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Improved treatment of tannery wastewater treatment plant effluent using polymeric coagulants

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ABSTRACT

This study examined the physico-chemical treatment of industrial tannery effluent from a wastewater treatment plant (WWTP) by coagulation with metal salts and polymers. Optimum dosage of coagulants like lime, alum, anionic polyelectrolyte (APE) and cationic polyelectrolyte (CPE) were studied in individual, combined dosage in lab and plant scale. Studies on dosage of seven different combinations were conducted with the primary settling tank influent. The optimum dosage of coagulants were found to be (alum – 650 ppm, lime – 800 ppm and CPE – 5 ppm). The percentage removal of turbidity, total suspended solids (TSS) and chemical oxygen demand (COD) were found to be in the range of 80–97%, 50–60%, 50–60%. The feasibility of using anionic and cationic polymers as coagulant aid with lime and alum were evaluated. Sludge production rate, cost of treatment and disposal, efficiency of different combination of metal salts and polyelectrolyte were studied. Treatment cost comparison studies were done for metal salts with polymers as coagulant aid and only for polymers as coagulants. The cost of sludge disposal remarkably reduced in the use of polymer alone as coagulant.

Keywords: Tannery wastewater; Coagulation/flocculation; Physico-chemical treatment

1. Introduction

Tannery effluent has long been known to have characteristics which make it unsuitable for discharge into surface water bodies, groundwater and soil. High levels of bio-chemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and total suspended solids (TSS) were commonly observed. Analysis of chemical characteristics of the wastewater discharged into tannery wastewater treatment plant substantiates this claim. This present study deals with tannery effluent discharged from semi finished to finished leather industries.

Coagulation/flocculation of wastewater plays a major role in the reduction of BOD, COD, TSS and heavy metals in the primary treatment. Coagulation/flocculation of wastewater occurs through several reaction steps which are as follows: (i) hydrolysis of multivalent metal ions and subsequent polymerization to multi nuclear hydrolysis species (ii) adsorption of hydrolysis species at the solid-solution interface (iii) aggregation of destabilized particles by inter particle bridging, (iv) aggregation of destabilized particles by particle transport and van der Waals forces (v) aging of flocs and precipitation of the metal hydroxide [1]. The efficiency of the treatment plant depends on choosing an appropriate combination of coagulant and its concentration present in the clarifier. Ferric chloride, Alum and lime, have been widely used as coagulants for the treatment of tannery effluent [2,3,4]. Disadvantage in using these inorganic coagulants are the quantity of sludge produced in the process and the efficiency. Metal salts act by two different mechanisms: charge neutralization and incorporation of impurities in an amorphous hydroxide precipitate [5] .

Polymeric coagulants are more effective than metallic salts and also minimize the amount of sludge produced. Selecting a suitable coagulant is important to enhance the dewatering efficiency, reduce total sludge quantity and disposal costs [6]. Usage of polymeric coagulants with metal

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salts has been reported to have number of benefits like less sludge volumes and moisture content. Bigger and compact flocs were observed with higher settling rates, which allows the use of higher surface overflow rates for primary settling tank [7–9]. Coagulation/flocculation studies of tannery wastewater using eleven different cationic polymers were conducted to find out the optimum concentration of the coagulant [3,10]. Several studies focused on optimization of coagulants with combination of metal salts for the primary treatment of wastewater. But very few studies have been reported on the application of anionic and cationic polymers for the enhanced primary treatment of tannery wastewater. Thus the present study was conducted with the following objectives: (1) Optimization of coagulants like lime, alum, anionic and cationic poly electrolyte were studied in individual, combination in lab and plant scale. (2) The feasibility of using anionic, cationic polymers as coagulant aid with lime and alum were evaluated. (3) Sludge production rate, cost of disposal and treatment, efficiency of different combination of metal salts and polyelectrolytes were studied.

