Iran. J. Chem. & Chem. Eng. Vol. 21, No. 2, 2002

Effect of Metal Salt Coagulants on Treatment of Activated Sludge Effluent in Sulfite Mill Pulp and Paper Plant

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ABSTRACT: *Pulp and paper effluents are considered as serious environmental hazards and their treatment, because of multiplicity of impurities and complexity of their chemical structures, is one of the most difficult and inconvenient industrial processes. As the most pulp and paper mill work on kraft process, there are few studies in literature on the treatment of neutral sulfite semi chemical (NSSC) process effluents. Sulfate lignin (SL) is the main concern of kraft process while lignosulphanates (LS) are primary concern for NSSC process. The high charge density of LS in the wide range of pH makes it more stable than SL. This experimental study examined the effect of metal salt coagulants (Alum, poly aluminum chloride, aluminum chloride and ferric chloride) on the treatment of activated sludge effluent in NSSC process used in Mazandaran pulp and paper industry. These coagulants were able to remove colour, turbidity and COD of the waste water up to 90, 95 and 70%, respectively. Results show that ferric chloride has the best performance among coagulants studied here. This feature of ferric chloride supports the idea that the Fe is more amenable to hydrolysis than Al.*

KEY WORDS: *Sulfite mill effluent, Alum, Ferric chloride, PAC, Aluminum chloride, Water treatment.*

INTRODUCTION

Treatment of pulp and paper effluent, because of numerous types or grades of effluents and complicity of their chemical structures, is one of the most difficult and expensive processes. The coloured effluents of pulp and paper plant cause serious disposal problems.The effluents, after primary treatment, are usually treated by some types of biological treatment (like activated sludge process or aerated lagoons), to decrease biochemical oxygen demand (BOD), and then clarification for reducing the suspended solids content. However, the colour and turbidity (associated with COD) are reduced only partially and these bodies are more difficult to remove [1].

Effluents from pulping and bleaching operations contain significantly higher concentrations of inhibitory and refractory organic compounds. Many of the compounds in these effluents are partially soluble in water and resist biological degradation or may exert significant toxicity toward the mixed microbial communities within biological treatment systems [2,3].

A conventional and effective method to remove these impurities is to use coagulation and flocculation processes. As these impurities are negatively charged , cations are capable of coagulating them in the form of large aggregates that may be removed by mechanical methods such as floatation, filtration and precipitation [4]. In addi-

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1021-9986/02/2/ 110 8/$/2.80

tion to lignin and lignosulphanates, other impurities in the pulp and paper effluent such as resin acids, tannins, long chain fatty acids, aromatic acids, phenols and terpenes have polar molecules and contain functional groups like hydroxyl or carboxyl groups. These groups provide small negatively charged species that can react with the iron and aluminum cations and form insoluble complexes [2,3]. Moreover the amphipathic (hydrophobic-ionic) compounds mentioned have high molecular weights, and are thus easily coagulated and precipitated. The coagulation and precipitation technologies have also the ability to remove natural organic materials (NOM) and synthetic organic chemicals (SOC) [5]. In addition, concentration of alkylhalides like trihalomethane (THM) and other chlorinated compounds, can be reduced during coagulation. Thus hydrolyzing metal salts are widely used as primary coagulants to decrease the concentration of organic compounds, suspended solids and colour in pulp and paper effluent.

There are two conventional methods for pulping process, i.e, Kraft (sulfate) and NSSC process (sulfite), but the kraft process is the most widely used in the world. Removing such fine admixtures as lignin is the main concern in the kraft process but lignosulphanates are the primary concern for sulfite pulp mill effluents. As the most pulp and paper mill works on kraft process, there are few studies in literature on treatment of wastewater in NSSC process.

Mazandaran wood and paper industry uses NSSC process. The main concern in the case of effluent from Mazandaran pulp and paper industry is high value of colour, turbidity and COD that are well above the environmental standards. Although at present high dosages of alum are used, they are not successful to decrease colour, turbidity and COD levels to standard limits. Thus finding suitable conditions for clarification of the effluent to reach the environmental standards are the main purpose of this research work.

MATERIALS AND METHODS

Source and characters of wastewater

The wastewater (effluent) used in this research work, was collected from inflow to the secondary (final) clarifier in Mazandaran wood and paper industry, in northern Iran, The flow sheet of the wastewater treatment plant is shown in Fig.1. The characteristics of the incoming wastewater to primary treatment, to secondary clarifier and the effluent from the final (secondary) clarifier are shown in Table 1. The average flow rate of raw wastewater is 664 m^3/day.

