Physicochemical and Biological Treatment of Vegetable Tannery Effluents for the Removal of Organic Matter

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Summary:Tannery wastewater samples were collected from vegetable tanneries located at Charsadda road Peshawar (Pakistan). The samples were chemically evaluated for parameters like; pH, dissolved oxygen (DO), total suspended solids (TSS), total dissolved solids (TDS), biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD). It was found that the effluents contained very high COD (>10,000 mg O_2/L) and high concentrations of TSS, TDS and BOD, which render it harmful for aquatic life when discharged into the Kabul River without any treatment. A process has been developed to detoxify the tannery effluents applying physicochemical followed by biological method (sequencing batch reactor, SBR). The TSS, COD and BOD_5 were substantially decreased employing the developed treatment technique. Overall, BOD and COD were both decreased by more than 87 and 81% respectively, whereas TSS was decreased by 98.74%. The resulting sludge from SBR was found to have good settling characteristics.

Introduction

About 130 different chemicals are used in leather processing, depending on the type of raw material and finished product. These chemicals may be divided into four major classes: pre-tanning chemicals, tanning chemicals, wet finishing chemicals and finishing chemicals [1]. During the tanning process, potable ground water, being the major source, is utilized. Tanneries produce all categories of waste, however, wastewater is the far most important environmental challenge being faced.

Kabul River is the main source of water for irrigation, fish crop and recreation. But due to heavy discharges from the nearby industrial units, the river is considered to be the main carrier for industrial wastes, resulting in the deterioration of water quality which is evident of periodic fish kills [2]. Tremendous work has been carried out throughout the world to monitor the quality of the effluents from tanneries and its possible treatment. Previously, characteristics of untreated and treated wastes of a tannery situated near Aurangabad, India have been studies [3]. Similar studies on the pollution of Kabul River and its tributaries [4] were also carried out which showed that Kabul River was very polluted and therefore proper treatment plants were suggested to be installed to treat the industrial effluents before discharging into Kabul River.

Air stripping to remove sulfide was also studied [5] by bubbling air through tannery wastewater. In Japan, a treatment process is used in which proteins and chemicals are recovered and water is reused in the tannery [6]. In another study, Fenton's treatment [7] i.e. homogenization, chemical oxidation, neutralization, flocculation and finally sedimentation were applied for making the tannery effluents safe for discharge. The wastewaters from the textile and tanning industries were also carried out with activated sludge short-term respiration measurement [8]. In another method, aeration-biochemical system for treatment of tanning wastewater was applied [9] in which COD was decreased from 750 to 150 mg/L and BOD_5 was decreased from 396 to 20 mg/L. In another study, tannery wastewater was treated by coagulation, precipitation, biological contact oxidation, and biological filtration [10]. Treatment of tannery wastewater by biofilm sequencing batch reactor (SBR) was also undertaken [11] in the past. Reverse osmosis and ultra filtration techniques have also been applied for the treatment of tannery wastewater [12] for the removal of chromium (III). Studies have also been undertaken [13] for the removal of NH_3-N in various processes of leather industry. Bentonite[14] clay has also been used to treat tannery wastewater for the removal of Cr (III). Removal of chromium and other toxic substances from spent chrome tannery effluents by precipitation with lime, NaOH and NH_4OH were carried out [15] and lime was found highly effective. Zinc polysilicate have also been employed as flocculants for the removal of COD (>80%), turbidity (>98%), total chromium and sulfide (>90%) [16].

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The aims of the present study is to develop an economically feasible, and viable method for the detoxification of tannery wastewaters in order to reduce its harmful effects on the nearby water bodies.

Results and Discussion

a. Characterization of Effluents

Higher BOD_5, COD, dissolved and suspended matters in water bodies adversely affect the dissolved oxygen level and consequently the respiration, the spawning and hatching process of fish [2]. Presence of high oxygen demanding wastes, which are indicated by high BOD_5 and COD values, deplete ambient dissolved oxygen and thus the oxygen supply is cut off to the aquatic population. Furthermore, a higher concentration of suspended solids also prevents penetration of sunlight in water bodies and retards the growth of algae and microplankton. These two effects create a suffocating environment and food shortage to fish population. Such effects have previously been reported by Khan *et al.* [17].