2. Materials and methods

2.1. Study area and sample collection

The effluent was collected from a tannery wastewater treatment plant (WWTP) in south Chennai, which receives 400 m^3/d of effluent from ten industries which are processing semi-finished to finished leather. The schematic representation of process flow diagram of the WWTP is given in Fig. 1. The effluent from the tanneries was collected in a receiving sump and pumped to an equalization tank. Aerators were used to mix the effluent in the equalization tank. In the primary physico-chemical treatment stage, effluent from the equalization tank was pumped to the flash mixer for the addition of different coagulants. The effluent from the flash mixer was sent to the primary clarifier via baffle channels. The sediments from the primary clarifier were removed and dewatered in a filter press before being dried in sludge drying beds. The effluent from primary treatment was sent to the secondary treatment stage, which was an activated sludge process. The effluent was sent to a secondary clarifier in which the biological sludge settles. Part of the biological sludge was recirculated back to the aeration tank for maintaining the level of mixed liquor suspended solids (MLSS) in the system. The secondary treated effluent was sent to multi grade filter for removing the residual organics.

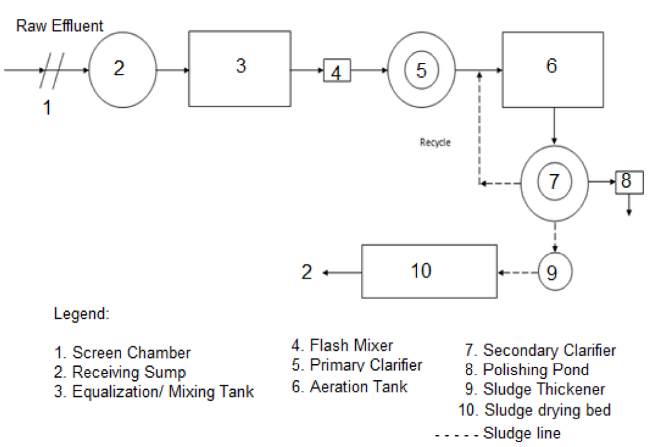


Fig. 1. Process flow diagram of the wastewater treatment plant.

2.2. Chemicals

Commercial grade lime $Ca(OH)_2$, alum ($AlSO_4 \cdot 18H_2O$) and polyaluminum chloride (PACl) were used in experimental studies. NaOH and H_2SO_4 (Merck) at analytical purity were used for the pH neutralization of raw wa stewater. Two different polyelectrolytes (anionic and cationic) of commercial grade were used for experimental and plant trial studies.

2.3. Analytical methods

The physical parameters including pH, TSS, TDS, COD of raw and treated tannery effluent were measured. A portable pH meter (PCS tester) was used for pH measurements. Total dissolved solids (TDS) and TSS were determined gravimetrically. COD samples were digested by (DRB 200 HACH digester) and titrated with ferrous ammonium sulfate. Particle size analysis was done using laser diffraction technique and zeta potential measurement was done using electrophoretic light scattering technique in Horiba LS 300 particle size analyzer. All these parameters were measured in accordance with standard methods [8]. Residual aluminium concentration present in the wastewater and sludge were determined by ICP-OES (Perkin Elmer Optima-5300 DV). Removal efficiency was measured in terms of reduction in TSS, TDS, pH, alkalinity and COD before and after treatment. The efficiency of the chemical dosage was measured in terms of reduction in total suspended solids (expressed in mg/L), total dissolved solids (expressed in mg/L), chemical oxygen demand (expressed in mg O_2/L) and turbidity (expressed in NTU) in the treated effluent. The main objective of the improved treatment was to comply the discharge limits of COD of 250 (mg O_2/L) and TSS (30 mg/L) [12].

2.4. Coagulation/flocculation experiments

The jar test is the most widely used method for evaluating and optimizing the coagulation/flocculation processes. Jar test apparatus was supplied by Scientific Engineering Corporation, Delhi. Batch experiments were conducted in six beakers which involve rapid mixing, slow mixing and sedimentation. Different concentration of coagulants were added to 500 ml wastewater samples and agitated in a jar test apparatus at 250 rpm for 1 min and 50 rpm for 3 min. After slow mixing, the flocs formed were allowed to settle for 3 h. Optimization studies were conducted for different concentration of lime (400, 500, 600, 700 and 800 ppm), alum (200, 300, 400, 500 and 600 ppm), anionic polyelectrolyte (APE) (1, 2, 4 and 10 ppm) and cationic polyelectrolyte (CPE) (1, 2, 3, 4, 5 ppm) in PST influent. The flocs were allowed to settle for 3 h. After settling, the turbidity, TSS, and COD of the supernatant were determined.

