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STUDIES ON PHYSICO-CHEMICAL TREATMENTS OF CHROME TANNERY EFFLUENTS

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Treatment of the composite tannery effluent with floculating and coagulating agents, such as lime with activated carbon, ferric chloride, aluminum sulphate and potash alum, caused considerable reduction in BOD_5, COD, Chromium, and suspended solids value. Microbial study of the effluent after each chemical treatment was also carried out.

Key words: Effluent, Coagulating agents, Activated carbon.

Introduction

Major pollutants in tannery wastewater are COD, BOD, calcium, chlorides, dissolved solid, ammonium salts, chromium, sulphides, suspended solids and alkalinity. In general tannery wastewater is terribly muddy, having a milky or dark colour which is due to suspension of very small particles of matter that does not sediment for a long time. Due to highly toxic nature of pollutants it is necessary to treat this before its discharge into sea, river, or elsewhere. Tannery effluents have variant nature, in volume and quality [1]. The effluents from various tannery processes are required to be stored for 4-8 hrs in an equalization tank to have a uniform composition [2].

Chemical coagulation is by far the most important unit operation for the treatment to reduce the pollution load from wastewater [3]. In present study the coagulating agents such as $FeCl_3$ (ferric chloride), $Al_2(SO_4)_3$ (aluminum sulphate) and K_2SO_4, $Al_2(SO_4)_3 24H_2O$(potash alum) were applied to the mixed tannery wastewater.

Treatment with the lime (CaO) with subsequent treatment of activated carbon, that is capable to remove dissolved organic matter [3], was also studied. Before each treatment sulphides were removed by air oxidation. The wastewater before and after each treatment was analysed for the parameters such as BOD_5, COD, D.S., S.S., or Kjeldhal nitrogen, chlorides, and total hardness [4-7]. Bacteriological study was also carried out [8-12].

Material and Methods

Composite tannery effluents were collected from Naullha, situated at Korangi Industrial Area, where so many tanneries discharge their effluent. This untreated effluent flows frequently to the local sewerage system and in the last finds its way towards the sea. This effluent was subjected for the following treatment.

(i) *Sulphides removal.* Five litres effluent was aerated for 10 hrs in a glass tank to oxidise the sulphides. Aeration was carried out with the help of a compressor pump. The contents of the tank was allowed to settle down. The liquid was decanted into another glass tank in order to separate the sludge.

(ii) *Treatment with ferric chloride ($FeCl_3$), aluminum sulphate ($Al_2(SO_4)_3$and potash alum $K_2(SO_4)Al_2(SO_4)_3$ 24 H_2O.* After sulphides removal three samples, each five litre, of composite tannery effluent were treated with three different coagulating agents, $FeCl_3$, $Al_2 SO_4$ and $K_2 (SO_4) Al_2 (SO_4)_3$. 24 H_2O in glass tanks. Every time 10% solution was added dropwise in the effluent and addition was stopped when effluent's pH reached 6.0. The pH was checked by a pH meter and stirring was carried out by mechanical stirrer at 30 R.P.M.

(iii) *Treatment with lime (CaO) + carbon dioxide (CO_2) gas and activated carbon.* Gradual increase of lime percentage with passage of time was carried out during stirring of effluent. Maximum sedimentation was observed at 8% addition of lime with one hour stirring. This lime treated effluent was allowed to settle for overnight. The liquid was decanted into another glass tank in order to separate the liquid from the sludge. The liquid was again treated with carbon dioxide gas until the pH reached 7.0. The liquid was decanted to separate it from calcium carbonate formed during the CO_2 gas bubbling.

One litre of this lime + CO_2 treated effluent was allowed to pass through a glass column (3 cm x 45cm) and charged with 50g of activated carbon granules. Flow rate was found to be 200ml/min. which was the maximum flow rate. The effluent was analysed chemically and microbiologically after each traetment.

