Treatment of Paper and Pulp Mill Effluent by Coagulation

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Abstract—The pulp and paper mill effluent is one of the high polluting effluent amongst the effluents obtained from polluting industries. All the available methods for treatment of pulp and paper mill effluent have certain drawbacks. The coagulation is one of the cheapest process for treatment of various organic effluents. Thus, the removal of chemical oxygen demand (COD) and colour of paper mill effluent is studied using coagulation process. The batch coagulation process was performed using various coagulants like: aluminium chloride, poly aluminium chloride and copper sulphate. The initial pH of the effluent (Coagulation pH) has tremendous effect on COD and colour removal. Poly aluminium chloride (PAC) as coagulant reduced COD to 84 % and 92 % of colour was removed at an optimum pH 5 and coagulant dose of 8 ml l^{-1}. With aluminium chloride at an optimum pH = 4 and coagulant dose of 5 g l^{-1}, 74 % COD and 86 % colour removal were observed. The results using copper sulphate as coagulant (a less commercial coagulant) were encouraging. At an optimum pH 6 and mass loading of 5 g l^{-1}, 76 % COD reduction and 78 % colour reduction were obtained. It was also observed that after addition of coagulant, the pH of the effluent decreases. The decrease in pH was highest for AlCl$_3$, which was followed by PAC and CuSO$_4$. Significant amount of COD reductions was obtained by coagulation process. Since the coagulation process is the first stage for treatment of effluent and some of the coagulant cations usually remain in the treated effluents. Thus, cation like copper may be one of the good catalyst for second stage of treatment process like wet oxidation. The copper has been found to be good oxidation catalyst then iron and aluminum.

Keywords—Aluminium based coagulants, Coagulation, Copper, PAC, Pulp and paper mill effluent, Wastewater treatment

I. INTRODUCTION

INTEGRATED pulp and paper mill generates wastewater with very high BOD and COD, toxic substances, recalcitrant organics, pH, turbidity, high temperature and intense color. The colouring body present in the wastewater from pulp and paper mill is organic in nature and is comprised of wood extractives, tannin resins, synthetic dyes, lignin and its degradation products formed by the action of chlorine on lignin [1]. Paper industry consumes large amount of water (about 250-300 m^3 per tones of paper) and generate an equal amount of wastewater [2]. Black liquor (originating from the chemical pulping stage) contains lignin, carbohydrates, organic acids, sulfur compounds, phenolic compounds, terpenes, resin, etc. Pulp and paper effluents contain a number of compounds which are harmful to receiving waters and are inhibitory or recalcitrant to biological treatment. Conventional treatment processes like chemical pre-treatment [3], lagooning [4], and activated sludge treatment [5, 6] are not adequate to meet the regulatory effluent standards for being discharged into sewers. Therefore, the pulp and paper industry has to use tertiary polishing stage to meet the effluent discharge standards.

Several treatment methods are in use in large mills including physcio-chemical and biological. The biological treatment is also not very effective in reducing colour [7], although BOD and COD reduction has been found to be satisfactory. However, lignin and its derivatives show high stability to degradation [8, 9]. Wet air oxidation (catalytic and non-catalytic) has been found to reduce BOD, COD and colour to a large extent. However, the energy requirement and the use of high pressure reactors and associated equipment make the wet air oxidation of large volume of wastewater uneconomical. Chemical precipitation (and/or coagulation) using alum, ferric chloride, lime, ferrous sulphate and poly aluminium chloride (PAC) have been studied extensively [10-14]. Although economical, in comparison to other methods, the precipitation method has other associated drawbacks like dewatering and disposal of the generated sludge.

Primary treatment methods like physical, chemical and thermal pre–treatment may be followed by anaerobic, aerobic and enzymatic treatment methods to remove the residual organics, which is largely degradable. Coagulation/ flocculation can, however, be used as an effective primary treatment method to remove much of the toxicity, colour, and COD (and BOD). This treatment will make the secondary treatment cost effective as well as efficient in the removal of residual toxic organic compounds and colour.

