



# Characterization and treatability studies of tannery wastewater using chemically enhanced primary treatment (CEPT)—A case study of Saddiq Leather Works

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## ABSTRACT

Chemically enhanced primary treatment (CEPT) is a technology that uses coagulants for enhanced pollutants removal at the primary stage of the wastewater treatment. This paper presents the detailed characteristics of tannery wastewater. It also explains effectiveness of CEPT in removing pollutants from tannery wastewater using various metal salts. The results of this study demonstrated that the tannery effluent had high concentrations of organic matter, solids, sulfates, sulfides and chromium. Alum, ferric chloride and ferric sulfate were tested as coagulants using jar test apparatus. Alum was found to be the suitable coagulant for tannery wastewater in a dose range of 200–240 mg/L as  $Al_2(SO_4)_3$ . With alum, percentage removal efficiency for turbidity, total suspended solids (TSS), chemical oxygen demand (COD) and chromium was found to be 98.7–99.8, 94.3–97.1, 53.3–60.9, and 98.9–99.7%, respectively. National effluent quality standards for total suspended solids and chromium were met after CEPT. However, COD content was high, emphasizing the need of secondary treatment for the tannery effluent.

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## 1. Introduction

Tanning industries in Pakistan are causing severe environmental problems due to the disposal of their untreated effluents on land and in water bodies. In the past few decades, developing countries have witnessed a sharp increase in leather production because such activities have declined in the developed world due to more stringent environmental pollution control requirements and high labour costs. Accordingly, Pakistan witnessed a rise in its leather export from US\$ 672 million in 2002 to 1.13 billion in 2007, which indicates an increase of 68% in a short span of 5 years [1]. The number of tanneries increased rapidly during this time period, which currently stands at approximately 650.

Wastewater characterization is an important step in designing effective treatment facilities for industrial wastewaters. This is especially true for tanneries which exhibit significant differences in their production processes generating effluents of unique and complex nature. Characterization is also needed for assessing the performance of individual unit operations and processes.

Most pollutants in wastewaters appear to exist either in particulate form or are associated with particulates [2]. This understanding

led to the wastewater treatment strategy of removing particulate and colloidal matter in the primary step using suitable coagulants. The process is commonly termed as chemically enhanced primary treatment (CEPT). After CEPT, the dissolved matter remaining in wastewater is dealt within the secondary step. Apart from removing commonly known pollutants, CEPT is reported to assist removal of heavy metals, PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons), which are strongly associated with particles [3]. There are other advantages of CEPT. The application of CEPT reduces the footprint of primary settling unit as it permits the use of high surface overflow rates. Similarly, reductions in terms of space and cost of subsequent biological unit are achieved due to the decreased organic loadings following CEPT. With minor retrofits, CEPT can also be applied to existing overloaded treatment plants to improve their efficiency. In addition, CEPT can effectively be employed for the removal of phosphorus in the effluents to control eutrophication.

Wastewater treatment in Pakistan is evolving. Application of secondary biological treatment to industrial and municipal wastewaters is not widely practiced due to a number of reasons which include high capital costs, lack of operation and maintenance skills, and the absence of stringent enforcement of environmental standards. In this scenario, best management practices must be used that are commensurate with available financial resources and skills. CEPT is a technology that appears to have potential in Pakistan

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to cope with evolutionary demand of environmental protection. This experimental study was undertaken to investigate the potential of CEPT for the treatment of tannery wastewater. The objectives of the study were: (1) to characterize the tannery wastewater and (2) to examine the treatability of tannery wastewater using different types of commonly used chemical coagulants and jar test methodology.

## 2. Materials and methods

### 2.1. Sampling

This study was carried out on tannery wastewater from Sadiq Leather Works (SLW), which is a large size tannery processing 18,000 kg of raw hides per day and producing finished leather for garments and shoes. The tannery is equipped with a primary treatment plant (PTP) consisting of screens, equalization basin, primary sedimentation tank, decanter for sludge and sludge drying beds. At present, addition of coagulants is not practiced during primary treatment at SLW. Average wastewater flow from the tannery is 1150 m<sup>3</sup>/day, which discharges into a local river.

Wastewater samples were collected from the equalization tank of PTP. The equalization tank had an average detention time of 8.5 h. It was equipped with mechanical mixers and dome type aerators for the purpose of mixing and homogenization. Samples were collected between 10 and 11.30 A.M. During this period the wastewater from almost all the tannery production processes had reached the equalization tank. For characterization, sampling was done weekly over a period of 14 months from May 2006 to July 2007. This period was considered sufficient to take into account all possible fluctuations in the production processes and all types of working routines which ultimately affect the effluent quality. For the purpose of jar tests, 60 L of sample was collected at a time from the equalization tank and transported within 30 min to the Institute of Environmental Engineering and Research laboratory. The collected sample was stored at 4 °C for subsequent use.

### 2.2. Wastewater characteristics

The wastewater samples from SLW were analyzed for temperature, pH, total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), settleable solids (SS), non-settleable solids (NSS), volatile suspended solids (VSS), fixed suspended solids (FSS), total alkalinity, total hardness, calcium hardness, chlorides, sulfates, sulfides, chromium, five day biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), phosphorus (P) and total kjeldahl nitrogen (TKN).