The data in Table 1 show the chemical analyses of tannery effluents. The parameters of tannery effluents have also been compared with that of the National Environmental Quality Standards (NEQS). The results reveal that organic strength as indicated by its BOD_5 and COD of tannery effluents were significantly higher than the threshold limits of NEQS. BOD_5 of vegetable tannery effluents lies in the range of 5233-6450 mg O_2/L which is 65-81 times higher than the NEQS [18]. Similarly BOD_5 of chrome based effluent lie in the range of 1700–6540 mg O_2/L which is 21-82 times higher than the NEQS limits. COD of vegetable and chrome tannery effluents respectively lie in the range of 6496-11244 mg O_2/L (43-75 times higher) and in the range of 8848-12941 mg O_2/L (59-86 times higher) than the NEQS.

The results (Table 1) show that TSS in effluents from vegetable tanneries are 126-135 times higher and chrome tanneries 10-49 times higher as compared to NEQS permissible limits. Similarly TDS from vegetable tanneries are 3-16 times higher and chrome tanneries 1-12 times higher than the threshold limits of NEQS [18].

The data of heavy metal ions concentration i.e. chromium (Cr^{+3}), lead (Pb^{+2}), copper (Cu^{+2}) and total iron both in the vegetable and chrome tanneries are presented in Table 1. The Cr^{+3} was found in higher concentration in chrome tannery effluents, the concentration being in the range of 14.5-15.53 mg/L (14-15 times) higher than the NEQS. The lead concentration varied from 0.45–0.66 mg/L whereas its permissible limit is 0.5 mg/L and is slightly higher than the permissible limit. The copper was only detected in Sample 2 from vegetable tannery (0.78 mg/L), which is within the NEQS. The total iron concentration in vegetable tannery effluent was in the range of 13.20-21.0 mg/L (3-4 times) higher than NEQS. Similarly iron in chrome tanneries was found in the range of 11.3-13.2 mg/L (2-3 times) higher than the NEQS permissible limits.

The presence of heavy metal ions in tannery effluents is due to the use of their respective chemicals in different processes. Chrome tannery use $K_2Cr_2O_7$ as tanning agent and therefore the presence of Cr^{+3} in higher concentrations is justified. Both vegetable and chrome tanneries use $FeCl_3$ alongwith lime as a decolourizing and precipitating agent, therefore its presence in higher concentrations is also logical [19]. The source of Pb^{+2} both in vegetable and chrome tanneries are not very clear, however its

Table-1: General characteristics of vegetable and chrome based effluents collected from different tanneries

PARAMETERS	Vegetable tannery effluents		Chrome tannery effluents		NEQS
	1	2	3	4	
pH	11.4	3.4	9.2	8.60	7-9.2
BOD_5 (mg O_2/L)	5233	6450	1700	6540	80
COD (mg O_2/L)	6496	11244	12941	8848	150
TSS (mg/L)	18840	20320	1476	7400	150
TDS (mg/L)	10120	55300	4832	40320	3500
Cr^{+3} (mg/L)	BDL	BDL	15.53	14.50	1.0
Cu^{+2} (mg/L)	BDL	0.78	BDL	BDL	1.0
Pb^{+2} (mg/L)	0.65	0.56	0.45	0.66	0.5
Total iron (mg/L)	13.20	20.93	11.30	13.20	5.0

BDL Below detection limit

Table-2.: Effect of neutralization on the concentration of various parameters

Parameters	Original effluent	Removal		
		After neutralization	After coagulation*	Total
pH	9.0	7.0	-	-
TSS (mg/L)	1588	172	20	98.74%
TDS (mg/L)	22844	27356	27076	18.53% (increase)
BOD (mg O_2/L)	4290	2569	2280	48.39%
COD (mg O_2/L)	8219	4922	4368	46.86%

* At optimum dose of potassium aluminum sulphate (0.75 g/L)

Table-3: Effect of air stripping on the composition of tannery effluents after potash alum (0.75 g/L) treatment

Parameters	Aeration time (hours)			
	0	3	6	24
pH	8.5	8.3	8.16	7.78
Temperature (°C)	29.5	31.5	32.0	33.0
DO (mg O_2/L)	1.0	0.10	0.10	0.10
TSS (mg/L)	992	688	1084	1756
TDS (mg/L)	25264	24108	21376	20788
BOD_5 (mg O_2/L)	2640	2600	2520	2445
COD (mg O_2/L)	4401	4276	4146	4020

presence in effluents can be associated with their presence in different chemical that are used during processing of hides.

b. Treatment of effluents

i. Physicochemical methods

Physicochemical followed by biological methods was used for the treatment of tannery effluents. Physicochemical methods include three main steps like; neutralization (pH adjustment), coagulation and air stripping. These steps were applied in sequence and the results of these steps are presented in Tables 2–3. Biological method (SBR process) was applied on the resulting effluent after physicochemical treatment.