It has been seen that most of the reported research work used aluminium, ferrous salts and its polyelectrolyte for the coagulation/ flocculation process, to remove the toxic organic materials from the wastewater in order to make it amenable to secondary treatment, like wet air oxidation (WO) or biological treatment. The present paper deals the COD and colour removal of pulp and paper mill effluent using aluminium salts like aluminium chloride and polyaluminium chloride and also the new coagulant cuprous sulphate. As per our knowledge, no one has studied the CuSO$_4$.5H$_2$O as coagulant. Since, pH has tremendous effect in coagulation process, hence in present studies, at constant mass loading, the initial pH is varied using alkali and acid, which saves the coagulants doses. This type

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of studies has not been found in past literatures. They have maintained the initial pH of wastewater and added the coagulants, which causes less COD reductions even at high mass loading of coagulants.

II. MATERIALS AND METHODS

A.Effluent

Black liquor was obtained from a local integrated kraft pulp and paper mill. This liquor was having a COD of about 7×10^5 mg l^{-1}. Synthetic wastewater was prepared by diluting this black liquor with distilled water to obtain a COD value of about 7000 mg l^{-1}. The average characteristics of the synthetic wastewater are presented in Table I.

TABLE I

CHARACTERISTICS OF DILUTED BLACK LIQUOR

Parameter	Values
Chemical oxygen demand (COD) (mg l^{-1})	7000
Biochemical oxygen demand (BOD) (mg l^{-1})	1400
pH	10.45
Total solids (TS) (mg l^{-1})	7 240
Total dissolved solids (TDS) (mg l^{-1})	6 680
Total suspended solids (TSS) (mg l^{-1})	560
Conductivity (µmhos cm^{-1})	51760
Color	Dark brown

B.Coagulants and Chemicals

Analytical reagent (AR) grade chemicals have been used for the analysis of the parameters during coagulation/ flocculation studies. Laboratory reagent (LR) grade $AlCl_3$ and analytical grade (AR) $CuSO_4.5H_2O$ obtained from s. d. fine Chemicals Ltd., Mumbai (India) and the commercial grade aqueous solution of polyaluminium chloride (PAC) was obtained from M/s Jubilant Organosys Limited, Gajraula, India, which were used in the experiments. The characteristics of the PAC, $AlCl_3$ and $CuSO_4.5H_2O$ are given in Table 2. The X-ray diffraction pattern of the solid PAC sample supplied by another company was performed earlier by Srivastava et al. [12]. The major components identified were $AlCl_3$, Al_2O_3, Al_2SiO_5 and $3Al_2O_3.2SiO_2$. The scanning electron micrographs of the PAC at $100\times$ and $1000\times$ magnification showed small particulate structure in a matrix and also the larger porous particles embedded into it [12].

TABLE II
CHARACTERISTICS OF PAC, $AlCl_3$, $CuSO_4.5H_2O$

Characteristics	PAC	$AlCl_3$	$CuSO_45H_2O$
Appearance	Pale yellow liquid	Pale yellow solid	Dark sky blue
Specific gravity	1.486	-----	-----
Al/Cu content	3.33 mg/ml	0.202 mg/mg	0.2545 mg/mg
pH of 1% solution	3.39(V/V)	1.96 (w/v)	4.30
Sulphate	Nil	0.01%	38.476%

C. Experimental method

0.20 dm^3 of pulp and paper mill effluent was taken in a 0.50 dm^3 glass beaker. The pH of the effluent was noted. A known amount of the coagulant was added to the effluent and the initial pH (pH$_0$) was adjusted by adding aqueous NaOH (1 M) or H_2SO_4 (1 M) solution, than it is flash-mixed for 5 minutes by a stirrer and, thereafter, slowly mixed for 15 minutes. The effluent sample was then taken in a glass cylinder and kept quiescent for 6 h. The supernatant liquor was centrifuged and analysed for its COD and colour value. These steps were repeated at different dosages of the coagulant. Thus, the experiments were planned with the objectives: (i) Optimizing pH for maximum COD removal (ii)To get optimum coagulant dose at optimum pH for maximum COD removal.

