Effect Of Varying Load Of Organochlorine Compounds On Activated Sludge Process

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ABSTRACT

Pulp and paper mills generate an appreciable amount of organochlorine compounds collectively expressed as "AOX" (adsorbable organic halogens). These compounds have varying degree of toxicity. In the present study the impact of AOX compounds on performance and microbial community structure in activated sludge process have been presented. Three laboratory scale reactors based on activated sludge process were run continuously with varying load of AOX compounds. Well dense structure of microbial flocs started breaking and resulted in diffused and pin point flocs when operated at higher AOX load of 84±3 g/m^3/day. Though the AOX reduction remained more or less same in the range of 39-46 % at lower (14- 33 g/m^3/day) and higher AOX load but there was 5-7 % less COD reduction at higher AOX load. The sludge volume index (SVI) value was above 100 at higher AOX load. During biodegradation, the major mode of AOX removal was mineralization and only 1.6-2.3% AOX compounds were adsorbed on waste activated sludge. The concentration of AOX compounds in sludge was dependent on the AOX concentration in influent. Excess sludge generation was 0.29±0.05 and 0.18±0.06 g/g of CODs removal during low to moderate and higher AOX load respectively.

***Keywords**: activated sludge process, AOX, microbial floc, organochlorines, reactor performance*

Abbreviations

AOX	:	Adsorbable Organic Halogen
ASP	:	Activated Sludge Process
C_D	:	Chlorine Dioxide Substituted Chlorination Stage
CODs	:	Settlable Chemical Oxygen Demand
D	:	Chlorine Dioxide Stage
DO	:	Dissolve Oxygen
E_{OP}	:	Alkaline Extraction Stage
MLSS	:	Mixed Liquor Suspended Solids
MLVSS	:	Mixed Liquor Volatile Suspended Solids
R_c	:	Control Reactor
R_{hl}	:	Reactor at Higher AOX Load
R_{rl}	:	Reactor at Reduced AOX Load
TSS	:	Total Suspended Solids
VSS	:	Volatile Suspended Solids
WBL	:	Weak Black Liquor

Introduction

The pulp and paper mill is one of the major consumers of fresh water. Sustained efforts are being exerted in the pulp and paper mill around the world to reduce water consumption and regulate the discharge of pollutants in the receiving aquatic body. The strategies for water conservation result in higher concentration of dissolved and particulate organics and colour. Aerobic biological treatment, principally activated sludge process (ASP), is followed for degradation of biodegradable organic compounds in the wastewater of the pulp and paper mills either as a sole clean-up process or as a polishing one. The removal of biodegradable organic substances; both soluble and finely dispersed, is accomplished by biological oxidation with the help of microbial consortia principally bacteria. The ecology, or to be more precise the balance of microbial species, in activated sludge process is the significant factor for the behavior of the biomass in the bio-oxidation and subsequent clarification [1]. The activated sludge process works well as long as the consortia of microorganisms, typically termed as sludge, grow in a healthy way, and settle and compact in the secondary settling tank to the extent that the return sludge concentration is high enough to maintain the mixed liquor suspended solids (MLSS) concentration at a desired level [2].

Organochlorine compounds are formed during the bleaching of wood pulp with chlorine (Cl_2) and chlorine derivatives such as chlorine dioxide (ClO_2). These compounds can be monitored by several techniques; AOX (adsorbable organic halogen) is the most commonly used parameter to measure it quantitatively [3]. The AOX compounds have varying degree of toxicity to the aquatic organisms [4]. Regulatory agencies world-wide have imposed more and more stringent limits on the discharge of AOX, the industry and regulatory agencies in India have mutually accepted to regulate the release of organochlorines in the aquatic body of 1.0 kg AOX per ton of paper from April, 2008 under the Charter on Corporate Responsibility for Environmental Protection (CREP).

High molecular weight fraction (>1000

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Da) of bleached kraft mill effluent affects the microbial activity and growth [4]. This fraction is the principal source of AOX compounds (80%) and have stimulatory effect on microbial activity as measured by biomass growth and substrate utilization. During biological treatment of wastewater containing AOX compounds, mineralization of 25-60 % of the same has been reported [5-7]. The effect of pH, temperature, HRT and SRT on morphology of sludge and performance of ASP has been reported by many researchers [8, 9]. The role of AOX compounds on morphology and performance of activated sludge process is very little studied. The present paper communicates the impact of different load of AOX compounds on microbial community, performance of activated sludge process, and mechanism of removal of AOX compounds during biological treatment of effluent.