Analysis and measurement of studied parameters

Jar tests were carried out to assess effectiveness of the various coagulants in clarifing the biologically treated effluents (inflow to seconidary clarifier). A Phipps & Bird jar test apparatus (Richmond VA 23228) was used in this work.Addition of the various coagulants and coagulant aids with rapid mixing (3 minutes at 250 rpm) was fol-

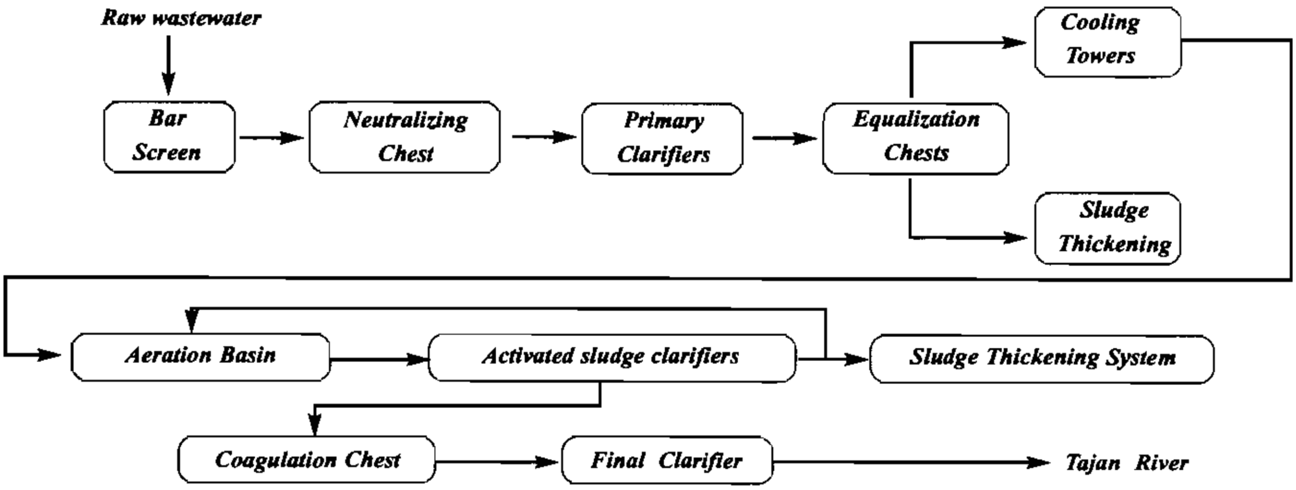

Fig. 1: Flow sheet of the wastewater treatment unit in Mazandaran wood and paper industry

Table 1: Characterization of various wastewaters in Mazandaran wood and paper industry

Parameter	Raw influent	Effluent of activated sludge clarifier (biotreated water)	Effluent of final clarifier
pH	5.5-7	7.5-8.5	7.5-8.5
Colour (Pt-Co)	4000-6500	1500-2600	>250
Turbidity (NTU)	250-400	100-120	> 30
COD (ppm)	2784	450-580	300-350
TSS (ppm)	500-1000	-	30
BOD_5 (ppm)	1157	-	20
Temperature (°C)	35-45	20-25	20-25

lowed by a slow stirring at 50 rpm for 15 minutes. The samples were then settled for half-hour and the supernatants was analyzed for turbidity, colour and COD. Turbidity of samples was measured at 450 nm on a Hach 2100 AN turbidimeter and calibrated against formazin standards. Colours were assayed at 455 nm on a Hach 2100 AN turbidimeter and calibrated against Platinum-Cobalt standards which are usually report as Pt-Co or CU (colour unit).

COD was measured according to standard methods [6] and samples were digested on a Hach COD meter thermoreactor and Hach DR 2000 spectrophotometer was used for determination of COD [7].The coagulants used in this work were: $Al_2(SO_4)_3$, $AlCl_3$, $FeCl_3$ and poly aluminum chloride (Sachtoklar 39, Germany). An anionic polymer (Prosedim ASI 25) was used as coagulant aid.

