Treatment of Black Liquor from Pulp Mills-A Step Wise Approach

Swamy Y.V, Tripathy H.K., Mohanty J.N., Murthy B.V.R. and Tripathy A.K.

ABSTRACT

The black liquor from small scale agro-based paper plant, having Biochemical Oxygen Demand (BOD) in the range of 2700-3100 mg/l and total solids 22-25 g/l, is treated step wise to generate design data for large scale treatment plant. Prior to treatment, the liquor is conditioned with acid for effective coagulation followed by flocculation using a cationic polyacrylamide. The settling characteristics are studied besides other physical parameters to design a 500 lit/batch treatment plant. The results obtained in 500 lit/batch trial run are in good agreement with the laboratory data generated earlier. It is possible to reduce BOD to the range of 450-550 mg/l with substantial reduction in suspended solids in the treated liquor. Efforts are being made to further bring down the BOD value to less than 100 mg/l on larger scale by advanced oxidation process.

INTRODUCTION

The pulp and paper industry is segmented as wood/forest based, agro and waste paper based. There are about 406 paper mills in India with 34 in the large scale sector and 372 in the medium and small scale sector. The problem of pollution is more in the small-scale pulp and paper sector, largely due to out dated processes and inadequate pollution prevention and control technologies. The large and medium scale pulp and paper mills are substantially better in controlling and managing the environmental pollution. The small and medium agro-based units discharge the black liquor to the surroundings along with unrecovered chemicals resulting toxicity to aquatic life. The presence of caustic in black liquor results in increased dissolved solids in waste water stream, thus rendering the water unfit for drinking and if the discharge is on land the sodium concentration contaminates the soil. The discharge of black liquor not only results in a loss of valuable chemicals but also results in high levels of Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) load in the effluent. It is estimated that the discharge from a 30 tonnes per day agro-based mill is equal to the pollution load from a 100 tonnes per day mill with a chemical recovery system in place.

Chemical coagulants have been used primarily for removal a suspended solids and partly colour. Coagulation with CaO, $Fe_2(SO_4)_3$, $FeCl_3$, $AlCl_3$, $Al_2(SO_4)_3$ has the colour removal efficiency of 25-95%. The high chemical dosage results in slow settling of the sludge and create problems for dewatering and disposal [1]. In another chemical treatment process [2], all most all the suspended solids and more than 50% of the dissolved solids are removed by clariflocculation followed by lime/sludge treatment.

Regional Research Laboratory (CSIR)
Bhubaneswar-751 013 (Orissa)

The BOD could be reduced to 400-600 mg/l from the initial value of 2400-3200 mg/l. The fibre particles in Chinese alkaline straw pulp liquor (3) have been coagulated to reduced COD by treating with 5.5% aluminium sulphate. The COD of the remaining filtrate is reduced using 10% carbon residue of cinder. Application of activated carbon for colour removal from pulp wastes has been tried [4] and this process is found to be economical, if reuse of treated effluent is considered for massive lime treatment [7] for colour removal. This method achieved 90% colour removal besides 20-40% reduction in COD. Granulated activated carbon known as pyrochar prepared from paper mill sludge has been successfully used for removal of colour and organic matter along with heavy metals from various waste waters [6-8].

Most of the paper industries practice the conventional chlorine based bleaching process. The bleaching sequence involves chlorination, alkali extraction and hypochlorite treatment. The effluent generated from the bleaching section contains oxygenated halogens and other associated compounds that are well known carcinogens. Hence, many units are trying to make the bleaching process completely free from elemental chlorine. Alternate bleaching chemicals such as oxygen, chlorine dioxide and hydrogen peroxide are being considered for use after the hypo stage. This change is expected to reduce the quantity of total oxygenated halogen compounds, and the effluent generated can be recycled and reused in the initial stages of the process.

Hydrogen peroxide (H_2O_2) is useful in removing colour by those materials, which are easily oxidisable. The Ozone (O_3) having the highest oxidation potential, can completely oxidize phenol to carbon dioxide and water [9, 10].