Experimental

Materials

Wastewater from partially chlorine dioxide substituted chlorination (C_D) and alkaline extraction (E_{OP}) stages of a pulp mill having $C_DE_{OP}DD$ bleaching sequence were mixed in 2:1 ratio. These two streams are the major source of pollution generation especially of AOX compounds. Weak black liquor (WBL) was added to it to adjust the COD concentration. The concentration of AOX compounds from C_D and E_{OP} stages was 90 ± 20 and 55 ± 15 mg/l respectively. The CODs concentration of WBL, C_D and E_{OP} stage wastewater was 150000, 1150 ± 225 and 1225 ± 235 mg/l respectively (Table 1). These three wastewaters were mixed in different proportion to get required level of COD and AOX in the feed. The pH of the resulting wastewater was adjusted to 7.0, it was filtered; the filtrate was used as the substrate for feeding into the activated sludge process. The above wastewaters and WBL were periodically collected from the mill and stored in the refrigerated condition at 4-5 ^{0}C.

Activated sludge from the effluent treatment plant of the same pulp and paper mill along with cow dung were used as seed in the biological reactors. Cow dung was first screened with coarse screen. Proportion of the two was equal on the basis of MLVSS content. Microscopic analysis of the secondary sludge indicated that it was comprised of excessive filamentous organisms (Figure 1) with diameter of 1-1.4 m; average length varied from 113 to 181m.

The mixed sludge was acclimatized in laboratory environment in a batch reactor with an arrangement of diffused aeration and continuous mixing with mechanical stirrer. Supernatant was decanted and fresh feed was added every day along with the required amount of nutrients. After 20 days of operation the nature of sludge was transformed from filamentous to floc forming one. 1.0-1.5 mg/l of DO in the reactor was found to be adequate to control the proliferation of filamentous organisms.

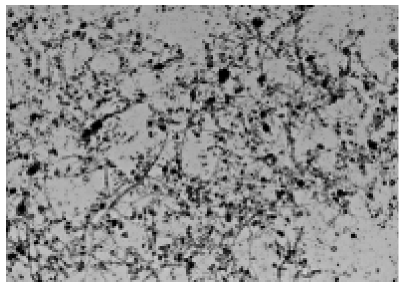

Figure 1:
Morphology of secondary sludge from ASP of pulp and paper mill

Three laboratory scale reactors (Figure 2) with volume capacity of 6 liter were used as aeration tank, followed with two settlers in series with 4.0 liter volume of each. The substrate was fed into reactors through peristaltic pumps (Cole Parmer, USA). Inlet feed solution was kept at a temperature of 10-12 ^{0}C to control biodegradation. Urea and technical grade phosphoric acid were used as the source of nitrogen and phosphorous and fed on the basis of CODs removal: N: P ratio of 100:5:1.

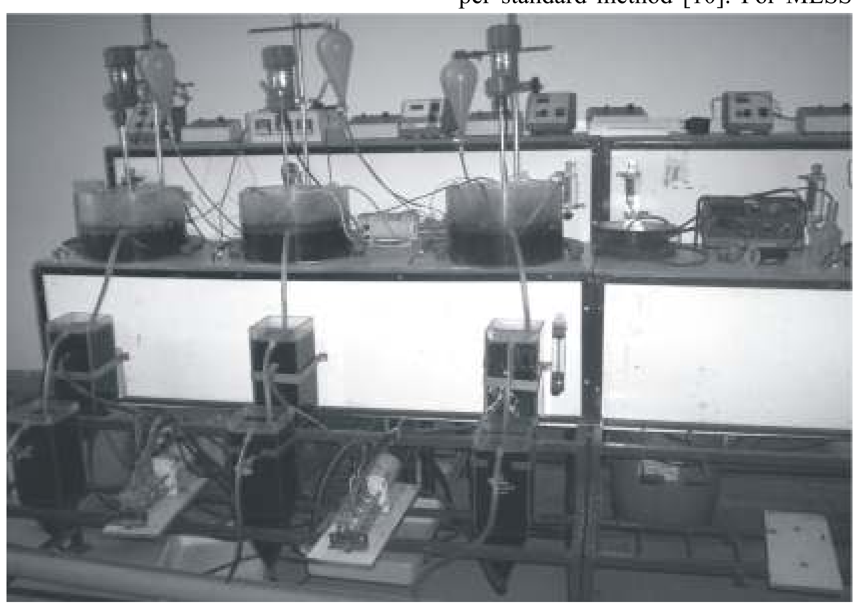

Figure 2: Laboratory scale biological reactors (ASP)

