PROJECT REPORT

COLOUR AND TDS REMOVAL FROM ECF BLEACH PLANT EFFLUENT

1. Broad Area of Technology	Effluent Treatment
2. Project Duration	12 months
3. Organisation	Tamil Nadu Newsprint and Papers Ltd., Kagithapuram, Karur, Tamil Nadu Pin - 639136
4. Other Investigating Agency	Central Leather Research Institute, Chennai,(Council of Scientific and Industrial Research, Govt. of India)
5. Actual Location where the Project is being carried out	Tamil Nadu Newsprint and Papers Ltd., Kagithapuram, Karur, Tamil Nadu Pin - 639136
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Funded by
Development Council (Paper), DoIPP,
Govt. of India

Supported by
Indian Paper Manufactures Association

Tamil Nadu Newsprint and Papers Ltd., Kagithapuram, Karur,
Tamil Nadu - 639136

Title	**: Colour and TDS removal from ECF bleach plant effluent**
Project area	**: Effluent treatment**
Sponsoring agency	**: Development Council (Paper), DoIPP, Govt. of India.**
Executing agency	**: Tamil Nadu Newsprint and Papers Limited**
Participating agency	**: Central Leather Research Institute, Chennai (Council of Scientific and Industrial Research, Govt. of India)**
Total budget	**: RS 47.66 lakhs**

SUMMARY

The biological treatment of HW EOP filtrate in the FAACO reactor has resulted in a reduction of 50 to 60 % in COD and Colour and this was enhanced slightly by Fenton dosage. However, COD & Colour was still high and it is not suitable to treat in membrane process for TDS reduction. Treatment of D_{HT} filtrate in FACCO reactor, with Fenton and ammonium persulphate has brought about 50 to 60% reductions in COD & Colour, but the cost of treatment has increased considerably. High COD at FACCO outlet caused fouling in the RO membrane thereby reducing the recovery efficiency. The cost of hardness/TDS removal by lime-soda treatment and membrane filtration works out to Rs 80 /m^3. Pretreatment methods to remove silica, heavy metals and hardness, such as, lime treatment, followed by anaerobic and aerobic process for improved biological treatment need to be explored to make the process more economical. Ion exchange techniques and Resin filtration for Colour/COD/TDS removal have to be experimented further to find a viable method for tertiary treatment to remove TDS and other non-process elements especially for ECF bleach plant effluent.

The results of present studies will be very useful input to design a Zero Liquid Discharge system which is technically more advanced and economically viable. Based on results

obtained from the present study TNPL has already initiated a ZERO LIQUID DISCHARGE program and proposed to setup 5 m^3/hr pilot plant to find out feasibility of treating bleach plant effluent combining both biological and membrane process.

INTRODUCTION

The pulp and paper mill operation consumes large volume of water when compared to other manufacturing industries. Water is used as medium where all the pulp and paper making process are carried out and it is also used as vehicle to transport the pulp in the mills from one unit operations to another and gets contaminated during various processes. This contaminated water (effluent) is treated and discharged later as wastewater. In the 80's water consumption per ton of paper produced was as high as 250 m^3/MT, and at present it ranges from 100 to 150 m^3/ MT. In the past one decade considerable efforts were made in both national and international level to develop and operate closed loop configuration in the pulp and paper mills to minimize environmental impact on the surrounding ecosystem. The concept is being accelerated in the recent years due to increasing awareness about environmental among the public and consumers (Johnson *et al,* 1996). The concept is slowly accepted within the industry that close looping is essential for long term sustainable production. Nonetheless, when water circuit is closed, concentration build-up of contaminants especially chlorides and other non-process elements cause problem in process operation by way of erosion, corrosion and scaling, forcing to purge or develop new systems to treat contaminants in the wastewater.

RELEVANT SCIENTIFIC CONCEPTUAL INFORMATION

Pulping of the fibrous raw materials involves combination of chemicals and the physical process conditions (temperature and pressure) that dissolve lignin present in raw material to liberate cellulosic fibre. The fibres retain its length and strength and sent for further processing. The dissolved lignin and other organic and inorganic components are washed counter currently from the pulp, concentrated by evaporation and subsequently burned in the recovery boiler to generate energy and recover spent chemicals. Up to this stage it is possible to close loop the process without discharging any wastewater using modern pulping and washing technology.

Cooked unbleached pulp has a brown, colour, due to presence of residual liginin and other oxidisable materials and it cannot be used as such for bleached products like printing and writing paper. Further treatment is necessary to increase the pulp brightness to a white colour. Residual lignin and other oxidisable material are removed by oxygen delignification and bleaching with moderate pressures and temperatures. The amount of bleaching chemical added in the first bleaching stage is directly proportional to the Kappa number of the unbleached pulp i.e. a low kappa number prior to bleaching results in chemical savings and reduced organic and inorganic discharge through wastewater from the bleach plant. However, reduction in pulp yield and pulp strength limits Kappa number to below certain level (McDonough 1998, Gellerstedt 2009).

Chlorine, Calcium hypochlorite and Sodium hypochlorite are the inexpensive and highly effective bleaching agent used widely until the 1990s and this technology was phased out due to high amount of chlorinated organic compounds generated in bleaching collectively measured as AOX. Chlorine and hypochlorite were also stopped in the pulp bleaching to avoid chloroform generation and to preserve pulp strength (McKenzie 1994, Pryke and Reeve 1996, Amec 2008, Gellerstedt 2009)

The modern bleaching sequence commonly known as Elemental Chlorine Free bleaching (ECF) mainly consists of chlorine dioxide (ClO_2), oxygen (O_2) and hydrogen peroxide (H_2O_2) (Amec, 2008, Gellerstedt 2009) and in some mills Ozone (O_3) is also used rarely (Sonnenberg 1998, Monta and Van Tran 2008). In addition to the above, ECF sequence also includes alkali stages (E) reinforced with either oxygen (O), or hydrogen peroxide (P), or both called (EO), (EP) and (EOP) stages (Gellerstedt 2009). Acid (usually sulfuric acid (H_2SO_4) is charged to some acidic stages for pH control. The Chlorine dioxide bleaching is also conducted at higher temperature of around 85 to 90 ^oC reduces the chemical consumption and AOX discharge (Ragnar 2005). Chlorine dioxide is the most selective bleaching agent used in ECF bleaching and to produce pulp with 90% ISO brightness, high strength, cleanliness, and brightness stability. The content of AOX in the bleach plant wastewater reduced to 0.2 to 0.4 kg /ADt pulp with a combination of modified cooking, oxygen delignification and bleaching with ClO_2 as the only chlorine-containing chemical.

The environmental effects of bleach plant effluents and whole mill effluents have been studied by various investigations (Walsh *et al.,* 1991, Ljunggren *et al.,* 1998, Stinchfield and Woods 1995, Lehtinen and Tina 1998, Deardorrf *et al.,* 1998). The above studies indicate AOX from that treated wastewater from well-managed pulp and paper mills using ECF bleaching reduced to minimum level. But colour and Total dissolved solids especially the inorganic compounds are still an issue in spite of many measures taken to reduce. For example, Modified or Continuous cooking, oxygen delignification (Fiskari, 2004, Johnson *et al*., 2008), ECF bleaching and modified ECF bleaching (Van Tran, 2006, Ragnar 2005), Ozone bleaching (Monta and Van Tran 2008, Colodette *et al.*, 1998), reuse or recycling of bleach plant filtrates such as alkaline and acid filtrates (Amec, 2008). Because much of the technology development associated with kraft mill bleach plant closure for colour and TDS reduction in wastewater involved reduction of water consumption and reuse and recycling of bleach plant waste water in side the plant leading to undesirable consequences, such as, scale deposits, corrosion, loss of bleaching efficiency, increased evaporative loads, reduced production capacity, and loss of operational flexibility. Amec 2008) these issues have caused many companies to reconsider the role of complete process closure in minimizing effluent impacts. In many cases, the optimal solution identified has been partial closure of bleach plant coupled with external secondary and tertiary treatment of the remaining mill process effluent (Amec, 2008).

Recent review indicates that combination of physical (microfiltration, Ultrafiltration, Nanofiltration and Reverse osmosis) coupled with chemical and biological process are found to be an alternative solution to reduce the colour and TDS in the pulp and paper mill wastewater especially in bleach plant (Adnan *et al.*, 2010, Dube *et al*., 2000, Pierre and Eric R. Hall 2001, Ramamurthy and Wearing 1998, Milestone *et al.*, 2004, Wingate *et al.,* 2004, Srivastava *et al.,* 2005, Jain *et al.,* 2009). The present study was carried out to have decentralized treatment system for bleach plant effluent to reduce colour and TDS using patented process developed by a Central government research laboratory which has been proved to be successful in removing the colour and organic TDS in effluent in combination with membrane process to remove the inorganic TDS. The only source of high colour and high TDS being the bleach plant effluent, treating the selected volume through the dual stage treatment will result in substantial reduction in colour, TDS and AOX in the final effluent and also to certain extent reusing this treated effluent in the mill result in water conservation.

