Effluent Treatment Technologies Based on Adsorption and Coagulation For Environmental Management in Pulp And Paper Industry

Sahu A.K. and Patel M.

ABSTRACT: Effluent treatment technologies based on adsorption and coagulation are described vis-a-vis colour reduction with flow diagrams. The decolourisation efficiency has been optimized by studying the treatment of effluents at different solid concentration, pH and retention time. Reductions in BOD and COD in the different treatment processes have been compared. Advantages and disadvantages of the different processes studied are discussed.

INTRODUCTION

It is forecasted that industries, attaining environmental stewardship (1), remaining lean, clean and green (2, 3) and giving adequate emphasis on safety and quality (4) will be the most successful ones in the 21st century. The environmental spend in US pulp and paper industry will rise to as much as 30% of total investment in late 90s which was 5% and presently it is around 15% (5). TCF (Total Chlorine Free), ECF (Elemental Chlorine Free) and zero effluent discharge with AOX (Adsorbable Organic Halides) level of as low as 0.15-0.2 kg/ADT (4) and COD limitation of 25 kg/t (4) are theme of environmental management attempts abroad today. By biobleaching, it is expected in Germany that these figures may be 0.1 kg/t and 20 kg/t (4).

The tolerance limits for discharge of industrial effluent into surface water (BIS-1974) do not impose any limit for colour of the waste water to be discharged. Recently, EPA in USA has proposed a colour limit of 75 kg/t for bleached paper grade kraft mills (5). Environmental legislation for forest products industry varies from country to country. In Germany local authorities issue emission permits to all industrial units based on (8) minimum requirement. Germany has water emission fee system. Fees are based on units of damage. Similarly in Spain there is limit for various pollutants which form the basis for calculating discharge fees. Though quantitatively colour is not directly proportional to COD and BOD, colour removal directly reflects on minimisation of COD and BOD load of the effluent.

Typical mill effluent colour discharges are as follows (7):

- Bleached kraft mill - 150 kg colour/ton
- Bleached sulfite mill - 62 kg colour/ton
- Bleached thermomechanical pulp mill - 60 kg colour/ton.

The above amounts mentioned are from kraft mill, having bleaching sequence CEDED with no possibility for countercurrent filtrate recovery.

Before 1970, the colour discharged from bleached plant was 70% of the total mill effluent colour. The pulp mill had minimum spill control, and the screen room was operated with continuous purge to mill effluent. This area counted for more than 20% of mill

Pulp and Paper Research Institute
Jaykaypur-765 017
Distt. : Rayagoda (ORISSA)

colour. In the 1980's there was dramatic reduction in mill colour discharge in abroad because of oxygen delignification, with its filtrate following countercurrently through the screen room, wash room, evaportors and recovery. Only 60% lignin remains to be bleached cut after the oxygen stage. There has been further improvement in 1990's with introduction of ozone, peroxide etc. with advanced spill containment systems.

It has been reported that approximately 30-60% of the colour in effluent is from the pulp mill. Depending upon the pulping process and the bleaching process, the effluent colour load can vary significantly. The pulping process can contribute up to 70% of the colour load in the effluent (21). The remaining colour usually results from bleaching operations and spills. The colour in pulp mill effluent has low BOD per unit of colour and, therefore, the rate of biodegradation is relatively low. This can have the following effects on water stream:

(a) Reduction in light penetration

(b) Reduction in photosynthetic activity

(c) Reduction in oxygenation capacity

(d) It accumulates in lower velocity regions or in ponds and lakes

(e) It can affect aquatic life systems

(f) It can affect aesthetic quality and recreational use.

COMPOSITION OF COLOUR

The colour can be because of both suspended solids and colloidal solids. The apparent colour refers to colour from suspended solids, while true colour refers to colour after removal of turbidity. It is the true colour that leads to presistant colour problem. The colloidal colour bodies include tannins, humic acids and humates from the decomposition of lignins. These lignin derivatives are highly coloured and quite resistant to biological attack, resulting persistence in the environment. It is the lignin of the wood which is separated from the cellulose fibres into the process liquids and give the colour.