Aluminum sulfate and aluminum chloride with reagent grade were obtained from Merck Co. (Darmstadt, Germany).Poly aluminum chloride (PAC) has a structure formula as $[\ Al_2(OH)_{6-x}\, Cl_x \, . \, yH_2O\ ]_z$ (z=15 in the case of hydrolyzing in water). PAC solution (34% in water) was obtained from Sachtoklar Co.

Ferric chloride solution (41%) was purchased from Nirou Chlor Co. (Isfahan, Iran). Anionic polyelectrolyte was prepared from Degremont Co. (France).Lime, sodium hydroxide and sulfuric acid were used for pH adjustment.

Lime and H_2SO_4 were obtained from Merck Co. and NaOH (with purity 99%) was purchased from Nirou Chlor Co.(Isfahan, Iran).

RESULTS AND DISCUSSION

The effect of alum treatment of wastewater (inflow to final clarifier), without any pH adjustment, is shown in fig.2. It shows the percent removal of turbidity and colour versus dose of alum. The results illustrate that alum at high dose (> 800 ppm), removes most of turbidity and colour from the effluents. Removal of colour and turbidity up to 90% and 95% respectively , is possible by using less than 1 g/lit of alum. The curve showing turbidity reduction is very similar to that of colour reduction. This similarity suggests that tiny particulate materials in effluent are almost organic.

Residual COD of effluents versus alum dosages is shown in fig. 3. It shows that removal of COD up to 50, 60 and 70% are obtained at dosages of 700, 800 and 900 ppm alum, respectively. It can be seen that the initial COD of effluent is 534 mg/lit.

Fig. 4 shows the effect of pH on alum performance in reducing the colour of sample.

Results show that alum, as a coagulant, has the best performance in secondary clarifier in the range of pH 4.5-6.5.The reasons of such behavior are:

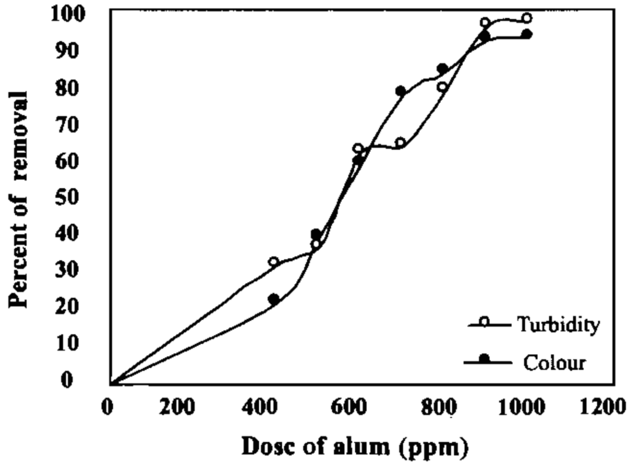

Fig. 2: Removal of colour and turbidity of effluent versus dose of alum added.

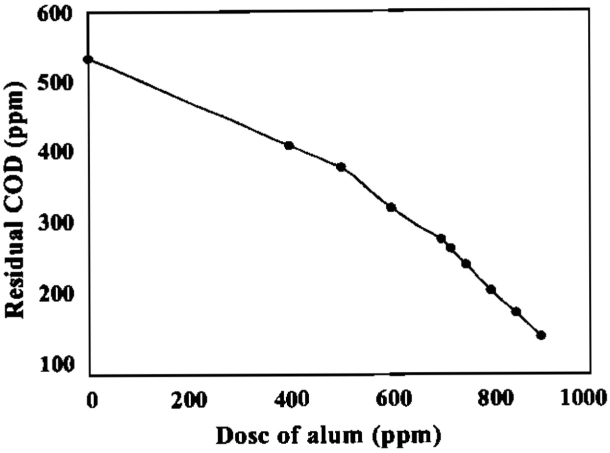

Fig. 3: Residual COD of effluents after alum coagulation.