BROAD OBJECTIVE OF THE PROJECT:

To develop a method to remove colour and TDS from bleach plant effluent by Patented process by Central Govt Research agency for industrial effluents – to remove organic TDS and colour Membrane technology to remove inorganic TDS and reuse of Sodium chemicals.

METHODOLOGY:

- Analysis of Bleach effluent from bleach plant of hardwood and bagasse pulp mill
- Preliminary colour and organic TDS removal using the patented process to determine the extent of removal and number of passes required
- Evaluation of Membrane technology to assess the removal of inorganic TDS from pre-treated effluent
- Concentrate handling – recovery of sodium chemicals and process for handling solid waste.

QUANTIFIED DELIVERABLES OF THE PROJECTS:

- Colour reduction in effluent
- Reduction in AOX in effluent
- Recovery of Sodium chemicals
- Reduction in COD, BOD and TDS in final effluent
- Recycling 100% bleach plant effluent

PILOT PLANT LAY OUT AND DESCRIPTION

Total Capacity of the pilot plant is 1.2 m^3/ hr and it is supplied by M/s Vens Marketing, Chennai. The plant consists of six sections/ modules viz. 1. Pretreatment section, 2. FACCO reactor, 3. Ozonator, 4.Ultra filtration modules, 5. Reverse Osmosis modules, and 6. Nano filtration. All the modules are interconnected and have bypass arrangements to take trials with various combinations by eliminations of one or two sections are modules.

The pretreatment section: It is provided with.1. Raw effluent storage tank having Cap 2000 lit to store the untreated wastewater. 2. Static mixers for mixing chemicals such as Lime and Ferric chloride with the wastewater. 3. Lime reservoir with 2300lit capacity to store milk of lime. 4. Lime dosing pump (0 to 100 lit/hr). 5. Dosing pumps to dose $FeCl_{3,}$ Sodium carbonate and ferrate/fenton (0 to 4 lph). 6. Clarifier 1000 liter capacity to settle the sludge generated after lime addition. 7. Sludge tank with 2300 liter capacity to store the sludge drawn from the bottom of the clarifier. 8. Screw pump to pump the sludge to filter press. 9. Hydraulic type filter press to dewater the sludge for disposal. 10. Mini mixing tank to mix sodium carbonate. 11. Settling chamber of 2000 liter capacity to settle the calcium carbonate formed after soda addition. 12. Intermediate tank with 1000 liter capacity to store the pretreated effluent.

2. FACCO reactor: It is a 25.6 m^3 capacity FRP coated tank. Reactor consists of 6000 kg of stone pebbles, 3 to 50 mm in the bottom of the reactor and 2200 kg of catalyst (a mixture of Silica, Ferric oxide, Cerium oxide, Copper oxide and Boron oxide) impregnated activated carbon in the top layer. Distribution arrangement for the uniform flow of wastewater at the top and bottom of the reactor. Lateral distributors are provided inside the reactor for air /ozone distribution at the top and bottom of the carbon bed. A strainer is also provided near the outlet at the top to prevent carryover of carbon with the effluent

3. Ozonator: It generate around 8 gram/hr ozone from air/oxygen and a reactor with ventury mixer to mix ozone with wastewater and a 5000 liter collection tank to collect the ozonated wastewater.

4. Ultra filtration modules: The module consists of a bag filter 7"*32" - 5 micron polypropylene make to remove the suspended solids. Ultrafiltration feed storage tank having 1000 liter capacity. UF module can process up to1000 lit/hr consisting of a PLC system sand filter, 100µ cartridge filter and UF 100 KD polysulphonate membrane hollow type to remove the colloidal silica and fine suspended solids.

5. Reverse Osmosis modules: This module consists of 1000 liter RO feed tank and RO filtration consists of activated carbon filter, 10µ cartridge filter, a high pressure pump (10 bar) and 4" dia*40"long polyamide membrane.

6. Nano filtration: This module consists Nano feed tank of 1000 liter capacity to store RO reject and Nano filtration unit consists of a sand filter, activated carbon filter and iron filter as a premodule. Then a 10µ cartridge filter, high pressure pump (10 bar) and 4" dia * 40" long Nano membrane to separate the monovalent and divalent salts and a 1000 liter capacity rejects tank.

RESULTS

PART – I : Treatment of Hard wood ECF EOP filtrate

Pretreatment with Lime and Ferric chloride: The Pilot plant was commissioned on 12.07.09 and initially bleach plant alkaline filtrate from EOP stage was taken for the study. The EOP effluent was treated with lime and ferric chloride and mixed thoroughly with static mixer and send to Clarifier to remove sludge containing colloidal silica, heavy metals and some organics. The overflow was collected in a 1000 lit intermediate tank. The pH after lime treatment was 11.0. A marginal reduction in COD and Colour was observed. The effluent was then passed through a 5 micron Polypropylene bag filter, to remove the suspended solids.

Treatment with FACCO Reactor: Ferrate (a mixture of 75 ppm each of Ferric nitrate and Sodium hypochlorite) was dosed as Oxidising agent online and the wastewater was send to FACCO reactor (Fenton activated carbon catalytic oxidation) in upward flow mode @1500 lit/hr, to remove Colour and COD. FACCO process consists of two stages; first stage is to breakdown dissolved organics and in the second stage oxidation of organics takes place at the active sites of the carbon-silicon mesoporous catalyst using stoichiometric quantity of oxygen abstracted from air at ambient temperature and pressure. This process does not generate any sludge. The hydraulic retention time in the reactor was about 16 hours. The chemical reaction in the reactor is as follows where hydroxyl radical is the active species for catalytic oxidation

$$Fe(NO_3)_2 + HOCl \rightarrow OH. + RH + OOH. \rightarrow CO_2 + H_2O$$

The COD was initially found to reduce from 1830 to 346 ppm (81 %) and Colour from 600 to 90 ppm (85.0 %). The entire process was run continuously for ten days. The out let of the FACCO was treated in the ozonator with 16 ppm ozone charge to reduce the COD further. The COD came down to 160 ppm (TABLE - 1). An increase in COD and Colour was observed after the tenth day (550 to 1196) in the FACCO outlet. This is due to the presence of refractory organics in the effluent and saturation of the carbon bed in the reactor. When COD was above 400 ppm, the pumping of effluent to UF unit was stopped to prevent fouling of membrane.

The study was continued with various chemical dosage and flow rates. Raw EOP pH was ranging from 9.5 to 10.5 after lime addition pH was increased to 10.5 to 11.0. Treated wastewater was then neutralised with acid to around 7 to 7.5 pH. The results are presented in TABLE 1, 2, 3, 4, 5 & 6. BOD reduced from 573 to 200 ppm (60 %).The average reduction in COD and Colour was 58 %.The settled sludge from the Clarifier was drained once in 4 hours and analysed for its composition and results are presented in TABLE 7. The sludge after lime treatment contains more organics and calcium and it is suitable for use in Cement plant

TABLE - 1: Results of HW EOP filtrate Lime and ferric chloride pretreatment

S. No	Parameter	Units	**Raw EOP effluent**	**Lime-$FeCl_3$ treated effluent**
1	pH		10.1	11.2
2	Colour	mg/lit	850	670
3	COD	mg/lit	1850	1640
4	Total hardness as $CaCO_3$	mg/lit	120	60
5	Calcium as $CaCO_3$	mg/lit	80	50
6	Magnesium as $CaCO_3$	mg/lit	40	10
7	TDS	mg/lit	4400	4950
8	Sodium as Na	mg/lit	1400	1340
9	Sulphates as SO_4	mg/lit	220	230
10	Chlorides as cl^-	mg/lit	200	210
11	Silica	mg/lit	40	18

TABLE – 2: Results of HW ECF EOP wastewater, after pretreatment -FACCO up-flow treatment (1000 to 1200 lit/hr flow) with 1000 ppm Lime and Oxidizing agent (Ferric chloride 80 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm), COD reduction index:0.70 gm /gm of carbon / hr.

