The Fate of Adsorbable Organic Halogens (AOX) in Activated Sludge Process of Agro-based Pulp and Paper Industry

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ABSTRACT

The performance of wastewater treatment plant based on Activated sludge process treating effluent from bagasse based integrated pulp and paper mill has been investigated to find out the extend of AOX (Adsorbable Organic Halogens) reduction during vaqrious stages of treatment along with other conventional pollutants like Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand. The overall reductions were 93, 77 and 98 percent for Suspended solids, Chemical oxygen demand and Biochemical oxygen demand respectively. It was found that AOX reduction across the wastewater treatment plant was 69.3%, out of which 53.8% was removed in the activated sludge biological treatment, out that 43.7% was found to be removed by microbial metabolism while remaining was getting carried away along with waste activated sludge.

INTRODUCTION

In any manufacturing process, it is possible to identify several sources of discharges having potential adverse effect on the environment. In paper manufacturing process pulp mill plays an important role where un-bleached pulp is made by chemically degrading and dissolving lignin content of the raw materials like wood, bagasse, bamboo etc. Since, complete lignin removal at this cooking stagte result in deterioration of the pulp strength, a small portion is allowed to remain in the pulp . This residual lignin which makes the pulp brown color and has to be removed by bleaching before the pulp is used for making writing and printing paper.

Bleaching is the multistage process involving various bleaching chemicals, such as, chlorine, hypochlorite, chlorine dioxide, oxygen, hydrogen peroxide and ozone. Among the above bleaching agents, chlorine and chlorine compounds have been used predominantly. This is because, they are highly efficient and economical. An alkaline extraction stage using NaOH usually follows each bleaching stage to extract the products formed by the bleaching reaction. They are mainly fragments of lignin macromolecules that have been modified during the bleaching process, for example, chlorinated lignin or oxidized lignin.

The presence of chlorinated lignin or chlorinated organic compounds in the bleach plant effluent found to have some detrimental effect on the environment[1]. Therefore, various government agencies have proposed stringent dischare regulation on discharge of these compounds to surrounding environment. These compounds are collectively called Total organically bound chlorine (TOCI). They include, polychlorinated

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organic compounds, such as Chlorophenol, Chloroguaiacols, Chlorocatechols, 2,3,7,8- terachloro-dibenzodioxin and 2,3,7,8- tetrachlrodibenzofuran. Estimation of TOCI gave low value because of incomplete recovery from resin column. An alternate method was soon evolved and being known as Adsorbale Organic Halogen (AOX) Analysis. Major pulp and paper producing countries around the world enforced regulations for AOX discharge in the final treated effluent[2,3,4]. including India[5].

Several studies have been carried out on AOX degradation and removal, for example, by aerobic bacteria[6,7], anaerobic bacteria[8], ultrafilteration followed by anaerobic and aerobic system[9], activated sludge process and aerated stabilization basin[10]. Extensive studies were carried out in Europe, North America and Scandinavian countries on AOX toxicity, degradation and removal efficiency where they use wood as raw materials mainly Softwood[11]. The nature of organic chlorine synthesis during bleaching, degradation and removal efficiency by microbial system differs considerably according to raw materials and process used to manufacture pulp[12,13].

Most of our mills in India use agrobased raw materials and practically no information is available on AOX degradation and removal by microbial system. Therefore, the present study was carried out to understand the microbial degradation efficiency of AOX along with other parameters such as pH, Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand in the activated sludge process of largest agro based pulp and paper industry.

EXPERIMENTAL

The effluent treatment plant receive effluent from two streams, one with high BOD which contains mostly bagasse washing and bagasse-yard effluent and other one contains bleach plant and paper machine effluents. The second stream (Figure:1) was selected for present study, because, chlorinated organics are produced during bleaching process. Composite samples were