Microbial analysis. Samples of the composite tannery effluent, before and after the treatment as described earlier, were inoculated into microbial media for assessment of bacterial and fungal count. The medium used for bacterial study is Nutrient Agar, for fungal, medium used is sabourauds. All incoulated plates were incubated at 35^0 for 24 hrs, after that results were noted, using plate count method.

Dilution of the inoculum used in each experiment

Efluent sample = 0.1 ml

Autoclaved distilled water = 10 ml
Dilution of the inoculum = 1:100
Out of this diluted sample = 0.1 ml
Used in 10 ml media (Plating) ultimate dilution = 1:10000

Composition of medium used for bacterial plating in each experiment: Nutrient Agar.

Polypeptone = 5 g
Beef extract = 3 g
Agar = 15 g
Distilled water = 1 litre

Composition of medium used for fungal plating in each experiment.

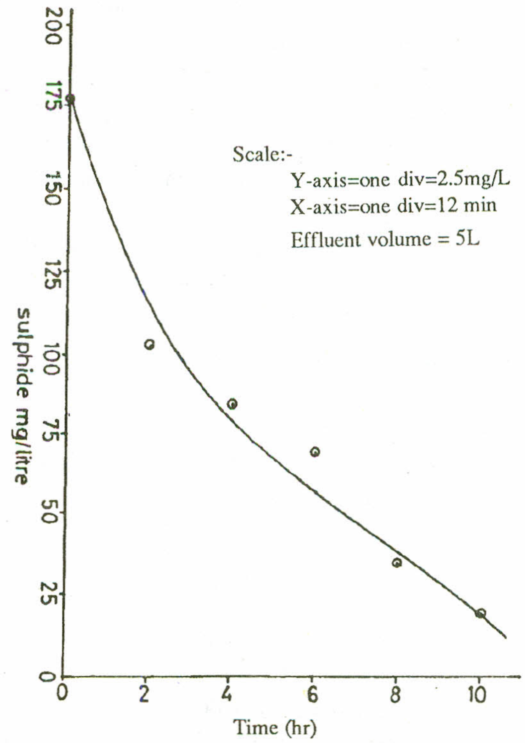
Neopeptone = 10 mg
Bactor dextroes = 40 g
Bacto agar = 15 g
Distilled water = 2 litre

Results and Discussion

Table 1 shows the reduction of sulphides content with aeration time. By plotting graph between concentration (mg/L) of sulphide vs. time (hrs) of aeration it is found that in the first two hrs, 42.69% of the total sulphides have been removed, while other 42.2% of sulphides were removed in eight hrs. After aeration slight reduction in pH value was observed. Increase in sulphate (SO_4) value shows that most of sulphides have been oxidised into sulphate. However there can be some other oxidative products those were not checked. Sulphate is one of the most expected product of air oxidation of sulphides.

Table 2 shows the results of composite tannery effluent just after the mixing of the liquors of each tannery process, soaking, unhairing liming, deliming/bating, pickling/chroming, neutralization/ retanning, fat liquoring and dyeing. During mixing large flocs were formed. Before and after settling of these flocs the effluent was analysed. The results showed that only settling of sludge carrying 20.94% BOD_5, 11.9% COD 26.8% total solids, 0.9% S.S., 44.44% chromium, and 10.6% Kjeldhal nitrogen. No reduction was found in sulphides and chloride values. This could be due to the solubility of these compounds. The reduction in pollution load shows that sludge formation, during mixing, carried some of the organic and inorganic compounds with it.

Table 3 shows results of effluent treatment with lime and carbon dioxide gas. In this treatment 42.4% reduction in BOD_5, 33.89% in COD, 12.43% in total solids, 9.36% in dissolved solids, 86.68% in suspended solids, 42.37% K-nitrogen and 13.55% total hardness has been found. The chromium that was only 60 ppm has been eliminated completely. The formation of $Ca(OH)_2$ which raised the pH value, eliminated chromium salt present in the liquor. Coagulating action of lime reduces



Relation between concentration of sulphides in effluent and time of aeration.