- *Neutralization (pH adjustment)*

The pH of the effluent was adjusted with acid or alkali, depending upon the nature of tannery wastewater. In the present studies the effluent having pH 8.60-11.4 was taken for neutralization and therefore different concentrations of HCl were applied to neutralize the effluent. It was found that 1M HCl (10-12 ml) was required to neutralize one litre of the above mentioned effluent. Neutralization with commercial HCl decreased the pH of the original effluent from 9 to 7 and as a result TSS was decreased from 1588 to 172 mg/L, the reduction being 89.17% (Table 2). Neutralization also decreased BOD and COD from 4290 and 8219 mg O_2/L to 2569 and 4922 mg O_2/L respectively, which showed 40.11% and 40.10% removal of BOD and COD respectively. COD removal could be associated with the adsorption of organics on the settleable matter during neutralization. Neutralization had however increased the soluble salt concentration from 22844 mg/L to 27356 mg/L, the increase being 18.53%.

- *Coagulation*

After neutralization, the wastewater was subjected to coagulation (Figures 1-2) in order to remove suspended matter using two different concentrations of potash alum ($K_2SO_4Al_2(SO_4)_3.24H_2O$). The results in Figure 1 show the effect of potash alum concentration on the settleability of mixed liquor suspended solid (MLSS). The data in Figure 1 suggest that lower concentration of potash alum (0.75 g/L) shows better settling characteristics of the suspended matter in tannery effluents compared to the higher concentration of potash alum [20]. Dose optimization (Figure 2) of the coagulant was carried out and settling characteristics of the resulting precipitate of MLSS were evaluated. The data in Figure 2 show an optimum dose of 0.75 mg/L of potash alum, the reagent below and beyond this concentration was not suitable. Dose below 0.75 mg/L of potash alum did not remove most of the suspended matter whereas, high doses caused further turbidity showing that the coagulant did not contribute to settle down suspension but instead it deteriorated the quality of the resulting effluent by increasing potash alum concentration in the supernatant. Referring to the data in Table 2, coagulation with 0.75 mg/L (optimal dose) of $K_2SO_4Al_2(SO_4)_3$ further decreased TSS from 172 to 20 mg/L which is 9.57%, the overall reduction by both neutralization and coagulation processes was 98.74%. Coagulation also decreased BOD and COD from 2569 and 4922 mg O_2/L to 2280 and 4368 mg O_2/L respectively with a further decrease of 8.28% in BOD and 6.76% in COD. The overall reductions in BOD and COD by both processes were respectively 48.39% and 46.86%.

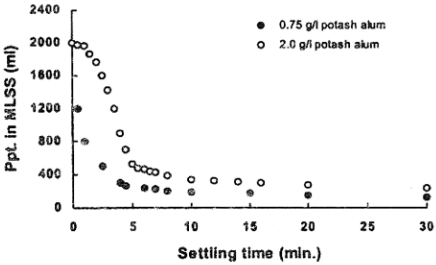

Fig. 1: Settling characteristics of different concentration of potash alum on the settleability of MLSS.

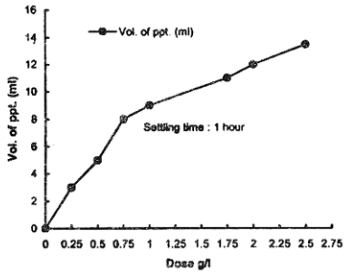

Fig. 2: Dose optimization of potash alum for the effective removal of suspended matter in tannery effluents

- *Air stripping*

Air stripping was applied to the tannery effluents to get rid of volatile organics and gaseous inorganic compounds like H_2S and free NH_3 so as to further improve the quality of effluents by reducing COD and BOD_5. Air stripping of the resulting wastewater after 0.75 mg/L potash alum treatment was carried out. Air stripping was continued for an extended period owing to the specific nature of tannery effluents. The data related to air stripping are given in Table 3.

