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Assessment of water pollution in different bleaching based paper manufacturing and textile dyeing industries in India

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Abstract Paper industries using different raw materials such as hard wood, bamboo, baggase, rice-straw and waste papers and bleaching chemicals like chlorine, hypochlorite, chlorine dioxide, hydrogen peroxide, sulphite and oxygen were studied to estimate organic pollution load and Adsorbable Organic Halides (AOX) per ton of production. The hard wood based paper industries generate higher Chemical Oxygen Demand (COD) loads (105–182 kg t^{-1}) and Biochemical Oxygen Demand (BOD) loads (32.0–72 kg t^{-1}) compared to the agro and waste paper based industrial effluents. The bleaching sequences such as C–EP–H–H, C–E–H–H, C–E–Do–D1 and O–Do–EOP–D1 are adopted in the paper industries and the molecular elemental chlorine free bleaching sequence discharges low AOX in the effluent. The range of AOX concentration in the final effluent from the paper industries was 0.08–0.99 kg t^{-1} of production. Water consumption was in the range of 100–130 m^3 t^{-1} of paper production for wood based industries and 30–50 m^3 for the waste paper based industries. Paper machine effluents are partially recycled after treatment and pulp mill black liquor are subject to chemical recovery after evaporation to reduce the water consumption and the total pollution loads. Hypochlorite bleaching units of textile bleaching processes generate more AOX (17.2–18.3 mg l^{-1}) and are consuming more water (45–80 l kg^{-1}) whereas alkali peroxide bleaching hardly generates the AOX in the effluents and water consumption was also comparatively less (40 l kg^{-1} of yarn/cloth).

Keywords Paper industry · Textile dyeing industry · Bleaching processes · AOX · Chlorine · Water pollution

Introduction

Bleaching process is one of the major water polluting sources in pulp and paper manufacturing and textile dyeing industries. The average wastewater generation is in the range of 150–250 m^3 t^{-1} of paper/pulp and 80–120 m^3 t^{-1} of textile products. Soluble organics of raw materials and chemicals used in the processes contribute higher Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand and Adsorable Organic Halides (AOX) and Total Dissolved Solids (TDS). Effect of the dissolved organics and dissolved inorganic salts on aquatic environment has been well documented whereas introduction of AOX is a recent subject. AOX are a family of chemicals produced when the halogens such as chlorine, bromine and partially iodine react with organic matter. The halogens bind with organic compounds to form more stable organic halides that consist of hundreds of individual chemicals with a unique property of adsorption on activated carbon. Presence of AOX in

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the environment is a worldwide concern as they are persistent, and reported to be carcinogenic, bioaccumulative and also have adverse effect on the flora and fauna in the aquatic system. When the AOX chemicals are concentrated and released in large quantities to receiving water bodies such as lakes and rivers they can cause chronic toxicity to the aquatic organisms. Chronic or sub-lethal effects may affect an organism's size, growth rate, sexual maturation or ability to reproduce (Colodey and Wells 1992; Tarkpea et al. 1999).

Demand of paper is steeply increasing and now it exceeds 330 million tons per annum all over the world (PPI 2005). Paper is a cellulose fiber obtained after digestion of wood using alkali/sulphide, which requires bleaching to impart whiteness to preparation of better quality paper. The bleaching agent conventionally used is elemental chlorine, which is reasonably cost-effective but it causes group of toxic compounds in effluents. Chloroligno sulphonic acids, low chlorinated Poly Aromatic Hydrocarbons (PAH) and dioxin in the level of 3–120 pg l^{-1} tetrachloro dibenzo dioxin (TCDD) and 7–2,200 pg l^{-1} tetrachloro dibenzo furan (TCDF) have been identified by various researchers (Harriman Chemsult 1989; Loon 1992) in paper industries effluents. A series of compounds such as methyl-, polymethyl-, and alkyl polychlorodibenzofuranes were also determined in the wastewaters and sludges of paper industries by Buser et al. (1989). As the application of chlorine leads to generation of more toxic compounds, alternative agents such as chlorine dioxide, hydrogen peroxide, elemental oxygen and ozone are used in India. The discharge limit for AOX in case of large paper industrial effluents notified as 1.0 kg per ton of paper production (CPCB 2003a, b). Textile industry is one of the oldest industries in the world and there are about 10,000 garment manufactures and 2,100 bleaching and dyeing industries in India (Annual Report Ministry of Textiles 2004). In textile industries bleaching and coloring are the major wet processes with wastewater generation of about 40–120 m^3 t^{-1} of production. Bleaching is employed to oxidize impurities like lignin, pectin and gum to make the yarn/cloth white and also favorite unit for dyeing of cloths. It is carried out either by using hypochlorite or alkali/hydrogen peroxide. It consumes more water and most of them are discharged as wastewater. In India, limit for AOX discharge by the textile industries is yet to be fixed whereas in European countries, the limit in wastewater should not exceed 1 mg l^{-1} for discharge into surface water and municipal treatment plants (Helcom land 2001).