TABLE 1. RELATION B/W CONCENTRATION OF SULPHIDES IN EFFLUENT AND TIME OF AERATION.

Time of aeration hr	Concentration of sulphides mg/L	SO_4 mg/L	
		Before aeration	After aeration
0	176.25	1210.60	1522.55
2	101.25		
4	83.75		
6	69.75		
8	33.75		
10	16.25		

TABLE 2. PERCENTAGE OF REDUCTION IN POLLUTION LOAD AFTER SETTLING OF SLUDGE.

Contents	Composite effluent before settling	After settling	Percentage removal
pH	8.2	8.0	-
BOD_5	1967.53	1555.5	20.94
COD	5360.0	4720.0	11.94
T.S.	22262.0	16284.0	26.85
D.S.	15788.0	15638.0	0.95
S.S.	6474.0	646.0	90.02
Cr	108.0	60.0	44.44
Sulphides	176.0	176.25	Nil
K-Nitrogen	924.0	826.0	10.60
Chlorides	7950.0	7950.0	Nil
T.Hardness	-	2360.0	-

the quantity of total solids and suspended solids.

CO_2 gas treatment is carried out to bring down pH value from 11.9 to 6.8, During this process most of the Ca $(OH)_2$ has been precipitated as $CaCO_3$ this resulted in the reduction of total hardness and dissolved solids value. Therefore reduction in total solids was not only due to S.S. removal but also due to removal of dissolved solids.

Table 4 shows that carbon treatment is also effective for tannery effluent. A considerable reduction is found in BOD_5 value i.e. 58.7% in COD value this reduction is only 7.79% and 17.64% reduction is found in Kjeldhal nitrogen. From results it is evident that some of the organic matter was adsorbed by activated carbon, while it was observed that there was no reduction in chloride value. pH was also not effected, that can be due to normal flow of effluent without any pressing or vacuum application, during perculation of effluent through the column.

TABLE 3. TREATMENT WITH LIME (CaO) AND CARBON DIOXIDE (CO_2). DOSE = 40g/L.

Contents	Settled effluent	Treated with lime + CO_2	Percentage removal
Ph	8.0	6.8	-
BOD_5	1555.5	895.4	42.4%
COD	4720.0	3120.0	33.89
T.S.	16284.0	14260.0	12.43
D.S.	15638.0	14174.0	9.36
S.S.	646.0	36.0	86.68
Cr	60.0	Nil	100.00
K-Nitrogen	826.0	476.0	42.37%
Chlorides	7950.0	7900.0	-
T.Hardness	2360.0	2040.0	13.55%

TABLE 4. TREATMENT OF LIME (CaO) + CO_2 TREATED, EFFLUENT WITH ACTIVATED CARBON. DOSE = 40g/L.

Contents	Lime + CO_2 treated effluent	Effluent treated with activated carbon	Percentage removal
pH	6.8	6.8	—
BOD_5	895.4	360.33	58.7
COD	3120.0	2880.00	7.69
K-Nitrogen	476.0	392.00	17.64
Chlorides	7900.0	7900.00	Nil

TABLE 5. TREATMENT WITH $Al_2(SO_4)_3$. DOSE = 1.6 g/L.

Content	Settled effluent	Treated with $Al_2(SO_4)_3$	Percentage removal
pH	8.0	6.0	—
BOD_5	1555.5	740.0	52.42
COD	4720.0	3360.0	28.8
T.S.	16284.0	16440.0	0.95 increase
D.S.	15638.0	16180.0	3.46 " " "
S.S.	646.0	260.0	59.75
Cr	60.0	<0.02	100.00

Table 5. Results after the treatment with aluminium sulphate shows 52.42% reduction in BOD_5 value and 28.8% in COD value, suspended solids are refuced to 59.75% while an increase of 0.95% in total solids and 3.46% in dissolved solids is found. Chromium may be present in liquid in a concentration below the detection limit i.e. 0.02 mg/L of the test methods [5] other wise almost 100% chromium is eliminated.

