Al = 0.428	0.170	39.72	0.258	60.28
4.	$FeSO_4\cdot7H_2O$	Fe = 1.007	0.874	86.80	0.133	13.20

rise in the curve towards lower pH (for alum curve). At lower pH (<6.0), COD removal again increased rapidly. It is evident from the figure that at pH 5.0, the residual COD of the treated wastewater reduced to ca. 6340 mg l^{-1} compared to ca. 13 340 mg l^{-1} at pH 6.0. It is clear from the two curves in Fig. 1 that the addition of H$_2$SO$_4$ reduced the residual COD from 14 500 mg l^{-1} to 11 330 mg l^{-1} at pH 5.0. Therefore, the reduction in COD due to alum addition is 4990 (=11 330–6340) mg l^{-1}. At pH 4.0, the effect of H$_2$SO$_4$ on COD reduction is much greater than that of alum. Presence of alum reduced the overall COD of the treated effluent to 6170 mg l^{-1} (total COD reduction = 14 500–6170 = 8330 mg l^{-1}) at this pH. Out of 8330 mg l^{-1}, COD reduction due to alum addition is only 2630 (=8800–6170) mg l^{-1} that is around one third of the total reduction. From the above, it can be inferred that the maximum COD reduction in the presence of alum can be achieved at an optimum pH 5.0. This result is in agreement with the previous findings [15]. It has also been reported that the soluble organic matter can be removed in the pH range of 5.3–5.7 using aluminium salts as the coagulant [28].

In the absence of alum, a further decrease in pH reduces the residual COD of the treated effluent as seen from Fig. 1. The rate of COD reduction is found to be much faster from pH 5.0 to 3.0. Thereafter the rate of reduction slows down. The COD–pH curve can be split in two parts: the first linear part showing a faster COD removal at the rate of ca. 2330 mg l^{-1} per unit pH, followed by the second part which showing a slower COD removal at a rate of ca. 600 mg l^{-1} per unit pH.

During the course of the experiment, it was found that very large volumes of H$_2$SO$_4$ were required to reduce the pH of the wastewater to 1.5 or below. Therefore, the removal of COD at a pH 1.5 does not appear to be attractive enough because of steep escalation in the treatment cost. This will also necessitate larger amount of alkali to raise the pH of the treated effluent. However, pH 1.5 is taken as the optimum pH giving 61% overall COD removal
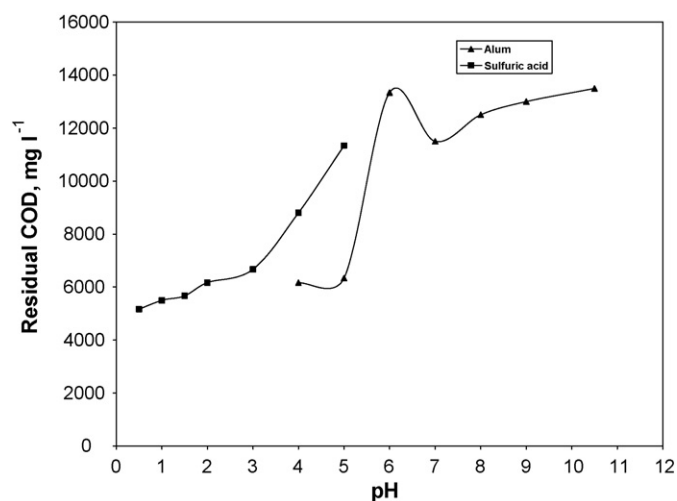
(final COD = 5670 mg l^{-1}). Similar results have been reported in the past [29], wherein rapid increase in lignin removal (ca. 53%) was observed in the pH range of 4.0–5.98 and extremely slow lignin removal at pH less than 3.23.

4.4. Effect of alum mass loading on COD and colour removal

The effect of alum mass loading (1–8 g l^{-1}) on the COD and colour removal of the synthetic wastewater (COD$_i$ = 7000 mg l^{-1}) was studied at room temperature (=25 °C). The results were compared with that obtained without the addition of alum under similar conditions. Initial pH of the wastewater was set at 5.0 before the start of a run.