Settleable solids (SS) were determined on both volume and weight basis as described in Section 2540F of the *Standard Methods* [4]. Results on weight basis were used for comparison purposes. Non-settleable solids (NSS) were determined by subtracting the content of SS (on weight basis) from total suspended solids (TSS). NSS represent colloidal solids, which do not settle in primary sedimentation tanks at normal surface overflow rates. BOD<sub>5</sub> and COD tests were conducted on both raw and filtered samples of wastewater to estimate total and soluble contents of these parameters. Whatman GF/C filter, of pore size 1.2 μm, was used for filtration of wastewater. Wastewater samples were analyzed for the above mentioned parameters using test procedures outlined in *Standard Methods for the Examination of Water and Wastewaters* [4].

### 2.3. Coagulants tested

Alum Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O, ferric chloride FeCl<sub>3</sub>·6H<sub>2</sub>O and ferric sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O were tested as coagulants. 2% stock solu-

**Table 1**  
Mixing regime for jar tests

| Step            | rpm <sup>a</sup> | Velocity gradient, G (s <sup>-1</sup> ) | Time (min) |
|-----------------|------------------|---|------------|
| Rapid mix       | 300              | 380                                     | 1          |
| Medium mix      | 60               | 54                                      | 5          |
| Medium-slow mix | 40               | 32                                      | 5          |
| Slow mix        | 20               | 14                                      | 10         |
| Settling        | 0                | –                                       | 30         |

<sup>a</sup> Revolution per minute.

tion of each coagulant was prepared and fed into the jars at required dosages. Doses of above coagulants referred in this paper are without water of hydration. Thus all the alum doses are as Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, ferric chloride doses are as FeCl<sub>3</sub> and ferric sulfate doses are as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

### 2.4. Jar test methodology

Phipps and Birds Programmable Jar Tester with six acrylic square beakers, each having a capacity of 2 L, was used. Sampling port was provided with each beaker for drawing sample. Table 1 shows the mixing regime used for all the jar tests. As given in Table 1, after adding coagulants to the jars, the contents were rapidly mixed at 300 rpm for a period of 1 min. Rapid mixing was then followed by a tapered slow mix (flocculation) at three different speeds, i.e. 60 rpm for 5 min, 40 rpm for 5 min and 20 rpm for 10 min. Velocity gradient (G) values for various rpm employed have been shown in the Table 1.

The mixing speeds and times were selected from the experience of similar studies published in the literature [5–12]. A small portion, approximately 20 mL, was wasted to flush out the sampling tube when taking sample from each jar after 30 min of settling [13,14]. Jar tests were conducted in the following three series:

#### 2.4.1. Series 1

A series of preliminary jar tests were carried out with the objectives: (1) to examine the comparative suitability of various metal salts tested; and (2) to determine their optimum dose range. Only turbidity measurements were made on samples drawn from jars using Hach 2100AN turbidimeter. Coagulant dose was varied from 0 to 100 mg/L, in increments of 20 mg/L. Raw wastewater was given a pre-settling time of 30 min before conducting jar tests. Jar tests were performed on wastewater sample having pH of 7.5.

#### 2.4.2. Series 2

Best coagulant from series 1 was selected and used in this series at a dose range of 0–400 mg/L, in increments of 40 mg/L. Jar tests were conducted on raw (unsettled) wastewater samples as well as on samples after subjecting them to 30 min settling. The objective of this series was to study the effect of pre-settling on the efficiency of the coagulant. This could provide insight into the evaluation of using pre-settling tank before the coagulation step. The parameters tested to evaluate the efficiency of coagulant were turbidity, TSS, TCOD and chromium.

#### 2.4.3. Series 3

In this series, jar tests were performed at pH of 7.5 and 9.5. These pH values were the two extremes in which the pH of the tannery wastewater varied during the period of study (Table 2; serial no. 2). Pre-settled wastewater was used for this series. Best coagulant from series 1 was selected and its dose was varied from 0 to 400 mg/L, in increments of 40 mg/L. The objective of this series was to study the effect of pH on the removal of different pollutants, i.e. turbidity, TSS, TCOD and chromium.