Table 1: Influent characteristics

Sample	CODs (mg/l)	BOD:CODs Ratio	AOX (mg/l)	Colour (Pt-Co)
C_D stage wastewater	1150 ± 225	1:1.9	90 ± 20	600 ± 30
E_{OP} stage wastewater	1225 ± 235	1:3.8	55 ± 15	1500 ± 90
WBL	150000	1:5.7	-	471400

2.2 Methods

AOX content of liquid and solid samples was estimated as per ISO 9562: 1989 and DIN 38414 (P18) respectively using Euroglass make AOX analyzer and p-chlorophenol (Merck, Germany) as standard; solid samples were disintegrated by probe sonicator before analysis.

pH, CODs, colour were determined as per standard method [10]. For MLSS and MLVSS, 100 ml of mixed sludge sample was centrifuged and washed with distilled water before transferring to pre-weighed silica crucible. The centrifuged mass was oven dried at 105 ^{0}C over night for determination of MLSS; the same crucible was ignited at 550 ^{0}C and loss in weight was taken as MLVSS. DO was determined by using YSI make DO meter and morphology of organisms was characterized with image analyzer (Buehler, USA; Ominimet model). The motility of rotifers and protozoa was observed at

5x resolution by taking one drop of mixed liquor from the reactor on glass slide.

Estimation of sludge yield

Substrate removal was measured by evaluating CODs removal; produced biomass (sludge) was estimated through mixed liquor VSS, and sludge generation was expressed as g biosolid/g of CODs removal. Influent-SS concentration, biomass loss in effluent as TSS, excess biomass withdrawal, sample taken for MLSS estimation and change of biomass concentration in aeration tank were accounted for estimation of sludge yield. The TSS concentration in both influent and effluent was more or less equal and concentration varied from 20-30 mg/l. The excess sludge was removed every day in the morning by transferring the complete biomass from settlers and tubes to reactor. Equivalent amount of treated wastewater was added to the reactor to compensate the volume of excess sludge withdrawn.

Sludge yield=

$$\left[\left\{(A*6) + B + C + \frac{D\,(A*6)}{(6-D)}\right\} - \{E + (F*6)\}\right] / G$$

A: MLVSS concentration in reactor (g/l)

B: Amount of MLVSS taken for analysis (g)

C: MLVSS concentration in effluent (g/d)

D: Volume of MLSS removed for excess sludge (l)

E: VSS concentration in influent (g/d)

F: MLVSS concentration in reactor on previous day (g/l)

G: CODs removal (g/d)

Results and discussion

The water conservation measures in pulp and paper mill have significantly reduced water consumption. The recycling of wastewater in paper machine and bleaching process has resulted in increasing the organochlorine concentration in the effluent.

Operation of ASP reactors at moderate AOX load

Before the change of AOX load, all the three reactors were run continuously for 20 days under standard environmental and operating conditions (Table 2). The standard conditions were used to grow flocculating bacteria. Though the pH of feed was near to 7.0, the same of treated wastewater was higher (7.7 to 8.1) in all the three reactors due to change of alkalinity. Temperature and DO were maintained at 34-37 ^{0}C and 0.9-1.5 mg/l respectively. SVI of the sludge in three reactors was in the range of 16-24 ml/g. Reduction in CODs and AOX was 68-72% and 39-43% respectively in the reactors. Good and dense flocs were developed with very few filamentous organisms coming out of flocs in all the three reactors. Abundance of active higher organisms like protozoa, rotifer and nematode etc. was quite high in all the three reactors.

