CHAPTER V

REMOVAL OF SUSPENDED SOLIDS

5.1 INTRODUCTION

Particulates in water consist of finely divided solids, larger than molecules, but generally not distinguishable by the naked eye. Suspended solids of tannery effluents include inorganic, organic and biogenic materials. Suspended solids causes scattering of incident light and degrades visibility within the water. Consequently the photosynthesis of the plant species that grow in water is restricted and in turn the fish that depend on vegetation will be affected. Suspended solids also interfere with disinfection during water treatment as microorganisms adsorbed on particulate material may be shielded against disinfectants. In addition certain particulates can exert a disinfectant demand. Hence removal of suspended solids from the effluents is very essential to maintain the environmental balance/ harmony and also to improve the efficiency of water treatment in down stream operations.

Different chemical coagulants can bring about the destabilization of suspensions in different ways. Four distinct mechanisms namely compression of the double layer, adsorption leading to charge neutralization, enmeshment in a precipitate and adsorption to permit inter particle bridging are well known. Generally alum and ferric alum are the widely used inorganic
coagulants in wastewater treatment. The stability of the colloidal, quasi-
colloidal dispersion was found to diminish upon the addition of the
aluminum- and Fe(III) salt coagulant. The loss of stability results in principle
from the one of the following processes.

a) The Al\(^{3+}\) or Fe\(^{3+}\) ions added to the water are adsorbed on the surface
of the colloidal, quasi colloidal particles which carry a high
negative electric charge, altering the electric charge of the solids
and lowering their Zeta-potential to zero. The electrostatic
repulsion forces between the particles are thus minimized allowing
the particles to aggregate.

b) Owing to the partial hydrolysis of the Al\(^{3+}\) or Fe\(^{3+}\) ions water-
soluble aluminum-or iron(III)-hydroxide complexes are formed,
which contain a few Al or Fe atoms and which carry a positive
charge. These complexes enter into durable bonds with the
negatively charged particles (they are adsorbed on the surface of
the latter) changing thus their originally high surface charge
(reducing it virtually zero). The particles aggregate thereafter.

c) Hydrolysis of the Al\(^{3+}\) or Fe\(^{3+}\) ions produces with in a brief period
of time (a few seconds) aluminum, or iron(III) hydroxide sols
which contain much water and carry a positive charge. The sols are
therefore adsorbed on the solid particles present in surface waters,
changing the high negative electric charge of the latter. The
ensuring metal-hydroxide – solid particle complex has a resultant
electric charge of the -5.0 – 0.0 mV Zeta potential order and is thus suited to effective, rapid aggregation.

d) The hydrolysis products of the Al\textsuperscript{3+} or Fe\textsuperscript{3+} ions aggregate at high rates into large aluminum- or iron(III)-hydroxide flocs, which owing to their large size "enmesh" or "sweep" the colloidal particles to be removed (sweep coagulation) (Licsko 1997).

In the present study, coagulation of suspended solids was achieved by incorporating soluble anodes such as aluminum and iron. The mechanism of coagulation and their separation by electrically generated bubbles was discussed. The importance of bubble size and the kinetics of flotation are also discussed. Finally the factors that influence the separation process were outlined.

5.2 RESULTS AND DISCUSSION

5.2.1 Size distribution of suspended solids in raw tannery effluent

The size distribution of the suspended solids of raw tannery effluent was shown in Fig.5.1a. From the figure it is evident that the suspended solids are distributed in a wide range from 0.04 micron to 100 microns. The mean size of suspended solids was observed to be 18 microns. The specific gravity and the quantity of volatile matter of the suspended solids were also estimated and found to be 1.05 and 80% respectively.

From the above results it could be inferred that the suspended solids are low in density and more of volatile in nature.
Fig. 5.1a Size distribution of the suspended solids of raw tannery effluent

5.2.2 Effect of electrode material on coagulation and flotation

The effect of different electrodes on the removal of suspended solids from tannery effluents was studied and the results obtained were presented in Table 5.1. From the results it is evident that the separation of suspended solids is near total in the presence of iron and aluminum and only partial in the presence of titanium electrode. Size distribution of suspended solids that remained in the electroflotation cell (non-float) was analyzed and the results were presented in Figs. 5.1b and 5.1c. The particle size analysis of the resultant effluents clearly indicate the presence of colloidal solids ranging from 0.04 to 10 microns when titanium was used as anode. In other words these colloidal solids have not responded to flotation. On the other hand, suspended solids ranging from 10 to 50 microns were found in the remaining
5% of the effluent where iron was used as anode. It may be noted that 95% of the suspended solids were removed and only 5% of the suspended solids were left out in aqueous solution.