**Table 2**  
Characteristics of raw homogenized wastewater of SLW for 14 months

| S. no. | Parameter <sup>a</sup>  | N <sup>b</sup> | Range         | Mean <sup>c</sup> |
|--------|---|----------------|---------------|-------------------|
| 1      | Temperature (°C)  | 33             | 20.4–34.2     | 29.3 ± 3.9        |
| 2      | pH  | 34             | 7.55–9.51     | –                 |
| 3      | Total solids (TS)   | 34             | 5330–15,912   | 9580.6 ± 2226.9   |
| 4      | Total suspended solids (TSS)                                  | 34             | 568–2132      | 1232.7 ± 277.4    |
| 5      | Total dissolved solids (TDS)                                  | 34             | 4466–14,572   | 8265.5 ± 2086.3   |
| 6      | Settleable solids (SS) (mL/L)                                 | 34             | 20–88         | 43.7 ± 14.7       |
| 7      | Settleable solids (SS)  | 28             | 448–1690      | 942.1 ± 243.9     |
| 8      | Non-settleable solids (NSS)                                   | 28             | 102–486       | 272.1 ± 104.4     |
| 9      | Volatile suspended solids (VSS)                               | 34             | 226–1344      | 804.9 ± 203.4     |
| 10     | Fixed suspended solids (FSS)                                  | 33             | 260–788       | 420.9 ± 117.9     |
| 11     | Total alkalinity (as CaCO <sub>3</sub> )                      | 34             | 520–1720      | 1227.3 ± 311.2    |
| 12     | Total hardness (as CaCO <sub>3</sub> )                        | 34             | 368–1050      | 770.8 ± 181.6     |
| 13     | Ca hardness (as CaCO <sub>3</sub> )                           | 34             | 208–700       | 404.4 ± 119.4     |
| 14     | Chlorides   | 34             | 1000.2–4548.9 | 3067.2 ± 900      |
| 15     | Sulfates  | 34             | 564.5–121.4   | 1246.2 ± 354.7    |
| 16     | Sulfides  | 34             | 14.8–424.5    | 156.9 ± 98.5      |
| 17     | Chromium  | 31             | 22.9–122.4    | 68.1 ± 24.5       |
| 18     | Total five day biochemical oxygen demand (TBOD <sub>5</sub> ) | 34             | 390–1320      | 774.9 ± 225.9     |
| 19     | Soluble BOD (SBOD <sub>5</sub> )                              | 34             | 200–765       | 526.6 ± 139.5     |
| 20     | Total chemical oxygen demand (TCOD)                           | 34             | 1760–3320     | 2442.4 ± 376.9    |
| 21     | Soluble COD (SCOD)  | 34             | 740–2040      | 1326.8 ± 300.9    |
| 22     | Phosphorous (P)   | 3              | 0.5–1.1       | 0.8 ± 0.3         |
| 23     | Total kjeldahl nitrogen (TKN)                                 | 3              | 104.4–40.6    | 118.3 ± 19.3      |

<sup>a</sup> All parameters except pH in mg/L if not specified.

<sup>b</sup> Number of samples.

<sup>c</sup> Mean ± standard deviation.

Jar number 1, in all the above jar test series, was used as control jar or “zero chemical” jar. Coagulant was not added to this jar to simulate conventional primary treatment.

### 3. Results and discussion

#### 3.1. Wastewater characteristics

The results of the wastewater characterization are presented in Table 2, which indicate quite a strong character of raw homogenized tannery wastewater. The wastewater contained high organic, solids, sulfates, sulfides and chromium contents. It was alkaline in nature and its composition continuously varied due to batch production processes with different discharge timings. Total alkalinity and calcium (Ca<sup>2+</sup>) hardness were significantly high with a mean value of 1227 and 404 mg/L, respectively. These high values could be advantageous as high alkalinity helps in the formation of flocs when coagulants are used [6] and Ca<sup>2+</sup> hardness is needed by anionic polymers when used as coagulant aid with metal salts [5,8,15].

High sulfate and sulfide concentrations were observed with a mean value of 1240 and 156 mg/L, respectively. Similarly high chromium contents with a mean value of 68 mg/L were present in the raw wastewater. The wastewater appears to be high in BOD<sub>5</sub> and TKN. However, data in Table 2 suggest that P is the nutrient limiting parameter for biological treatment of the wastewater. A BOD:N:P of 100:5:1 is generally considered to be an optimum ratio [16]. This ratio, based upon average values of these parameters from Table 2, was 100:15:0.1. Thus phosphorus was deficient in SLW wastewater. This deficiency has also been reported by Ates et al. [17] in tannery wastewater.

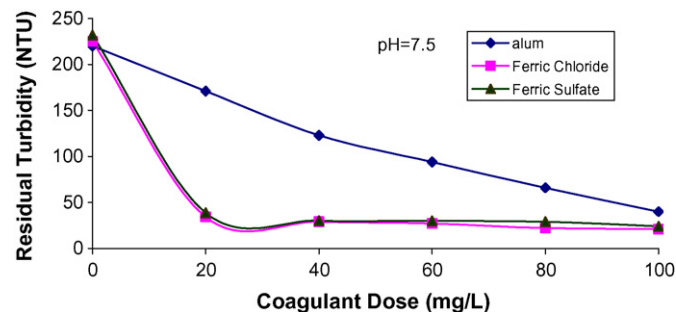
Experimental data were further examined to obtain useful relationship between major parameters as shown in Table 3. It can be seen in Table 3 that sufficient portion of TBOD<sub>5</sub> and TCOD was in the particulate form with mean values of 32 and 46%, respectively (serial no. 1 and 2). Practically, this entire portion can be removed at primary step using suitable coagulants. The value for particulate COD in Table 2 is comparable with the results obtained by Ates et al. [17] and Orhon et al. [18] for tannery wastewater. The mean

value of TCOD/TBOD<sub>5</sub> was 3.2 (serial no. 3), which appeared to indicate that a large portion of organic matter in tanneries wastewater was non-biodegradable or very slowly biodegradable. Out of total solids, on average, 86% were in the dissolved form (serial no. 5). Similarly in case of TSS, 80% were settleable (serial no. 6) and 70% of TSS were volatile in nature (serial no. 7) on the basis of mean values. Chromium, described as % of TSS, varied from 2.3 to 11.1% with a mean value of 5.2% (serial no. 8). This is comparable with the results obtained by Ates et al. [17] and Orhon et al. [18].