Table 2:
Operating conditions and performance of ASPs prior to change of AOX load

Parameter	R1	R2	R3
pH (inlet)	7.01 ± 0.01	7.01 ± 0.01	7.01 ± 0.01
pH (outlet)	7.91 ± 0.20	7.92 ± 0.22	7.90 ± 0.12
Temperature (^{0}C)	35.8 ± 1.2	35.6 ± 1.1	36.0 ± 0.9
DO (mg/l)	1.2 ± 0.3	1.1 ± 0.2	1.3 ± 0.3
HRT (h)	8.7 ± 0.2	8.5 ± 0.3	8.9 ± 0.2
MLSS (g/l)	4.12 ± 0.25	4.09 ± 0.35	4.00 ± 0.27
MLVSS (g/l)	3.44 ± 0.21	3.42 ± 0.27	3.34 ± 0.22
F/M ratio (d^{-1})	0.23 ± 0.02	0.25 ± 0.02	0.22 ± 0.05
Organic loading	0.80 ± 0.06	0.82 ± 0.02	0.84 ± 0.03
(kg CODs removal/m^3/d)			
SVI (ml/g)	20 ± 3	16 ± 3	24 ± 4
CODs feed (mg/l)	482 ± 10	482 ± 10	482 ± 10
CODs reduction (%)	69.8 ± 1.3	70.1 ± 1.2	69.9 ± 1.4
AOX feed (mg/l)	12.2 ± 0.4	12.2 ± 0.4	12.2 ± 0.4
AOX reduction (%)	41.3 ± 1.2	40.1 ± 1.3	41.7 ± 0.9

Operation of ASP with moderate, low and high AOX load

The first reactor was maintained as control (R_c) throughout the study (moderate AOX load) whereas the second and third reactors were run at reduced (R_{rl}) and higher (R_{hl}) AOX load respectively (Table 3). During Phase I (PI), MLVSS to MLSS ratio in R_{hl} decreased to 81.8 from 87.0% (Table 4) due to accumulation of salts present in wastewater from bleaching streams; the performance with respect to reduction of CODs also decreased to 66.0 ± 4.9 from 69.9 ± 1.4%. Reduction of AOX compounds was unaffected as compared to control (Table 5). In R_{rl} reduction of CODs also decreased to

Table 3:
AOX load in reactors at moderate, low and high concentrations

	Reactor	R_c	R_{rl}	R_{hl}
Phase I	AOX concentration (mg/l)	11.64	4.51	29.30
(First 10 days)	AOX load (g/m^3/day)	34.9	13.5	87.9
Phase II	AOX concentration (mg/l)	11.36 0.18	4.59 0.10	28.69 0.40
(Next 20 days)	AOX load (g/m^3/day)	34.1 0.5	13.8 0.4	86.1 1.2
Phase III	AOX concentration (mg/l)	10.94 0.42	4.70 0.57	27.61 0.95
(Next 30 days)	AOX load (g/m^3/day)	32.8 1.3	14.1 1.7	82.8 2.9

Table 4:
Operating conditions of ASP during moderate, low and high AOX load

Operating parameter		R_c	R_{rl}	R_{hl}
MLSS (g/l)	PI	4.06 0.11	3.96 0.16	4.23 0.10
	PII	3.97 0.16	3.86 0.16	4.42 0.19
	PIII	3.89 0.13	3.85 0.19	4.62 0.19
MLVSS (g/l)	PI	3.52 0.09	3.48 0.14	3.46 0.11
	PII	3.49 0.13	3.46 0.15	3.39 0.14
	PIII	3.44 0.12	3.50 0.18	3.32 0.13
F/M ratio (d^{-1})	PI	0.27 0.02	0.26 0.02	0.30 0.05
	PII	0.30 0.04	0.28 0.04	0.29 0.03
	PIII	0.27 0.04	0.27 0.03	0.26 0.04
HRT (h)	PI	8.7 0.3	8.9 0.4	8.5 0.1
	PII	8.4 0.5	8.5 0.8	8.6 0.3
	PIII	8.4 0.5	8.5 0.4	8.7 0.8
Organic loading (kg CODs removal/m^3/d)	PI	0.94 0.07	0.91 0.07	1.04 0.19
	PII	1.03 0.14	0.98 0.14	0.97 0.09
	PIII	0.94 0.13	0.94 0.11	0.85 0.13

Table 5:
Performance of ASP during moderate, low and high AOX load

Performance parameter		R_c	R_{rl}	R_{hl}
CODs (mg/l)	PI	480 14	522 19	523 12
	PII	505 34	525 29	540 22
	PIII	485 25	516 28	515 34
CODs reduction (%)	PI	70.9 2.5	64.0 2.7	66.0 4.9
	PII	71.5 4.9	65.5 2.7	64.2 3.5
	PIII	67.6 5.3	64.2 4.4	60.3 5.7
AOX reduction (%)	PI	43.7	39.2	44.8
	PII	46.8 1.3	43.5 1.7	43.8 0.5
	PIII	44.6 3.6	47.4 4.6	44.0 3.3
SVI (ml/g)	PI	35 5	19 2	29 1
	PII	44 11	28 12	46 14
	PIII	34 9	37 12	114 25