Date	Raw WW	Treated WW	Raw WW	Treated WW	**Reduction**	Raw WW	Treated WW	**Reduction**	Ozone Treated WW
	pH	pH	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**	COD
12.7.09	7.8	3.8	370	0	100	1240	226	81.8	168
12.7.09	8	3.5	380	0	100	1320	238	82.0	158
16.7.09	7.6	4.8	460	0	100	1780	280	84.3	
17.7.09	7.5	5.1	620	40	93.5	2163	230	89.4	
18.7.09	7.1	5.4	680	80	88.2	2341	270	88.5	
21.7.09	7.7	5.6	750	90	88.0	2214	334	84.9	
21.7.09	7.8	5.5	820	120	85.4	2170	318	85.3	142
22.7.09	7.5	5.8	820	170	79.3	2320	418	82.0	
22.7.09	7.9	5.2	830	220	73.5	2208	428	80.5	
22.7.09	8	6.2	820	220	59.5	2420	465	80.2	168
AVG	**7.7**	**5.0**	**600**	**90**	**85.0**	**1830**	**346**	**81.1**	

TABLE – 3: Results of HW ECF EOP wastewater FACCO up-flow treatment (800 to 1000 lit/hr flow) with 800 ppm Lime and Oxidizing agent(Ferric chloride 100 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm), COD reduction index:0.47 gm /gm of carbon / hr.

Date	Raw WW	Treated WW	Raw WW	Treated WW	**Reduction**	Raw WW	Treated WW	**Reduction**
	pH	pH	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**
3.8.09	8.5	4.9	800	560	**45.0**	1750	929	**46.9**
4.8.09	8.2	5.2	780	540	**34.6**	1984	1131	**43.0**
8.8.09	8.6	7.8	810	530	**34.5**	1942	928	**52.2**
10.8.09	8.6	7.5	850	550	**35.3**	1912	872	**54.4**
11.8.09	7.8	7.4	920	500	**45.7**	1835	999	**45.6**
12.8.09	7.9	7.2	870	420	**51.7**	1903	1242	**34.7**
13.8.09	8.2	6.9	870	420	**51.7**	2519	1162	**53.9**
14.8.09	8.1	6.9	1000	650	**35.0**	2195	1260	**42.6**
AVG	**8.2**	**6.1**	**900**	**510**	**43.3**	**2090**	**1065**	**49.0**

Average BOD of raw wastewater was 573 ppm & Treated and treated 200 ppm and the average percentage BOD reduction was **60.3.**

TABLE – 4: Results of HW ECF EOP wastewater FACCO up-flow treatment (600 to 800 lit/hr flow) with 800 ppm Lime and Oxidizing agent (Ferric chloride 80 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm), COD reduction index:0.56 gm /gm of carbon / hr.

Date	Raw WW	Treated WW	Raw WW	Treated WW	**Reduction**	Raw WW	Treated WW	**Reduction**
	pH	pH	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**
18.8.09	8.9	7.5	750	330	56.0	1980	1070	46.0
20.8.09	9.4	6.8	850	500	41.2	1450	910	37.2
21.8.09	8.7	6.7	840	550	34.5	1520	870	42.8
22.8.09	8.4	6.7	1000	500	50.0	1240	540	56.5
“	8.4	6.8	1000	480	42.0	1240	520	58.1
AVG.	**8.7**	**7.2**	**875**	**455**	**49.0**	**1610**	**795**	**52.0**

TABLE - 5: Results of HW ECF EOP wastewater FACCO up-flow treatment (600 to 800 lit/hr flow) with 1000 ppm Lime and Oxidizing agent (Ferric chloride 100 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm), COD reduction index:0.51 gm /gm of carbon / hr

Date	Raw WW	Treated WW	Raw WW	Treated WW	**Reduction**	Raw WW	Treated WW	**Reduction**
	pH	pH	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**
24.8.09	8.7	7.0	1000	520	48.0	1260	400	58.3
25.8.09	8.3	6.8	940	330	64.9	1060	504	52.5
			920	420	54.3	1135	538	52.6
26.8.09	9.2	7.0	1000	250	75.0	1950	520	73.3
			1050	310	70.5	1960	455	76.8
27.8.09	9.3	7.1	1120	280	75.0	1710	455	73.4
			1150	240	79.1	1748	358	79.5
28.8.09	9.7	7.2	1080	260	75.9	1932	494	74.4
			1160	280	75.9	1980	494	75.1
29.8.09	8.8	6.8	960	290	69.8	1653	622	62.4
			920	310	66.3	1733	690	60.2
AVG.	**8.7**	**7.0**	**960**	**320**	**66.7**	**1646**	**545**	**66.8**

TABLE - 6: Results of weekly average of HW ECF EOP wastewater FACCO up-flow treatment with various lime and oxidizing agent dosage

Parameters	Raw EOP-colour ppm	Treated colour ppm	Reduction %	Raw EOP COD ppm	FACCO Treated EOP COD, ppm	Reduction, %
Flow 1000 to 1200 lit/hr with 1000 ppm Lime and Oxidizing agent(Ferric chloride 80 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm)	600	90	85.0	1830	346	81.1
Flow 800 to 1000 lit/hr with 800 ppm Lime and Oxidizing agent(Ferric chloride 100 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm)	900	510	43.3	2090	1065	49.0
Flow 600 to 800 lit/hr with 800 ppm Lime and Oxidizing agent (Ferric chloride 80 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm),	875	455	49.0	1610	795	52.0
Flow 600 to 800 lit/hr with 1000 ppm Lime and Oxidizing agent (Ferric chloride 100 ppm and: Ferric Nitrate & Sodium Hypochlorite 75 ppm)	960	415	66.7	1646	545	66.8

TABLE -7: Results of Clarifier sludge analysis

S. No	Parameter	units	After Lime treatment
1	Loss on ignition	%	55.2
2	Silica	%	2.8
3	Mixed oxides	%	5.2
4	Calcium as CaO	%	31.8
5	Magnesium as MgO	%	4.2

Membrane filtration treatment: The FACCO outlet was taken to **Ultrafiltration**, at the rate of 1200lit/hr via a sand filter and cartridge filter to remove the colloidal silica, suspended solids and bacteria. The recovery in UF was 70 %. The UF rejects was drained and the permeate, containing TDS 4800 to 5800 ppm was taken to the **Reverse Osmosis (RO) membrane filtration system** at the rate of 650 lit/hr, @ 12 bar pressure, via a activated carbon filter & 10 micron filter. The RO permeate was found to contain only 100 to 150 ppm TDS and pH was 6.8 .The recovery was **50 %**. SMBS was used as antiscalant in RO and Nano filtration units.

Na**no filtration**

The RO rejects was passed through Sand filter, Activated carbon filter and Iron filter (filled with MnO_2 beads and green sand to remove dissolved iron) @ 650 lit/hr, passed through a 10 micron cartridge filter, pumped with a high pressure pump, at a feed pressure of 10 kg/cm^2 to the Nano membrane (MW >250 dalton) to remove the inorganic salts and COD. The Nano membrane with a negatively charged polymer film which rejects ions with higher charge density, such as, SO_4. The permeate **@** 100 lit/hr, containing water with monovalent ions was collected in the Nano permeate tank. The rejects @ 500 lit/hr was collected in the Rejects tank. The rejects contained more sulphates and sodium.

TABLE - 8: Results of membrane filtration treatment Reverse Osmosis (Average of three trials)

S. No	Parameter	units	RO feed	RO permeate	RO rejects
	Flow	lit/hr	650	320	330
1	pH		7.8	7.3	7.8
2	Colour	mg/lit	80	0	150
3	COD	mg/lit	168	0	280
4	Total hardness as $CaCO_3$	mg/lit	110	0	190
5	Calcium as $CaCO_3$	mg/lit	70	0	120
6	Magnesium as $CaCO_3$	mg/lit	40	0	70
7	TDS	mg/lit	5600	150	10840
8	Sodium as Na	mg/lit	1360	50	2620
9	Sulphates as SO_4	mg/lit	230	0	420
10	Chlorides as cl^-	mg/lit	210	0	380

TABLE - 9: Results of NANO filtration treatment (Average of three trials)

S. No	Parameter	units	Nano feed	Nano permeate	Nano rejects
	Flow	lit/hr	600	100	500
1	pH		7.8	7.5	7.9
2	Colour	mg/lit	150	40	260
3	COD	mg/lit	280	120	304
4	Total hardness as $CaCO_3$	mg/lit	190	60	260
5	Calcium as $CaCO_3$	mg/lit	120	40	200
6	Magnesium as $CaCO_3$	mg/lit	70	20	60
7	TDS	mg/lit	10640	5230	11680
8	Sodium as Na	mg/lit	2620	8410	1460
9	Sulphates as SO_4	mg/lit	420	120	480
10	Chlorides as cl^-	mg/lit	380	160	410

Conclusion

1. The Colour and COD reduction was achieved to the level of 80 to 85 % in the first ten days. The rate of COD reduction was 0.70 mg of COD / gm of carbon/hr of activated carbon in the FACCO reactor.