#### 3.2. Series 1 jar tests

Comparative performance of alum, ferric chloride and ferric sulfate at pH values of 7.5 is shown in Fig. 1.

Fig. 1 indicates that ferric chloride and ferric sulfate performed in a similar fashion and maximum turbidity removal occurred at a low dose of 20 mg/L with no further significant improvement. For alum maximum turbidity removal was observed at the maximum applied dose of 100 mg/L. However, both ferric salts produced dark black colour. Black colour was considered to be due to the formation of FeS by S<sup>2-</sup>, which is derived from the use of Na<sub>2</sub>S during unhairing process. Sulfide reduces Fe<sup>3+</sup> (ferric) to Fe<sup>2+</sup> to form FeS, which is soluble and black in colour [19,20]. Further investigation is required for the removal of this black colour and economical use



**Fig. 1.** Coagulant dose and residual turbidity at pH 7.5 for various coagulants.

**Table 3**  
Relationship between major pollution parameters

| S. no. | Parameter/relationship  | Range    | Mean | Comparison       |                   |
|--------|---|----------|------|------------------|-------------------|
|        |   |          |      | Ates et al. [17] | Orhon et al. [18] |
| 1      | Particulate <sup>a</sup> BOD <sub>5</sub> (% of TBOD <sub>5</sub> ) | 18–53    | 32   |                  |                   |
| 2      | Particulate COD (% of TCOD)   | 33–63    | 46   | 56               | 43                |
| 3      | TCOD/TBOD <sub>5</sub>  | 1.8–4.8  | 3.2  | 2.9              |                   |
| 4      | TCOD/TSS  | 1.3–4.2  | 2.0  | 2.2              | 2.9               |
| 5      | TDS/TS  | 0.7–0.9  | 0.86 |                  |                   |
| 6      | SS/TSS  | 0.6–0.9  | 0.8  |                  |                   |
| 7      | VSS/TSS   | 0.4–0.8  | 0.7  | 0.48             | 0.6               |
| 8      | Cr/TSS (%)  | 2.3–10.1 | 5.53 | 5.1              | 5.2               |

<sup>a</sup> Particulate BOD<sub>5</sub> = TBOD<sub>5</sub> – SBOD<sub>5</sub>.

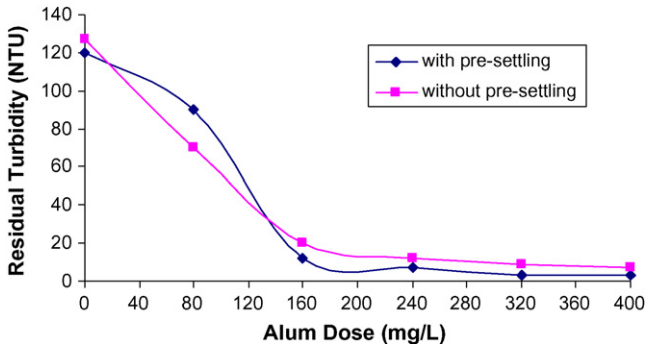


Fig. 2. Alum dose and residual turbidity with and without pre-settling.

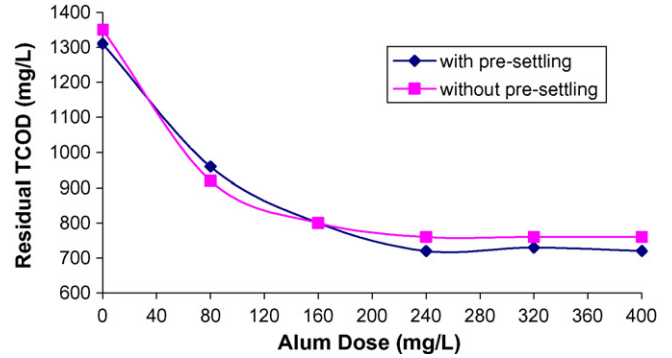


Fig. 4. Alum dose and residual TCOD with and without pre-settling.

of ferric salts. Alum on the other hand showed no such problem, rather it exhibited a tendency to completely remove colour already present in tannery wastewater.

Thus it can be observed in Fig. 1 that good initial turbidity removal was achieved with ferric salts at low dose. However, the production of black colour was the major hindrance for ferric salts to be used as coagulant. Thus on the basis of the preliminary tests, alum was selected as the metal salt of choice for tannery wastewater.

3.3. Series 2 jar tests

The results of series 2 jar tests are illustrated in Figs. 2–5.

It is evident from Figs. 2–5 that maximum turbidity, TSS, TCOD and chromium removal occurred at alum doses of 200, 240, 240 and 240 mg/L as Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively. Removals in pre-settled samples were slightly better than those without pre-settling. However, no significant differences existed at optimum dose for both types of samples in terms of turbidity, TSS, TCOD and chromium contents. Therefore, on the basis of the experimental results the

optimum dose range for alum was determined to be 200–240 mg/L as Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Additionally, the effect of pre-settling on the removal of pollutants was not significant. Thus the provision of a pre-settling tank may not result in any added benefit. The summary of results from series 2 jar tests and its comparison with plain sedimentation are shown in Tables 4 and 5.