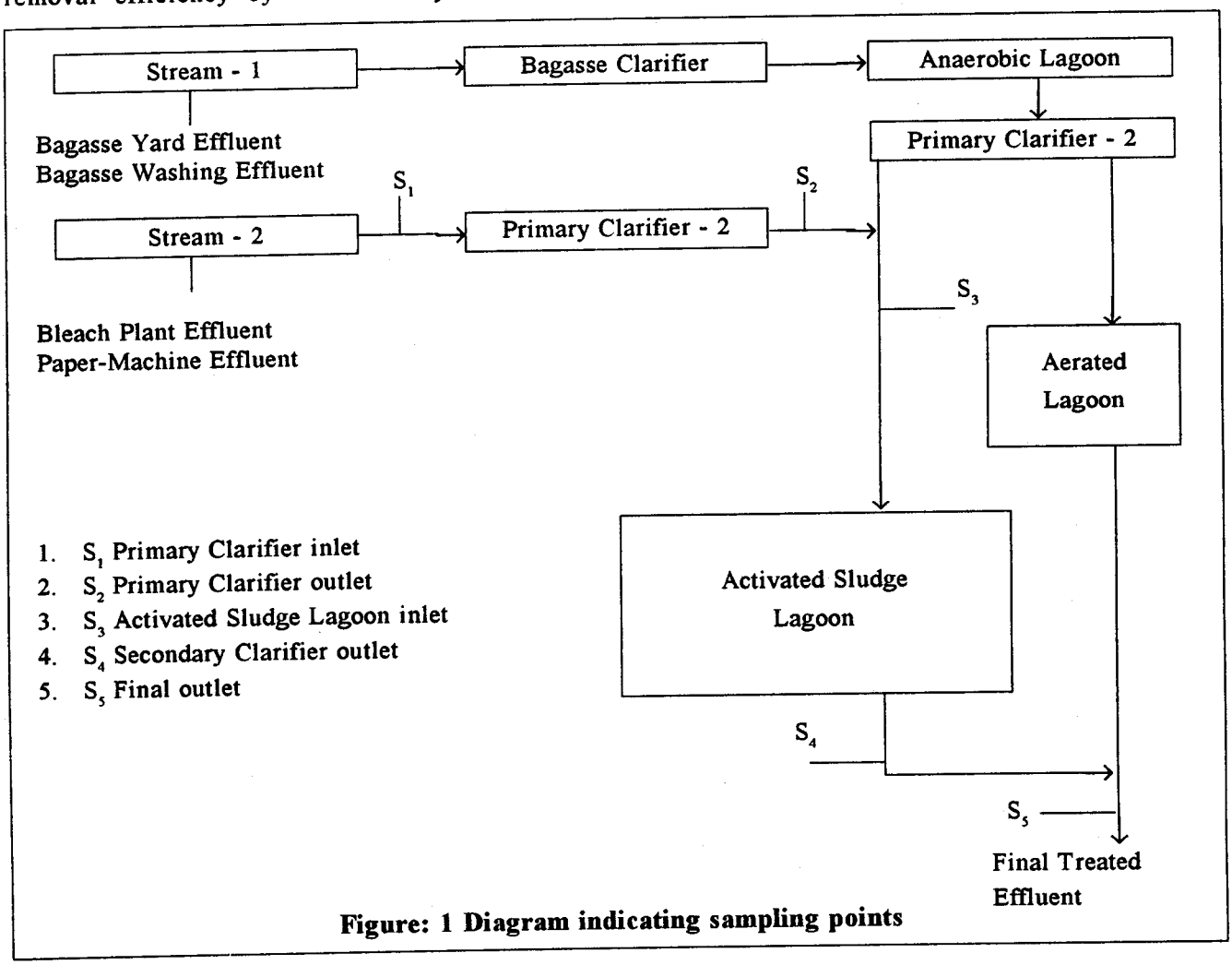


Figure: 1 Diagram indicating sampling points

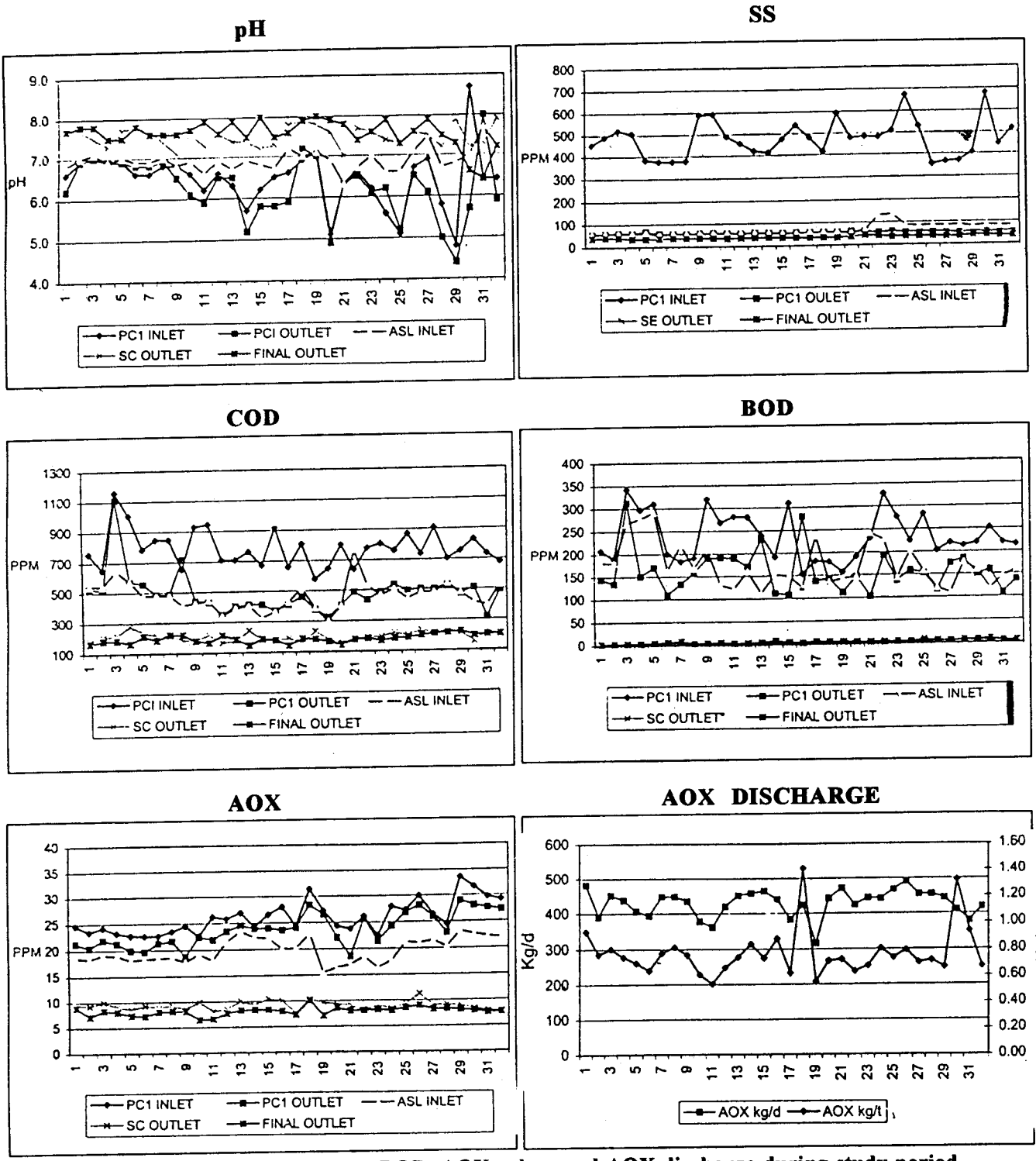


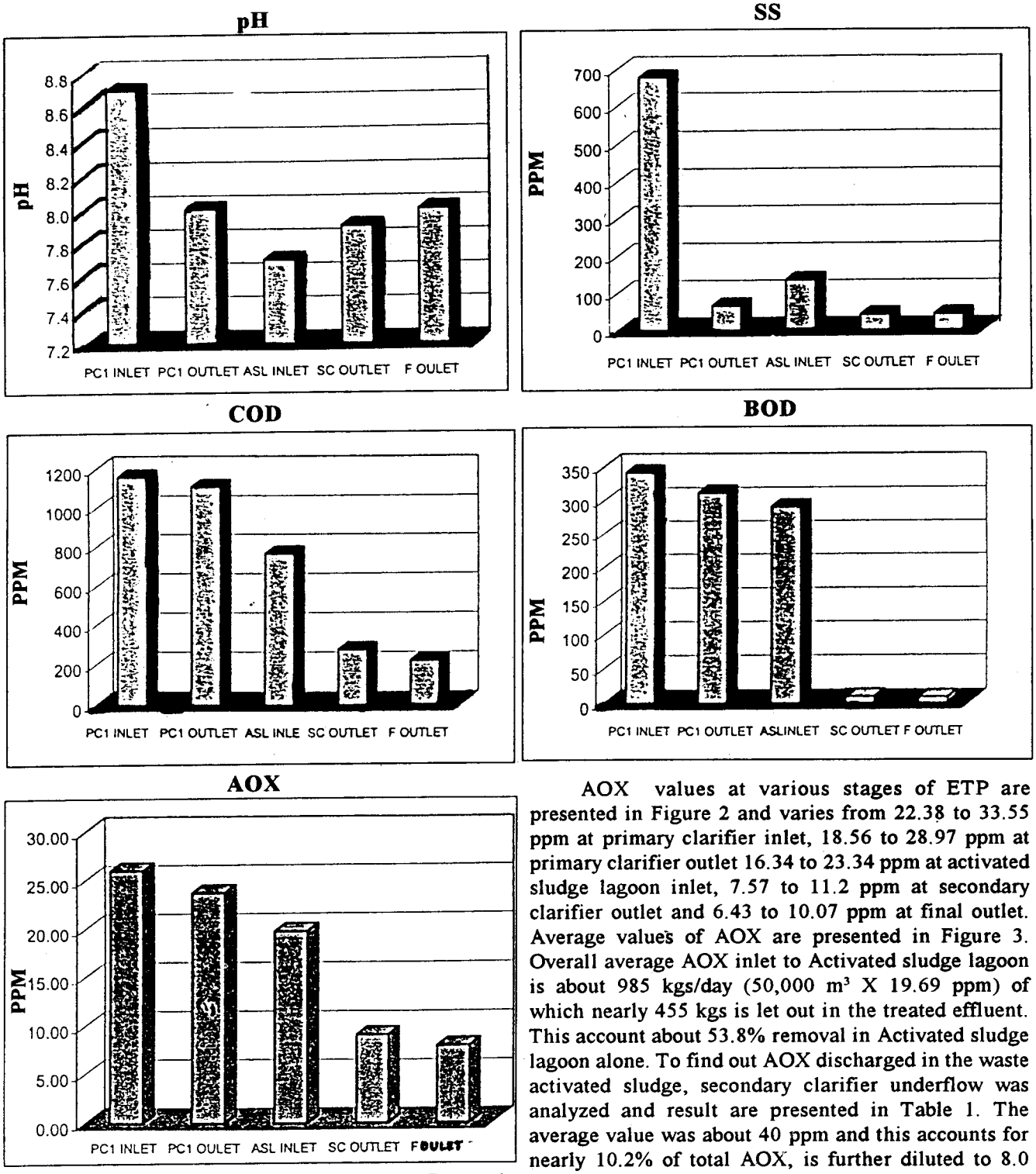
Figure: 2 Daily pH, SS COD, BOD, AOX values and AOX discharge during study period

collected and analyzed every day for about one month. pH, Suspended Solids, Chemical Oxygen Demand and Biochemical Oxygen Demand were analyzed as per the standard methods (SS:2540D, BOD : 521 0B & COD :22 B). AOX was analyzed using AOX analyzer (ECS 1200 AOX Analyzer, Euroglas Analytical Instruments, The Netherlands) as per the ISO column method (ISO 9562:1989-E)[15].

RESULTS

Daily values of pH, Suspended Solids, Chemical