64.0 ± 2.7 from 70.1 ± 1.2%. The lower reduction in CODs was due to use of higher amount of low biodegradable WBL to makeup the required COD concentration and lower amount of biodegradable substrate (C_D, E_{OP} effluent) to have low AOX content. The morphology of organism in all the reactors remained same throughout the operation. The motility of higher organisms in all reactors was also comparable.

During Phase II (PII), MLVSS content and reduction of CODs in reactor R_{hl} further decreased to 76.9 from 81.8% and 64.2 ± 3.5 from 66.0 ± 4.9 % respectively whereas, in R_{rl} the volatile content of the biomass increased to 89.8 from 87.9%. The morphology of microorganisms started to change after 10 days with change in AOX load. In R_{rl} there were good dense flocs with a few diffused one. Though filamentous organisms were also observed, SVI remained within 28 ± 12 ml/g. The motility of the higher organisms was also good. In R_{hl} a few well-built dense flocs started to get diffused with development of thin and pin point flocs (Figure 3). The motility of higher organism was slightly stressed.

In Phase III (PIII), the MLVSS content and reduction of CODs in R_{hl} further decreased to 71.9 from 76.9 and 60.3±5.7 from 64.2 ± 3.5% respectively. There was drastic change in morphology of sludge; SVI was in the range of 114±25 ml/g. Although filamentous organisms were not observed, most of the sludge was in the form of diffused flocs. A few new dense flocs started to grow at the end due to gradual adaptation in the changed conditions. Motility of higher organism was quite comparable to R_c.

Figure 3: Morphological characteristics during moderate, low and high AOX load

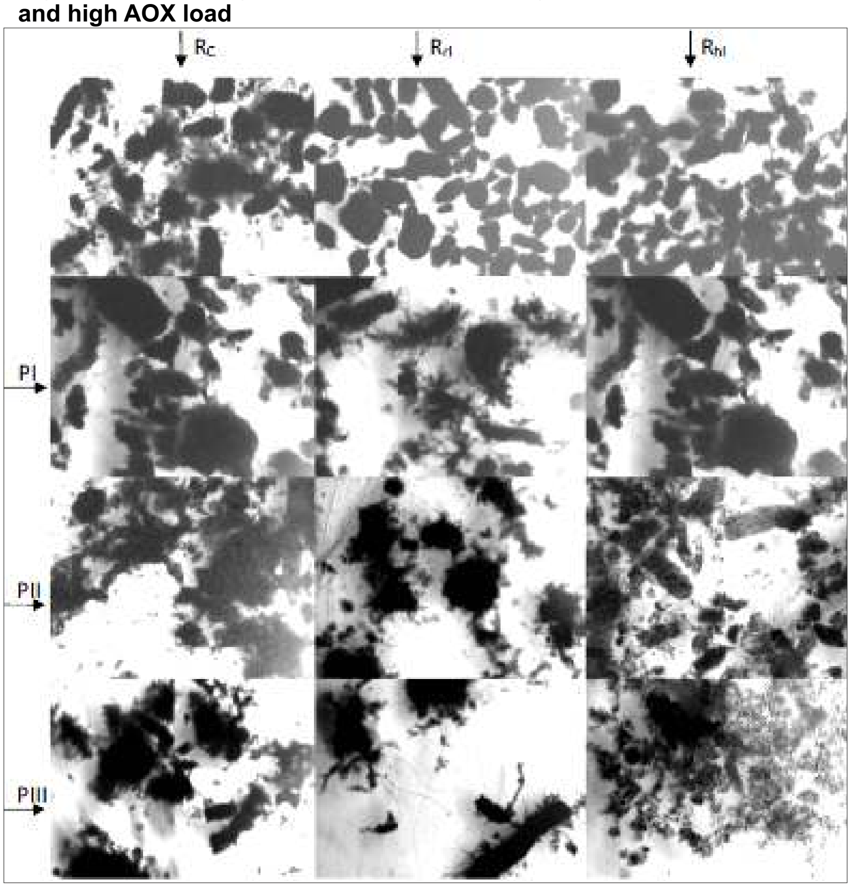

Table 6: Sludge generation at moderate and high AOX load

Parameter	Moderate load	High load
Inlet AOX conc. (mg/l)	9.35 1.87	23.67 5.41
AOX load (g/m^3/d)	28.1 5.6	71.0 16.2
AOX reduction (%)	40.8 6.0	41.3 3.7
Sludge yield (g/g CODs removal)	0.29 0.05	0.18 0.06