The organic pollutants in industrial water can be destroyed effectively by advanced oxidation process (AOP) of UV/H_2O_2, UV/O_3 and $UV/H_2O_2/O_3$. Intermediate addition of H_2O_2 and catalyst, Fe^{2+}, reduce COD of water within a reasonably short than one time addition of reagents [11]. the study on treatment of kraft and textile effluents [12] reveals that the UV irradiation in presence of TiO_2 and ZnO or silica gel supported ZnO, helps in substantial decolourisation with considerable reduction of total phenol concentration in the liquor. Solar de-toxification technology [13] using UV light from Sun or electric lamp to drive photo-catalytic reduction reaction helped in the destruction of toxic chemicals.

In this paper, step wise approach for treating black liquor, obtained from small scale agro-based paper plant, with special reference to the design of demonstration unit has been discussed.

EXPERIMENTAL

Black liquor generated in straw based paper plant collected from the sump was used in the study. The laboratory scale as well as large scale studies were carried out using these representative samples and the analysis of various forms of solids i.e., total, dissolved and suspended solids and BOD are shown in Table 1. The characteristics of chemical reagents and additives used in the study are shown in Table-2.

Table-1

Composition of Black Liquor

Parameters	Sample 1	Sample 2	Sample3
pH	8.9	8.8	8.9
Total solids g/l	23.7	22.7	25.1
Suspended solids g/l	5.0	4.5	6.2
Dissolved solids g/l	18.7	18.2	18.9
Silica g/l	1.28	1.40	1.45
BOD mg/l	3105	2743	2893
COD mg/l	11,250	12,600	14,500
Specific gravity	1.015	1.015	1.017

Table-2

Composition of Chemical Reagents and Additives

Lime:	CaO : 61.6%
	LOI : 20%
Flocculant :	Synthetic cationic polyacrylamide
	Bulk density- 0.7g/cc
	Particle size-98% less than 1400 micron
Acid :	Specific gravity- 1.84
	Normality-36N

TABLE-3

RESULTS OF LABORATORY SCALE EXPERIMENTS						
Sample	**Ist stage**			**IInd Stage**		
	Initial solids g/l	**BOD mg/l Initial**	**BOD mg/l Final**	**BOD mg/l Initial**	**BOD mg/l Final**	**Final solids g/l**
1	18.5	2325	1300	1300	390	6.5
2	24.0	2760	1380	1380	490	13.4

Experimental procedure

The black liquor was tested for flocculation in acidic and alkaline range of pH using cationic and anionic flocculants. In order to identify the suitable flocculating agent (cationic or anionic), the pH of the black liquor as varied from 8.5 to 4 and 8.5 to 10. The liquor was conditioned with acid to bring the pH to 4-5 prior to the addition of primary coagulant followed by flocculation using a suitable cationic polyacrylamide. The flocs were allowed to settle in settling tank and the clarified liquid was separated. The clear solution was treated with neutralizing agent to bring the pH to near neutral. The BOD and various forms of solid contents of liquor were determined at different stages. The BOD was estimated [14] using revised Winklers iodometric method IS 3025 (part 44): 1993, 296. The laboratory scale data obtained from these experiments were discussed earlier [2].

Experiments were also carried out in both 60 lit/batch and 500 lit/batch set up to establish the laboratory data. The set up used to carryout 60 lit/batch reactor was discussed earlier [2]. The reactor was a 60 lit. translucent PVC tank with conical bottom. The clarified liquor was collected from the three out lets at various depths in the reactor and sludge at the bottom of the conical portion. The reactor was graduated in order to measure the settling velocity.

500 litre/batch capacity unit was designed based on the data generated on 60 lit/batch. The process was tested on this 500 lit/batch unit and results were compared with those of laboratory scale studies.

