# TREATMENT OF TANNERY WASTEWATER WITHOUT SLUDGE GENERATION

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**Segregation of highly polluting streams**

- **Soak liquor and pickle liquor Evaporated in Solar Evaporation pans**

- **Chrome liquor Recovery of Chromium (III) and reuse**

Wastewater discharged from industries are being treated through unit operations

Screening
Equalisation
Primary clarification,
Secondary biological anaerobic treatment,
Aerobic biological treatment and
Tertiary treatment

(I) coagulation- flocculation,
(ii) sedimentation,
(iii) sand filtration,
(iv) carbon filtration,
(v) ultrafiltration,
(vi) nano filtration and
(vii) Reverse Osmosis.

## PRIMARY TREATMENT

**Equalisation ,**
**Coagulation –Flocculation**
**Sedimentation**

## CHEMICAL SLUDGE PRODUCTION

- 150-200 kg of sludge per ton of rawmaterial processed.

# SECONDARY BIOLOGICAL TREATMENT OF TANNERY WASTEWATER

**Many combinations of treatment**

- **Anaerobic biological treatment (UASB) and Aerobic biological treatment**
- **Aerobic biological treatment (Activated Sludge Process)**
- **Membrane Bioreactor ( MBR)**

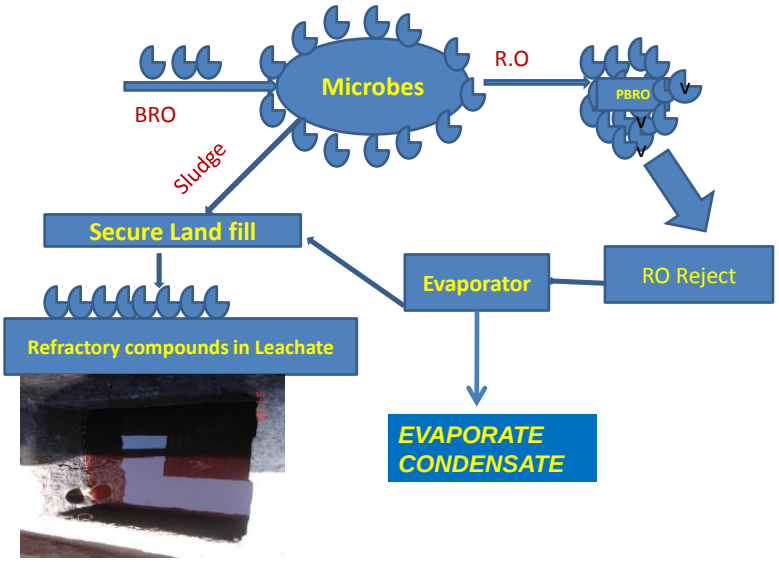
**Issues Identied:**

- **Huge sludge production**
- **Volatile organic compounds emission**
- **Excessive foam formation**
- **Residual COD or Biorefractory COD in the treated wastewater**
- **Fouling of membrane**
- **Membrane life is shortened**

**Reduction potential** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O(l)$

**Eo = 1.23 V**

**Fate of Bio refractory organic (BRO) compounds in wastewater**




## Possible pathway for controlling the oxidation of organics in wastewater

Hydroxyl radical may be considered as the oxidising agent with oxidation potential of 2.33V

| Compound | Symbol | Oxidation Potential (V) | Relative Power of Chlorine |
|---|---|---|---|
| Fluorine | $F_2$ | 3.06 | 2.25 |
| Hydroxyl Radical | •OH | 2.80 | 2.05 |
| Ozone | $O_3$ | 2.07 | 1.52 |
| Hydrogen Peroxide | $H_2O_2$ | 1.77 | 1.30 |
| Permanganate | $MnO_4^-$ | 1.67 | 1.23 |
| Hypochlorous acid | HOCl | 1.49 | 1.10 |
| Chlorine | $Cl_2$ | 1.36 | 1.10 |

# Nano Porous Activated carbon has been proved to generate hydroxyl radicals using molecular oxygen Patentd technology of CLRI

Characteristics of the mesoporous carbon

| S.no | Parameters | Values |
|---|---|---|
| 1 | $S_{BET}$ ($m^2/g$) | 438.9 |
| 2 | $S_{mic}$ ($m^2/g$) | 214.9 |
| 3 | $S_{meso}$ ($m^2/g$) | 224.0 |
| 4 | Micropore volume, $V_{micro}$ ($cm^3/g$) | 0.12 |
| 5 | Mesopore volume, $V_{meso}$($cm^3/g$) | 0.27 |
| 6 | Total pore volume, $V_{tot}$ ($cm^3/g$) | 0.39 |
| 7 | $V_{meso}$ /$V_{tot}$ (%) | 69.23 |
| 8 | Average pore diameter (A°) | 35.28 |
| 9 | Production yield of carbon (%) | 37.69 |
| 10 | Carbon (%) | 37.96 |
| 11 | Hydrogen (%) | 2.40 |
| 12 | Nitrogen (%) | 0.50 |
| 13 | Moisture (%) | 13.56 |
| 14 | Ash (%) | 45.58 |
| 15 | Decolorizing power (mg/g) | 69.32 |
| 16 | Point of zero charge (PZC) | 7.1 |
| 17 | | 0.56 |