Effect of moderate and high AOX load on sludge generation

In biological treatment processes, growth of cell occurred in concurrence with the oxidation of substrate. The ratio of biomass produced to the amount of substrate removed was defined as the sludge yield.

Sludge generation at moderate AOX load was 0.29 ± 0.05 g/g of CODs removal and the same trend was observed during continuous run of reactors at moderate AOX load for more than eight months. During low AOX load, the sludge generation was comparable to that during moderate load whereas at high AOX load the same was reduced to 0.18 ± 0.06 g/g of CODs removal (Table 6). The increased concentration of organochlorine compounds affected the growth of microorganisms and the performance efficiency of the process. The organochlorine compounds worked as metabolic uncouplers and resulted in low sludge generation while compromising with low CODs reduction and poor settling properties of sludge. The similar observations have been reported elsewhere [11-13].

AOX removal mechanism at moderate and high AOX load

Three set of samples were analyzed to evaluate AOX removal mechanism at different AOX load. At moderate load, 45.0 ± 4.1% AOX compounds were mineralized during biological

Table 7: AOX removal at moderate and high AOX load

Parameter	Moderate load	High load
Inlet AOX (mg/l)	9.95 1.77	23.43 4.57
Outlet AOX (mg/l)	5.29 1.30	12.63 2.93
Sludge AOX (mg/kg)	2690 969	7659 750
HRT (h)	8.6 0.2	8.9 0.5
CODs inlet (mg/l)	450 22	445 31
CODs outlet (mg/l)	152 3	171 34
Biomass (mg/g CODs removal)	0.29 0.05	0.18 0.06
AOX removal (%)	47.3 3.7	46.3 3.1
AOX mineralization (%)	45.0 4.1	44.7 3.3
AOX adsorbed on sludge (%)	2.3 0.6	1.6 0.2

degradation whereas 2.3 ± 0.6% of the same accompanied with waste activated sludge in adsorbed form (Table 7). The overall AOX removal was 47.3 ± 3.7%. Similarly, at high load, 44.7 ± 3.3% AOX compounds were mineralized whereas 1.6 ± 0.2% of the same accompanied with waste activated sludge. The overall AOX reduction was 46.3 ± 3.3%. The concentration of AOX compounds in sludge was dependent on concentration of the same in influent; it was 2690 ± 969 and 7659 ± 750 mg/kg at moderate and high AOX load respectively. Although the concentration of AOX compounds in secondary sludge was high, ranging from 2000-8000 mg/kg, major mode of AOX removal was mineralization (~95 % of the AOX removal). During biological treatment, 43-51% reduction in AOX compounds was observed and rest (49-57%) compounds were released with treated effluent; only 1.6-2.3% AOX compounds were drained as adsorbed on waste activated sludge. AOX compounds bearing sludge has been classified as hazardous waste under Schedule-I of the Hazardous Waste (Management and Handling) Amendment Rules, 2008, Govt. of India.

Conclusions

At higher AOX load (71±16 g/m^3/day) there was less biomass yield, 0.18±0.06 g/g of CODs removal and at low to moderate AOX load of 14-33 g/m^3/day, biomass yield was 0.29±0.05 g/g of CODs removal. Initially there was a change in morphology of sludge and motility of higher organisms was affected at higher AOX load. After a run of 20-30 days the organisms started to adapt with the changed conditions and there was formation of dense flocs; higher organisms also turned into active mode at higher AOX load. Moderate concentration and load of AOX compounds did not disturb the performance and sludge morphology of reactor. The activated sludge process can be operated at a high AOX load of 83-88 g/m^3/day with no appreciable change in reduction of AOX but with a compromise in COD reduction. During biological treatment 43-51% AOX compounds were removed; the major mode of AOX removal was mineralization (95-97%) and 3-5 % of the same was adsorbed on waste activated sludge.

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