The BOD_5 and COD were decreased from 2640 mg O_2/L to 2445 mg O_2/L (7.39% removal) and from 4401 mg O_2/L to 4020 mg O_2/L (8.66% removal) after 24 hours of air stripping. The dissolved oxygen level (Table 3) however did not increase despite reduction in BOD_5 and COD. TDS concentration also decreased from 25264 mg/L to 20788 mg/L (17.72% removal) by the extended aeration period of 24 hours. TSS concentration was increased from 992 mg/L to 1756 mg/L (77.02% increase). This increase in TSS which was mostly settleable could be associated with the conversion of soluble salts into insoluble form [10]. This is a normal behaviour, as some salts get precipitated with oxidation, e.g. iron salts can be precipitated by oxidation process [21].

ii. Biological treatment

Sequencing batch reactor (SBR) was employed on the resulting wastewater after completion of physicochemical methods. The supernatant, diluted for this purpose, was subjected to sequencing batch reactor (SBR) for the removal of carbonaceous BOD.

The BOD and COD of the influent were 470 and 827 mg O_2/L respectively. Aeration time was 1 hour whereas 30 minutes each was allowed for accomplishing anoxic and anaerobic treatment. The reactor was operated for 192 hours. The nitrogen requirement for the growth of biomass was duly maintained (data not presented here) so that growth limiting conditions could be avoided. The characteristics of the effluent was analyzed after every 24 hours, the results are presented in Table 4.

The data in Table 4 suggest two main aspects of the SBR; firstly, as BOD removal takes place DO level increased correspondingly from 0.20 to 5.10 mg O_2/L. Secondly, BOD removal took place upto 5 days and beyond this period growth limiting conditions were created. This is indicated by increase in BOD from 85 mg O_2/L at 120 hours to 140 mg O_2/L at 192 hours. During this growth limiting condition, DO is dropped from 5.1 mg O_2/L at 120 hours to as low as 2.7 mg O_2/L at 192 hours with a corresponding decrease in the biomass concentration from 522 mg O_2/L mixed liquor volatile suspended solids (MLVSS) at 120 hours to 343 mg/L MLVSS at 120 hours. Interestingly, COD of the effluent was found decreasing throughout the treatment period, the reason to this effect was not clear. The apparent reason of cell decay due to starvation, as depicted by the decrease in MLVSS and supported by decrease in DO level could be associated with low BOD (85 mg O_2/L) at 120 hours and beyond the treatment period. 85 mg O_2/L BOD is not enough for the sustenance of biomass especially when other limiting conditions might have also been involved, however it was not substantiated in the present study.

Table-4: Sequencing batch reactor process – effluent characteristics (after physicochemical treatment)

Parameters	Time (hours)								
	0	24	48	72	96	120	144	168	192
pH	7.75	7.72	7.70	7.75	7.80	7.83	7.70	7.85	7.87
DO (mg O_2/L)	0.20	0.30	0.20	3.30	4.10	5.10	2.80	2.90	2.70
MLVSS* (mg/L)	183	262	310	362	435	522	504	450	492
TDS (mg/L)	4950	4801	4498	4430	4286	4244	4092	4114	4178
BOD_5 (mg O_2/L)	470	380	290	250	150	85	120	110	140
COD (mg O_2/L)	827	771	727	654	418	343	321	246	239

* MLVSS mixed liquor volatile suspended solids

Sequencing batch reactor further decreased 71.0% BOD and 58.52% COD of the resulting wastewater from the physicochemical methods. Calculating the removal from the remaining portion of BOD, it comes to about 31.40% after 120 hours of SBR treatment. Similarly, COD removal in the remaining portion of the organics was nearly 26.03% after 120 hours (Table 4). As such, the total removal in BOD and COD from tannery wastewater both by the physicochemical and SBR methods are respectively 87.18% and 81.55%.

The quality of the resulting sludge was extremely good, the data being shown in Figure 3. It is apparent from the data that almost 96% of the mixed liquor suspended solid (MLSS) of the sludge was settled within 15 minutes. This substantiates that the settling characteristics of the sludge is quite good.