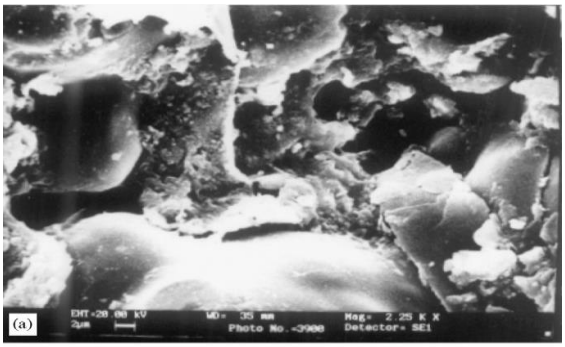
$S_{BET:}$ BET surface area;

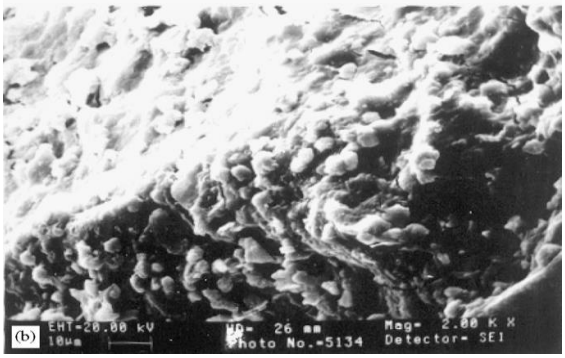
$S_{mic}$: micropore surface area;

$S_{meso}$: mesopores surface area.

Immobilised bacteria in NPAC

*Sekaran et al., Indian Journal of Chemical Technology*, 11(1)(2004), 95-102




❖*CATALYST DOES NOT REQUIRE REPLACEMENT*

❖*LIFE OF THE CATALYST IS MORE THAN 10 YEARS*

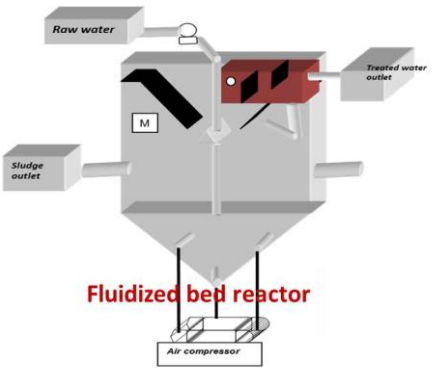
## CHEMO-AUTOTROPHIC ACTIVATED CARBON OXIDATION (CAACO) SYSTEM

### FEATURES

- **IMMOBILISATION OF *BACILLUS SP.***
- **NANO POROUS SILICA-CARBON COMPOSITE MATRIX**
- **OXIDATIVE MINERALISATION OF ORGANICS IN WASTEWATER**

Two Modes of treatment

## Fluidised Immobilised Cell Carbon Oxidation (FICCO)




Packed Bed reactor known as Chemo Autotrophic Activated carbon Oxidation (CAACO)

MERITS OF CAACO TECHNOLOGY DEVELOPED BY CLRI FOR THE TREATMENT OF WASTEWATER


- **Indigenous technology**
  **All the components of the technology are available in India**

- **Less land requirement**
  **CAACO technology requires 0.5 $m^2/m^3$ as it involves only three unit operations against the conventional technology**

**Less electrical and mechanical equipments**
**Only transfer pumps and an air blower for supplying air is required**

- …….contd.

- **Less detention period (1 hr)**

  **CAACO technology requires 1hour residence time while the conventional technology needs 24-36 hours**

- **Less power consumption**

  **CAACO technology requires 0.87 kwh/$m^3$**

# Issues:

**The refractory organic chemicals were not removed by CAACO system**

Poor removal of aromatic compounds

Alicyclic compounds escape aerobic biological treament

The longer chain fatty acids appear in aerobic biological treatment

During endogeneous decay of bacterial cells a wide spectrum of compounds are released into solution, they contribute to residual COD