Table 6. Results after the treatment with $FeCl_3$ show that 64.74% in BOD_5 value, 20.27% in COD value, 59.91% in

TABLE 6. TREATMENT WITH $FeCl_3$. DOSE = 4 g/L.

Contents	Settled effluent	Treated with $FeCl_3$	Percentage removal
pH	8.5	6.0	—
BOD_5	1888.85	666.0	64.74
T.S.	27848.0	29924.0	7.45 increase
D.S.	25164.0	28848.0	14.63 " " "
S.S.	2684.0	1076.0	59.91
COD	5920.0	4720.0	20.27
Cr.	24.0	<0.02	100.00

TABLE 7. TREATMENT WITH POTASH ALUM K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$. $DOSE_4$ =3 g/L.

Content	Settled effluent	Treatment with alum	Percentage removal
pH	8.5	6.0	-
BOD_5	1888.8	340.0	81.97
COD	5920.0	3980.0	32.77
Cr	24.0	0.02	100.00
T.S.	27848.0	31464.0	12.99 increase
D.S.	25164.0	31374.0	24.64 " " "
S.S.	2684.0	94.0	96.5

TABLE 8. PERCENTAGE REDUCTION DUE TO POTASH ALUM, LIME + CO_2, $FeCl_3$ AND $Al_2(SO_4)_3$.

	BOD_5 (%)	COD (%)	Chromium (%)	Suspended solids(%)	Total solids(%)	Dissolved solids (%)
(Lime+CO_2)	42.4	33.89	100	86.68	12.43	9.36
(Postash alum)					Reduction	Reduction
	81.97	32.77	100	96.5	12.99	24.67 Rise
($FeCl_3$)	64.74	20.27	100	59.91	7.45	14.63
[$Al_2(SO_4)_3$]	52.42	28.8	100	39.75	0.95	3.46

suspended solids value, and chromium has been removed about 100% while an increase in total solids i.e. 7.45% and in dissolved solids 14.63% is found.

Table 7. Potash alum treatment shows 81.97% reduction in BOD_5 32.77% in COD., 100% chromium, and 96.5% in suspended solids. A rise of 12.99% and 24.67% in total solids and dissolved solids is found, respectively.

Removal of the most of the chromium from mixed tannery effluent, as shown in Table 5 and 7, shows that the Cr+3 exists in the liquor in colloidal from which after the action of coagulants become settled down with flocs.

Table 8. The postash alum and lime + CO_2 treatment shows that BOD_5 value is reduced to 81.97% by potash alum while lime + CO_2 reduces only 42.2%. However COD value has been reduced nearly to the same level. Suspended solids value cut down by potash alum is more than the one reduced by lime + CO_2 treatment. So far as the total solids and dissolved solids are concerned lime + CO_2 treatment showed better results than potash alum since it reduced total solids to 12.43% and dissolved solids to 9.36% while potash alum treatment incresed total solids to 12.99% and dissolved solids to 24.67%.

$FeCl_3$ and $Al_2(SO_4)_3$ treatment increased the total solids and dissolved solids values while reduced some of the suspended solids but the value is less that the reduction value achieved by alum and lime+CO_2 tretament. $FeCl_3$ and $Al_2(SO_4)_3$ gives higher COD value as compared to potash alum and lime+CO_2 treatment. The increase in dissolved solids values could be due to formation of some soluble compounds of coagulants in effluent that reduced pH of effluent but on the other hand increased the dissolved solids.

From the results, it is evident that at the pH=6. Potash alum is much effective on tannery effluent as compared with $FeCl_3$ on the other hand lime treatment raises the pH of the effluent due to which CO_2 is applied to make it neutral and this treatment requires more time than the other three coagulants.

It is also found that any of above four coagulants can be applied for reductions of chromium, present in this type of effluent.