Residual values and percentage removals of various parameters resulting from plain sedimentation are compared with CEPT at optimum alum dose in Tables 4 and 5. This comparison (Table 4) shows that CEPT enhanced the removal of all the pollutants when compared with plain sedimentation. Turbidity removal was enhanced from 86.2 to 99.3% (effluent turbidity = 7 NTU). TSS removal enhanced from 76.8 to 97.1% (effluent TSS = 30 mg/L). Similarly TCOD removal enhanced from 18.5 to 60.9% (effluent TCOD = 720 mg/L) and chromium removal from 85.4 to 99.6% (effluent Cr = 0.4 mg/L). Similar observations can be made from Table 5. It can also be noted from Table 4 that soluble COD for the wastewater sample was 1000 mg/L whereas residual TCOD after CEPT was 720 mg/L. It clearly demonstrates the removal of some soluble COD

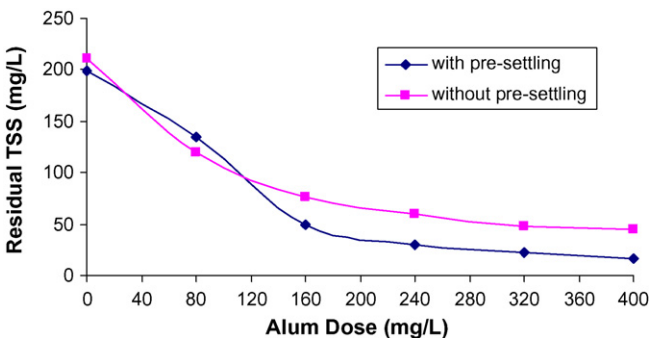


Fig. 3. Alum dose and residual TSS with and without pre-settling.

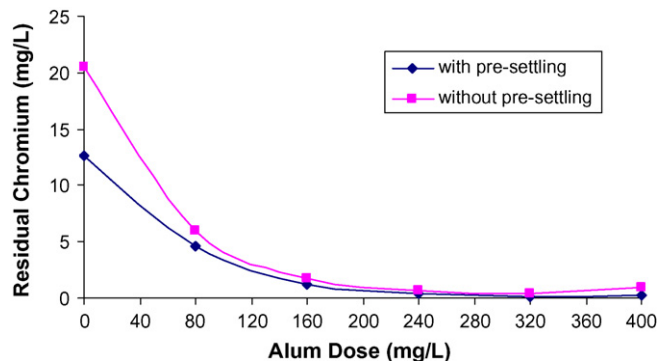


Fig. 5. Alum dose and residual chromium with and without pre-settling.

**Table 4**  
Comparison of plain sedimentation with CEPT for series 2 jar tests (with pre-settling)

| Parameter       | Raw unsettled wastewater | Plain sedimentation <sup>a</sup> |                          | Alum dose (mg/L) | CEPT           |                          |
|-----------------|--------------------------|----------------------------------|--------------------------|------------------|----------------|--------------------------|
|                 |                          | Residual value                   | Removal <sup>b</sup> (%) |                  | Residual value | Removal <sup>b</sup> (%) |
| Turbidity (NTU) | 955                      | 132                              | 86.2                     | 200              | 7              | 99.3                     |
| TSS (mg/L)      | 1056                     | 245                              | 76.8                     | 240              | 30             | 97.1                     |
| TCOD (mg/L)     | 1840(1000) <sup>c</sup>  | 1500                             | 18.5                     | 240              | 720            | 60.9                     |
| Chromium (mg/L) | 105                      | 15.3                             | 85.4                     | 240              | 0.4            | 99.6                     |

<sup>a</sup> Results of the pre-settled wastewater used as influent to all the jars.

<sup>b</sup> For % removal raw unsettled wastewater was taken as reference.

<sup>c</sup> Value in parenthesis is SCOD.

**Table 5**  
Comparison of plain sedimentation with CEPT for series 2 jar tests (without pre-settling)

| Parameter       | Raw unsettled wastewater | Plain sedimentation <sup>a</sup> |                          | Alum dose (mg/L) | CEPT           |                          |
|-----------------|--------------------------|----------------------------------|--------------------------|------------------|----------------|--------------------------|
|                 |                          | Residual value                   | Removal <sup>b</sup> (%) |                  | Residual value | Removal <sup>b</sup> (%) |
| Turbidity (NTU) | 955                      | 127                              | 86.7                     | 200              | 12             | 98.7                     |
| TSS (mg/L)      | 1056                     | 211                              | 80                       | 240              | 60             | 94.3                     |
| TCOD (mg/L)     | 1840(1000) <sup>c</sup>  | 1350                             | 26.6                     | 240              | 760            | 58.7                     |
| Chromium (mg/L) | 105                      | 20.5                             | 80.5                     | 240              | 0.6            | 99.4                     |

<sup>a</sup> Results of zero chemical jar, which simulate plain sedimentation.

<sup>b</sup> For % removal raw unsettled wastewater was taken as reference.

<sup>c</sup> Value in parenthesis is SCOD.

in CEPT. It might be due to the adsorption of soluble COD on  $Al(OH)_3$  gel formed during coagulation process with alum.

The enforced national effluent standards [21] for parameters tested are given in Table 6. By comparing residual values in Tables 4 and 5 with those in Table 6, it can be observed that CEPT generated effluent that met these standards for TSS (effluent TSS=30–60 mg/L; standard=200 mg/L) and chromium (effluent Cr=0.4–0.63 mg/L; standard=1 mg/L). Additionally, almost complete removal of chromium in CEPT would save any subsequent biological treatment from chromium toxicity. TCOD in the effluent from CEPT (720–760 mg/L) was still higher than the effluent standards (150 mg/L) thus emphasizing the need for secondary treatment.