Accumulation of biomass leads to release of SMP


# FENTON ACTIVATED CARBON CATALYTIC OXIDATION [FACCO] FOR THE TREATMENT OF REFRACTORY ORGANICS IN WASTEWATER

## Advanced Oxidation Processes (AOP)

❖**insitu generation of highly potent chemical oxidant hydroxyl radical (OH•)**

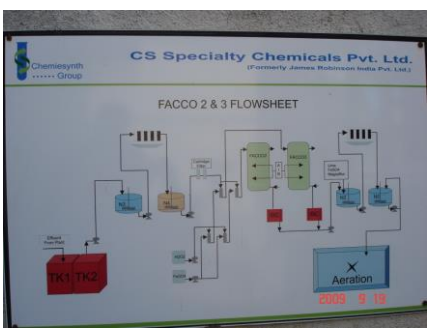
❖**with a high electrochemical oxidation potential (2.8V versus normal hydrogen electrode) for the destruction of wide range of organic compounds in wastewater**

**FACCO technology in TNPL, Karur, Tamilnadu**

❖Hydroxy radicals react with organics and break them down gradually into smaller fragments with higher bio degradation potential.

❖Sometimes (few occasions) dissolved organics are even completely degraded mainly into $CO_2$ and water.

❖ **Hydroxy radicals are generated by Fenton's reagent, a mixture of Ferrous iron and hydrogen peroxide**




FACCO technology in CS Speciality chemicals Pvt Ltd., VAPI

❖The large amount of ferric hydroxide sludge are generated during Fenton process, thus, causing an additional water pollution problem.

❖This may be regarded as the disadvantage of homogeneous Fenton's reagent .

❖ Attempts have been made to avoid the additional water pollution due to metal ions by substituting the heterogeneous catalysts for homogeneous Fenton catalyst .

❖The combination of sorption with destruction of the sorbates in wastewater by catalytic processes such as Fenton Activated Carbon Catalytic Oxidation using immobilised Fe(II) , Hydrogen peroxide and Nano Porous Activated Carbon.

## Two Modes of configuration

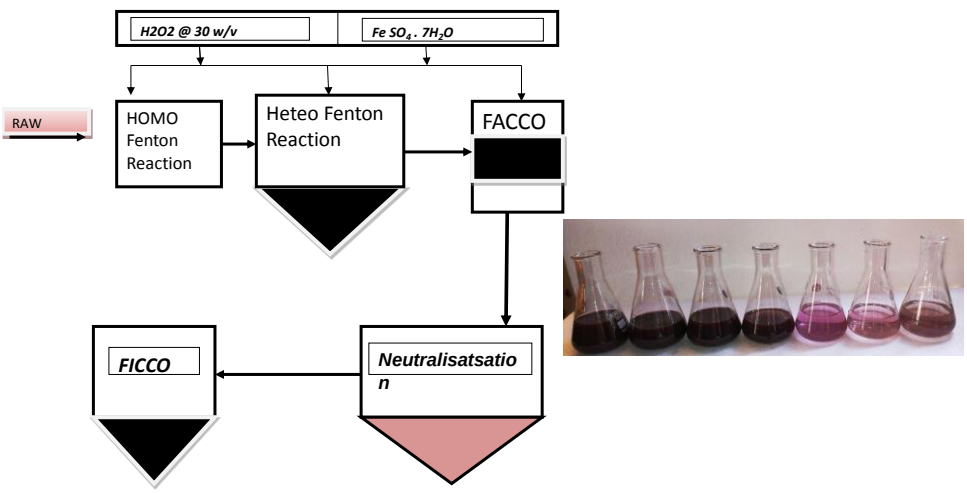
## 1.Fluidised Activated Carbon Fenton Oxidation

## (Hetero Fenton Oxidation system)

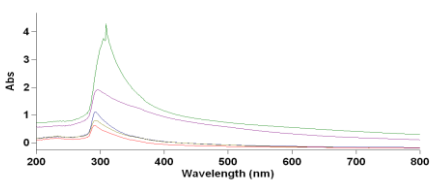
## 2. Packed Bed Activated Carbon Fenton Oxidation

## Fenton Activated Carbon Catalytic Oxidation (FACCO)

| Parameters | Raw wastewater | Homo Fenton Oxidation $H_2O_2$ (@30%w/v) 0.2ml/L; $FeSO_4.7H_2O$- 0.1g/L ; HRT- 1 hr | Hetero Fenton Oxidation $H_2O_2$ (@30%w/v) 0.2ml/L; $FeSO_4.7H_2O$ MAC,30g/L HRT:6 hrs | FACCO $H_2O_2$ (@30%w/v) $FeSO_4.7H_2O$- 0.1g/L HRT- 1hr | FICCO 24 HRS |
|---|---|---|---|---|---|
| pH | 6.71 | 3.5 | 3.41 | 3.4 | 7.1 |
| COD ,mg/L | 7060 | 4050 | 3520 | 1230 | 420 |
| $BOD_5$ ,mg/L | 2100 | 1220 | 1020 | 450 | 107 |
| $NH_3$,mg/L | 272 | 143 | 116 | 105 | 67 |
| Total Solids ,mg/L | 12100 | 11121 | 11073 | 10833 | 9890 |
| Total Dissolved Solids, mg/L | 11871 | 10931 | 10901 | 10672 | 9763 |
| Total Suspended Solids, mg/L | 229 | 190 | 172 | 161 | 127 |