Dominant fungi isolated from composite tannery effluent:

1. *Rhizopus* sp.
2. *Penicillium* sp.
3. *Aspergillus* sp. *niger*
4. *Aspergillus* sp. *flavus*
5. *Aspergillus* sp. brownish yellow.
6. *Aspergillus* sp. yellowish white.
7. *Aspergillus* sp. brownish white.
8. *Aspergillus* sp. light green.
9. *Penicillium* sp. light green.
10. *Penicillium* sp. bluish green.
11. *Rhizopus* sp.
12. *Mucor* sp.
13. *Alternaria* sp. black.
14. *Alternaria* sp. greenish black
15. *Sporotrichum* sp.

Dominant bacterial isolated from composite tannery effluent.

1. *Staphylococcus aureus*.
2. *Staphylococcus albus*.
3. *Staphylococcus citreus*.
4. *Streptococcus* sp.
5. *Bacillus subtilis*.

Table 9 shows that lime + CO_2 treatment is also effective for the reduction in bacteria and fungi. In combination with activated carbon it removes 99.07% bacteria and 90% in fungi from wastewater. After activeated carbon treatment fungal growth has been reduced while bacterial colonies are increased.

Table 10 shows the effect of potash alum and $FeCl_3$ treatment on microbial growth in mixed tannery effluent. Both of these treatments are found effective specially in case of bacterial growth, where potash alum and $FeCl_3$ both are comparable with 69.6% and 70.80% removal respec-tively. In

TABLE 9. MICROBIAL ANALYSIS OF COMPOSITE TANNERY EFFLUENT AFTER VARIOUS TREATMENTS.

Treatments	Colony count bacteria		Colony count fungi	
Nil	18854	Removal %	40	Removal %
Lime + CO_2	70	99.63	27	32.5
Activated carbon	175	99.07	4	90

TABLE 10. MICROBIAL ANALYSIS OF MIXED EFFLUENT AFTER POTASH ALUM AND $FeCl_3$ TREATMENTS.

Treatment	Colony count bacteria		Colony count fungi	
Nil	6320		21	
		Removal %		Removal %
Potash alum	1920	69.62	12	42.8
$FeCl_3$	1840	70.8	20	4.7

TABLE 11. EFFECT OF SETTLEMENT ON MICROBIAL GROWTH IN MIXED EFFLUENT.

Treatment	Colony count bacteria		Colony count fungi	
Before sludge settling	164		40	
		Removal %		Removal %
After sludge settling	40	75.6	17	57.5

TABLE 12. MICROBIAL EFFLUENT OF $Al_2(SO_4)_3$ TREATMENT ON COMPOSITE TANNERY EFFLUENT.

Treatment	Colony count bacteria		Colony count fungi	
Nil	640		10	
		Removal %		Removal %
$Al_2(SO_4)_3$	424	33.7	7	30

Table 13.

Effectivity of microbial population	Lime + CO_2 (%)	Activated carbon (%)	Potash alum (%)	$FeCl_3$ (%)	$Al_2(SO_4)_3$ (%)	Sludge settling (%)
1. Bacteria	99.63	99.07	69.62	70.8	33.7	75.6
2. Fungi	32.50	90.00	42.80	4.2	30.0	57.7

case of fungi, potash alum treatment is found effective with 42.8% removal, while $FeCl_3$ effect is negligible i.e. only 4.7%.

Table 11 shows effect of settling and no chemical was used here for treatment. It shows that only settling is also effective for bacterial removal as here is 75.6% for fungi its effect is also good i.e. 57.5%.

Table 12 shows effect of $Al_2(SO_4)_3$ treatment on bacterial and fungal population. From the Table it is clear that its effect on both is quite comparable i.e. 33.7% and 30% respectively. In Table 13, effectivity of all the above mentioned treatments, on the removal of bacteria and fungi, are compared, it is noted that in all chemical treatments, the combination of, lime + CO_2 and activated carbon treatment is remarkable good for bacterial and fungi removal, while taking into account all the treatments including settling. It is concluded that coagulation effect reduces not only the chemical pollution load but it is also effective for the bacterial removal from tannery waste water.

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