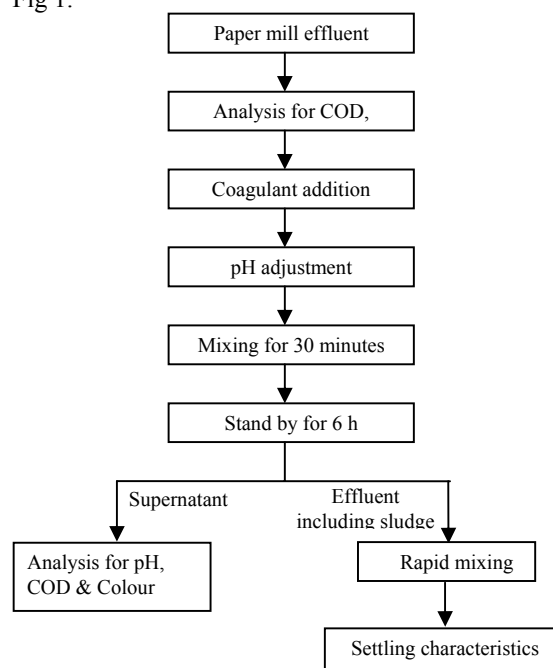Anexperimental detail of the coagulation study is given in Fig 1.

Fig. 1 Flow chart showing the steps for coagulation studies

D.Analytical Methods

The treated samples were centrifuged in a Remi Centrifuge (Model R 24, Remi Instruments, Mumbai, India). The COD of the effluent was determined by dichromate open reflux method as per standard method [15]. The colour of the initial and final effluent after the treatment was measured at a wavelength of 263 nm using UV/VIS spectrophotometer (Model Lambda 35 Perkin Elmer, Switzerland).

III. RESULTS AND DISCUSSION

The pulp and paper mill effluent contains reduced carbohydrates, lignin and resins, etc. The carbohydrates have mainly carboxylic and hydroxyl functional groups. The biorefractory molecule – lignin contains phenolic, hydroxyl and benzoylic hydroxyl groups. When aluminium chloride ($AlCl_3$), PAC and Copper sulphate are dissolved in water, the metal ions hydrate and hydrolyse to form monomeric and polymeric species : $M(OH)^+$, MOH^{2+}, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_2^0(s)$ and $M(OH)_4^-$ etc. At low pH (pH < 7), both Al^{3+} and Cu remain in the solution, and form precipitates of CuOH

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or $Al(OH)_3$ as the pH is increased or as the coagulant dosage is raised [16]. The general form of hydrolysis reaction of trivalent metals is represented as [17] :

$$x\, M^{3+} + y\, H_2O = M_x(OH)_y^{(3x-y)+} + y\, H^+$$

The metal hydroxide polymers have amorphous structure, very large surface area, and possess positive charge [18]. These hydroxides are hydrophobic, causing them to adsorb onto the organic anionic particle surface and become insoluble [16, 17].Copper and aluminium cations tend to associate and complex with a number of functional groups and ligands, especially with polar molecules and with oxygen containing functional groups like hydroxyl, phenolic and carboxylic groups [19-21]. The local negative charge of these groups is neutralised by the Al and Cu cations, resulting in colloid destabilization and precipitation of the metal (cations) – organics (anions) complexes. This phenomenon induces sweep flocculation and the adsorption and bridging enhancement of both particulate organics and inorganic solids to form large, amorphous flocs [22]. The precipitation is enhanced as the pH is lowered in the presence of multivalent cations.

E. Effect of pH on COD and Color Removal

Figure 2 and 3 show the effect of pH on the COD reduction as well as colour removal of the wastewater having an initial COD value of 7000 mg l^{-1} at ambient temperature (25 $^\circ$C) using different coagulants. The coagulant mass loading was kept uniformed as 5 g l^{-1} for $AlCl_3$ and $CuSO_4.5H_2O$ and 5 ml l^{-1} for PAC. The runs were taken at different initial pH (pH_0) values, i.e., at 2.0, 4.0, 5.0, 6.0, 7.0 and 8.0. The supernatant was then decanted off and its COD was measured. For aluminium chloride, the COD reduction was found considerable at $pH_0 \leq 5$ and maximum at the pH of 4.0 resulting in a COD reduction of 74 %. At $pH_0 > 5$, the COD reduction is found to decrease. For the coagulation by PAC, the maximum COD reduction (70 %) is noted at $pH_0 = 5$. After increasing or decreasing initial pH from 5, the COD reduction was found to decrease in both the cases. Similar COD reduction phenomena was noted for coagulation of biodigester effluent of an alcohol distillery plant using $AlCl_3$ and PAC [23]. For 5 gm l^{-1} of $CuSO_4$ the COD reduction was increased from pH_0 1.5 to 6.0, then decreased as pH_0 was increased from 6 to 8. The maximum 80 % COD reduction was obtained using this coagulant at pH_0 6. $CuSO_4.5H_2O$ showed better results (80% COD reduction) ,being the low molal feed *(5.1 mM Cu $\approx$ 5g/l $CuSO_4.5H_2O$)* than $AlCl_3$ (74% COD reduction) at higher molal feed *(7.57 mM $\approx$ 5g/l $AlCl_3$)*. This may be due to presence of greater unfield orbital in copper than aluminium. The anionic compounds of wastewater act as good reagents and electron donor to the Cu.