3. Results and discussion

The concentrations of coagulants like alum, lime, anionic and cationic polyelectrolyte individually or in combination, on Primary Settling Tank (PST) influent were optimized. The optimization studies done in the lab scale were applied in plant scale to evaluate the removal efficiency.

3.1. Studies on particle size analysis and zeta potential measurement

Studies on particle size analysis and zeta potential measurement were done for the primary inlet and treated effluent to identify the distribution of particle size and the charge of the particle. Coagulation will occur when the repulsive electrical forces between the particles are minimized. Particle size distribution of the PST inlet effluent varied from 0.05—15 µm and treated effluent varied from 0.05—28.5 µm. Increase in size of the particle distribution shows the formation of coagulated flocs. The zeta potential value of the tannery effluent chosen for study varied from —25 to —56 mV. Presence of negative charge particles can be neutralized with dosage of cationic polyelectrolyte. It would increase the removal of suspended particles in the primary settling tank influent [11].

3.2. Studies on single coagulant dosage optimization in PST

Fig. 2 shows the optimization of coagulants like lime and alum in PST influent. Removal efficiency was measured in terms of reduction of SS, TDS, pH, alkalinity, COD before and after treatment. For an increase in concentration of lime above 700 ppm above a gradual reduction of TSS, turbidity and COD values is observed in the treated effluent, but it increases the alkalinity as well as pH of the wastewater. For an increase in concentration of alum above 500 ppm a reduction of TSS, TDS and COD is verified in the treated effluent, but it increased the turbidity and alkalinity in the water. The optimized concentration of lime and alum for the primary treatment of tannery effluent were 700 ppm lime and 500 ppm alum. Results of single and combined coagulant studies shown that combined dosage of alum and lime proves to be effective in primary treatment of tannery effluent.

3.2.1. Optimization of anionic and cationic polyelectrolyte (APE, CPE) dosage in PST influent

The cationic polyelectrolyte used in this study was having active solids of 45–60%. It is a low molecular weight organic coagulant. Optimization studies on APE and CPE concentrations were done. The reduction in turbidity was measured for different concentrations and combinations of coagulants. It was observed that 1 ppm concentration of APE reduces turbidity to 741—645 NTU. For an increase in concentration of APE above 1–4 ppm does not change the effluent characteristics much in the treatment system. For an increase of CPE from 400 to 1000 ppm, there was an increase in the colour and sludge removal in the primary settling tank. The combination of 400 ppm of CPE, 400 ppm of alum and 2 ppm of APE works similar to the combination of 1000 ppm CPE and 2 ppm APE). It forms insoluble matter with the colored matter present in the tannery wastewater. It can be used alone or along with alum, ferrous sulphate or zirconius salts. The charge carried by the polymer was responsible for the abstraction of dissolved coloured matter present in the wastewater in the colloidal form, which was removed by sedimentation in the clarifier in the form of a thick sludge. It has effective high charge density at wide pH range of 3.5–5.5. Turbidity of the solution was also lower when compared to other combinations. Since CPE consumption was lower, this cost effective combination was chosen for implementation in field conditions. The results of the combination of CPE, alum, lime and APE coagulants used in the primary settling tank are shown in Table 1.