True colour of pulp and paper mill waste water is due to the presence of chromophore and auxochromes present in degraded lignin compounds. The major colour contributing compounds are the derivatives of chlorophenol, quinone, tannin, humic acid, chloroguicol, isoguicol, catechol, vanilin, PCDD and PCDF. The chromophores in the effluent contain lignin and its derivatives which are converted to quinoid structure (9, 10).

Chemical clarification i.e. treatment process can take place by (i) coagulation, (ii) flocculation and (iii) sedimentation. Various coagulants used for waste water treatment are alum, lime, iron salts like $FeCl_3$, $FeSO_4$ and polyelectrolyte etc. These clarification processes include the removal of suspended organic and inorganic materials, dissolved phosphates, heavy metals, salts of Ca, Mg, silica and fluorides.

Both organic and inorganic compounds, oxidisable are responsible for COD load of the effluent.

COAGULATION AND ADSORPTION

The coagulation mechanism is based on two theories involving the stability and instability of colloid systems (11). According to the chemical theory, coagulation takes place because of specific chemical reaction between the colloidal particles and the coagulant added. Effective coagulation depends on (12, 16, 17):

a- pH

b- concentration of cationic coagulant

c- salt in the system and

d- mechanical stirring.

According to physical theory reduction of electrostatic forces and zeta potential tend to keep the colloids apart through reduction of electrostatic force such as zeta potential.

Adsorption is essentially a surface phenomenon. The efficiency of an adsorbent depends upon the surface and structural properties, namely (BET) surface area, porosity, crystallinity and density. The silica present in fly ash plays a major role but if there is sufficient amount of unburnt carbon present, it also becomes important (13).

The present study is considered to be appropriate and economically viable technologies based on adsorption and coagulation phenomena. Fly ash generated from the boiler after burning of coal has been used for effluent treatment through adsorption while alum, lime and ferric chloride have been used for coagulation.

Effluent treatment study using fly ash has been reported recently with the effluent for discharge (14). We have carried more extensive work using effluents, generated at various other stages. The efficiency of colour reduction with fly ash has been compared here with processes based on coagulation also. As the products have been modified, it has been preferred to use the general term of adsorbent and coagulant.

EXPERIMENTAL

The experimental studies have been carried out at the laboratory level using adsorption columns (volume of 2 lt and 20 litres). For coagulation experiments, 1 lt graduated cylinders have been used.

The fly ash collected from the mill was sieved and only coarse fraction has been taken. The coagulation experiments have been conducted with alum, lime and $FeCl_3$; the former two were also collected from the mill. Milk of lime was prepared from the lime lumps for the settling experiments. The effluent samples were collected from the mill.

The colour measurement was made with UV/ Visible spectrophotometer by comparing against cobaltous chloroplatinate colour at 410 nm. BOD was determined in a BOD incubator. COD and suspended solids were determined according to standard methods (15).

In order not to make the histograms cumbersome, the effluents have been given no. and abbriviated as follows:

Effluent	No.	Abbreviation
Inlet to primary clarifier	1	IPC
Outlet of primary clarifier	2	OPC
Outlet of lagoon	3	OL
Outlet of secondary clarifier	4	OSC
Bleach plant effluent	5	BP.

The solids taken are termed as follows:

Original solid	Termed as	Abbreviated as	Concentration used
Fly ash	Adsorbent	A	200g
Alum	Coagulant I	C-I	100ppm
Lime	Coagulant II	C-II	4000ppm
Lime+Alum	Coagulant III	C-III	C-I= 50-300ppm
Lime+Ferric chloride	Coagulant IV	C-IV	C-II= 50-300ppm

The percentage reduction in colour has been calculated as follows:

$$\frac{I - F}{I} \times 100$$

I = Initial colour of effluent
F = Colour after treatment.