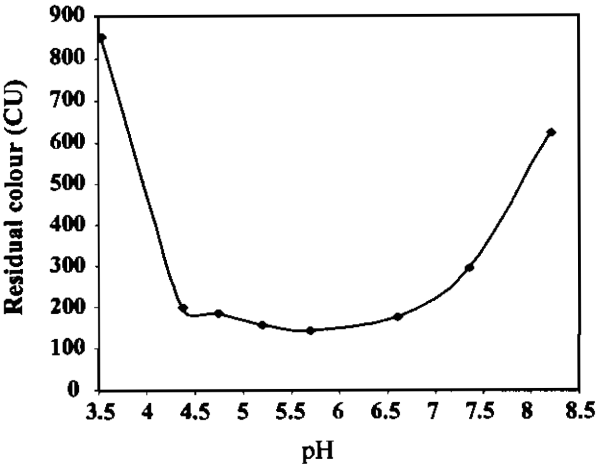

Fig. 4: Effect of pH on colour removal of effluent through allum coagulation

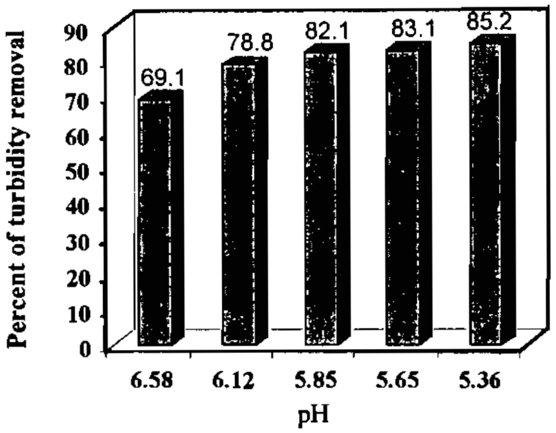

Fig. 5 : Colour removal from the effluent at 600 ppm alum at various pH levels.

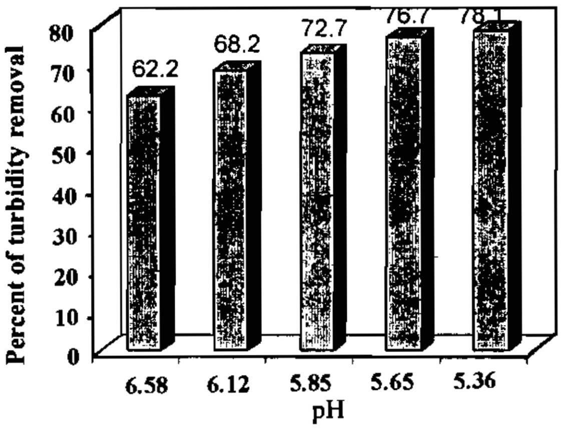

Fig. 6: Turbidity removal from the effluent at 600 ppm alum at various pH levels.

- At low pH, presence of monomeric aluminum species causes neutralization and then precipitation [8].

It should be noted that most of the wood extractive refractory components are insoluble under very acidic conditions [9].

- At low pH, the dissolved aluminum concentration decreases by decreasing the proportion of $Al(OH)_4^-$ formed, (this anionic aluminum hydroxide reduces the effectiveness of coagulation) hence improving precipitation [10].

Figures 5 and 6 show removal of colour and turbidity of effluent at various pH levels at a constant dosages of 600 ppm alum. Comparing, fig. 2 with fig. 5 indicates that for the dosages of alum in the range of 500 to 700 ppm, the colour removal increases up to 50% when the pH of effluent is adjusted to 4.5-6.

Aluminum chloride performance

The performance of aluminum chloride in reducing colour, turbidity and COD of the effluent is shown in comparison with that of alum in figures 7-9.

It is observed that at a given dose aluminum chloride is more successful than alum in reducing colour , turbidity and COD.

Effect of aluminum chloride in colour reduction has been shown in Fig.10.

It should be noted that pHs shown in this figure are the operating pH of effluent without any pH adjustment by chemicals except added AlCl3.