Table 5.1 Effect of anode material on the removal of suspended solids

Initial concentration of suspended solids: 1372 mg/L Flotation time: 900s, Current density: 46 mA cm⁻²

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Electrode system</th>
<th>Suspended solids after treatment (mg/L)</th>
<th>(%) Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al as anode and Fe as cathode</td>
<td>64</td>
<td>95.3</td>
</tr>
<tr>
<td>2</td>
<td>Fe as anode and Al as cathode</td>
<td>66</td>
<td>95.2</td>
</tr>
<tr>
<td>3</td>
<td>Titanium as anode and cathode</td>
<td>658</td>
<td>52.1</td>
</tr>
<tr>
<td>4</td>
<td>Coagulation and sedimentation Alum dosage: 250 ppm (CETP sample)</td>
<td>326</td>
<td>76.2</td>
</tr>
</tbody>
</table>
Fig. 5.1b Size distribution of the suspended solids in the resultant effluent after electroflotation [using Ti (Ta/Ir/Ru) oxide electrodes]

Fig. 5.1c Size distribution of the suspended solids in the resultant effluent (after electroflotation using Fe electrodes)
Histogram of the sample where iron was used as anode clearly shows that the population density of the colloidal solids was reduced. The same phenomenon was observed while aluminum was used as anode. This clearly suggests the coagulation of colloidal particles in the presence of iron and aluminum anodes and also the necessity of prior coagulation for their elimination by electroflotation.

Electroflotation tests were conducted on beam house effluent in the presence of different anodes at a current density of 47 mA/cm². The duration of electroflotation was maintained at 900 seconds in all the experiments. The effluents of beam house mainly comprise of sulfide ions, which are precipitated as metal sulfides. The coagulation of precipitates was further demonstrated by particle size analysis. The initial concentration of suspended solids was observed to be 1078 ppm. By using aluminum as anode, the concentration of the suspended solids could be brought down to 24 ppm, which is well within the standards. Whereas by using iron and Titanium, the suspended solids were brought down to 270 ppm and 687 ppm respectively. Though the bubble size and the flux are almost identical, floatability of suspended solids is observed to be better in the presence of iron and aluminum anodes and poor in the presence of titanium. The results of the same are presented in Fig. 5.2. In order to understand the effect of the anode material on flotation, size analysis of suspended solids was carried out using a particle size analyzer. The duration of electroflotation was varied from 120 to 900 seconds at a fixed current density of 47 mA/cm². After the experiment, the froth phase was subjected to mild agitation so that the entire solid phase is
Fig. 5.2  Electrocoagulation of suspended solids in the presence of different anodic materials

detached from the bubbles. The samples thus obtained were analyzed for particle size distribution and the results obtained are presented in Figs. 5.3a and 5.3b. By using aluminum and iron anodes, a gradual increase in size of the suspended solids is evident as the duration of electroflotation is increased. Coagulation of colloidal size solids was observed within 600 seconds and the size of the coagulum remains almost constant thereafter. Mean diameter of the solids increased to 34 microns with iron as anode and 61 microns in the presence of aluminum anode. This clearly suggests the coagulation of colloidal solids in the presence of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ ions released from the anode. These ions are generally preferred in the coagulation process because of their multivalent character and low solubility ($K_s = 10^{-32.7}$) of their hydroxides.
Fig.5.3a  Progress of coagulation with reference to electroflotation time in the presence of iron as anodes. (a) Initial effluent (b) after 120s (c) after 300s (d) after 600s (e) after 900s

Fig.5.3b  Progress of coagulation with reference to electroflotation time in the presence of aluminum as anodes. (a) Initial effluent (b) after 120s (c) after 300s (d) after 600s (e) after 900s
Aluminum or iron ions dissolved from anode form a range of coagulant species that destabilize and aggregate the suspended solid particles and precipitates. Thus the suspended solids were simultaneously coagulated and floated effectively in the presence of soluble anodes. In the conventional treatment, sulfate ions from alum and iron salts leads to secondary pollution. This could be avoided by the electroflotation technique as the metal ions dissolved from the respective anodes act as coagulant. It has been reported that the electrocoagulation process consumes less coagulant (Vic et al., 1984) and has an advantage of removing small colloidal particles because the applied electric field accelerates the motion, thereby facilitating the coagulation.