RESULTS AND DISCUSSIONS

The black liquor analysed from poacher at different washing stages indicates an average composition and characteristics similar to the sample obtained from sump. The laboratory data [2] showed an initial pH value of 8.9 and decreased to 6.2 within 42 hrs. and at the same time there is an increase in BOD with time. It was also observed from those experiments that initial conditioning of liquor by bringing down the pH to desired value, was required before going for primary coagulation. The study revealed that a cationic polyacrylamide was found to be effective for the flocculation of the solids. It was found that the BOD of the liquor could be brought down to 400-450 mg/l from an initial value of 2400-2800 mg/l by removing substanital amount of suspended and dissolved solids. The results are shown in Table 3. Almost 60-70% of the colour was removed at this stage. The data is further tested in 500 lit/batch unit, which is designed on the basis of laboratory scale experiments.

DESIGN OF 500 LITRE/BATCH CAPACITY UNIT

The treatment process requires mixing tanks and settling clarifiers. The mixing tank has impeller and baffle arrangements. Flat bladed turbine type impeller is used to thoroughly mix the liquor and its additives. The impeller is rotated at 100 rpm through motor. The baffles have been provided in a mixing tank to avoid swirling and vortex formation resulting due to rotation of impeller.

The clarifier has raking mechanism with three out let ports having provision for values for testing the pattern of settling at various heights. The rake arm has a rotational speed of 30 rph to facilitate settling of flocs. The bottom portion is made conical where a discharge port is provided through which sludge is discharged at different time intervals.

The process outlines the first stage treatment consisting of mixing of flocculants followed by clarification and the second stage with lime mixing followed by settling. while designing a 500 lit/batch unit for treatment of black liquor, attempt has been made to manage the entire process by one mixer and one clarifier in two stages.

MIXER

Mixing of fluid can be accomplished using mechanical impellers. A rotating impeller provides a thrusting and shearing action on the fluid in a vessel. The equipment takes many forms but common to each is an impeller attached to a rotating shaft. The most common impeller mixer configuration is the centre mounted top entering agitator. The shaft is vertical at the centre line of an upright cylindrical tank.

As the capacity of the mixer is low, i.e. 500 lit and the black liquor having specific gravity of 1.03, is of low viscosity ($\approx$ 0.9 cP), only one impeller has been considered and the height to diameter of tank has been decided to be 1. For such low viscous liquids, turbines are highly effective in developing radial currents and they also produce vertical flows particularly in baffled vessels [15]. Hence the following parameters are considered prior to further design exercises

No of blades of turbine type impeller : 6

No of vertical baffles in the tank : 4

In order to determine the physical specifications of the mixer the following shape factors are selected from the standard table [15].

$S_6 = H/D_t = 1.0$

$S_1 = D_t/D_a = 3.0$

$S_2 = E/D_a = 0.77$

$S_3 = L/D_a = 0.25$

$S_4 = W/D_a = 0.20$

$S_5 = J/D_t = 0.08$

Also, $J = D_t/12$

Where, H = Height of the liquid in tank, m

(Height of tank = H + 0.3 m)

D_t = Diameter of mixing tank, m

D_a = Diameter of the impeller, m

E = Distance between impeller bottom and tank bottom, m

L = Length of blade, m

W = Width of blade, m

J = Width of baffle in the tank, m

The following specifications of the mixer tank could be derived from the above parameters.

Height of tank = 1.16 m

Diameter of mixing tank = 0.860 m

Diameter of the impeller = 0.285 m

Distance between impeller bottom and tank bottom = 0.22 m

Length of blade = 0.075 m

Width of blade = 0.06 m

Width of baffle in the tank = 0.07 m

No of vertical baffles in the tank = 4

No of blades of impeller = 6

It is essential to complete in the mixing of flocculants and other additives with the balck liquor within a very short time (<30 seconds) in order to avoid the formation of flocs in the mixing tank. For such operation, the mixing has to be highly turbulent and Reynold Number (N_{Re}) of the impeller should be greater than 10,000 [16] and in this present design N_{Re} is assumed to be 10^5. In order to achieve such dynamics, the rotation of the impeller is estimated from the following:

$N_{Re} = nD_a^2\, \rho_f / \mu_f = 1{,}00{,}000$

n = Revolution per second

D = Diameter of impeller, m

ρ_f =Density of black liquor, kg/m^3

μ_f =Viscosity of black liquor, Poise

From the above, RPM is estimated to be 65 but for convenience in selection of geared motor, the RPM of the impeller is fixed at 100.