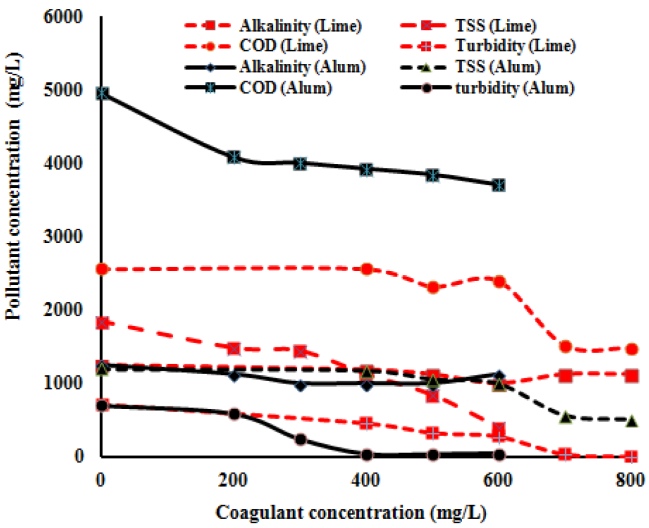


Fig. 2. Optimization studies on lime and alum concentration in PST influent.

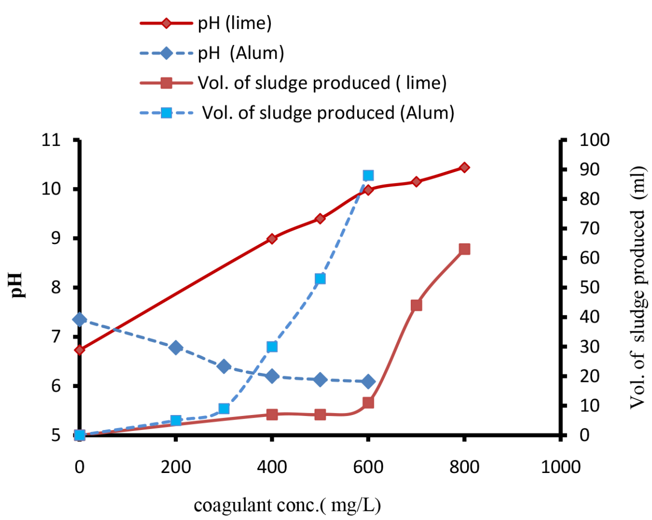


Fig. 3. Effect of pH and volume of sludge produced on lime and alum concentration in PST influent.

Table 1
Optimization studies on APE and CPE dosage in PST influent

S. No	Coagulant concentration (ppm)	Turbidity (NTU)	pH	Vol. of sludge (ml)
1	PST influent	741	6.78	0
2	1 ppm APE	615	6.9	23
3	4 ppm APE	606	7.0	22
4	1000 ppm CPE + 2 ppm APE	20	7.5	25
5	800 ppm CPE + 2 ppm APE	34	7.6	26
6	600 ppm CPE + 10 ppm APE	57	7.6	25
7	400 ppm CPE + 400 ppm Alum + 2 ppm APE	19	7.0	90

3.2.2. *Effect of combined dosage of lime and alum in PST influent*

Tannery wastewater with different combination of coagulants like alum and lime was mixed with 500 ml of PST influent kept in the jar test apparatus. After rapid mixing, the beakers were carefully removed from the jar test apparatus and any floc formed was allowed to settle for 3 h. The clear liquor ranging from the liquor level to 25 mm below the level was taken out for analysis. Optimization studies was conducted for combined dosage of lime and alum with different weight ratios in primary settling tank effluent. Physico-chemical characteristics like pH, volume of sludge settled, TSS, TDS, COD and turbidity were measured in PST influent before and after dosing different concentration of lime and alum. Physico-chemical characteristics of the PST influent for different combination of coagulant concentration are given in Fig. 4.

Performance of coagulation was increased in the order of (lime, alum, anionic polymer) < (lime, alum, CPE) < (lime, alum, APE and CPE). At optimum pH, coagulation and destabilization of particles is due to the coating of the inherently unstable aluminum hydroxide. This is possibly due to ionization on the surface of precipitate or adsorption of anionic ions [6]. Initial COD and TSS of the PST influent were 3280 mg/L and 1150 mg/L. For the combined dosage of (700 ppm lime, 500 ppm alum, 1 ppm of APE and 1 ppm of CPE) an increase in COD and TSS removal of respectively 70% and 92% were obtained in the PST influent. Whereas, the combination of coagulants (lime, alum and APE) results in TSS and COD reduction of 56% and 46% respectively. The enhanced primary treatment and reduction in sludge production were achieved by the addition of low concentration of polymeric coagulants [13].