As is evident from Fig. 2, only ~18% COD reduction was obtained at an alum dosage of 1 g l^{-1}. This is marginally higher than that observed without the addition of a coagulant (ca. 17%). Up to this point, no clear precipitation was observed. As the alum concentration was raised to 2 g l^{-1}, COD reduction increased to 59.5%. Above this alum concentration, the corresponding increase in COD reduction was insignificant (ca. 63% at alum dosage = 5 g l^{-1}). Further increase in alum dosage did not enhance COD removal.

Fig. 2 also illustrates the effect of alum dosage on the colour removal of the effluent. Colour removal also shows similar trend as that for COD reduction. Alum dosage 5 g l^{-1} resulted in a maximum colour removal of ~90%. However, the colour removal decreased slightly to 88% at an alum dosage of 8 g l^{-1}. This slight reduction in colour removal may be attributed to the colour imparted by alum itself. As reported by Ho et al. [30], colour reduction increases up to a certain point beyond which it begins decreasing with an increase in coagulant concentration. Colour removal at 2 g l^{-1} alum concentration was of the order of 85%. Major parameter affecting the colour removal is the presence of persistent organic compounds (like lignin) in the wastewater. Separation of these compounds not only reduces the COD but also removes significant amount of colour from the wastewater. Several studies have reported the colour removal from 80 to 100% depending upon the characteristics of the effluent and the operating conditions [8,10,27,31,32].
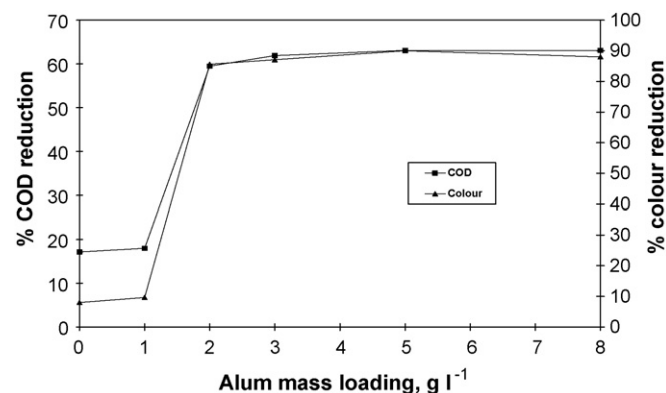

Fig. 1. Effect of pH on residual COD during diluted black liquor treatment using alum and sulfuric acid (initial COD = 14 500 mg l^{-1}, alum mass loading = 3 g l^{-1}, T = 25 °C).

Fig. 2. Effect of coagulant mass loading on the COD and colour of diluted black liquor (initial COD = 7000 mg l^{-1}, pH 5.0, T = 25 °C).
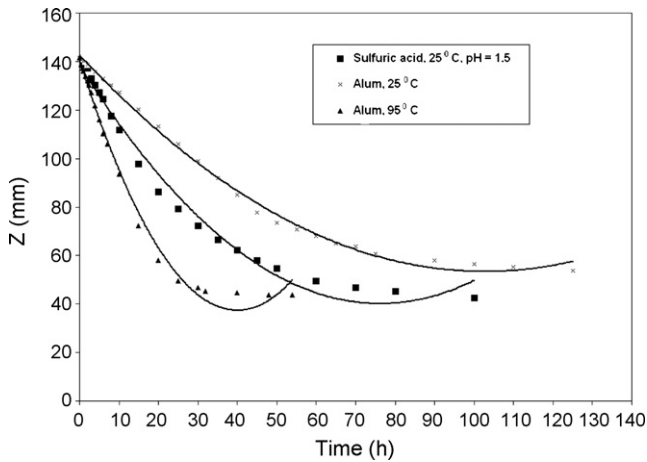
Fig. 3. Settling characteristics of the slurry produced after treatment of diluted black liquor with sulfuric acid and commercial alum (alum mass loading = 5 g l^{-1}, initial adjusted pH for coagulation runs = 8.0).

The pH of the treated wastewater was reduced to 3.45 from its initial value of 5.0. This decrease in the solution pH may be attributed to the several hydrolytic reactions that take place during coagulation process, forming multivalent charged hydroxide species and generating H_3O^+ ion during each step [33]. Stephenson and Duff [8] have also reported that the coagulant addition depresses pH to acidic levels.