Referring to the standard plot of blending-time factor (f_t) vs Reynold number (N_{Re}) for miscible liquids in a turbine agitated baffled tanks [16] and using the standard correlation, the blending time (t_T) is estimated as 15 seconds. Thus, the requirement of very fast mixing is achieved. The power transmitted to the liquid is estimated to belower than 1 kW. The sketch of the mixer is shown in Fig. 1.

CLARIFIER

Sedimenters are broadly classified into two categories, a) thickener and b) clarifier. In case of 'Thickener', concentrated sludge is the desired product whereas clean liquid is separated from the suspended particles using a clarifier. In the present case, solids from the treated black liquor is to be separated and hence an attempt has been made to design the clarifier to treat 500 lit/batch of black liquor.

The rate of sedimentation of a suspension containing very fine particles is low. The rate can be increased by adding flocculant in the mixing tank, which causes flocculation of colloidal particles [15]. The sludge obtained after primary clarification, contains higher residual moisture. The moisture content in the sludge varies depending on molecular weight and dose of the flocculant. The residual water content [17] is enhanced by the reduction in particle size and increase in surface area of particles. It is possible to lower the moisture content of sludge by adding the selected flocculants.

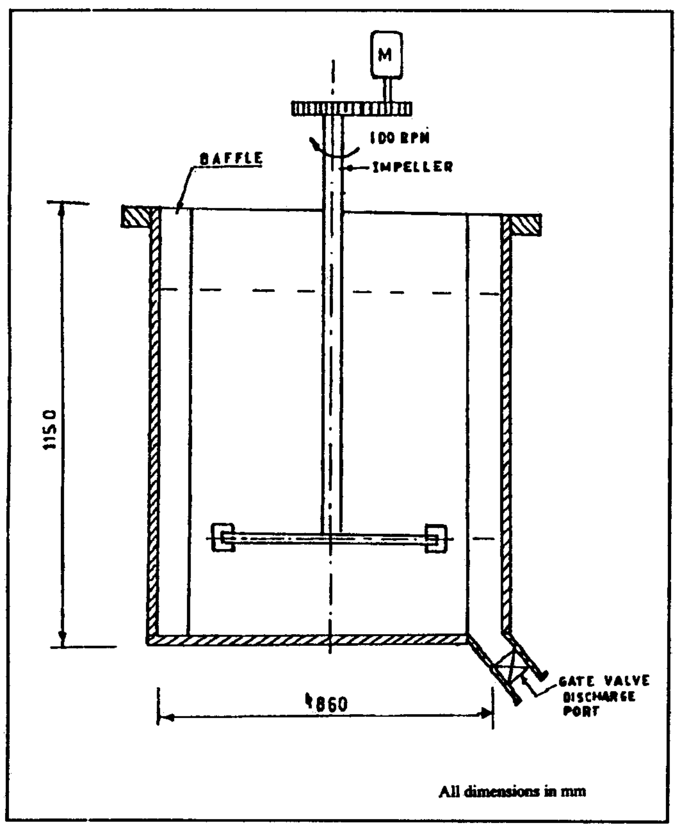

Fig. 1 Mixing tank

Here, an attempt has been made to design a model/prototype clarifier in order to estimate the size of clarifier required for small scale pulp industries in India with this type of flocculation characteristics.

There are various factors, which govern the design of a clarifier. The degree of thickening is controlled by the residence time of the particles in the tank, which depends on depth of tank below the feed inlet. Settling rate of flocs decreases with time. It is essential to have raking of the sediments for slow settling flocs. It assists in moving the concentrated sediments to the withdrawal point and it also helps in thickening the sediments by disrupting bridged floccules, permitting trapped fluid to escape and allowing the floccules to become more consolidated.