RESULTS AND DISCUSSION

The chemical analysis results of fly ash, alum and lime are given in Table 1, 2 and 3 respectively. In fly ash, the ash content is 82.4%, the remaining being fixed carbon (7.1%), volatile matter (9.1%) and moisture (1.4%). In the ash, SiO_2 is estimated to be 57.7% and Fe_2O_3 is 4.4%. Al_2O_3, TiO_2, CaO and MgO are the other ingradients in fly ash (22).

Table-1

Chemical analysis of fly ash

Property	%
Ash	82.40
Fixed carbon	7.10
SiO_2	57.70
Fe_2O_3	4.40
Moisture	1.42
Volatile matter	9.10

Table-2

Chemical analysis of alum

Property	%
Al_2O_3	14.97
Fe_2O_3	0.52

Table-3	
Chemical analysis of lime	
Property	%
CaO (available)	76.60
Cao (total)	91.00
SiO_2	0.40
Fe_2O_3	0.03
MgO	1.20
Al_2O_3	3.30

In alum, Al_2O_3 is 14.97% and Fe_2O_3 is 0.52%. Thus it is nonferric alum. Analysis results of lime in Table 3 show available Cao to be 76.6%, the total CaO being 91%, the remaining are Al_2O_3 (3.5%), MgO (1.2%), SiO_2 (0.4%) and Fe_2O_3.

The process of effluent treatment with fly ash is shown in Fig.1. The column design is very important in the adsorption phenomenon. With the present adsorbent, two columns (marked as I and II in Fig. 1) have been taken in series so that the back water from column-I flows to column-II. When column-I is loaded with the colouring matter which can be observed from the colour of the back water of column-I, the adsorbent has to be back washed. However, the adsorbent can be used for a limited cycle only. The back water from column-II was taken for reuse for bleaching of pulp while the back washed water is to be sent to the drain.

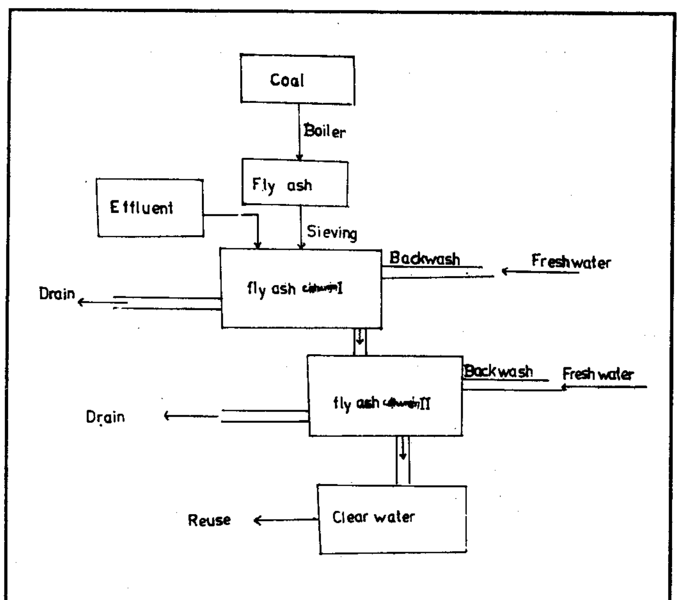

Fig-1 Treatment by adsorption process

Flow diagram in Fig. 2 shows the effluent treatment systems through coagulation mechanism using alum (C - I). The coagulant is brought to solution in a bucket, then the required doses are added to the settling column. The pH is adjusted with NaOH solution. Soon after addition of the coagulant, it is stirred with a glass rod for uniform mixing of the coagulant with the effluent. The settling rates are noted using a stop watch. After settling, it is decanted and the decanted portion is taken for measurement of colour, BOD and COD. The treated effluent has been taken for bleaching of pulp. The underflow sludge of used alum has been conceived for reuse.