4.5. Settling characteristics of the wastewater treated by alum and H_2SO_4

Settling characteristics of the wastewater treated with alum (treatment temperatures: 25 °C and 95 °C; initial pH 8.0 and alum dosage = 5 g l^{-1}) and H_2SO_4 (treatment conditions: 25 °C, pH 1.5) were chosen for the comparison. Fig. 3 shows change in the height of the suspension–supernatant interface (Z) with time (t).

As evident from the figure, all settling curves exhibited the same trend: fast settling in the hindered zone followed by slower settling in the compression zone (as discussed in Section 3.2). These two major zones are separated by a transition zone. Increase in settling velocity just after the start for sedimentation run was due to the rapid aggregation of the flocs [32]. Wastewater treated at ambient conditions with alum showed poor settling in comparison to H_2SO_4 treated wastewater (pH 1.5, 25 °C). However, the wastewater treated with alum at 95 °C gave much faster settling rate than that at 25 °C. This result is in agreement with the past findings [5,25,34]. At higher temperatures, floc formation is accelerated and the size of the flocs becomes larger than that produced at lower temperatures. Hindered zone is much larger for the wastewater treated at 95 °C than that observed for the other two suspensions. It can also be seen that the settling rates were very slow for all the three suspensions.

The settling data have been correlated using a second order polynomial [27,35] as given below in:
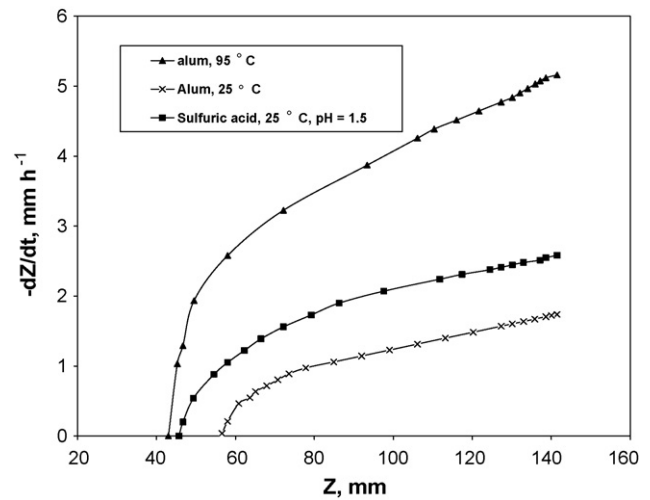
$$Z = at^2 + bt + c \tag{1}$$

Fig. 4. Velocity of suspension–supernatant interface vs. height for all three curves shown in Fig. 3.
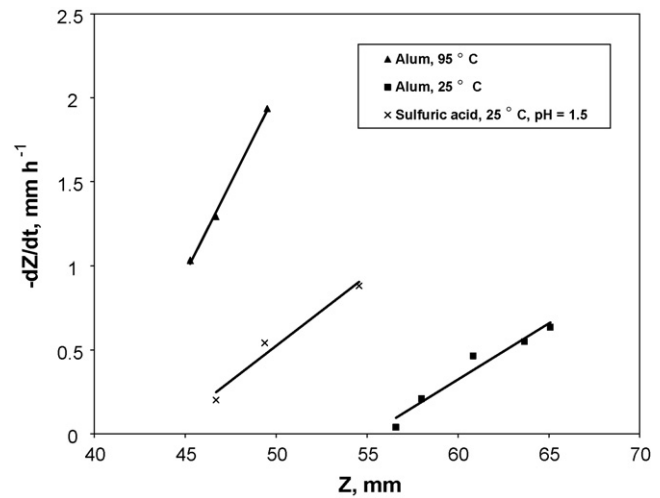

Fig. 5. Localization of critical points for all three settling curves.

where Z is height of the suspension at time t and a, b, and c are constants.

For all the three suspensions, the polynomial fits very well with the data obtained in the fast settling zone. The settling data for the wastewater treated with alum at 25 °C also showed a good correlation with Eq. (1) for the compression zone unlike the two other suspensions. This fact was also confirmed by lower regression coefficient (R^2) values for these two suspensions (i.e. one treated with H_2SO_4 and the other treated with alum at 95 °C). The values of constants a, b, c and regression coefficient (R^2) are shown in Table 3. High values of regression coefficients show that the equation fits well with the data obtained from settling tests.