The following correlations [15] are used for finalising the specifications of the clarifier based on laboratory batch settling experiments generated in both 5 litre and 60 liter capacity settling tanks.

$$C_L + C_f)Z_o/Z_i)$$

$$L.C_L /A = V \{)1/C_L) - (1/C_u)\}$$

$$L.C_L /A)_{min} = Q/A$$

$$Q = F.C_f$$

Where,

C_u = Concentration of solids in underflow, kg/m^3

ρ_s = Specific gravity of solid present in feed black liquor

ρ_f = Specific gravity of black liquor

C_L = Concentration of solid in a particular layer, kg/m^3

C_f = Concentration of solid in feed black liquor, kg/m^3

Z_o = Height of interface at time, t_o, m

Z_i = Height of interface at any given time, m

L = Volumetric rate of discharge of underflow sludge, m^3/sec

A = Cross sectional area of the clarifier, m^2

Q = Feed rate of slurry on dry basis, kg/sec

F = Volumetric feed rate of slurry, m^3/sec

V = Settling velocity at different time, m/sec

Settling velocity, V at different time is determined from the settling data as shown in Table-4.

% Solid in underflow = 9.0

% Liquid in underflow = 91.0

ρ_g, Specific gravity of solid present in feed black liquor -1.2

ρ_f, Specific gravity of feed black liquor = 1.03

Using the above correlations and data generated in laboratory scale settling studies, the following specifications of the clarifier was estimated:

Diameter = 900 mm

Depth = 1200 mm

The depth of tank below the feed inlet depends on the residence time of the particles in the tank. But for a batch type clarifier, where the residence time can be controlled as per desire, a convenient position is chosen for feed inlet. In this case the depth can be found out from the volumetric capacity of the tank once the diameter is estimated. A working allowance of 300 mm is added to the height of the fluid level for the tank depth.

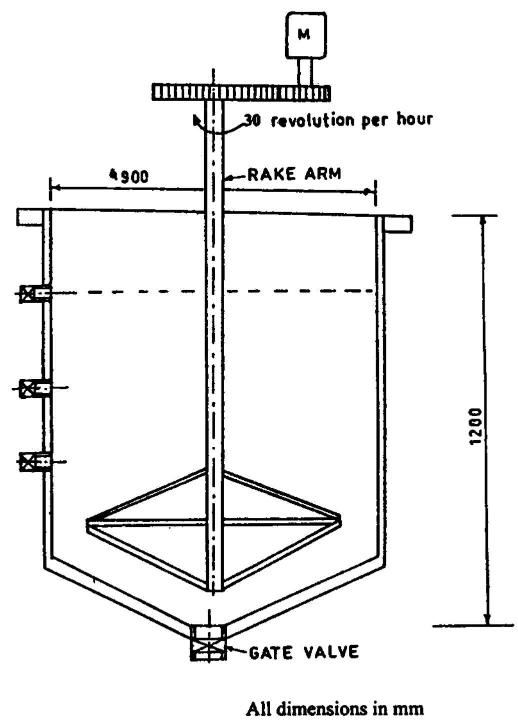

Fig. 2 Clarifier

Adopting the above design steps a clarifier is designed with an ID of 900 mm having a height of 1200 mm. The bottom portion of the tank is made conical shape with a discharge port at centre. A raking mechanism is incorporated which helps in compacting the sediments and sliding towards the discharge port. The speed of the raking arm is estimated at 30 rph for maintaining a peripheral speed of 1.4 m/min. The sketch of the clarifier is shown in Fig. 2.

TABLE-4

SETTLING VELOCITY OF THE TREATED LIQUOR			
Time, min	5 litre V_1, m/min	60 litre V_2 m/min	V m/min
15	0.001761	0.001689	0.001725
30	0.001315	0.001335	0.001325
40	0.001019	0.001031	0.001025
60	0.000611	0.000529	0.00057
80	0.000410	0.000436	0.000423

TABLE-5

RESULTS OF 500 LIT/BATCH TRIAL RUN						
Batch (Sample 2)	Ist stage			IInd Stage		
	Initial solids g/l	Initial BOD mg/l	Final BOD mg/l	Initial BOD mg/l	Final BOD mg/l	Final solids g/l
Batch I	23.7	3105	1575	1575	450	12.2
Batch II	22.7	2743	1600	1600	550	13.0
Batch III	25.1	2893	1525	1525	500	14.6