According to figures 4 and 10, alum and AlCl3 per-

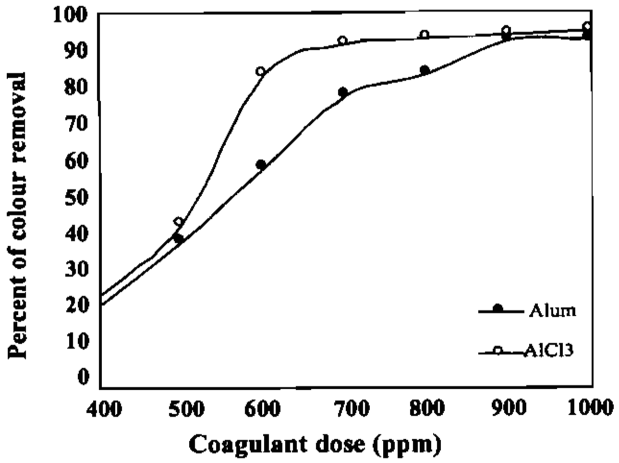

Fig. 7: Comparing the alum and $AlCl_3$ in colour removal

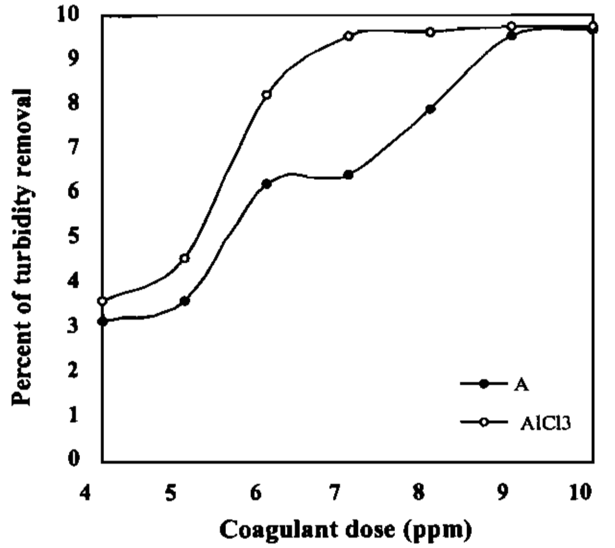

Fig. 8: Comparing the alum and $AlCl_3$ abilities in turbidity removal

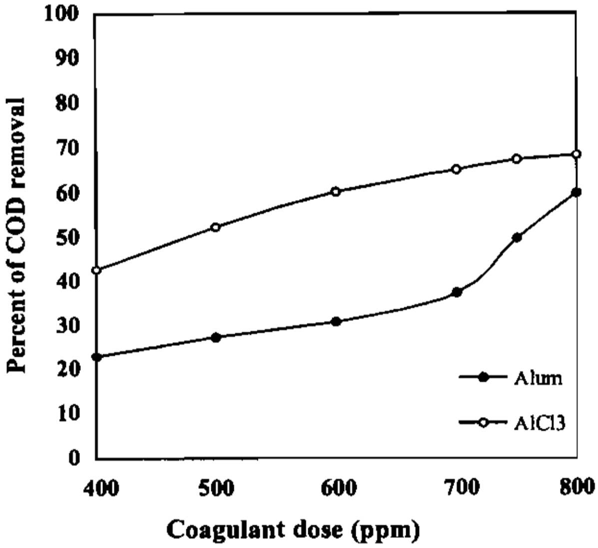

Fig. 9: Comparing the alum and $AlCl_3$ abilities in COD removal

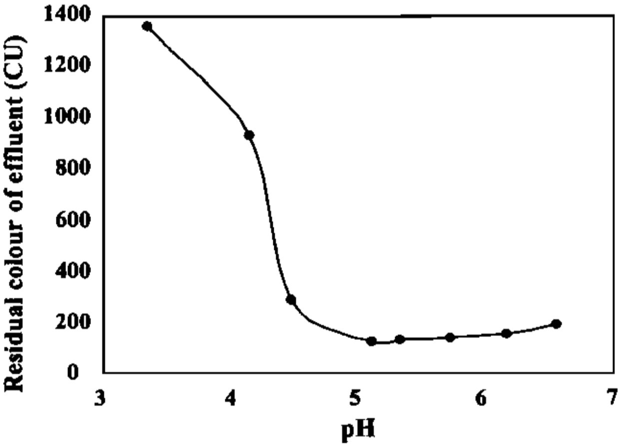

Fig. 10: Effect of $AlCl_3$ in reduction of colour at various pHs

form satisfactorily in reducing the colour, turbidity and COD in the pH range of 4.5-6.5 and the optimum pH range for these coagulants is almost the same.

Poly aluminum chloride (PAC) performance

Changes of residual colour, turbidity and COD of sulfite effluent due to addition of various dosages of 34% PAC solution are shown in figures 11 and 12. The initial values of the parameters were :

Colour: 2075 CU Turbidity: 100 NTU COD: 565 mg/lit

It was found that 500 ppm PAC can reduce colour, turbidity and COD, up to 92, 95 and 70%, respectively.

Fig.13 shows the effect of pH adjustment on PAC performance in reduction of colour and turbidity of the effluent.