The variation in colour reduction was also studied, it was found to be in order of COD reduction for all the coagulant (Fig 3). The decolourization is expressed as the percent decrease in the absorbance of the biodigester effluent sample from the untreated sample at λ = 263 nm. The optimum colour reduction is found to be 86 %, 78 % and 82 % for $AlCl_3$, $CuSO_4.5H_2O$ and PAC treated effluent at their optimum pH_0 : pH_0 = 4 for $AlCl_3$, pH_0 = 5 for PAC and pH_0 =

6 for $CuSO_4.5H_2O$. For the coagulation with $CuSO_4.5H_2O$, the COD reduction is highest in comprasion to $AlCl_3$ and PAC (Fig. 2), however, the colour removal is lower than these coagulants, which may be due to the colour of $CuSO_4.5H_2O$ itself. The $CuSO_4.5H_2O$ produces blue colour, when it is dissolved in water.
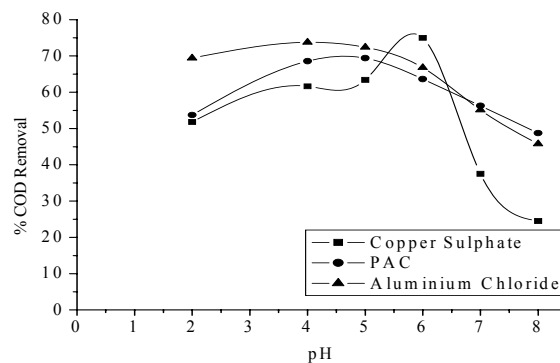
Fig. 2 Effect of pH on %COD removal for different coagulants.
($CuSO_4.5H_2O$ = 5 g l^{-1}, $AlCl_3$ = 5 g l^{-1}, PAC = 5 ml l^{-1})
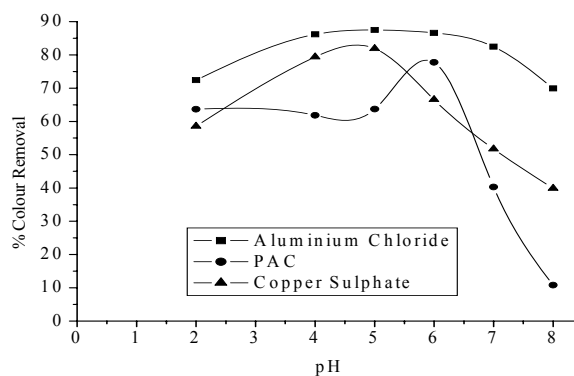
Fig. 3 Effect of pH on % colour removal for different coagulant.
($CuSO_4.5H_2O$ = 5 g l^{-1}, $AlCl_3$ = 5 g l^{-1}, PAC = 5 ml l^{-1})

The carboxylic and phenolic groups coordinate with metal cations at low pH as compared to hydroxyl and aliphatic hydroxyl groups. However, coagulation/flocculation at a particular pH will depend on the amount of the particular functional groups taking part in the coordination and complexation with metal cations. The removal of dissolved organics during coagulation and precipitation with metal salts at different pH values follows two distinct mechanisms. At low pH, the effluent containing anionic organic molecules coordinate with metal cations and form insoluble metal complexes. At higher pH and elevated coagulant doses, the organics adsorb onto pre-formed flocs of metal hydroxides and get precipitated. The net result of the two mechanisms is that the removal of dissolved organic compounds with different functional groups can occur over a wide range of pH, and that a maximum COD and colour removal may occur at a pH where the combined effect of both the mechanisms is maximum. Figures 2 and 3 also revel that the optimum pH_0 for COD and colour removal for all the coalulents fall in the acidic pH range and that the optimum pH_0 is specific to each

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coagulant. Thus, it may be concluded that the COD and colour reduction of pulp and paper effluent is a strongly dependent on the pH_0 value.