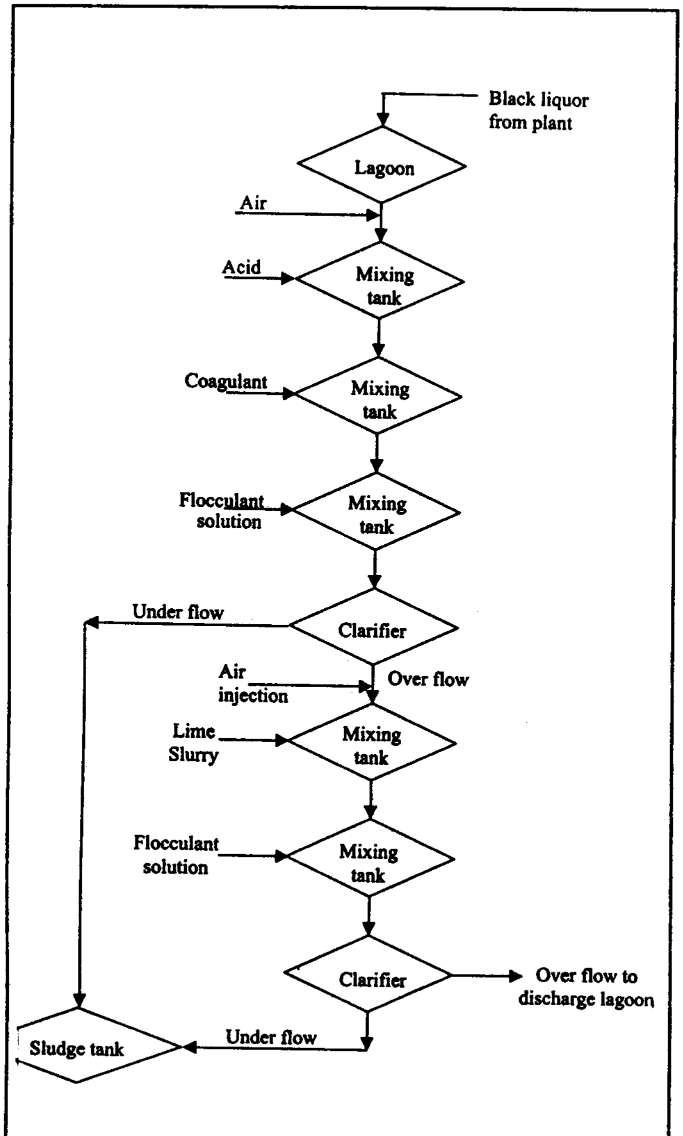

Fig. 3 Proposed process flow diagram for continous treatment of black liquor.

TRIAL RUN

The liquor from the sump of the straw based plant is left for ageing for certain time. The changes are manifested by lowering of the pH from 8.9 to a value of 5.0-6.0. The decrease in pH was also reported [18] in literature and it may be due to the degradable organic material forming acetone and formic acid. The process of degradation of organic material help in subsequent primary coagulation. Further conditioning of the liquor with acid (pH 4-5) helped in the coagulation of the solids in the liquor. After primary coagulation of solid, cationic polyacrylamide is added which helps in the formation of bigger size flocs after mixing for 30 seconds. After mixing, the entire liquor is discharged to a clarifier and the flocs are allowed to settle for 3 hrs. The overflow from the clarifier is collected after settling. subsequently, the pH of the overflow is adjusted to near neutral by the addition of lime in the same mixer and fed to the clarifier for further settling. This helps in bringing down the BOD considerably. The results obtained from trial runs are shown in Table 5- and the process flow sheet is shown in Fig. 3. The BOD of the treated effluent (400-550 mg/l) could be furhter brought down to liquid effluent discharge standards by Advanced Oxidative process (AOP) and the sludge could be utilised for making briquettes by blending with straw dust and other paper waste materials to recover energy [2].