It is well established that the mono and polymeric aluminum hydroxyl species thus formed can in turn interact with particles of opposite charge by electrostatic interaction and form a coagulum. Coagulated solids are subsequently lifted to the surface by hydrogen and oxygen bubbles generated electrolytically. Better floatability of coagulated particles could be attributed to favorable hydrodynamics. From the point view of hydrodynamics, the probability of particle-bubble collision is better if the bubble size and particle size are approximately the same Glembotskii et al., (1973) and Glembotskii et al., (1975) have reported that the bubbles generated by electrolysis of water are very small and generally vary from 15 to 80 microns depending on pH and current density. It may be noted that the size of the coagulated solids and the size of electrolytic bubbles are in the same range. Generally, the surface of solid should be hydrophobic to facilitate
bubble attachment. However, bubbles generated by electrolysis are able to float even hydrophilic precipitates. This is attributed to high capillary pressure inside the bubbles. At the moment of bubble formation, the pressure inside the bubble is estimated to be around $1.45 \times 10^6$ Pa (Melic-Gaikazyana et al., 1981). Bubbles with high pressure could spread even on hydrophilic surface and establish micro contact (Manohara et al., 1982).

Derjaguin and Dukhin (1960) have observed that the probability of particle-bubble collision will be high if the size of the bubbles and particles were of the same order. Models based on interception theories reveals that the collection efficiencies depends on the ratio $(dp/db)^n$ with the exponent usually in the range of 1.5 to 2.0. Calculations based on the assumption that the fraction of the bubble surface is available for transporting particles and without regard to how the particles reach the bubble, indicates that the transport is proportional to $Q_a f \frac{dp}{db}$ where ‘$Q_a$’ is aeration rate, ‘$f$’ is fraction of the bubble area covered, ‘$dp$’ is particle diameter and ‘$db$’ is bubble diameter. Thus the transportation of suspended solids will be high if the bubble size is low. A given volume of air will have more surface area if the bubbles are fine and can accommodate more solids on their surface. Thus high rate of flotation could be achieved by electroflotation.

It may be noted that the respective metal ions are released while using soluble anodes such as Fe and Al where as oxygen bubbles are generated by using stable anodes such as titanium. Anodic dissolution of metal ions could be represented as
\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \quad E^0 = +1.677V \\
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \quad E^0 = +0.440V \\
\end{align*}
\]

(5.1)  
(5.2)  

Fe\textsuperscript{2+} ions thus released in to aqueous solution may partly be converted to Fe\textsuperscript{3+} ions either by anodic oxidation or under oxidizing environment.

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad E^0 = -0.771V
\]

(5.3)  

The hydroxyl species formed have a pronounced tendency to undergo polymerization due to interaction between hydroxyl groups of adjacent molecules. In the case of iron, species such as FeOH\textsuperscript{2+}, Fe(OH)\textsubscript{2}\textsuperscript{+}, Fe(OH)\textsubscript{2}, Fe(OH)\textsubscript{3}, Fe(OH)\textsubscript{4}\textsuperscript{-} and FeO(OH) are formed according to the following

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{FeOH}^{2+} + \text{H}^+ \quad -\log K = 2.20 \\
\text{FeOH}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \quad -\log K = 3.50 \\
\text{Fe(OH)}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_{3} + \text{H}^+ \quad -\log K = 6.00 \\
\text{Fe(OH)}_{3} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_{4}^- \quad -\log K = 10.00
\end{align*}
\]

(5.4)  
(5.5)  
(5.6)  
(5.7)  

Similarly, aluminum also forms different species

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} & \rightarrow \text{AlOH}^{2+} + \text{H}^+ \quad -\log K = 4.97 \\
\text{AlOH}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_{2}^+ + \text{H}^+ \quad -\log K = 4.30 \\
\text{Al(OH)}_{2}^+ + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_{3} + \text{H}^+ \quad -\log K = 5.70 \\
\text{Al(OH)}_{3} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}_{4}^- \quad -\log K = 8.00 \\
2\text{Al}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{Al}_2(\text{OH})_{4}^{4+} + 2\text{H}^+ \quad -\log K = 7.70 \\
3\text{Al}^{3+} + 4\text{H}_2\text{O} & \rightarrow \text{Al}_3(\text{OH})_{4}^{5+} + 4\text{H}^+ \quad -\log K = 13.9
\end{align*}
\]