2. Due to the high sodium content (1400 ppm) and the refractory nature of the low molecular lignin compounds and saturation of the catalyst, the reduction has decreased in the subsequent trials to 40 to 50 %; COD reduction index was 0.47 mg/gm of carbon/hr. The COD reduction was slightly improved to 55% with increase of Ferrate dosage to 100 ppm.

3. The reduction was further improved to 60% by further optimization of flow (600 to 800 lit/hr) and with Fenton.

4. The efficiency of sulphate removal in Nano-filtration was found to be 90 %

5. The RO permeate i.e. the final treated wastewater was colourless, having very low TDS (150 ppm) which is suitable for recycling in the process.

6. The sludge after lime treatment from the clarifier contains more organics and calcium and it is suitable for use in Cement plant.

Limitations of the FACCO process

1. Size of the reactor used to process 1.2 m^3/hr was 25 m^3, which is very large which needs further study to make it economically viable for treatment.

2. COD and Colour reduction was not consistent at different levels of inlet COD; at higher levels of COD and flow rates, the reduction achieved was only 48 to 52 % .The outlet COD also increases after seven days of operation due to

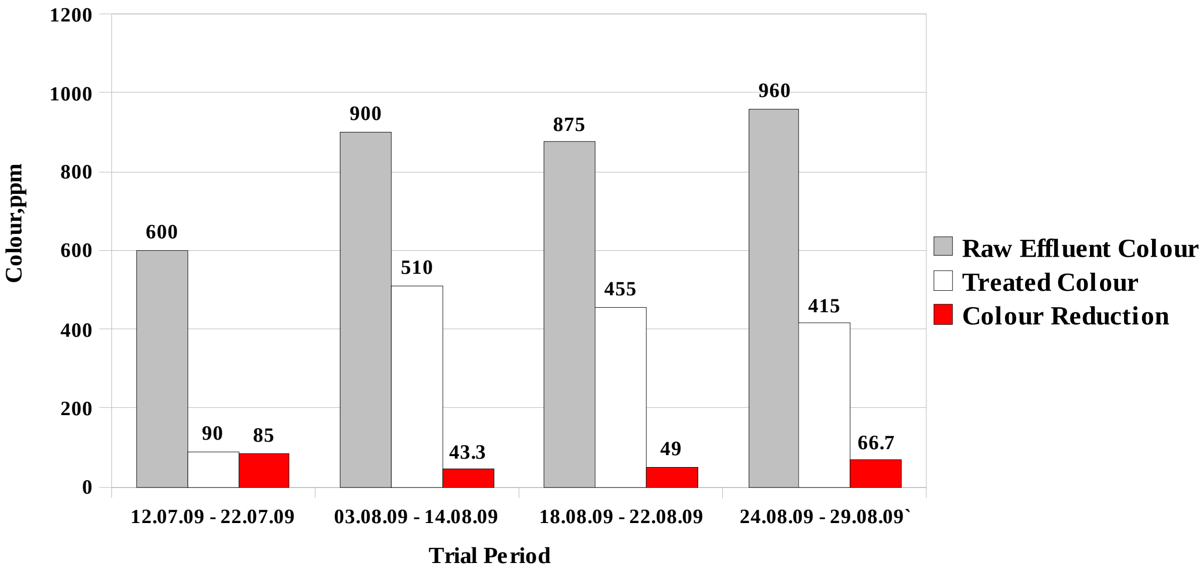
3. Acid for neutralization before reactor increases the sulphate content. This increases the inorganic TDS load to the Membrane filtration unit. Choking of bag filters was observed.

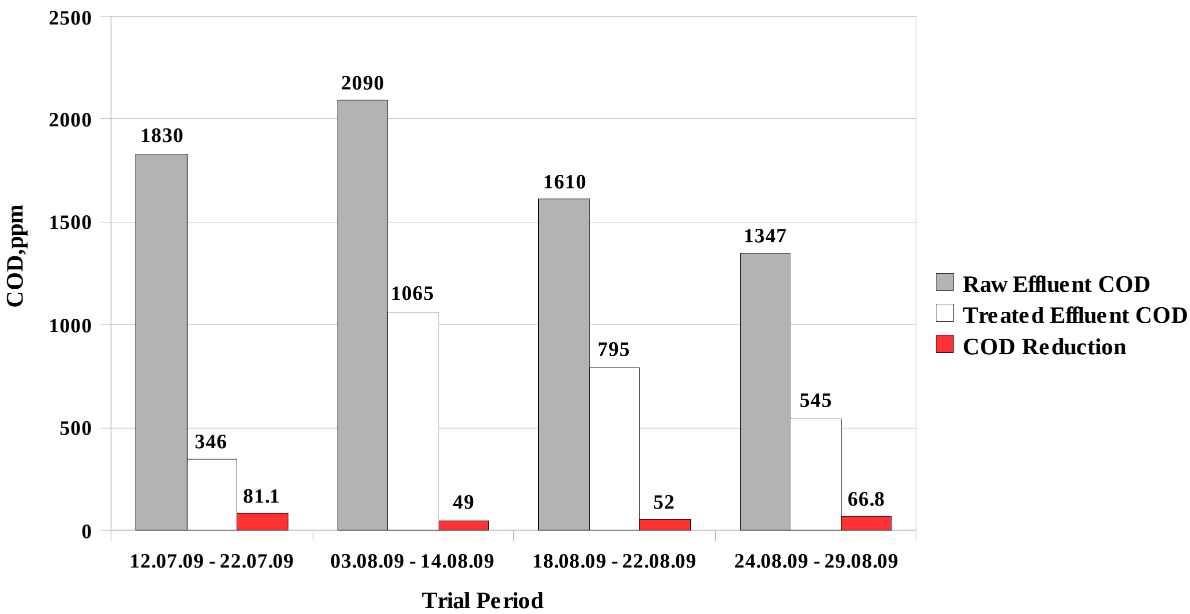
4. Carryover of fine carbon particles in the outlet was observed when flow was increased, which causes choking problems in the subsequent stages resulting in increase in bacwash frequency.

5. Air distribution disturbs the carbon bed during the upward flow mode at higher flow rates resulting in improper aeration.

6. Higher COD at the FACCO outlet due above reasons causes fouling of the RO & Nano filtration membranes, which reduces the recovery efficiency leading to frequent cleaning of RO unit.

HW – EOP filtrate effluent treatment
PILOT PLANT TRIAL (WITH FACCO REACTOR)





PART – II: Treatment of Hard wood ECF D_{HT} filtrate

Lime-Soda Treatment: The D_{HT} filtrate @ 750 lit/hr, from HW ECF plant was cooled, treated with lime in a Clarifier to precipitate the Magnesium salts, colloidal silica and some of the organics. The pH after treatment was ranging from 11.0 to 11.5. The sludge contains organics and inorganic salts and found to be suitable for use in Cement plant. The overflow goes to the second stage, where it is treated with soda (Na_2CO_3) and allowed to settle in a settling tank to precipitate the Calcium salts as $CaCO_3$. The results are shown in TABLE 10. The settled sludge can be used in SRP lime kiln to produce lime. Results of sludge analysis from clarifier after lime treatment and settling tank after soda treatment is presented in the TABLE 11 and 12 and it mostly contains organics and calcium carbonate. Lime soda treatment reduces hardness and COD to a level by 30 %, but TDS and Sodium levels are increased. The pH is then adjusted to 3.5 to 4.0(for FACCO) using dilute Sulphuric acid, which also reduces the alkalinity.

TABLE – 10: Results of Lime soda treatment of D_{HT} wastewater

S. No	Parameter	units	Raw DHT effluent	Lime-soda treated effluent
1	pH		2.2	11.6
2	Colour	mg/lit	550	270
3	COD	mg/lit	2300	1740
4	Total hardness as $CaCO_3$	mg/lit	1720	120
5	Calcium as $CaCO_3$	mg/lit	1480	80
6	Magnesium as $CaCO_3$	mg/lit	240	40
7	TDS	mg/lit	9370	11300
8	Sodium as Na	mg/lit	1800	4600
9	Sulphates as SO_4	mg/lit	3170	4570
10	Chlorides as cl^-	mg/lit	1560	1540

The main advantage of Lime-Soda treatment is removal of colloidal silica, heavy metals, suspended solids, portion of organics, reduction of colour to about 50%, reduction of COD 25% and removal of total hardness. The sludge generated contains mostly Calcium carbonate, silica and Magnesium hydroxide and can be used for cement plant or SRP. The softened effluent contains only Sodium sulphates and Chlorides and it is easier to separate by Membrane filtration.