3.3. *Coagulant optimization studies in PST influent in lab and plant scale*

There was always a gap between the performance of chemicals in laboratory and plant trials. To identify the gap between the performance of the trials conducted in lab and plant. Coagulation/flocculation experiments have been conducted in the WWTP site. The optimum concentration of the coagulants for the field trials were identified as the combination of (650 ppm Alum, 800 ppm lime and 5 ppm CPE). There is an increase in consumption of coagulants concentration because of the presence of more soluble COD present in the influent. The turbidity of the influent reduced from 2028 to 35 and 15 NTU, corresponding to removals of respectively (99.26% and 98.12%) for two different trials. Results of the optimized dosage of two different lab trials are shown in Table 2.

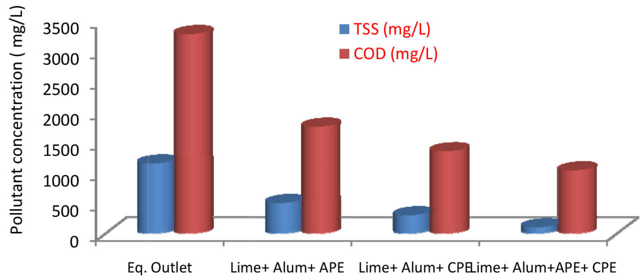


Fig. 4. Comparison of different combinations of coagulants for PST influent treatment.

Table 2
Optimization of coagulant concentration in plant and lab scale

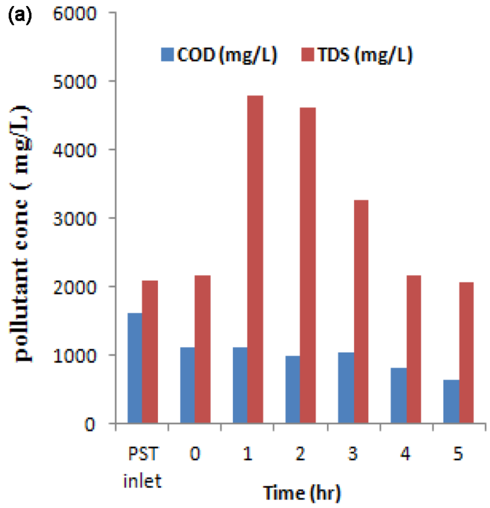
Description	Turbidity (NTU)	pH
PST influent	2028	7.49
Primary outlet (Trial 1) (Alum – 650 ppm + Lime – 800 ppm + Poly – 5 ppm)	35	8.12
Primary outlet (Trial 2) (Alum – 650 ppm + Lime – 800 ppm +Poly – 5 ppm)	15	7.96

3.3.1. *Plant trails on evaluating the performance of CPE in PST influent*

The best combination of coagulant concentration [CPE (10% solution) – 400 ppm, alum (10% solution) – 400 ppm and APE – 5 ppm] chosen from laboratory experiments were dosed in PST influent. Performance parameters like reduction in TSS, pH, COD, turbidity and TDS were measured with respect to time in the PST outlet. Existing combination of coagulant dosage reduces the TSS by 38% and COD by 28%. The addition of CPE reduces the TSS content around 59% and the COD reduction of 42% was observed with the new combination of coagulants in PST outlet. TDS, turbidity and pH of the wastewater does not vary much when compared to previous combination of coagulant concentration. Performance of CPE in the treatment of the PST influent is given in Fig. 5.

3.4. *Residual aluminium concentration estimation*

Aluminium concentration present in the treated wastewater and in the sludge leachate were determined by



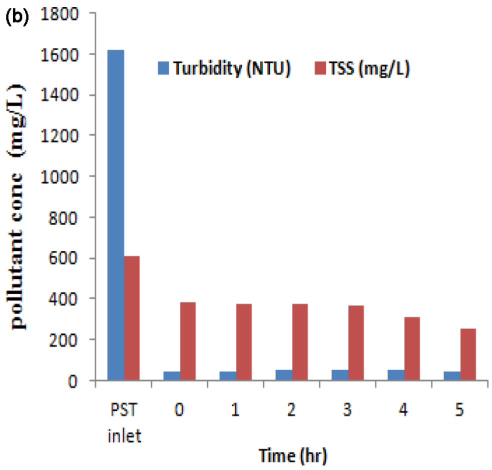


Fig. 5. Performance of CPE in PST outlet sample (alum — 650 ppm, lime — 800 ppm and CPE — 5 ppm).