F. Effect of Mass Loading on COD and Colour Removal

The addition of different coagulants in the effluent and its flash mixing, creates proper coagulation condition. Gentle mixing thereafter initiates floc formation, complexation and adsorption of the organics resulting in the precipitation and settling of the insoluble solids.

For different coagulants, the effect of mass loading on the COD reduction of the synthetic wastewater ($COD_0 = 7\ 000$ mg l^{-1}) was studied at ambient temperature of 25 ^oC at their optimum pH_0 (Fig 4). The coagulant mass loading was varied from 1 to 9 g l^{-1} for $AlCl_3$ and $CuSO_4.5H_2O$, and 1 to 9 ml l^{-1} for PAC. From the figure, it is observed that as PAC coagulant dose is increased, the COD reduction is increased till 8 ml l^{-1} coagulant dose, after which, the COD reduction is almost unchanged. Thus, the 8 ml l^{-1} of PAC dose is optimum, resulting in 84 % COD reduction. For $CuSO_4.5H_2O$ coagulant, the COD reduction has been found to increase till 5 g l^{-1} dose, giving maximum COD reduction of 76 %. After increase in coagulant loading, the COD reduction decreases, indicating, 5 g l^{-1} as optimum dose to $CuSO_4.5H_2O$. The decrease in COD reduction at higher dose of copper sulphate may be due to excess amount of cations (Cu^+) causing the repletion in itself, providing less chances for coordinating copper cations of coagulant with anions present in wastewater. For $AlCl_3$ coagulant, the COD reduction has increased considerably till its loading of 5 g l^{-1}, giving ~ 74 % COD reduction, After an increase in its loading, the COD reduction increased marginally till 7 g l^{-1} and beyond which, the COD reduction has decreased.
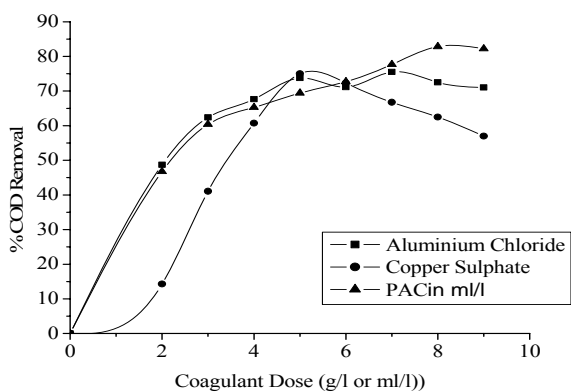

Fig. 4 Effect of coagulant dose on % COD removal at their corresponding optimum pH_0
($pH_0 = 6$ for $CuSO_4.5H_2O$, $pH_0 = 4$ for $AlCl_3$, $pH_0 = 5$ for PAC)

The colour reduction at optimum pH of coagulation for different coagulants is presented in Fig 5. For optimum mass loading of $CuSO_4.5H_2O$ (5 g l^{-1}), $AlCl_3$ (5 g l^{-1}) and PAC (8 ml l^{-1}) at optimum pH_0, the colour reductions are found to be 75 %, 88 % and 92 %, respectively.
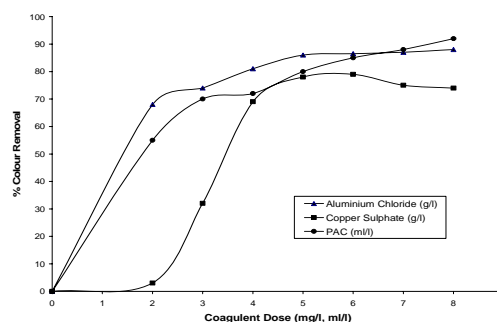