### 3.4. Series 3 jar tests

The results of the jar tests conducted under this series are shown in Figs. 6–9.

It can be seen in Figs. 6–9 that maximum removal of turbidity, TSS, TCOD and chromium occurred at alum doses of 200, 240, 240 and 240 mg/L as  $Al_2(SO_4)_3$ , respectively. Moreover, removals were slightly better at pH 9.5 than at 7.5. However, the differences were not significant. This clearly demonstrated that pH range normally associated with homogenized SLW wastewater had no appreciable effect on the optimum dose of the coagulant. Similar findings were reported by Ates et al. [17] regarding tannery wastewater. The present investigations suggest that no pH adjustment is needed for tannery wastewater before coagulant is applied as long as an adequate equalization basin is provided. It can be seen in Figs. 6–9 that the initial concentrations of turbidity, TSS, TCOD and chromium

**Table 6**  
Effluent standards in Pakistan [21]

| Parameter | Effluent standard (mg/L) |
|-----------|--------------------------|
| Turbidity | NA <sup>a</sup>          |
| TSS       | 200                      |
| COD       | 150                      |
| Chromium  | 1.0                      |

<sup>a</sup> Not applicable.

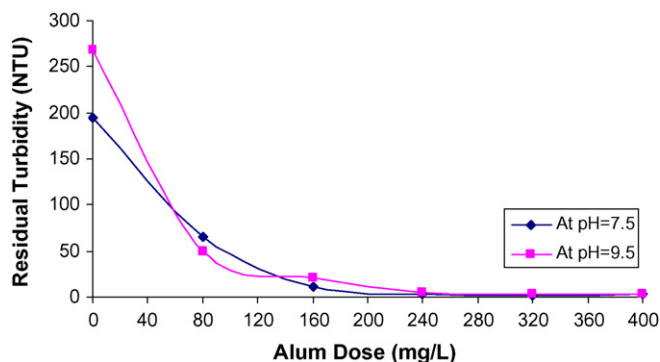


Fig. 6. Alum dose and residual turbidity at different pH.

were different for the two jar tests. This was due to the different samples used for these tests. Differences were even observed when only one wastewater sample was used for multiple jar tests. These differences arose due to sub-sampling of the bulk sample initially obtained from the equalization tank. In addition, multiple jar tests on the same bulk sample were performed on different days. Therefore, aging of initial sample could be another reason for these differences. It is clear from Figs. 6–9 that at optimum dose, resid-

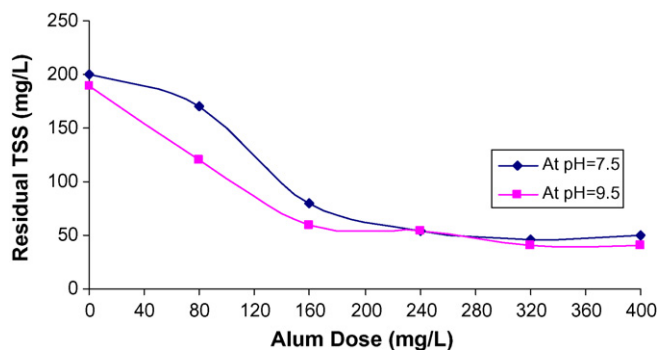


Fig. 7. Alum dose and residual TSS at different pH.

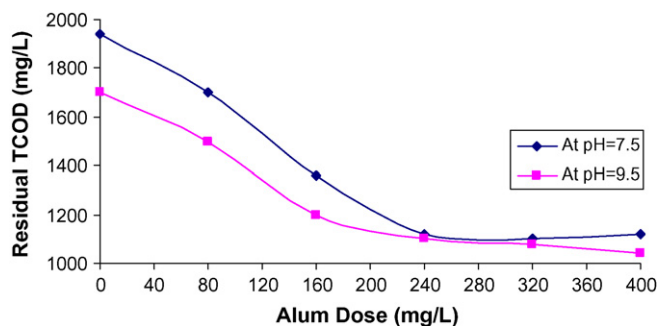


Fig. 8. Alum dose and residual TCOD at different pH.

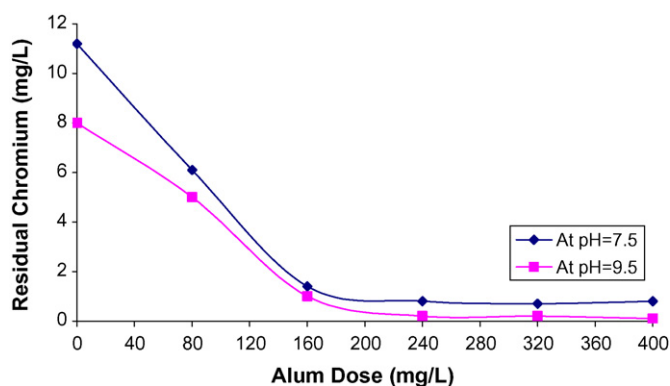


Fig. 9. Alum dose and residual chromium at different pH.

ual values of various parameters for the two jar tests were in close agreement thus nullifying the initial concentration differences to a large extent.