Table 3
Sludge generation per day

Coagulant dosage	Rate of sludge generation		
	kg per day	kg per month (80% moisture)	Total cost per month ($)
Lime + Alum + APE	820	4100	473.1
Alum + CPE	360	1800	207.7

NOTE: * one dollar approximately ~ 65 INR.

ICP-OES (Perkin Elmer Optima 5300 DV). The aluminium concentration in the primary treated wastewater and sludge were 1.5–3 mg/L and 16.23–34.7 mg/L. Aluminium concentration present in the secondary treated wastewater was 0.2–0.4 mg/L which was close to the discharge limits imposed of 0.2 mg/L [12].

3.5. Rate of sludge generation in primary settling tank influent

The rate of sludge generation in the primary treatment was due to the amount of organic matter present in the wastewater, type of coagulant used and the operating conditions. The volume and settling characteristics of the sludge was determined for metallic salts and polyelectrolyte dosage. The presence of anionic polymer alter the coagulation by hydrolyzing metal ions in terms of replacement of hydroxyl ion or the kinetics of precipitation. Sludge generation due to polymer combination of coagulant and existing metal salt dosage were studied to calculate the sludge disposal cost. The amount of sludge produced per cubic metre of treated effluent was reduced from 2 to 0.9 kg due to the new combination of coagulant dosage. Quantity of sludge generation (360 kg) was reduced up to three times when compared to existing combination of coagulant dosage (820 kg). It reduced the sludge disposal cost by two fold per month (from $473 to $208).

3.6. Cost comparison for combination of coagulants for PST influent

Cost is an important factor for the CETP operator in deciding the acceptability of the proposed interventions. Optimum coagulant dosage for various combinations of alum, lime, and anionic were carried out by parallel teams. Cationic was tried with metal salt coagulants were found to yield highly favorable results in terms of COD reduction and colour removal in the tannery wastewater. Table 4 compares the daily operating costs for chemical usage and power. The calculations were made for 420 m^3 of wastewater treated for 20 working h/d. Costs considered for the comparison of the primary treatment were coagulant cost and sludge disposal cost.

4. Conclusion

Results shows that the combination of polymer coagulants can be used as a suitable replacement of metal salts

Table 4
Cost comparison for combination of coagulants for PST influent

Coagulant combination	Consumption per day	Cost/month ($)	Cost of sludge disposal ($)	Total cost ($/ month)
Alum (650 ppm) + Lime (800 ppm) + APE (10 ppm) + CPE (600 ppm)	Alum – 260 kg, Lime – 320 kg, APE – 150 g, CPE – 240 g	9819.8	2800*0.12 = 332	10,155.8
CPE (1000 ppm + APE (10 ppm)	CPE – 400 g, APE – 150 g	9256.7	1800*0.12 = 216	9,472.7

*Alum – 0.26$ /kg, Lime – 0.23$ /kg, APE – 5.7 $/kg, CPE – 0.76 $/kg. Disposal sludge cost – 0.12$/kg. Usually, sludge disposal cost was calculated for sludge with 80 % moisture.

for the tannery wastewater. The optimum concentration of the CPE and APE for the treatment of PST influent were 1000 and 20 ppm without the addition of metal salts. The optimum concentration of metal salts with CPE was determined as (alum — 650 ppm, lime — 800 ppm and CPE — 5 ppm). The percentage removal of turbidity, TSS and COD were 80–97%, 50–60%, 50–60% for the pre treatment of tannery wastewater. Primary treated wastewater was further treated in biological treatment, secondary settling tank and filtration to meet the standards. The results suggests that the combination of metal salts with suitable cationic polyelectrolyte could be a viable option to enhance the primary treatment of the tannery effluents.

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