Fig. 5 Effect of coagulant dose on colour removal at their corresponding optimum pH
(pH_0=6 for $CuSO_4.5H_2O$, pH_0= 4 for $AlCl_3$, pH_0=5 for PAC)

The addition of metal ions in wastewater decreases its pH. The decrease in pH is proportional to amount of metal ions. Fig 6 shows variation of pH with dose of coagulants. The decrease in pH is less for dose of 8 ml PAC in comparison to dose of 5 g $AlCl_3$. It shows low amount of aluminium content in PAC than $AlCl_3$. Having the low amount of aluminum in PAC than $AlCl_3$, it gives high COD and colour reductions. It may be due to polymeric structure of the PAC. The multivalent Al cations of PAC coordinate with the anions present in pulp and paper mill effluent. And result in complexation. The gel structure of PAC also enmeshes the organics present in wastewater. Thus the complexation (and consequent precipitation) and the capture of the organics in the gel are responsible for the higher COD/colour reduction by PAC as compared to those obtained with $AlCl_3$ and $CuSO_4. 5H_2O$.

G. Variation in pH of Effluent by Adding Coagulants

Figure 6 shows the variation of pH after addition of different dose of coagulants. The decrease in pH after the addition of coagulant may be due to the several hydrolytic reactions, which are taking place during coagulation, forming multivalent charged hydrous oxide species and generating H_3O^+ ion during each step, thus reducing the pH value [24]. Chaudhari et al. [23] have also reported that the coagulant addition depresses pH to highly acidic levels, as the coagulant dose is highly correlated with pH. Higher doses of coagulants without the need of optimization are reported due to two reasons [24]: one for the increment in the aggregate rate and the other by enmeshing particulates into large aggregates. As it is reported earlier that (Fig 2), $pH_0 = 4$, $pH_0 = 6$ and $pH_0 = 5$, are the optimum pH for coagulation with $AlCl_3$, $CuSO_4.5H_2O$ and PAC, respectively. After adding optimum amount of coagulants in the wastewater, the pH of the solution changes, which are near to optimum pH_0 of the individual coagulant. Thus, further adding of alkali/ acid is not needed to adjust the initial pH_0 of coagulation.
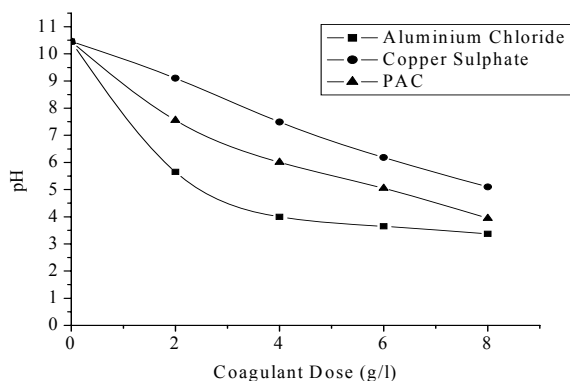
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Fig. 6 Effect of coagulant dosing on pH of effluent

H. Comparison of Different Coagulant for COD Removal

The effect of different coagulants, such as, PAC, aluminium chloride and copper sulfate on the COD and colour reduction are presented in Fig 7. From the figure, it may be seen that at their optimum dose, 8 ml l^{-1} for PAC, and 5 g l^{-1} for $CuSO_4.5H_2O$ and $AlCl_3$, the COD reduction is maximum (84 %) for PAC which is followed by $CuSO_4.5H_2O$ (76 %) and $AlCl_3$ (74 %).

The corresponding colour reductions 92 % for PAC, followed by 86 % for $AlCl_3$, and 78 % for $CuSO_4.5H_2O$.