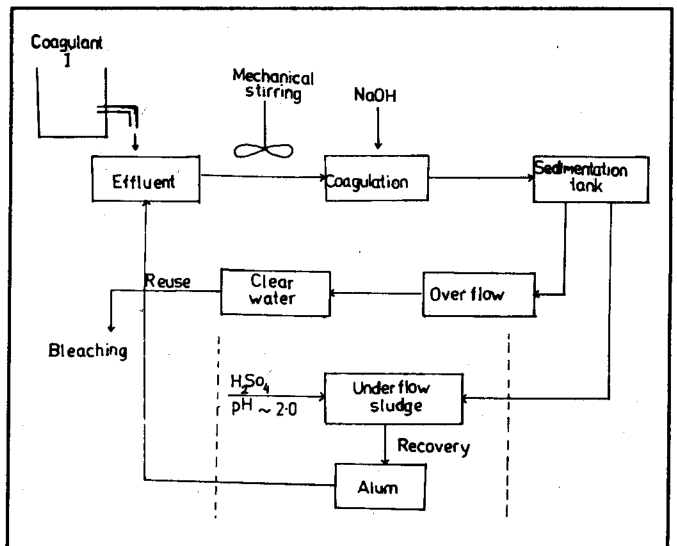

Fig-2 Treatment by coagulation process (C-I)

The coagulation process shown in Fig. 3 contains lime as the coagulant (C - II). The overflow after slaking of lime is decanted and milk of lime is taken as

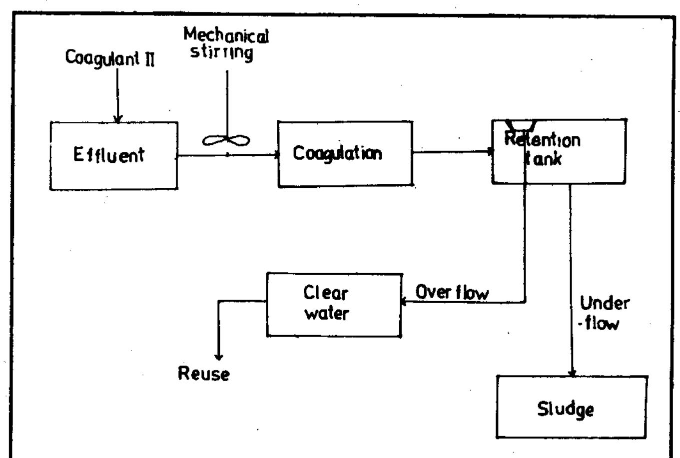

Fig 3 Treatment by coagulation process (C II)

coagulant. The lower part is rejected as it is mostly lime grit. The coagulant is added in the required dose in the settling column as in case of alum. Here the sludge volume is substantial which is found at the bottom of the cylinder, the overflow being the clear water for reuse.

Coagulant-III is combination of alum and lime while coagulant-III is lime + $FeCl_3$. As the processes are similar, no flow diagram has been drawn for IV.

The percentage of colour reduction with the adsorbent (A) and the two coagulants (C-I and C-II) are presented in form of histograms in Fig. 4 for different effluents taken from the mill. In case of the