# RECOMMENDED SCHEME FOR TANNERY WASTEWATER

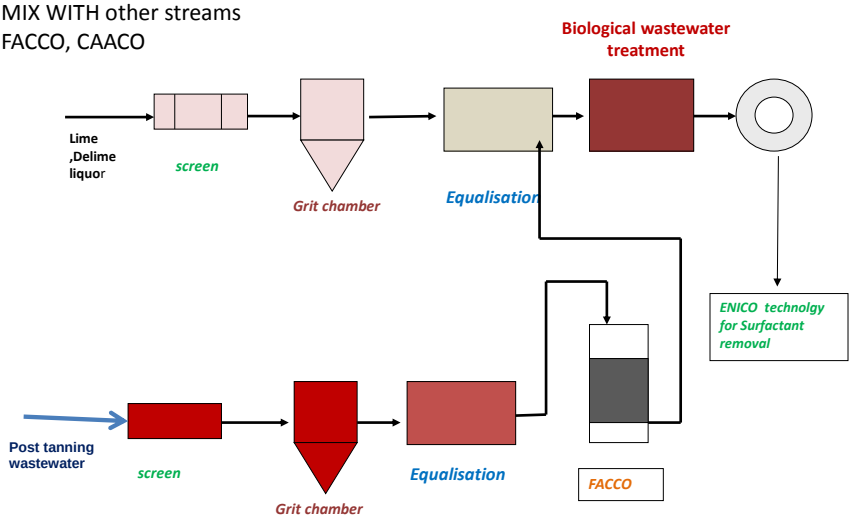
**Tanning industry**

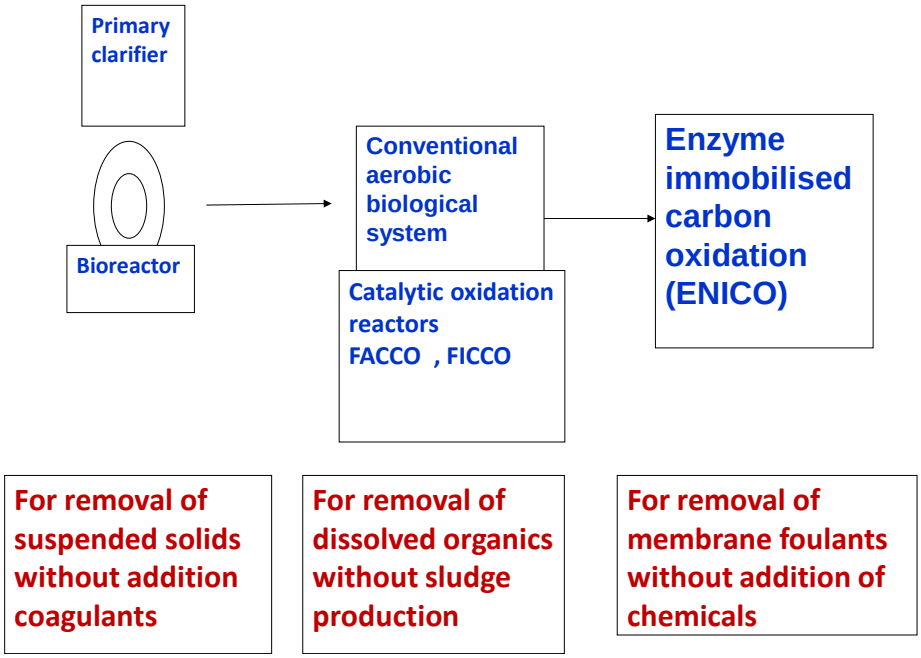
Segregation of Chrome and Pickle stream ,
Post tanning wastewater.
Post tanning wastewater is treated through hetero fenton catalytic oxidation reactor,
MIX WITH other streams
FACCO, CAACO

**CONVENTIONAL TECHNIQUES:**

**PRIMARY TREATMENT- ANAEROBIC-AEROBIC**

**ISSUE: SLUDGE PRODUCTION , NOT MEETING THE STANDARD**






## *CONCLUSIONS*

❖***Segregation of soak liquor and pickle liquor and treatment to reuse the salt***

❖***Treatment of post tanning wastewater using advanced oxidation process***

❖***Pre treatment of beamhouse wastewater***

❖***Combined biological treatment of treated post tanning wastewater and pretreated beamhouse wastewater to reduce sludge generation***


THANK YOU FOR YOUR KIND ATTENTION