The critical points for the three curves in Fig. 3 were located by plotting Tory graphs ($-dZ/dt$ vs. Z) [25]. For all the three suspensions, the derivatives of Eq. (2) were determined and then plotted

Table 3
Values of constants and regression coefficient for three suspensions.

Suspension	a	b	c	R^2
Alum, 95 °C	0.0645	−5.1602	140.54	0.9934
Alum, 25 °C	0.0085	−1.7393	142.67	0.9964
H_2SO_4, 25 °C, pH 1.5	0.0170	−2.5815	138.40	0.9873

Table 4
Values of critical solid concentrations for suspensions obtained after the addition of alum at different temperatures and H_2SO_4.

Suspension	C_0 (kg m^{-3})	Z_0 (mm)	Z^* (mm)	$C_{critical}$ (kg m^{-3})
Alum, 95 °C	5.04	141.5	49.5	14.40
Alum, 25 °C	5.04	141.5	65.1	10.96
H_2SO_4, 25 °C, pH 1.5	2.85	141.5	54.6	7.40

Table 5
Comparison of characteristics of solid residues (obtained after diluted black liquor treatment using alum and H_2SO_4) with black liquor, coal and wood.

Parameters	Black liquor	Residue obtained after treatment with alum	Residue obtained after treatment with H_2SO_4	Indian coal [37]	Wood chips [38]
C (%)	20.00	43.24	59.71	38.9	49.1
H (%)	4.504	5.805	5.351	2.6	6.0
N (%)	0.007	0.166	0.00	0.7	0.6
S (%)	2.709	2.787	2.624	0.6	0.06
C/H atomic ratio	1:2.70	1:1.61	1:1.08	1:0.80	1:1.46
High heating value (MJ/kg)	12.14	26.90	25.84	16.5	19.53
Ash (%)[a]	32.4	12.34	3.34	43.1	2.13
Volatile matter (%)[a]	58.0	60.21	74.24	31.4	92.03
Fixed carbon (%)[a]	9.6	27.25	22.42	25.5	5.84

[a] Moisture-free basis.

against the height of the interface between suspension and the supernatant in the vertical cylinder (Fig. 4).

Thus the settling rate of the wastewater treated with alum at 95 °C was almost thrice and twice than that obtained for the wastewater treated at 25 °C using alum and H_2SO_4, respectively. The initial settling velocity for the wastewater treated with alum at 95 °C was 5.16 mm h^{-1} as against 1.74 mm h^{-1} and 2.58 mm h^{-1} for the wastewater treated at 25 °C with alum and H_2SO_4, respectively. The critical points were estimated using the procedure given by Larue and Vorobiev [27]. The critical points are located at the lower end of the straight line in the hindered zone of settling. In order to calculate the critical points for the three curves, the lowest straight part of the Tory plots were magnified and illustrated in Fig. 5. The values of the estimated height of the critical points (Z^*) for suspensions can be used to determine the critical solid concentrations using the relation given below [36]:

$$C_{critical} = \frac{C_0 Z_0}{Z^*} \qquad (2)$$

where C_0, initial solid concentration; Z_0, initial level of interface; $C_{critical}$, critical solid concentration at the interface height of the interface, Z^*.

The values of the critical solid concentration and the height of critical points are given in Table 4.

It is evident from this table that the critical solid concentration was higher for the suspension having better settling characteristics. The solid concentration for wastewater treated with alum at 95 °C was found to be 14.4 kg m^{-3} as compared to 10.96 kg m^{-3} found for the wastewater treated at ambient temperature. The suspension formed after mineral acid treatment showed lower critical solids concentration of 7.4 kg m^{-3} despite having better settling characteristics than the suspension obtained after the treatment at 25 °C with alum. This may possibly be ascribed to the lower initial suspended solids concentration in the acid treated wastewater (2.85 kg m^{-3} than 5.04 kg m^{-3} for alum treated suspensions at 25 °C). Higher solids concentration in the alum treated suspensions is expected due to the precipitation of alum species. The interface height was the lowest for the suspension settled faster than the other two (49.5 and 65.1 mm for alum treated wastewaters at 95 and 25 °C, respectively and 54.6 mm for H_2SO_4 treated wastewater). This shows the compactness of the solid residue. The well settled solid residue will be handled easier than the bulky suspension.