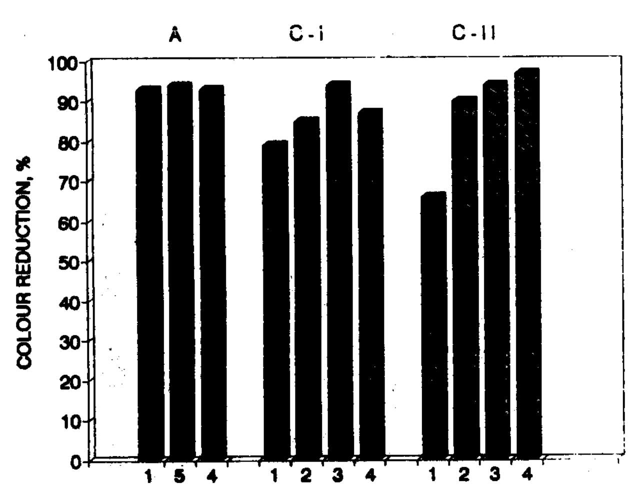

FIG-4 - TREATMENT WITH COAGULANT C-I & C II AND ADSORBENT-A

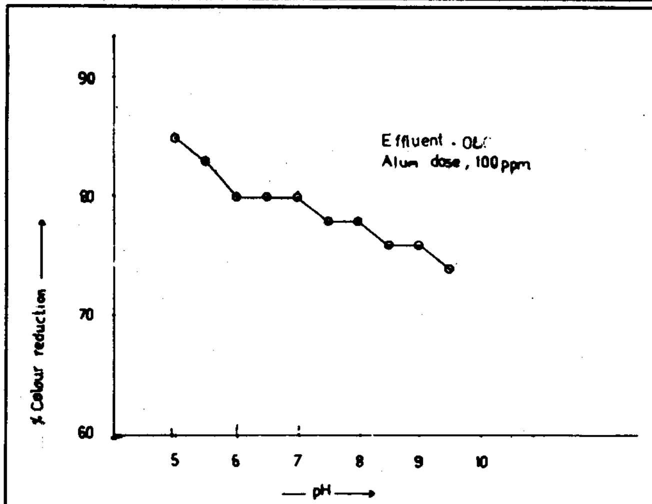

Fig-5 Colour reduction Vs pH

adsorbent, (IPC), (SC) and (BP) effluents have been taken. The colour reduction is excellent (≥ 92%) in all the three effluents with the adsorbent. In case of C-I, the efficiency of colour reduction is found to be variable according to the effluent, the maximum being with OL (~95%) and the minimum being 78% with IPC. In case of C-II, the efficiency of colour reduction is appreciable (> 90%) with OPC, OL and OSC but for IPC, it is as low as 62%.

It can be seen in Fig. 5 that the colour reduction with alum is dependent upon pH. Higher the pH, lower is the colour reduction; at pH = 5, the % reduction is 85 while at pH = 9, it is 73%. As alum is acidic, the pH decreases with increase in alum dose. Effluent treatment with pH 5.5 - 6 with resulting pH on addition of alum has been carried out with alum concentrations of 100 to 1000 ppm.

The next coagulant system, (C-III) used is the combination of lime and alum. The alum dose is varied from 50 to 300 ppm and lime from 50-300 ppm in 7 different combinations. As amount of sludge generation is very high with lime of 3000 ppm, attemps have been made to reduce the lime content by addition of alum and $FeCl_3$. The results of lime-alum systems are given in Fig. 6 and lime- $FeCl_3$ systems in Fig. 7. Addition of alum - $FeCl_3$ has been done in 5 different combinations. The colour reductions in both the systems vary from 50 to 80%.

The BOD reduction with the adsorbent and

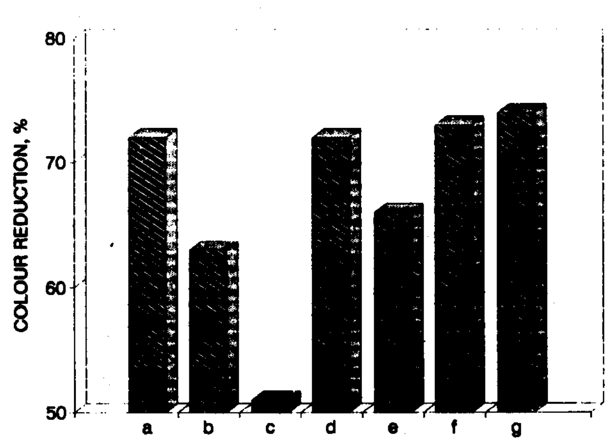

Fig-6 Treatment with coagulant - C-III
EFFLUENT - IPC Coagulant I + II
a) 50 + 100 ppm
b) 100 + 50 ppm
c) 100 + 200 ppm
d) 200 + 100 ppm
(e) 200 + 200 ppm
(f) 200 + 300 ppm
(g) 300 + 200 ppm