Fig. 13 illustrates that there is only a narrow range of pH (near 5) for optimum performance of PAC in reducing the colour and specially turbidity. It is obvious that narrow range of pH for PAC limits its usage in effluent treatment.

Ferric Chloride performance

Performance of ferric chloride on colour, turbidity and COD removal is shown in figures 14-15. It can be

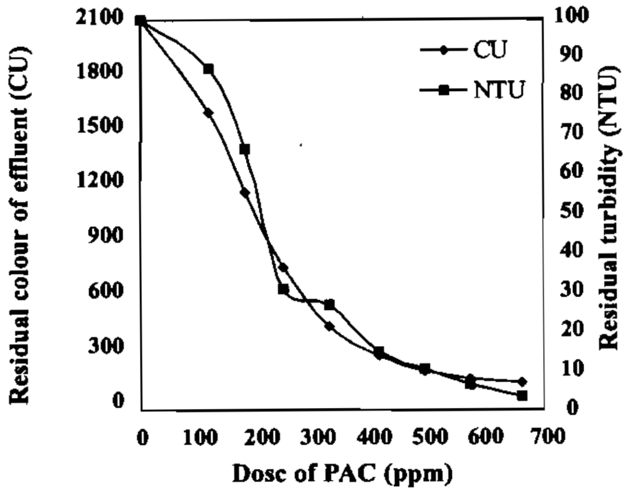

Fig. 11: Residual colour and residual turbidity of effluent when treated with various dosages of PAC.

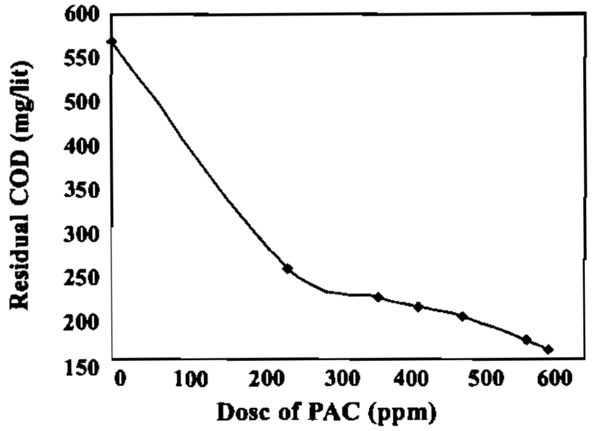

Fig. 12: Residual COD of effluent after coagulation versus dos of PAC.

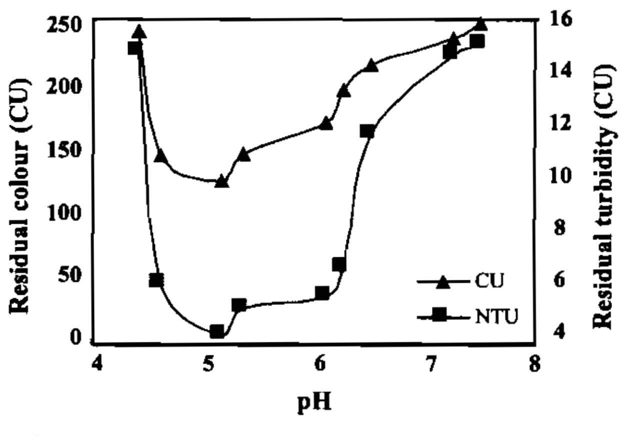

Fig. 13: Effect of pH adjustment on PAC performance in reduction of Colour and Turbidity of effluent.

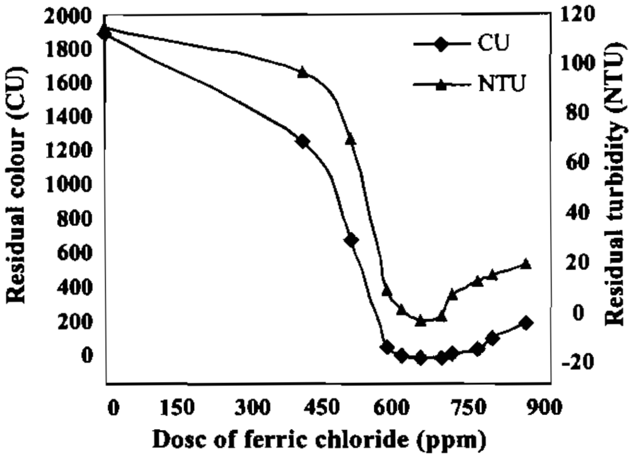

Fig. 14: Effect of ferrice chloride dosage on colour and turbidity of effluent.