CONCLUSIONS

The following conclusions can be drawn from the study:

The agro-based paper plant effluent with high BOD and total solids could be effectively treated by clariflocculation.

Based on settling data and other physical parameters 500 lit/batch mixer and clarifier was designed.

The experiments on 500 lit/batch reactor proved to be in agreement with the laboratory scale data.

It is possible to reduce BOD to 400-550 mg/l and total solids to 12-14 g/l in 500 lit/batch set up through clariflocculation followed by lime treatment at near neutral pH.

REFERENCES

1. Ollhof, M.G. and Eckenfelder, W.W. (Jr.), "Colour removal from pulp and paper waste water by coagulation", Water Res. 853 (1975).

2. Swamy, Y.V., Mohanty, J.N., Murthy, B.V.R., Tripathy, H.K. and Tripathy, A.K., "Treatment of black liquor and utilization of waste materials generated in small paper plants", IPPTA Vol. 12 (4), pp 53-60 (2000).

3. Zhou, Xiaohua, Tan, Huiling and He, Quionghua, "Treating alkaline straw pulp liquor by coagulation and adsorption", Water Treatment, Vol. 6 (4), pp. 461-464 (1991).

4. Lang, E.W.: Timpe, W.G. and Miller, R.L., "Activated carbon treatment of unbleached Kraft effluent for reuse", EPA-660/2-75-044 (1975).

5. Spruill, E.L. (Jr.), "Colour removal and sludge disposal process for Kraft mill effluents", EPA-660/2-74-008 (1974).

6. Bhide, A.D.; Thergaonbar, V.P.; Patil, A.D.; Ramteke, D.S.; Process for the manufacture of pyrochar (Activated) from waste material, Patent No. 438/Del/83 (1983).

7. Rakteke, D.S., Patil, A.D., Tarfadar, P.K., Thergaonkar, V.P. and Bhide, A.D., "Use of pyrolytic char as an adsorbent", Indian J. Env. Hlth, 300-308 (1981).

8. Ramteke, D.S., Moghe, C.A., Thakre, R.A. and Thergaonbar, V.P.., "Activated pyrochar from solid wastes from paper mills", J. Pulp and Paper, 37, 6-13 (1983).

9. Eisenhower, H.R., J. Wat. Pollut. Control Fed., 36, 1116 (1964).

10. Pospisil and Ettlel, Pharm. J., 23, (1975).

11. De, A.L.; Chaudhuri, D.; Bhattacharjee, S. and Dutta, B.K., "A practical application of the advanced oxidation processes for waste water treatment", Indian Chem. Engr., Section A, Vol. 41, No. 2, April-June, T 63-66 (1999).

12. Peralta-Zaniora, Patrico et.al., "Evaluation of ZnO, TiO_2 and supported ZnO on the photoassisted remediation of black liquor, cellulose and textile mill effluents", Chemosphere, Vol. 36 (9), 2119-2133 (1998).

13. Pache, J.E., Hoslund, C.A. and Holmes, J., "Rapid destruction of organic chemicals in ground water using sunlight", Solar Thermal Collector Technology Division, Sandia National Laboratories, Hazardous Materials Management Conference, Rosemont, IL, March, (1989).

14. Methods of sampling and test (physical and chemical) for waster and waste water, bureau of Indian Standards, IS 3025 (part 44), (1933).

15. Narayana, C.M. and Bhattacharya, B.C., "Mechanical operations for chemical Engineers", Khanna publishers, Dehli.

16. Mc Cabe; Warren L and Smith, Julian C.; "Unit operations of chemical engineering", Mc Graw-Hill Kogadusha, LTD., (1976).

17. Li, Shifeng et at., "Surface chemistry" Central South University of Technology Publishing House, Chanajsha, p. 69 (1991).

18. Ranade, D.R., "Microbiological aspects of anaerobic digestion", Seminar on Energy Recovery from Municipal Wastes Proceedings, IWWA, August 27-28, N-1-N-5 (1988).