The main Disadvantages are increase in TDS level by 2000 ppm and Sodium level by 1500 ppm. Also the addition of H_2SO_4 to reduce the alkalinity before FACCO increase the Sulphate level from 1400 to 3000 ppm and high chemical cost of treatment.

TABLE -11: Results of sludge analysis from clarifier after lime treatment and settling tank after soda treatment

S. No	Parameter	units	After Lime treatment	After soda treatment
1	Loss on ignition	%	53.3	42.5
2	Silica	%	5.4	0.5
3	Mixed oxides	%	2.9	0.2
4	Calcium as CaO	%	31.8	*53.6
5	Magnesium as MgO	%	2.6	0.2
6	Sodium as Na_2O	%	1.2	2.4

* 95.7 % as $CaCO_3$

TABLE – 12: Particle size analysis sludge generated during lime soda treatment

S. No	Parameter	units	After Lime treatment	After soda treatment
1	Settling time	mts	45	30
2	Sludge volume index	ml/g	136	2.11
3	Mean particle size - HORIBA particle size analyser	µm	21	38.6
4	Particle size range	µm	0-45	0-66

The Lime -soda treated effluent is neutralised with diluted Sulphuric acid, (@1500 ppm) to reduce the pH to 3.5,at which fenton works effectively, and collected in an Intermediate tank and send to FACCO reactor, for treatment.

FACCO treatment study 1 : The HW ECF Wastewater after the Lime soda treatment was treated using Fenton (a mixture of ferrous sulphate and hydrogen peroxide) and Ammonium per-sulphate as oxidising agents using downward flow mode @ 2400 lit/hr with air and ozone distribution for catalytic oxidation in the FACCO reactor. The hydraulic retention time in the reactor was fixed as four hours. The results showed a COD reduction of 45 to 67 % and Colour 55 to 70 % and marginal reduction in TDS (TABLE 13). The BOD reduction was 76.6 %. This shows that most of the biodegradable organics were removed in the catalytic oxidation process. But the residual COD (TABLE 14) and colour indicates only, some of the refractory organics are not removed. The pH after treatment was 5.2 to 5.5, due to the formation of hydroxyl ions. The results are given in TABLE 13 and 14

TABLE – 13: Results of Lime soda treated HW ECF Dht wastewater before and after FACCO treatment-Hardness & TDS levels

S. No	Raw WW	lime-soda treated WW	Raw WW	lime-soda treated WW	FACCO treated	Raw WW	FACCO treated WW	Reduction
	Hardness ppm	Hardness ppm	TDS, ppm	TDS, ppm	TDS, ppm	BOD ppm	BOD ppm	%
1	2160	180	6520	8090	7190	944	197	79.1
2	2200	200	6820	8416				
3	2100	190	7720	8964	8152			
4	2220	200	6372	8410		833	280	66.4
5	2300	260	8000	9138	8814			
6	2500	320	8910	10142	9296			
7	2520	220	8530	10060	9438	796	125	84.3
8			8690	9870	10686			
Avg.	**2286**	**224**	**7820**	**9237**	**8930**	**858**	**201**	**76.6**

The TDS increases by 15 %; Silica in the untreated eff was 60 mg/lit and 20 mg/lit in the treated effluent.

TABLE -14: Impact of FACCO treatment on colour and COD on Lime soda treated HW ECF wastewater.

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	**%**	COD Ppm	COD ppm	**%**
12.9.09	460	220	52.2	1602	700	56.3
12.9.09	480	210	56.3	1684	810	51.9
13.9.09	480	180	62.5	1702	1150	32.4
14.9.09	490	160	67.3	2430	1400	42.4
18.9.09	460	180	60.9	2100	1040	50.5
19.9.09	510	300	41.1	2080	880	57.7
AVG.	**480**	**210**	**56.3**	**1930**	**996**	**48.4**

FACCO treatment study 2: The flow of effluent to FACCO reactor was kept @2400 lit/hr and Fenton dosage (FeSO4 100 ppm and H2O2 60 ppm) and Ammonium persulphate (100 ppm) was increased to improve the reduction efficiency with air and ozone at 4 ppm distribution at the bottom of the reactor. The reactor performance was found to improve slightly. The COD reduction was found to be around 56 % (i.e. from 1807 to 810 ppm) and colour by 60 % (i.e. from 535 to 213 ppm) with a marginal reduction in TDS level. The COD reduction index across the reactor is 0.75 mg of COD /gm of carbon / hr. The Peroxy monosulphate ion $HSO5^-$ from Ammonium persulphate, having higher oxidation potential than OH^-, is an effective oxidising agent and found to degrade the refractory organics in the acidic effluent.The pH after treatment was 5.5 to 6.0; The results are given in TABLE 15.

TABLE – 15: Results of FACCO treatment study 2

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**
1.10.09	520	200	61.5	1443	586	59.4
	520	220	57.7	1443	453	68.6
2.10.09	560	180	67.9	1866	853	54.3
	540	200	63.0	1813	720	60.3
5.10.09	540	210	61.1	1840	906	50.3
	540	220	59.3	1840	852	53.7
6.10.09	530	300	43.4	2106	1120	46.8
	530	210	67.9	2106	986	53.2
Avg.	**535**	**213**	**60.2**	**1807**	**810**	**56.0**

FACCO treatment study 3: The FACCO reactor performance was reviewed after second experiment and the chemical dosage was increased with Fenton ($FeSO_4$ 100 ppm and H_2O_2 75 ppm) and Ammonium persulphate (120 ppm) to improve the reduction efficiency with same wastewater flow rate @2400lit/hr, air and ozone (4 ppm) distribution at the bottom. FACCO reactor performance was found to improve further with COD reduced by 72 % (From 2020 to 573 ppm) and colour by 78 % (from 440 to 98 ppm) with marginal reduction in TDS level. The COD reduction index across the reactor is 1.17 mg of COD /gm of carbon / hr which is fairly good. The BOD reduction was 76.6 % (from 850 to 201 ppm).The pH after treatment was 5.2 to 5.6, The results are presented in TABLE 16.

TABLE – 16: Results of FACCO treatment study 3

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD Ppm	%
8.10.09	500	100	80.0	1760	453	74.3
9.10.09	450	170	62.2	1973	560	71.6
10.10.09	420	130	69.0	2053	586	71.5
12.10.09	440	70	84.1	2133	640	70.0
13.10.09	400	60	86.4	2120	613	71.1
13.10.09			85.0	2080	586	71.8
Avg	**442**	**98**	**77.8**	**2020**	**573**	**71.7**
Raw wastewater BOD 858 ppm and treated wastewater BOD 201 ppm						

FACCO treatment study 4: The DHT effluent without Lime-Soda treatment was treated with Fenton ($FeSO_4$ 100 ppm and H_2O_2 75 ppm) and Ammonium persulphate (120 ppm) with downward flow of @2400lit/ hr along with air and ozone distribution in FACCO reactor for catalytic oxidation. The COD was reduced by 67 % (From 1928 to 638 ppm) and colour by 68 % (From 450 to 140 ppm) in the outlet and only a marginal reduction in TDS level. The COD reduction index across the reactor was 1.41 mg of COD /gm of carbon / hr. The pH increased to 6.4, due to the formation of hydroxyl ions during the process. The results are given in TABLE 16.