The colour compounds present in the paper mill effluent are negatively charged, which get neutralized from the positively charged coagulant and remove the colour of the wastewater. The colour reduction increases up to a breakpoint, after which it starts decreasing due to increase in the coagulant concentration.
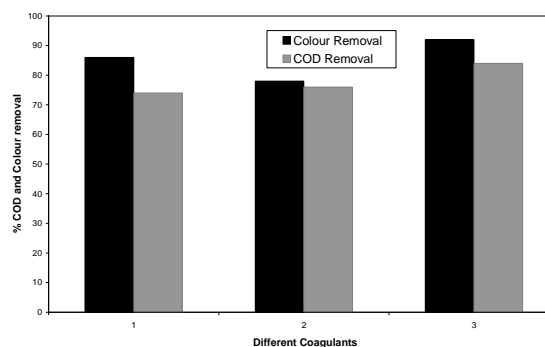

Fig. 7 Comparison of different coagulant for maximum COD and colour removal at corresponding to optimum pH and optimum dose. 1. Copper sulphate, 2 Aluminium Chloride, 3. PAC

TABLE III
DIFFERENT COAGULANTS USED AND THEIR CORRESPONDING REMOVAL FOR PULP AND PAPER MILL EFFLUENT IN VARIOUS LITERATURES

Coagulants	Concentration	Effluent type	Initial TC/COD	Parameter	(%) removal	References
Alum	100 mg l^{-1}	Paper machine		COD	96	[11]
		Alkali extraction		COD	50	
				Colour	80	
		Bleaching effluents		COD	20	
Ferric chloride	10 g l^{-1}	BCTMP/TMP		TC	75	[10
	7.5 g l^{-1}			Colour	90	
	7.5 g l^{-1}			Turbidity	98	
Aluminium chloride	10 g l^{-1}	BCTMP/TMP		Colour	90	
B+ Alum	100+300 mg l^{-1}	Paper and pulp		Colour	About 91	[14]
CaB + Alum	1000+300 mg l^{-1}	industry wastewater			About 91	
BrS + Alum	400 +300 mg l^{-1}				About 95	
BS + Alum	1000+ 300 mg l^{-1}				About 93	
PAC(Poly aluminium chloride)	3 g l^{-1}	Alkaline black liquor and acid wastewaters	2380 mg l^{-1}	COD	80	[12]
				Colour	90	
Copper sulphate	5 g l^{-1}	Black liquor	7000 mg l^{-1}	COD	61.4	[13]
PAC	8 ml l^{-1}	Black liquor	7000 mg l^{-1}	COD	83	Present work
				Colour	92	
Copper Sulphate	5 g l^{-1}			COD	74	
				Colour	76	
Aluminium chloride	5 g l^{-1}			COD	72	
				Colour	84	

A. Comparison of Results

Results obtained by other researchers to treat paper mill effluent have been compared in the Table 3, showing, the % COD and % colour removal along with the effluent type, coagulant type and their concentration. Stephenson et. al. (1996) [10] obtained 90% colour removal using 10 g l^{-1} dose of aluminium chloride. The dose is quite high in comparison

to 86.30% colour removal at 5 g l^{-1} dose in present work. Copper sulphate is used by Garg et al. for thermal precipitation of pulp and papper mill effluent [13], who have observed 61.4% COD removal. The better result (74% COD removal) in present work (using $CuSO_4$ coagulant) may be due to different process used by Garg et. al. They have performed thermal precipitation reaction at 95 °C. In the present work, the coagulation is performed at room

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temperature ~ 25 °C. Poly aluminium chloride has given better result as 82.85% COD removal and 91.81% colour removal, which is better to that obtained by Srivastava et al. [12].

IV. CONCLUSIONS

The pH of effluent has found to tremendous effect on COD and colour removal by coagulation process. The pH 4, 5 and 6 were optimum values for $AlCl_3$, $CuSO_4$ and PAC respectively.

The maximum COD and colour removal of 84 % and 92 % respectively were obtained using PAC (8 ml l^{-1}) as compared to 72 % and 84 % with aluminium chloride (5 g l^{-1}) and 74 % and 76 % with copper sulphate ((5 g l^{-1}) at their optimum pH_0.

After addition of coagulants, the pH of the effluent had decreased. The decrease in pH was maximum for $AlCl_3$, which was followed by PAC and $CuSO_4$.

The addition of catalyst followed by pH adjustment to its optimum value can save the coagulant dose considerably.

PAC is found to be a better coagulant in comparison to other two coagulants. However, copper sulphate may also be considered as a better prospective coagulant because the Cu content in supernatant works as a good catalyst for wet oxidation in the next stage of treatment by wet oxidation.

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