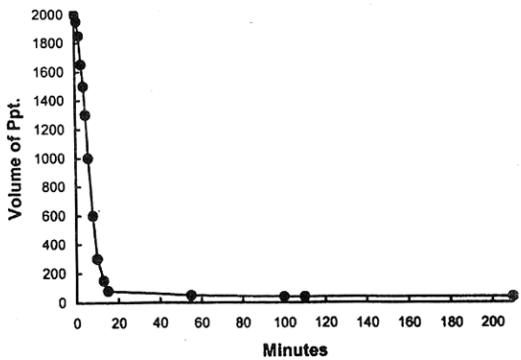

Fig. 3: Settling characteristics of activated sludge

Experimental

Standard methods [22] were employed in all determinations. pH was measured with a Metler Delta-320 pH meter. Suspended solids were determined by filtering an aliquot of sample through Whatman-42 filter paper followed by drying it alongwith its contents at 105°C. Total dissolved solids were determined in the filtrate by evaporating the liquid on a water bath and then drying in an oven at 180°C.

Biological oxygen demand (BOD_5) in wastewater samples were determined by finding out the difference between the initial and final dissolved oxygen (DO) concentration after incubation at 20°C for 5 days divided by the decimal fraction of sample. BOD bottles of 300 ml were used for this purpose. DO levels were measured by Winkler's Azide modification method [22]. Appropriate aliquot of sample was used and suitable dilutions were made wherever needed. Dilution water was aerated for about 1 hour before use.

Chemical oxygen demand (COD) of samples was measured by open reflux method [22]. For this purpose, an aliquot of sample was digested in strong acidic environment (H_2SO_4 reagent) in the presence of standard $K_2Cr_2O_7$ solution and digesting the solution for 2 hours. The sulphuric acid reagent contained mercuric sulphate and silver sulphate that are used to catalyse the oxidation of organic matter in the sample. After digestion, the un-reacted $K_2Cr_2O_7$ was titrated against standard ferrous ammonium sulphate solution using ferroin indicator. A blank was also run in parallel. Ferrous ammonium sulphate solution was standardized on the same day when COD was carried out owing to its oxidation and its subsequent decrease in concentration with the course of time.

Heavy metals in wastewater were determined by atomic absorption spectrophotometer using AAS Hitachi, model Z-8000 Japan, following the standard methods [22].

Treatment Methodology

Effluents from tanneries near Peshawar (Pakistan) were subjected to different treatments. A total working volume of 35-L tannery effluent was

used in each treatment. 2-L graduated cylinder was used in experiments related to assessment of settling characteristics. Potash alum in concentrations; 0.75 g/L and 2.0 g/L was separately used as coagulant. The effluent was neutralized with concentrated HCl (@ 12 ml/L). The mixture of coagulant and effluent was mixed for 2-3 minutes and allowed to settle. The supernatant sample was drawn for BOD_5 and COD determination. The wastewater in the same tank was subjected to coagulation. Relevant parameters including BOD and COD were measured at the end of each individual treatment. Finally, air stripping of the supernatant was carried out by vigorous aeration of the supernatant.

Sequencing batch reactor (SBR) was employed on the resulting wastewater after physico-chemical methods. The supernatant was subjected to sequencing batch reactor (SBR) for the removal of carbonaceous BOD.

Sequencing batch reactor [23] is regarded as a completely mixed reactor without continuous flow through it. A "batch" of effluent is placed into the vessel with biomass and allowed to react to completion as microorganisms grow on the pollutants present. As growth proceeds, reaction conditions change and consequently, so does the growth environment. Batch processes are very flexible and are particularly well suited for situation with low or highly variable flows. Furthermore, by changing the nature of the electron acceptor, it is also possible to accomplish nutrient removal in a single bioreactor because their operation follows a sequence of events; oxic, anoxic and anaerobic.

Conclusions

Tannery effluents were characterized and the organic carbon (a major cause for depletion of dissolved oxygen) discharged into Kabul River, was evaluated in terms of BOD_5 and COD besides other parameters. The results have indicated that the tanneries at Peshawar discharge effluents that can be regarded as high strength wastewater.

On the basis of the laboratory scale studies, the extent of pollution due to tannery effluents was decreased and comparatively an economical method of treatment has been developed. This method is based on filtration, neutralization, coagulation, air stripping in sequence followed by sequencing batch reactor method. 0.75 g/L of $K_2SO_4 \cdot Al_2(SO_4)_3$ was found to be an optimal dose for most of the tannery effluents for the removal of more than 98% of TSS. BOD and COD of the tannery wastewater were decreased by more than 87 and 82% respectively, by employing both physicochemical and SBR methods.

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