TABLE – 16: Results of FACCO treatment study 4

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
14.10.09	360	140	61.1	2024	556	72.5
15.10.09	500	190	62.0	1739	435	75.0
19.10.09	520	110	78.5	1870	710	62.0
20.10.09	420	120	71.4	2080	850	59.1
Avg.	**450**	**140**	**68.3**	**1928**	**638**	**67.2**

FACCO treatment study 5 (recycling) : The FACCO treated effluent was collected in a storage tank of 5000 lit cap and re-circulated through the FACCO reactor with additional Fenton dosage to study the impact of recycling. The COD was found to reduce from 850 to 450 ppm (47 %) in the first cycle and from 450 to 320 ppm (28 %) in the second cycle and the color reduced to 80 ppm from 120 ppm. The results are given in TABLE 17

TABLE – 17: Results of FACCO treatment study 5

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
21.10.09	120	120	0	850	573	32.6
22.10.09	120	90	25.0	850	514	39.5
22.10.09	120	85	29.2	850	455	46.5
23.10.09	120	80	33.3	455	320	28.8

FACCO treatment study 6 (without Ammonium persulphate) **:** The progress was reviewed along with CLRI personnel. The overall reduction of COD & Colour was 84 % with recycling and decided to increase the dosage levels of Fenton, without the use of Ammonium persulphate. Further studies are also underway to study the effect of flow rate, Ozone dosage levels and chemical dosage. Fenton dosage was increased ($FeSO_4$ 150 ppm and H_2O_2 150 ppm) without Ammonium persulphate to improve the reduction efficiency. Wastewater flow rate, after lime-soda treatment was fixed @2400lit/hr to FACCO inlet with air and ozone (4 ppm) distribution at the bottom of the reactor. FACCO reactor performance was studied for about a week. COD was reduced by 57 % (from 1971 to 854 and Colour by 53 % (from 460 to 223) with only a marginal reduction in TDS level. The COD reduction index across the reactor is 0.73 mg of COD / gm of carbon / hr, which is comparatively lesser than with Ammonium persulphate treatment. The pH increased to 6.2, due to the formation of hydroxyl ions during the process. The results are tabulated in TABLE 18

TABLE – 18: Results of FACCO treatment study 6 (without Ammonium persulphate)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	**%**	COD ppm	COD ppm	**%**
26.10.09	450	220	51.1	1984	952	52.0
27.10.09	550	190	65.5	1706	940	45.0
28.10.09	480	230	52.1	2233	860	61.5
29.10.09	450	220	51.1	1933	800	58.6
30.10.09	450	210	53.3	2000	720	64.0
Avg.	**460**	**223**	**52.6**	**1971**	**854**	**56.7**

The FACCO reactor performance was reviewed after a week and the chemical dosage was increased with Fenton ($FeSO_4$ 250 ppm and H_2O_2 250 ppm) without Ammonium persulphate to improve the reduction efficiency. COD reduced was found to be 68 % (from 1820 to 565 ppm) and Colour 69 % (from 460 to 145 ppm) which is slightly higher ten the previous study. The COD reduction index across the reactor is 0.76 mg of COD / gm of carbon / hr, which is comparatively lesser than with earlier one. The results are tabulated in TABLE 19.

TABLE – 19: Results of FACCO treatment study 6 (without Ammonium persulphate)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
2.11.09	480	200	58.3	1520	560	63.2
3.11.09	550	180	67.3	2266	480	78.8
4.11.09	400	140	65.0	2107	540	74.4
5.11.09	450	100	77.8	1813	440	75.7
6.11.09	440	90	79.5	1600	560	65.0
7.11.09	440	90	79.5	2120	570	73.1
Avg.	**460**	**145**	**68.9**	**1820**	**565**	**68.1**

FACCO treatment study 7 (without Ammonium persulphate and Lime soda treatment)**:** The chemical dosage was kept at Fenton ($FeSO_4$ 250 ppm and H_2O_2 250 ppm) without

Ammonium persulphate to improve the reduction efficiency. The wastewater flow rate to FACCO reactor was reduced 1500lit/hr with air and ozone (4 ppm) distribution at the bottom of the reactor. The COD reduced was found to only 34 % (from 2040 to 1350 ppm) and Colour 10 % (from 340 to 300) in the outlet, due to the presence hardness in the wastewater. The COD reduction index across the reactor is 0. 48 mg of COD / gm of carbon / hr, which is comparatively lesser than the lime-soda treated effluent TABLE 20.

TABLE – 20: Results of FACCO treatment study 7 (without Ammonium persulphate and lime soda treatment)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
10.11.09	430	340	20.9	2150	1330	38.1
11.11.09	320	290	9.4	1970	1400	28.9
12.11.09	310	300	3.2	2080	1440	30.8
13.11.09	300	280	6.7	1960	1230	37.2
Avg.	**340**	**300**	**10.0**	**2040**	**1350**	**33.8**

The results of TDS and BOD reduction across FACCO reactor was found to 10.5 % and 61% respectively (TABLE 21)

TABLE – 21: Results of FACCO treatment study 7 (without Ammonium persulphate and lime soda treatment)

Date	Raw WW	FACCO treated	Raw WW	FACCO treated	**Reduction**
	TDS ppm	TDS ppm	BOD ppm	BOD ppm	%
10.11.09	8750	7710	954	418	
11.11.09	8599	8326	1220	385	
12.11.09	8422	8156	1254	361	
13.11.09	8083	7515	1071	598	
16.11.09	8203	6183	1008	371	
17.11.09	8244	7130	-	-	
Avg.	**8383**	**7503**	**1101**	**427**	**61.2**

FACCO treatment study 8 (with Ammonium persulphate and without Lime soda treatment) **:** The chemical dosage was kept at Fenton ($FeSO_4$ 250 ppm and H_2O_2 250 ppm) with Ammonium persulphate 120 ppm and wastewater flow rate to FACCO @1500lit/hr with air and ozone (4 ppm) distribution at the bottom of the reactor. The COD reduction was only 55 % (from1830 to 780 ppm) and Colour 58.5 % (from 380 to 160 ppm) in the FACCO outlet. The COD reduction index across the reactor is 0. 72 mg of COD / gm of carbon / hr. The results are presented in TABLE 22.

TABLE – 22: Results of FACCO treatment study 8 (with Ammonium persulphate and without lime soda treatment)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
16.11.09	332	129	61.1	1840	790	57.1
17.11.09	430	190	55.8	2080	986	52.6
Avg.	**380**	**160**	**58.5**	**1960**	**888**	**54.9**

FACCO treatment study 9 (with Ammonium persulphate and Lime soda treatment): After discussions with CLRI personnel, the lime soda treated wastewater was taken to FACCO at the rate of 2000 lit/hr (higher taken the previous study). with 120 ppm Fenton and 120 ppm and ammonium persulphate along with air and 4 ppm Ozone dosage (4 ppm) the bottom. The COD was reduced by 51.7 % and color by 16.6 % and COD reduction index was 0. 62 mg of COD / gm of carbon / hr. The results are presented in TABLE 23

TABLE – 23: Results of FACCO treatment study 9 (with Ammonium persulphate and lime soda treatment)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
20.11.09	290	230	20.7	1200	560	53.3
21.11.09	400	350	12.5	1440	720	50.0
Avg.	**345**	**290**	**16.6**	**1320**	**640**	**51.7**
FACCO inlet pH 3.3 and outlet increased to pH 5.0 with Sulphuric acid. This increased the Sulphates to 4150 ppm and after FACCO sulphates were only 340 ppm						

FACCO treatment study 10 *(*Two stage treatment with Ammonium persulphate and without lime soda treatment)

The lime soda treated effluent having pH 11.5 was collected in the intermediate tank and adjusted the pH to 3.5 with dilute sulphuric acid. It is then dosed with Fenton 120 ppm and ammonium persulphate 120 ppm. The wastewater was dosed downward in the FACCO reactor @ 2000 lph with air was distributed in the bottom. The COD was reduced by 41.7 % and color by 23.3 %. The colour removal was percentage was improved further with reduced flow. However there is no improvement in COD reduction. The COD reduction index was 0. 55 mg of COD / gm of carbon / hr. Reduction in COD and colour was only marginal in the second stage. The TDS and sulphates in the raw wastewater and treated wastewater was also tested. The treated effluent was ozonated in the ozonator with 16 ppm ozone and no improvement was observed (TABLE 24)

TABLE – 24: Results of FACCO treatment study 10 (two stage with Ammonium persulphate and lime soda treatment)

Date	Raw WW	Treated WW	Reduction	Raw WW	Treated WW	Reduction
	Colour, ppm	Colour, ppm	%	COD ppm	COD ppm	%
24.11.09	420	322	23.3	1440	840	41.7
3.12.09	450	190	57.7	1330	960	27.8
6.12.09	190	190	57.7	960	880	33.8