Residual values and percentage removals of various parameters, at different pH values, resulting due to plain sedimentation are compared with CEPT in Tables 7 and 8. It can be seen in these tables that reasonable removals of turbidity, TSS and chromium occurred even with plain sedimentation whereas removal for TCOD was minimal. With CEPT, at optimum alum dose (Table 7), removals for turbidity enhanced from 85.4 to 99.8% (effluent turbidity = 2.3 NTU), TSS from 86.5 to 96.4% (effluent TSS = 54 mg/L), TOCD from 16.3 to 53.3% (effluent TOCD = 1120 mg/L) and chromium removal enhanced from 84.2 to 98.9% (effluent Cr = 0.8 mg/L). CEPT effluent met effluent standards for TSS and chromium whereas TCOD values were still high. Removal of some portion of soluble COD was also observed. Similar trends are exhibited in Table 8.

The possibility of using CEPT at the existing PTP was also studied under two options. First option was to augment the existing PTP with a rapid mix and tapered flocculation unit prior to primary sedimentation tank (PST). Second option was to skip the above arrangement and add alum directly into the equalization

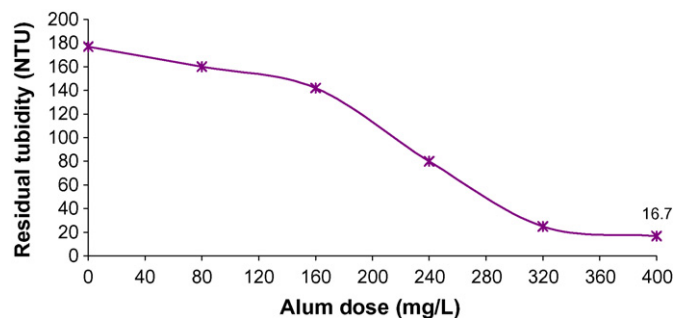


Fig. 10. Alum dose and residual turbidity for the addition of alum in equalization tank.

tank where it would be mixed with wastewater prior to primary sedimentation. The first option was completely simulated by series 2 and 3 jar tests where wastewater was rapidly mixed at a  $G$  value of  $380 \text{ s}^{-1}$  followed by tapered flocculation at three different  $G$  values, i.e. 54, 34 and  $14 \text{ s}^{-1}$  (Table 1). In order to simulate the second scenario in the laboratory, the velocity gradient ( $G$ ) in the equalization tank was determined from the power input of motor for the aerators and volume of the equalization tank. It was found to be  $150 \text{ s}^{-1}$ . Thus jar test was run at this  $G$  value for a period of 8.5 h (average detention time in the equalization tank) followed by 30 min of settlement. Turbidity test was used to evaluate the quality of effluent as shown in Fig. 10

The optimum dose for second option in Fig. 10 appears to be 400 mg/L as  $\text{Al}_2(\text{SO}_4)_3$ , which is almost double as compared to the optimum dose (200–240 mg/L as  $\text{Al}_2(\text{SO}_4)_3$ ) for first option. This clearly demonstrates the effect of proper rapid mix and flocculation on the removal of pollutants. Thus if rapid mix and flocculation units are avoided, the chemical cost for CEPT would almost become double.

CEPT results for the treatment of tannery wastewater have been compared with other treatment methods in Table 9. Three different parameters, i.e. TSS, COD and chromium have been selected for the purpose of comparison. Values of these parameters for raw and treated samples and percentage removals have been presented. Five different treatment methods, namely: (1) aerated lagoons; (2) activated sludge; (3) upflow anaerobic sludge blanket (UASB); (4) powdered activated carbon (PAC) coupled with membrane bioreactor (MBR); and (5) vegetated wetlands have been included in this comparison.

It is evident from Table 9 that CEPT gives good results for percentage removal and effluent TSS when compared with aerated lagoon, activated sludge and UASB. Best results for TSS removal are obtained with PAC + MBR. The effluent TSS for vegetated wetlands is also lower than CEPT. However, it should also be noted that the value for raw TSS for vegetated wetlands is also quite low. COD removal with CEPT is comparable to UASB and vegetated wetlands whereas aerated lagoon, activated sludge and PAC + MBR give better

Table 7  
Comparison of plain sedimentation with CEPT at pH 7.5

| Parameter       | Raw unsettled wastewater | Plain sedimentation <sup>a</sup> |                          | Alum dose (mg/L) | CEPT           |                          |
|-----------------|--------------------------|----------------------------------|--------------------------|------------------|----------------|--------------------------|
|                 |                          | Residual value                   | Removal <sup>b</sup> (%) |                  | Residual value | Removal <sup>b</sup> (%) |
| Turbidity (NTU) | 1370                     | 200                              | 85.4                     | 200              | 2.3            | 99.8                     |
| TSS (mg/L)      | 1508                     | 203                              | 86.5                     | 240              | 54             | 96.4                     |
| TCOD (mg/L)     | 2400 (1200) <sup>c</sup> | 2010                             | 16.3                     | 240              | 1120           | 53.3                     |
| Chromium (mg/L) | 77                       | 12.2                             | 84.2                     | 240              | 0.8            | 98.9                     |

<sup>a</sup> Results of the pre-settled wastewater used as influent to all the jars.