(5.8)  
(5.9)  
(5.10)  
(5.11)  
(5.12)  
(5.13)
Aqueous solutions of aluminum ions at neutral pH have been reported to contain highly charged poly-nuclear hydroxy aluminum (III) complexes such as $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al(OH)}_6^{3-}$, $\text{Al(OH)}_7^{4+}$ and $\text{AlO}_2^-$ (Morgan 1967). Parthasarathy and Buffle (1985) succeeded in demonstrating experimentally that with in a wide (4.0-6.5) range of pH values and Al concentrations ($10^{-3}$ to $10^{-1}$ M) and at OH-Al ratio between 2.5-2.9 : 1, over 75% of all the Al present in the form of water soluble complex $[\text{Al}_{13}(\text{OH})_{32}]^{7+}$. They have proved that this type of polymeric complex with positive charge is highly effective coagulant.

Species distribution diagrams of iron and aluminum are shown in Figs. 5.4 and 5.5. From Fig. 5.4, it is evident that at pH 8.0 the species such as Fe (OH)$_3$ is predominant. Below this pH, positively charged ferric hydroxide species will exist. In the very alkaline range it will become negative. In the case of aluminum, neutral amorphous Al(OH)$_3$ is predominant around pH 7.0. Positive species will exist below this pH and negative species above this pH. Since the poly-nuclear metal hydroxyl complexes with positive, negative and neutral charge are good coagulants, the suspended colloidal solids are adsorbed on highly active polymer molecules and form coagulum. Such coagulation was not observed in the case of titanium electrode coated with Ir/Ta/Ru, since it is insoluble. Though carbon was released from graphite electrode due to mechanical instability, it could not aid coagulation of suspended solids.
Fig. 5.4  Species distribution diagram of Fe (III)-Water system at Fe (III) concentration of $1 \times 10^{-6}$M

Fig. 5.5  Species distribution diagram of Al (III)-Water System at Al (III) concentration of $1 \times 10^{-6}$M
5.2.3 Flotation Kinetics

Removal of suspended solids by electroflotation was studied at different current densities using aluminum as anode. At each current density, samples were collected at different time intervals and the results are presented in Table 5.2. The kinetic data obtained at the current density of 31mA/cm² has been fitted into the following kinetic models established by the earlier investigators (Ek 1991; Mayer and Klimpel 1984).

Model-1

\[
R = R^* (1-e^{-kt}) \quad (5.14)
\]

\[
-kt = \ln \left(\frac{1-R}{R^*}\right)
\]

\[
k = \frac{-[\ln \left(\frac{1-R}{R^*}\right) / t] }{}
\]

Model-2

\[
R = R^* \left(\frac{kt}{1+kt}\right) \quad (5.15)
\]

\[
k/(1+kt) = \frac{R}{R^*}
\]

\[
ktR^* = (1+kt)R
\]

\[
ktR^* = R+Rkt
\]

\[
ktR^* - Rkt = R
\]

\[
k(tR^*-Rt) = R
\]

\[
k = \frac{R}{(tR^*-Rt)}
\]
Model-3

\[
R = R^*^2 \left[ kt/(1+R^* kt) \right] \quad (5.16)
\]

\[
R(1+ R^* kt) = R^*^2 kt
\]

\[
R^* kt - R^*^2 kt = -R
\]

\[
k(R^* t - R^*^2 t) = -R
\]

\[
k = -R / (R^* t - R^*^2 t)
\]

Model-4

\[
R = R^* \left[ 1 - \{ln(1+kt)/kt\} \right] \quad (5.17)
\]

\[
(R - R^*)kt = - R^* \left[ ln(1+kt) \right]
\]

Where R is recovery at time t, R* is ultimate recovery and k is rate constant.

From the results shown in Fig. 5.6, it is apparent that the best fit to the experimental data was observed for the first order model represented in equation (5.14). The first order rate equation was extended to the data obtained at different current densities (Table 5.2). The rate constants for first order equation were found to be 0.0077 s\(^{-1}\), 0.00815 s\(^{-1}\) and 0.00898 s\(^{-1}\) at current densities of 31 mA cm\(^2\), 46 mA cm\(^2\) and 62 mA cm\(^2\) respectively.

Assuming that concentrations of hydrogen bubbles and particles would influence the recovery, kinetics should obey second order rate equation. Since the hydrogen bubbles liberating from cathode was large compared to the number of particles, the significance of the bubbles could be
Fig. 5.6 Flotation kinetics-model fitting
negligible. De Bruyn and Modi (1956) have observed first order rate for the flotation of fine particles (< 65microns), if the solids content in the pulp is less than 5.2%. Tomlinson and Fleming (1963) have also observed first order process when the solids concentration in the pulp is small (uninhibited flotation) and zero when the concentration is high. Results of the present study are in good agreement with the above observations.