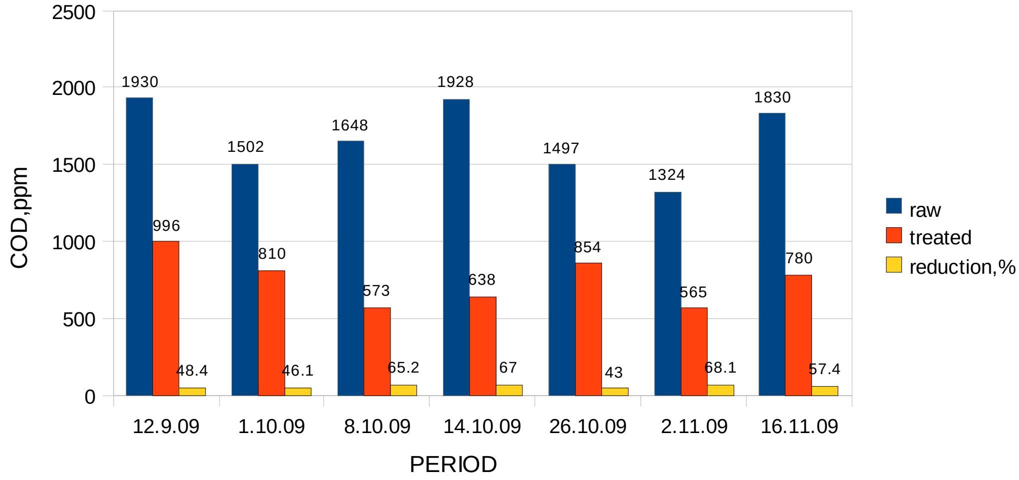
TABLE - 25: Overall results of DHT wastewater treatment in FACCO reactor

S .No	Chemical dosage ppm	Raw WW colour ppm	Treated WW colour	Reduction %	Raw WW COD ppm	FACCO Treated WW COD	Reduction %	COD reduction index
1	Fenton 80	480	210	56.3	1930	996	48.4	0.61
2	Fenton + APS 100	535	213	60.2	1502	810	46.1	0.75
3	Fenton + APS 120	442	100	77.8	1648	573	65.2	1.17
4	Fenton + APS 120	450	140	68.3	1928	638	67.0	1.17
5	Fenton 150	460	220	52.6	1497	854	43.0	0.73
6	Fenton 250	460	145	68.9	1324	565	68.1	0.76
7	Fenton 250 + APS 120 w/o lime soda	380	150	58.0	1830	780	57.4	0.72
8	Fenton 250 + APS 250,w/o lime soda	430	190	55.8	2080	986	52.6	.72
9	Fenton 250+ APS 120,w/o lime soda	420	230	45.2	1200	560	53.3	0.62
Note : Fenton -Ferrous sulphate & Hydrogen peroxide ; APS -Ammonium persulphate								

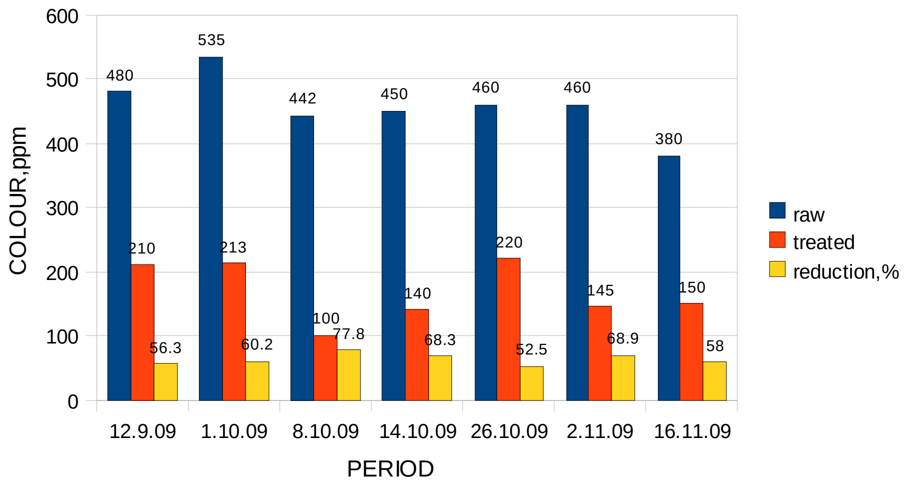
The COD reduction index expressed in mg of COD / gm of carbon / hr in the reactor varies from 0.6 to 1.2. The effect of flow without lime soda and increase in chemical dosage in the reactor. Ammonium persulphate was found to be effective oxidising agent, but even a 120 ppm dosage increases the cost of treatment by Rs16/m^3. The partial reduction in COD in

FACCO reactor necessitates further biological treatment. The dissolved oxygen at the outlet of the reactor was 2-3 ppm.

HW – D_{HT} filtrate effluent treatment
PILOT PLANT TRIAL (WITH FACCO REACTOR)
COD Reduction %



COLOUR Reduction %



Studies were conducted using membrane filtration studies, to remove TDS and COD, with FACCO treatment for about three week and the results are presented below.

Ultrafiltration: The FACCO treated effluent from the final tank was pumped to the UF feed tank. It is then sent to a sand filter @ 1700 lit/hr and at 1kg/cm^2 pressure through 100 micron cartridge prefilter and then to the UF Polysulphonate membrane (hollow type) to retain particles (colloidal silica, bacteria and fine suspended solids) of about 0.005µ or larger (MW >100 dalton). The permeate **@** 1200 lit/hr, containing low molecular substances was sent to the RO feed tank. The rejects @ 500 lit/hr was drained. The recovery efficiency was 70.6 % with COD reduction of around 200 ppm. There was no reduction in TDS and colour. The results are presented in the TABLE 26.

TABLE – 26: Results of HW ECF D_{HT} ultrafilteration with FACCO treatment

S. No	Parameter	units	UF feed	UF permeate	UF rejects
1	pH		7.6	7.5	7.8
2	Colour	mg/lit	270	260	290
3	COD	mg/lit	1740	1520	1880
4	Total hardness as $CaCO_3$	mg/lit	120	110	160
5	Calcium as $CaCO_3$	mg/lit	80	90	120
6	Magnesium as $CaCO_3$	mg/lit	40	20	40
7	TDS	mg/lit	11300	11200	11050
8	Sodium as Na	mg/lit	4600	4500	4800
9	Sulphates as SO_4	mg/lit	4570	4460	4760
10	Chlorides as cl^-	mg/lit	1540	1520	1600

***RO Membrane filtration*:** The UF permeate was filtered through activated carbon filter @ 650 lit/hr and passed through 10 micron cartridge filter. It is then pumped with a high pressure pump to the RO membrane (Hydraunatics make-spiral wound type) at 10 kg/cm^2 feed pressure. Dissolved salts and organic substances >50 dalton were removed here and allows only relatively pure water collected in RO permeate tank **@** 320 lit/hr. The permeate was found to be colorless with less dissolved salts and COD TABLE 27 & 28. The rejects @ 330 lit/hr (the volume was reduced to 50 %) was collected in the Nano feed tank.

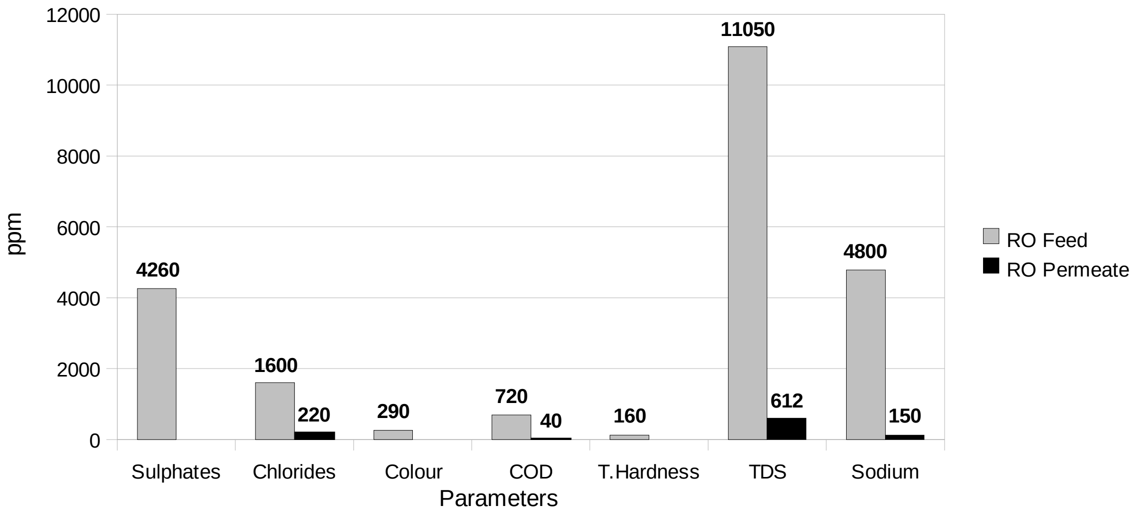
TABLE – 27: Results of HW ECF D_{HT} RO membrane filtration after FACCO treatment (average of three trials) and ultrafilteration