4.6. Characteristics of the sludge obtained after the treatment of wastewater with alum and H_2SO_4

Precipitates formed after treatment with alum (dosage = 5 g l^{-1}) and H_2SO_4 at 25 °C were characterized by performing elemental and proximate analyses and determining their HHVs (Table 5). The results were compared with that of black liquor, Indian coal [37] and wood chips [38]. HHV of the sludge obtained after treatment with alum and H_2SO_4 resemble with that of lignin (ca. 27 MJ/kg)

[19]. The heating values of the sludge were found to be much higher than conventional Indian coal, wood chips and black liquor. However, the sulfur content in the pulp mill residue ranged from 2.6 to 2.8%. On the other hand, coal and wood chips have much smaller values (0.6 and 0.06%, respectively) of sulfur. Ash content in H_2SO_4 treated sludge (ca. 3.3%) was around 1.3 times that of wood chips (ca. 2.1%) but much lower than that found in coal, alum treated sludge and black liquor. Solid residues obtained after treatment had higher carbon content (ca. 43% and 59%) as against that obtained from the black liquor (ca. 20%). However, this is comparable to that for wood chips (ca. 49%). Volatile matter in coal is only ca. 31% in comparison to >90% in wood chips and 58–75% in pulp mill derived black liquor and solid residues. As a consequence of lower levels of volatile matter in coal, heating of the combustion chamber is slow in comparison to other materials discussed here since heat is generated rapidly as volatile materials are oxidized.

It is apparent from the thermal characteristics that the solid residues may be used as fuel or a co-fuel in energy recovery operations. The major constraint with this material is the presence of high sulfur. This drawback can be overcome by co-firing this material with wood chips [39]. Apart from this, the waste residues need to be dried (either in air or by providing external energy) before using for energy recovery due to high water content present in precipitated slurry. The sludge treated with alum also has high aluminium concentration (~37 g/kg of sludge). Since the residue is originally derived from wood, it contains almost 100% biogenic fraction that is considered 'carbon neutral' [40]. Hence, CO_2 emissions from co-combustion will not contribute to greenhouse gas (GHG) emissions and resulting in the reduction in net CO_2 emissions. The potential outlets for this fuel may include coal-fired power plants, cement kilns, paper mill boilers and gasification plants since these facilities are constantly aiming to reduce GHG emissions for meeting global requirement and cut the fuel prices to make the energy recovery process less expensive. As an alternative, such facilities can use biomass rich waste derived materials (available at no or low cost) as a co-fuel in the processes [40]. The above discussion leads us to believe that the energy recovery from the pulp and paper mill wastewater in the form of combustible precipitate is a distinct possibility.

5. Conclusions

All aluminium-based coagulants and ferrous sulfate were found to be equally efficient in removing COD of the diluted black liquor (ca. 60% reduction for a substrate having an initial COD = 7000 mg l^{-1}). Commercial alum was found to be the most economical coagulant among these tested coagulants. The capability of a coagulant for reducing COD and colour strongly depends on the pH of the wastewater. Using commercial alum, the maximum COD and colour reductions of 63% and 90% were obtained at an optimum pH of 5.0. The pH of the resulting effluent after treatment with

alum was decreased. Acid precipitation using H_2SO_4 exhibited substantial COD reduction at a pH < 4.0. The COD removal was mainly due to the separation of non-readily biodegradable lignin from the wastewater. Further COD reduction can be achieved by treating the supernatant using biological methods or wet oxidation processes or adsorption.

Settling characteristics of the resulting slurry were found to have improved with an increase in treatment temperature. The settling rate of the wastewater treated at 95 °C was almost 3 times of that treated at 25 °C. The solid residue obtained after coagulation and acid precipitation was found to have considerably high heating value and can be used as a renewable source of energy in several energy intensive industries for electricity production and heat recovery. It can be concluded that this kind of fuel will be in demand because of low or negligible cost, biogenic fraction, better thermal characteristics and continuous depletion in coal reserves. However, a detailed laboratory and pilot scale study on the probable emissions from the combustion of the residue and the impact of aluminium on emissions need to be investigated before using the residue for energy recovery processes.

Further studies should also be aimed to determine the effect on optimum dosage of coagulants at higher treatment temperatures.

Acknowledgements

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