<sup>b</sup> For % removal, raw unsettled wastewater was taken as reference.

<sup>c</sup> Value in parenthesis is SCOD.

**Table 8**  
Comparison of plain sedimentation with CEPT at pH 9.5

| Parameter       | Raw unsettled wastewater | Plain sedimentation <sup>a</sup> |                          | Alum dose (mg/L) | CEPT           |                          |
|-----------------|--------------------------|----------------------------------|--------------------------|------------------|----------------|--------------------------|
|                 |                          | Residual value                   | Removal <sup>b</sup> (%) |                  | Residual value | Removal <sup>b</sup> (%) |
| Turbidity (NTU) | 1183                     | 390                              | 67                       | 200              | 5.4            | 99.5                     |
| TSS (mg/L)      | 1308                     | 321                              | 75.4                     | 240              | 54             | 95.9                     |
| TCOD (mg/L)     | 2480 (1220) <sup>c</sup> | 2050                             | 17.3                     | 240              | 1100           | 55.6                     |
| Chromium (mg/L) | 61                       | 7.6                              | 87.5                     | 240              | 0.2            | 99.7                     |

<sup>a</sup> Results of the pre-settled wastewater used as influent to all the jars.

<sup>b</sup> For % removal, raw unsettled wastewater was taken as reference.

<sup>c</sup> Value in parenthesis is SCOD.

**Table 9**  
Different treatment methods and their performance for tannery wastewater

| S. no. | Treatment methods       | Parameter  |                |             |            |                |             |            |                |             |
|--------|-------------------------|------------|----------------|-------------|------------|----------------|-------------|------------|----------------|-------------|
|        |                         | TSS        |                |             | COD        |                |             | Chromium   |                |             |
|        |                         | Raw (mg/L) | Treated (mg/L) | Removal (%) | Raw (mg/L) | Treated (mg/L) | Removal (%) | Raw (mg/L) | Treated (mg/L) | Removal (%) |
| 1      | CEPT (Table 7)          | 1508       | 54             | 96          | 2400       | 1120           | 53          | 77         | 0.8            | 98.9        |
| 2      | Aerated lagoon [22]     | 1824       | 258            | 85.9        | 4321       | 1180           | 72.7        | 28         | 0.6            | 97.8        |
| 3      | Activated sludge [23]   | 750        | 110            | 85.3        | 3600       | 200            | 94.4        | 56         | 0.8            | 98.6        |
| 4      | UASB [23]               | 1398       | 587            | 58          | 1135       | 566            | 50.1        | 76         | 11             | 85.5        |
| 5      | PAC + MBR [24]          | 976        | 4              | 99.5        | 4051       | 832            | 79.5        | –          | –              | –           |
| 6      | Vegetated wetlands [25] | 79         | 23             | 70.8        | 2093       | 745            | 64.4        | –          | –              | –           |

removals. Similarly, excellent chromium removals can be obtained with CEPT as shown in Table 9. These removals are comparable with those obtained using aerated lagoon and activated sludge process, and better than those obtained using UASB. It can, therefore, be concluded that with respect to TSS and chromium, CEPT outperforms other treatment methods. However, it gives moderate removal of COD and hence further treatment to this effect is required.

#### 4. Conclusions

Following conclusions can be drawn from the above studies:

1. Homogenized wastewater of SLW from equalization tank showed variations in characteristics. It contained high organic, solid, sulfate, sulfide and chromium contents. Phosphorus was found to be deficient for satisfactory biological treatment.
2. CEPT could be a suitable treatment strategy for SLW wastewater which had high alkalinity and sufficient amount of various pollutants in the particulate form. Alum was found to be suitable coagulant for use in CEPT of tannery wastewater in a dose range of 200–240 mg/L as  $Al_2(SO_4)_3$ , in case rapid mix and flocculation units were provided prior to primary sedimentation tank. However, without these units, if alum was added to the equalization tank, a dose of 400 mg/L as  $Al_2(SO_4)_3$  was required to obtain comparable results.
3. Ferric chloride and ferric sulfate generated black colour when used as coagulant for tannery wastewater. Nevertheless, an appreciable removal of turbidity was achieved at lower doses. Further investigations are needed for the removal of black colour and economical use of these coagulants.
4. Results indicated that pH range normally associated with homogenized SLW wastewater had no significant effect on CEPT efficiency using alum at its optimum dose. Similarly results for CEPT with and without pre-settling of wastewater for 30 min showed only slight difference in effluent quality. Hence CEPT without pre-settling would be more beneficial in terms of the capital cost.
5. With alum doses of 200–240 mg/L as  $Al_2(SO_4)_3$ , removals of turbidity, TSS, TCOD and chromium were found to be 98.7–99.8, 94.3–97.1, 53.3–60.9 and 98.9–99.7%, respectively.

6. At optimum dose, CEPT with alum removed almost all particulate COD and some portion of soluble COD (in a range from 7 to 28%) probably due to the adsorption of soluble portion on  $Al(OH)_3$  gel. However, organic matter remaining after CEPT was still high and in the dissolved form and required secondary treatment to meet effluent standards.
7. At optimum dose, CEPT with alum generated an effluent with TSS (30–60 mg/L) and chromium (0.2–0.8 mg/L) concentration that met the enforced effluent standards. However, effluent standard for COD could not be qualified.

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