Table 5.2  Effect of current density on the removal of suspended solids

| Sl. No. | Flotation Time (s) | % Removal of Suspended solids
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>31 mA cm(^{-2})</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>93</td>
</tr>
</tbody>
</table>

By increasing the current density, the bubble flux and in turn the collision probability and flotation rate are expected to increase. However, electroflotation tests conducted at different current densities (Table 5.2) have shown a marginal increase in the removal of suspended solids. This may be due to liberation of sufficient hydrogen bubbles even at a current density of 31mA cm\(^{-2}\). An equation to predict the recoveries of suspended solids has been deduced by employing multi linear regression.

\[ R = x_1 C + x_2 I + x_3 T + x_4 \]  

(5.18)
Where R is removal of suspended solids expressed in %, C is the initial concentration of suspended solids expressed in g/L, T is the flotation time in seconds. The constants \( x_1, x_2, x_3 \) and \( x_4 \) are calculated and the values are found to be 2.087, 0.2352, 0.3641 and 0.0021 respectively. Using these constants, theoretical removal of suspended solids are calculated and plotted against experimental results as shown in Fig. 5.7. A close look at Fig. 5.7 indicates that there is a good correlation between theoretical and experimental results. The constants \( x_1, x_2, x_3 \), and \( x_4 \) are obtained by performing multilinear auto regression analysis. The details of multilinear auto regression analysis are as given below.

\[ X = A^{-1} q \]  \hspace{1cm} (5.19)

where

\[
A = \begin{pmatrix}
\Sigma C & \Sigma I & \Sigma T & 4 \\
\Sigma C^2 & \Sigma CI & \Sigma CT & \Sigma C \\
\Sigma CI & \Sigma I^2 & \Sigma IT & \Sigma I \\
\Sigma CT & \Sigma IT & \Sigma T^2 & \Sigma T
\end{pmatrix}
\hspace{1cm} (5.20)

\[
q = \begin{pmatrix}
\Sigma R \\
\Sigma RC \\
\Sigma RI \\
\Sigma RT
\end{pmatrix}
\hspace{1cm} (5.21)

\[
X = \begin{pmatrix}
x_1 \\
x_2 \\
x_3 \\
x_4
\end{pmatrix}
\hspace{1cm} (5.22)
Fig 5.7. Correlation between theoretical and practical removal of suspended solids by electroflotation.

Flotation time: 60, 120, 180, 240 and 300 seconds.

Series 1. Initial conc. of suspended solids: 5.080g/L, Current density: 31mA/cm²
Series 2. Initial conc. of suspended solids: 5.080g/L, Current density: 47mA/cm²
Series 3. Initial conc. of suspended solids: 5.080g/L, Current density: 62mA/cm²
Series 4. Initial conc. of suspended solids: 1.390g/L, Current density: 31mA/cm²
Series 5. Initial conc. of suspended solids: 1.390g/L, Current density: 47mA/cm²
Series 6. Initial conc. of suspended solids: 1.070g/L, Current density: 31mA/cm²
Series 7. Initial conc. of suspended solids: 1.070g/L, Current density: 47mA/cm²
Series 8. Initial conc. of suspended solids: 1.070g/L, Current density: 62mA/cm²
Series 9. Initial conc. of suspended solids: 3.040g/L, Current density: 31mA/cm²
Series 10. Initial conc. of suspended solids: 3.040g/L, Current density: 46mA/cm²
Series 11. Initial conc. of suspended solids: 3.040g/L, Current density: 62mA/cm²
A MATLAB script has been written to perform the multilinear auto regression analysis using equations from (5.19) to (5.22).

From the above discussion, it could be concluded that aluminum and iron were found to be very effective for the removal of suspended solids compared to titanium coated with Ir/Ta/Ru oxides and graphite electrodes. It was observed that the colloidal size suspended solids are coagulated in the presence of aluminum and iron anodes. The floatability of suspended solids that are below 10 microns was observed to be poor with the small bubbles generated by electrolysis. They can be floated after coagulation in the presence of either aluminum and iron anodes. The kinetics of flotation of suspended solids by electrolytic bubbles was found to obey first order rate expression. The pH of the effluent, current density, initial concentration of the effluent and the time were found to influence the overall elimination of the suspended solids.