Figure: 3 Average values of pH, SS COD, BOD, AOX in various stages of ETP



Oxygen Demand and Biochemical Oxygen Demand across ETP plant are presented in Figure 2 and average values are presented in Figure3. The overall reductions were 93, 77 and 98 percent for Suspended solids, Chemical oxygen demand and Biochemical oxygen demand respectively.

AOX values at various stages of ETP are presented in Figure 2 and varies from 22.38 to 33.55 ppm at primary clarifier inlet, 18.56 to 28.97 ppm at primary clarifier outlet 16.34 to 23.34 ppm at activated sludge lagoon inlet, 7.57 to 11.2 ppm at secondary clarifier outlet and 6.43 to 10.07 ppm at final outlet. Average values of AOX are presented in Figure 3. Overall average AOX inlet to Activated sludge lagoon is about 985 kgs/day (50,000 m^3 X 19.69 ppm) of which nearly 455 kgs is let out in the treated effluent. This account about 53.8% removal in Activated sludge lagoon alone. To find out AOX discharged in the waste activated sludge, secondary clarifier underflow was analyzed and result are presented in Table 1. The average value was about 40 ppm and this accounts for nearly 10.2% of total AOX, is further diluted to 8.0 ppm by mixing with aerated lagoon outlet and discharged as treated effluent. Total AOX discharged per day and per tone of production is given in the Figure 3 and average was about 429 kg/day and 0.77 kg/tonne.