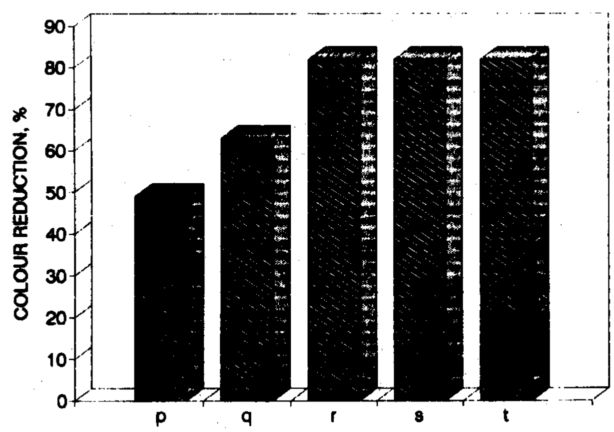

Fig 7: Treatment with coagulant - IV

EFFLUENT - IPC Coagulant II + Fecl$_3$

p - 500 + 0 ppm
q - 500 + 250 ppm
r - 500 + 500 ppm
s - 1000 + 250 ppm
t - 2000 + 250 ppm

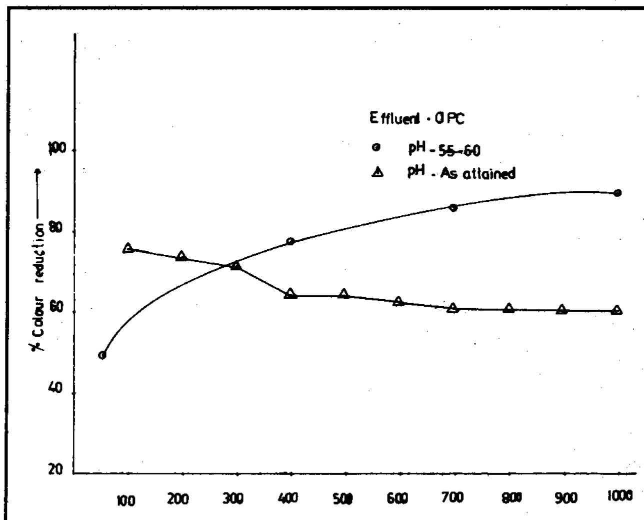

Fig-9 Alum, as Al_2O_3 ppm

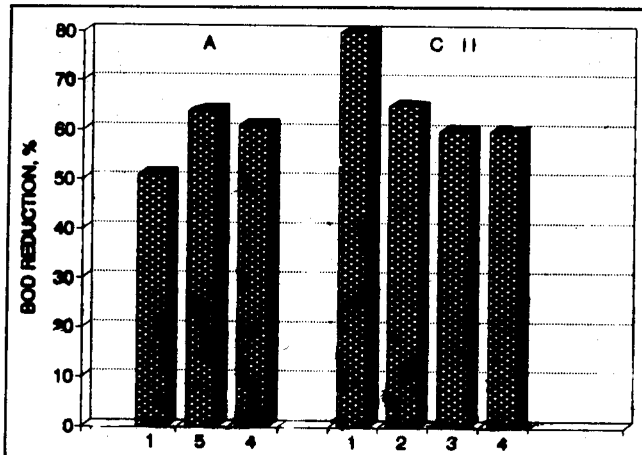

Fig-8. Treatment with coagulant - C-II and adsorbent - A

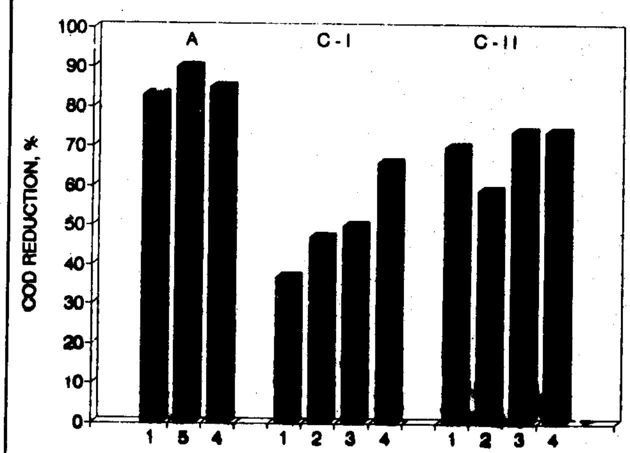

Fig-10. Treatment with adsorbent - A and coagulant C-I & C-II

coagulant C-II are shown in Fig. 8 with different effluent samples. The highest reduction in BOD is with the effluent of inlet to primary clarifier (80%). In both the solids, 50 - 60% reduction in BOD is certain with other effluent samples. The corresponding COD values along with coagulant C-I are shown in Fig. 8. The adsorbent shows highest COD removal of 90% compound to 40 - 70% with C-I and C-II.

In Fig. 9, the alum dose has been varied from 100 to 1000 ppm to find out whether further improvement in colour reduction can be there and it is observed that it cannot be beyond 92%. The effluent taken here is outlet of primary clarifier.

Fly ash serves better for reduction of COD (90% for BP) Fig. 10, for while BOD reduction is better with lime (80% with IPC) than the other products. All the three solids taken, remove colour fairly well (> 90%).

INDUSTRIAL APPLICATION

According to the results obtained, the colouring compounds in the effluent of paper mill, can be eliminated with any one of the solids studied. However, the industrial applicability of the technologies depend upon the economical criteria, namely cost factor. Fly ash is a waste product though efforts are going since long for production of bricks, cement, (-) other ceramic products and for road construction. For the time being, it may be considered as a waste material. However, transport and handling problem of fly ash are to be seen.

Moreover, enough fly ash should be available for treating the large volume of effluent generated.

Alum is easily available and it is already in practice for water treatment. The amount of alum requirement being 100 ppm, it appears to be most practicable.

Use of alum for treatment of IPC will help saving cost of aeration and overall maintenance of lagoon.

Lime is also easily available but the sludge handling may not be easy, as the requirement is 4000 ppm i.e.; 40 times more than that of alum.

It is therefore conceived that the bleach plant effluent may be treated as much as possible with the fly ash generated in the mill and alum addition should be made in the effluent of inlet to primary clarifier. This requires adequate space and infrastructure arrangement which may not be easy for an existing plant but such a combination can always be conceived for a mill which is at the project stage. Simple alum treatment is, however, possible in all the mills but the cost of treatment will be quite significant.

If the treated water can be planned to be reused such a proposition will be quite cost effective.