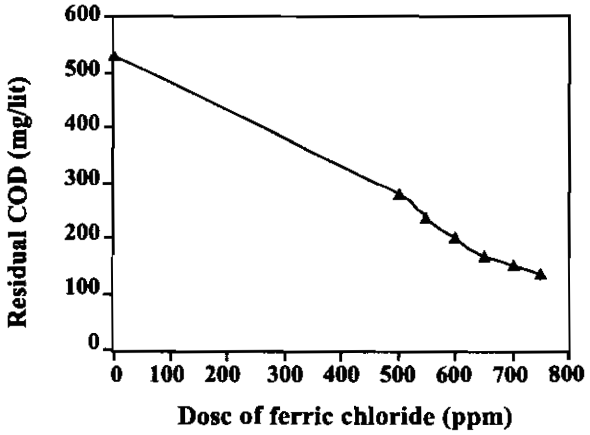

Fig. 15: Effect of ferrice chloride dosage on COD removal of effluent.

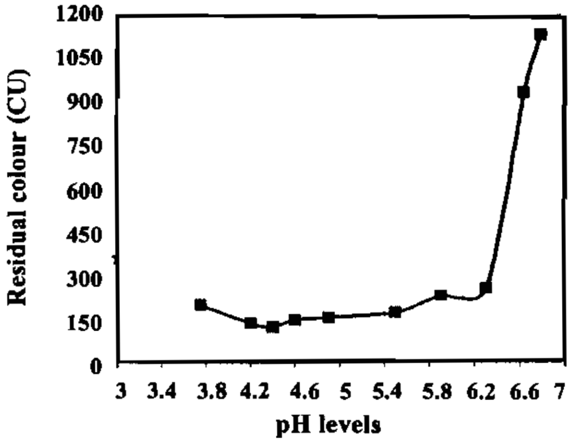

Fig. 16: Effect of pH adjustment on removal of effluent colour by 650 ppm ferric chloride.

seen that 600-700 ppm of ferric chloride is effective for coagulation of the suspended solids in the effluent. Removal up to 93,96 and 74% of colour, turbidity and COD were obtained through precipitation using ferric chloride. It should be mentioned, in these figures, pH of effluent has not been adjusted.

Since ferric chloride is a coloured solution it should be expected that exceeding of coagulant dose results in significantly higher colour levels in supernatant. This is in agreement with the observation by Ho *et al* [11] that colour reduction with iron salts is sensitive to coagulant dose after reaching a breakpoint.

Effect of pH adjustment on coagulation with ferric chloride

Effect of pH adjustment, before ferric chloride addition, on removal of colour is shown in fig. 16. The dosage was 650 ppm and the final pHs of samples were recorded.

It shows that the best pH range for optimum performance of ferric chloride is 3.8-6.2. The sharp increase in residual colour in pHs higher than 6.2 is due to formation of complex compounds such as $Fe(OH)_4^-$, $Fe(OH)_2^+$ and $Fe(OH)_2^+$ [12].

CONCLUSION

Metal salt coagulants, were examined to remove suspended solids in secondary clarifier of pulp and paper industry. Removal up to 90, 95 and 70% of colour, turbidity and COD of effluents were achieved. Ferric chloride has the best performance among the others.

It has been found that adjustment of the pH has a primary effect on the behaviour of each coagulant.The optimum pH ranges for alum, aluminum chloride, poly aluminum chloride (PAC) and ferric chloride were: 4.5-6.5, 4.8-6.2, 4.5-6 and 3.8-6.2, respectively.

Similarity in trends of colour and turbidity reduction with COD revealed that most of suspended solids in biotreated waste water (inflow to final clarifier) were organic.

Similar behaviour of colour analyses with turbidity results was emerged when they both were drawn in the same figure, i.e., figures 2, 11, 13 and 14. Based on this finding, it seems that colour and turbidity are not independent parameters, at least for effluent of pulp and paper industry.

Finding of this research work encourages that problem of high colour, turbidity and COD in the effluent of pulp and paper industry can be solved.

The results show that satisfying EPA standard requirement can be achived by using ferric chloride instead of alum and the performance of coagulant can be enhanced by adjusting pH of effluent during coagulation.

Received : 20th November 2000 ; Accepted : 29th May 2002

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