Table-1 AOX Concentration at Secondary clarifier under flow sludge

S. No.	AOX ppm
1.	44.30
2.	45.03
3.	38.38
4.	35.38
5.	30.55
6.	44.26
7.	39.68
8.	39.75
9.	38.92
10.	40.15
Avg.	**39.68**

DISCUSSION

Wastewater treatment plant in pulp and paper industry are primarily designed to reduce the conventional pollutants like Total solids, Total dissolved solids, Suspended solids, Chemical oxygen demand and Biochemical oxygen demand. However, it has been found that wastewater treatment like aerated stabilization basin and activated sludge process, primarily designed to treat conventional pollutants also found to remove or reduce AOX produced during bleaching process. The percentage reduction of AOX was reported to vary 14 to 65%[16,17] and in the present study i.e. wastewater treatment process using agrobased pulp and paper mill effluent accounts for about 69.3% reduction in AOX along with other conventional pollutants like Suspended solids (93%), Chemical oxygen demand (77%) and Biochemical oxygen demand (98%). Among the overall 69.3% AOX reduction in ETP, actual reduction in the activated sludge lagoon is only 53.7%. There are two principal mechanism by which AOX is removed in the biological treatment system.. They are 1. Microbial degradation, 2. Adsorption on to the sludge.

MICROBIAL DEGRADATION

In microbial degradation, AOX compounds having molecular weight below 1000 are ingested by bacterial cells and metabolized and in the fungal system, the AOX reduction is by dechlorination of Chlorinated phenolic compounds which result in release of Chlorine and phenoxy radicals, Phenoxy radicals undergo further non enzymatic reactions with other compounds present in the systems resulting polymerization[2].

These repolymerized compounds are considered to be resistant to microbial degradation and adsorbed on sludge or send out along with treated effluent. Earlier studies indicates that biodegradation of AOX by microorganism reduce the concentrations of these compounds in the bleach plant effluent, but not completely[18]. This is in accordance with present study where actual microbial degradation accounts for about 43.7 percent as evidenced by other studies[17,19]. Most of non degraded compounds are found to accumulate in the sediments of water body and degraded slowly by anaerobic biota widely distributed in the sediments. But it is premature to conclude that complete dechlorination could take place under anaerobic condition.[18,20] The deficient dechlorination capability of aerobic and anaerobic biological system is due to the selection of readily available degradable compounds during bleaching and other process by microbial flora in the treatment system.[21]

ADSORPTION ON TO THE SLUDGE

Most of the hydrophobic chlorinated organic compounds adsorb to on the solid surface like fiber fines, clay and bacterial flocs present in sludge. Generally AOX compounds resistant to microbial degradation are carried away by the treated effluent or sludge. This is evidenced by the presence of AOX content in the sludge (39.68ppm) and secondary clarifier outlet. Nearly 100 kg was removed by sludge by adsorption which accounts for about 10.2% of total AOX entering to activated sludge lagoon.

Fears have been expressed that groundwater would be contaminated by the AOX present in sludge, however we have found that during the composting of sludge along with waste pith and bagasse, the AOX compounds are getting mineralized and the leachate from composting contains little or no AOX. Therefore, the role of terrestrial micro and higher organisms and their metabolic capabilities will differ from aquatic or wastewater treatment environment and it is found that higher terrestrial organisms are mainly capable of accumulating chlorophenolic compounds.[19,21]

Other studies indicate that degradation of AOX varied according to raw materials used to manufacture pulp and kappa number. For example, for pine pulp with 30.2 and 25.7 kappa number the AOX reduction was 48% and 57% and for birch pulps with kappa number 17.6 and 16.4 the reduction was 59% and 65%

respectively.[22] This indicates that low kappa number of the pulp favors, high reductions of AOX in the activated sludge proces probably due to the higher degradation of lignin during pulping. In our case, the total reduction was 69.3% which is quite high due to the low kappa number of bagasse pulp and may be due to structure difference of lignin present in the bagasse and AOX produced during bleaching process when compared to other raw materials.

To conclude, it is a fact that major fraction of organochlorine compounds of bleach plant effluents occurs in the form of high molecular weight materials and their structure is not fully elucidated. Unless the structure of these compounds are fully characterized, their biodegradation or biotransformation potentials cannot be assessed completely. At the same time it is important to note that all the chlorinated organic compouds are not the exclusive products of chemicals and paper industry. Many hundredds of chlorinated organic compounds are natural metabolites of bacteria, fungi, algae, lichens and higher plants.[23] To what extent these natural and industrial process contribute to global balance of organochlorine is unknown factor. Studies need to be focused in this area. Till then, the total estimation techniques like AOX will give fare idea about their persistence, biodegradation and biotransformation in industrial and natural habitat.

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