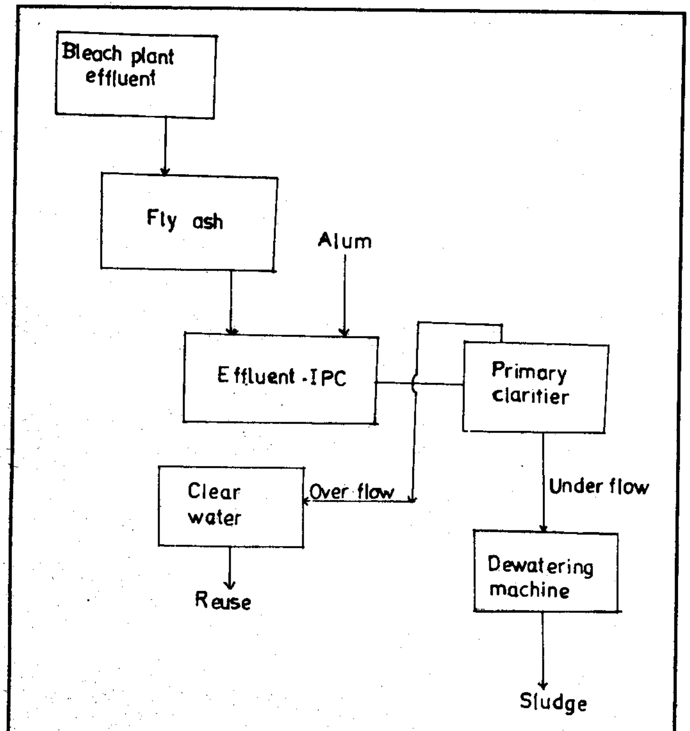

Fig-11: Treatment by adsorption and coagulation

Depending upon the location of a plant where rainfall may be very less such alum treatment and reuse of water should be a practical proposition.

In view of the adsorption capacity of fly ash, if not at the mill, it can always be dumped in the area before discharge of the effluent to water. The problem here will be again the suspended solids emanating from the fly ash itself which may be carried to the river water. Fly ash lime seepage walls can be tried to avoid this problem.

The fly ash can also be used in the drying bed in the mill. The various applications with advantage and disadvantages are given in Table 4 - 6 while the proposition of fly ash - alum combined treatment systems are given in Fig. 11.

Table-4

Advantage and Disadvantage with Adsorbent (Fly Ash)

Advantages	Dis advantages
1. It is waste product, hence no cost.	1. Difficult to handle for treating high volume of effluent.
2. Colour, BOD, COD and organically bound chlorine compounds can be removed in considerable amount.	2. Disposal of treated fly ash

Table-5

Alum for effluent treatment

Advantages	Dis advantages
1. Easy to handle and treat the effluent from inlet to primary clarifier.	1. Chemical Cost
2. It can be used in existing system.	2. AOX removal may not be possible.
3. Sludge loading in primary clarifier will be minimum.	
4. Colour, BOD and COD removal is significant.	
5. Further water treatment may not be required.	

Table-6

Lime for effluent treatment

Advantages	Dis advantages
1. Coagulation is faster.	1. Difficult to handle.
2. Colour and BOD removal are better	2. Additional sludge formation.
	3. High dosing (4000 ppm) is required.
	4. Sludge dewatering will be difficult and it will create operational problem.

REUSE OF THE TREATED EFFLUENT

The effluent after reduction of colour to 70%, the water product, appears colourless and from aesthetic points of view, it can be used for general purpose such as:

Gardening
Plantation
Cleaning of floors in the mill
Coal Yard area for spray in summar season
Safety purpose
Cleaning of drains etc.
Cleaning of bamboo/wood logs

Effluent water after primary clarifier is already being used in some industries (18, 19) for cultivation of rice. It has also been tried for growing sugarcane and many vegetables. Our experience shows that effluent water helps in better growth of eucalyptus than ordinary water. Therefore, use of water heated through adsorption and coagulation can very well be used for agricultural purpose.

In the process also, it can be reused for bleaching purpose on decolourisation above 85-90%. It was established that such water does not effect the optical and strength properties. It can be used for washing unbleached pulp.

CONCLUSIONS

Colour reduction of the paper mill effluent can be achieved along with that of BOD and COD by treatment of the effluent with adsorbent (fly ash) and coagulant (alum, lime and ferric chloride). The effluent treatment process recommended is in 2 stage; treatment of the bleach plant effluent with fly ash and then the primary clarifier effluent with alum which will help - reduction of colour, BOD and COD upto ~90%and it is likely to reduce AOX/ or chloro organic compounds also. The treated effluent can be reused for bleaching purpose apart from the general use for gardening, plantation, floor cleaning and in yard areas.

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