S. No	Parameter	units	RO feed	RO permeate	RO rejects
1	Flow	lit/hr	650	320	330
2	pH		7.8	7.3	7.8
3	Colour	mg/lit	290	0	296
4	COD	mg/lit	720	40	1030
5	Total hardness as $CaCO_3$	mg/lit	160	0	310
6	Calcium as $CaCO_3$	mg/lit	120	0	220
7	Magnesium as $CaCO_3$	mg/lit	40	0	72
8	TDS	mg/lit	11050	612	21168
9	Sodium as Na	mg/lit	4800	150	9316
10	Sulphates as SO_4	mg/lit	4260	0	8510
11	Chlorides as cl^-	mg/lit	1600	220	2930

TABLE – 28: Results of HW ECF D_{HT} RO membrane filtration after FACCO treatment (average of three trials) and ultrafilteration-Mass balance (flow*mg/lit).The rate of recovery was **50 %**

S. No	Parameter	units	RO feed	RO permeate	RO rejects	Removal, %
	Flow	lit/hr	650	320	330	--
1	COD	kgs/hr	468	12.8	340	97.2
2	Total hardness	kgs/hr	104	0	104	100
3	Calcium	kgs/hr	78	0	78	100
4	Magnesium	kgs/hr	26	0	26	100
5	TDS	kgs/hr	7182	196	6986	97.3
6	Sodium	kgs/hr	3120	48	3072	98.5
7	Sulphates	kgs/hr	2769	0	2769	100
8	Chlorides	kgs/hr	1040	70.4	969.6	93.2

RO membrane filtration - D_{HT} Effluent



***NANO Membrane filtration*:** The RO reject was passed through Sand filter, Activated Carbon Filter and Iron filter (filled with MnO_2 beads to remove dissolved iron) @ 650 lit/hr and then through 10 micron cartridge filter the reject was pumped with a high pressure pump 10 kg/cm^2 pressure to the Nano membrane (MW >250 dalton) to remove the inorganic salts and COD. The Nano membrane with a negatively charged polymer film rejects ions with higher charge density, such as SO_4. The permeate **@** 100 lit/hr containing water and monovalent ions was collected in the Nano permeate tank. The reject @ 550 lit/hr was collected in the reject tank. The reject contained more sulphates and sodium (TABLE 29 & 30).

TABLE – 29: Results of HW ECF D_{HT} NANO membrane filtration after RO filtration (average of three trials)

S. No	Parameter	units	Nano feed	Nano permeate	Nano reject
1	Flow	lit/hr	600	100	500
2	pH		7.8	7.6	7.9
3	Colour	mg/lit	296	57	96
4	COD	mg/lit	1030	258	1184
5	Total hardness	mg/lit	310	60	100
6	Calcium	mg/lit	220	20	60
7	Magnesium	mg/lit	72	40	40
8	TDS	mg/lit	21168	7620	23886
9	Sodium	mg/lit	9316	6460	9874
10	Sulphates	mg/lit	8510	410	9420
11	Chlorides	mg/lit	2930	1804	4772

TABLE – 30: Results of HW ECF D_{HT} NANO membrane filtration after RO filtration (average of three trials)-Mass balance

S. No	Parameter	units	Nano feed	Nano permeate	Nano rejects	Removal %
	Flow	lit/hr	600	100	500	
1	COD	kgs/hr	618	26	592	95.8
2	TDS	kgs/hr	12700	762	1938	94.0
3	Sodium	kgs/hr	5590	648	4942	88.4
4	Sulphates	kgs/hr	5106	41	5065	99.2
5	Chlorides	kgs/hr	1758	181	1577	89.7

The chloride content in Nano reject may be reduced by better selection of the membrane and reject may be further concentrated either by using Mechanical Vapor Compression technology or in an evaporator. The recovered Sodium sulphate can be concentrated to 80 gpl and mixed with WBL and use in SRP as make-up chemical. The sodium chloride in the permeate may be further concentrated and disposed to industrial users like Dyeing industry.

The cost of lime-soda pretreatment was found to be high with HW DHT effluent due to high hardness level (1400 ppm). The improvement in the quality of raw materials, such as, debarked Casuarina and matured wood will lower the concentration of non-process elements entering in the HW pulp line and would reduce treatment economically viable and this needs further study. Moreover, the volume of effluent reject handled would also come down due to the aforesaid measures. Reduced TDS level in the effluent in subsequent cycles, if the RO generated water is used in the HW bleaching process, resulting in reduction of the overall pollution load and water consumption

S. No	Parameters	Cost in Rs
1	Cost of equipment & installation charges	45 lakhs
O & M Cost of treatment HW DHT effluent treatment cost in pilot plant/ m^3		
2	Chemicals for pretreatment - lime, soda, sulphuric acid	62
3	Power - 8.36 kwh @ Rs 2.06	17
4	Cost of evaporating the Nano rejects (from 8 gpl to 80 gpl) @150kg of steam/t of water	47
5	Biological treatment (FACCO process)	18
6	**Total**	**134**
Savings expected upon treatment of Dht effluent /m^3		
7	Quantity of water that can be recycled thro' DM water(.5*12)	6
8	Savings expected in ETP2.4	12
9	Sodium (in terms of caustic lye) 2.5 kgs	39
10	Lime sludge 3.0 kgs & Calcium carbonate, 3.0 kgs	
11	Sodium sulphate ,2.8 kgs	25.2
12	**Total**	**84.4**
Net cost / m^3		**50.4**

Limitations of the CLRI FACCO process

- Size of the reactor used to process 1.2 m^3/hr was 25 m^3, which is very large and is not economically viable for treatment.
- COD and Colour reduction was not consistent at different levels of inlet COD. The reduction efficiency comes down with increasing level COD and colour.
- Use of sulphuric acid for neutralisation increases the sulphate content and inorganic load to the Membrane filtration unit.
- High cost of Ammonium persulphate (Rs 140/kg) increases the cost of treatment.
- Two stage FACCO treatment is not technically feasible due to high volume of reactor, chemical dosage and residence time.

Other issues for consideration

- The membranes used were of 4" dia, which may not be sufficient for simulating plant scale process to achieve the desired flux levels. The operating pressure at the membrane was only 10 to 12 bar, unlike the requirement in the plant scale, which is in the order of 60 bar and above.
- TDS levels and separation of monovalent and divalent salts in the Nano filtration permeate was not satisfactory. The concentration of reject was lower which produces high volume wastewater for further processing in an evaporator.
- The recovery rate in the RO and the Nano filtration system was very low, in the range of 35 to 40%.
- High COD and Colour levels in the FACCO treated effluent caused frequent fouling and reduced the efficiency of the Membrane systems.

CONCLUSION

The biological treatment of HW EOP filtrate in the FAACO reactor has resulted in a reduction of 50 to 60 % in COD and Colour and this was enhanced slightly by Fenton dosage. However, COD & Colour was still high and it is not suitable to treat in membrane process for TDS reduction. Treatment of D_{HT} filtrate in FACCO reactor, with

Fenton and ammonium persulphate has brought about 50 to 60% reductions in COD & Colour, but the cost of treatment has increased considerably. High COD at FACCO outlet caused fouling in the RO membrane thereby reducing the recovery efficiency. The cost of hardness/TDS removal by lime-soda treatment and membrane filtration works out to Rs 80 /m^3. Pretreatment methods to remove silica, heavy metals and hardness, such as, lime treatment, followed by anaerobic and aerobic process for improved biological treatment need to be explored to make the process more economical. Ion exchange techniques and Resin filtration for Colour/COD/TDS removal have to be experimented further to find a viable method for tertiary treatment to remove TDS and other non-process elements especially for ECF bleach plant effluent.

The results of present studies will be very useful input to design a Zero Liquid Discharge system which is technically more advanced and economically viable. Based on results obtained from the present study TNPL has initiated a ZERO LIQUID DISCHARGE program and proposed to setup 5 m^3/hr pilot plant to find out feasibility of treating bleach plant effluent combining both biological and membrane process.

ACKNOWLEDGEMENTS

The authors are thankful to Development Council (Paper), DoIPP, Govt. of India and TNPL management for funding and support to complete the project. Thanks to IPMA for the continued support and encouragement, Central Leather Research Institute for licensing of technology and special thanks to Dr. G. Sekaran, Scientist, CLRI for his coordination, advice for successful completion of this work and others those who are directly and directly supported for completing this work.

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Membrane Filtration Plot Plant Unit

	
Ultra filtration Module	**R O Module**
	
Nano Module	**Nano Pre-filtration**

Membrane Filtration Results

Pretreatment and Ultra Filteration

RO and Nano Filtrations

Membrane Filtration Results