Despite the adverse effects of AOX on human health and the environment, removal of the same from paper industries waste waters has been studied by different authors and found in vain. The removal of AOX averaged 46% for the two-stage activated sludge systems and 34% only in aerated stabilization pond (Bryant et al. 1992). Anaerobic treatment of effluent of a pulp bleaching plant has been studied with the focus to remove the adsorable organic halogens and reports 50% only at a hydraulic retention time (HRT) of 15 h (Yu and Welander 1994). In view of these reasons, cleaner technologies are being followed in pulp and paper industries and in bleaching operations of textile sectors through out the world to reduce the discharge of AOX. As per the directions of statuary bodies or as a commitment by the exporting agency, the bleaching operations are converted to non-elemental chlorine processes. The main objective of the present study is to quantify AOX generation and organic loads with reference to the different bleaching operations and raw materials used at various paper manufacturing and textile industries and the results are compared.

Experimental work

Eight paper industries and three textile bleaching units were selected for collection of information such as, production capacity, raw materials and bleaching chemicals used, water consumption, wastewater generation and available treatment technologies (Table 1). The wastewaters from the above industries were also collected to determine water pollutants and AOX contents during the studied period (2003–2005). Composite samples (8 h)/grab samples from bleaching units, inlet and outlet of Effluent Treatment Plants (ETP) of paper industry have been collected and analyzed for general and specific parameters (APHA 1998; CPCB 2001). The parameters such as pH and total residual chorine (TRC) were determined in the field and other general parameters were analysed in laboratory. A known quantity of effluents (250 ml) was taken separately in amber bottles, treated with Na_2SO_3 for removing residual chlorine, if any, acidified using AR grade HNO_3 and preserved at icebox till analysis of AOX. Further samples (1,000 ml) collected separately

Table 1 Paper manufacturing and textile dyeing industries monitored

Industry	Raw material used	Current production ($t\ d^{-1}$)	Bleaching steps	Water required ($m^3\ d^{-1}$)	Wastewater generation ($m^3\ d^{-1}$)
Paper industry unit-I	Hard wood (>90%) and WP	520 (90)	C–EP–H–H	71,820	64,200
Paper industry unit-II	Hard wood and bamboo (80%), IP	330 (30)	C–EP–H–H	35,600	33,540
Paper industry unit-III	Hard wood and bamboo	299	C/D–EP–Do–E–D1	38,500	34,455
Paper industry unit-IV	Hard wood and bamboo, (>90%), IP and WP	295 (50)	O–Do–EOP–D1	55,000	38,000
Paper industry unit-V	Paddy straw, bagasse and WP	80 (20)	C–E–H–H	11,000	7,894
Paper industry unit-VI	Paddy straw and WP	30 (10)	C–E–H/ C–H–H	3,000	2,150
Paper industry unit-VII	Rice straw, kraft pulp and WP	135 (70)	C–E–H	10,500	8,450
Paper industry unit-VIII	WP	70	H	3,200	2,700
Textile bleaching-I	Cloth	0.40	H	34	32
Textile bleaching-I	Cloth	0.70	H	34	32.00
Textile bleaching and dyeing unit-III	Cloth	0.42	P	17.5	17

C Chlorine, *EP* Extraction with alkali, *H* Hypochlorite, *D* Chlorine dioxide, *EOP* Extraction with oxygen and peroxide, *P* Peroxide. Values given in brackets are waste paper (WP)/imported pulp (IP).

for heavy metals were analysed having preserved with nitric acid and concentrated by evaporation before analysis. The instrument GBC Atomic Absorption Spectrophotometer was used for analysis of heavy metals.

AOX was analysed by adding 100 ml of diluted sample with $NaNO_3$ solution at pH 2.0 and 50 mg of activated carbon following batch mode adsorption for 1 h and filtered using polycarbonate filters. The folded polycarbonate filters burnt at high temperature (950°C) and converted into hydrogen halides. These product gases are dehydrated and cleaned in a scrubber and are introduced into the titration cell and are subsequently determined by volumetric titration with Ag NO_3 using Metrohm AOX Analyzer (ISO 1989). All the glassware and chemicals used were of borosil glass and Analytical Grade (AR/GR), respectively. Analysis was done in duplicate and the experimental error was with in 5%.

Results and discussion

Paper manufacturing process and wastewater generation in India

Paper and its products are cellulose materials derived from forest-based or agro-based raw materials such as wood, bamboo, bagasse and straw by processing at pulp mill, bleaching unit and paper machine of pulp and paper industries. The raw materials contain 50–54% of cellulose and the rests are organics like hemicelluloses, phenolic compounds, lignin and other extractives like fats, terpenes and resins. The compounds other than cellulose are removed in industry by chipper, digester and bleaching and finally made into paper sheet in the paper machine. The wood is made into small pieces at wet condition in the chipper and are conveyed to digester house for cooking using white liquor (10% NaOH and Na_2S) at 160°C for 4 h. The contents are separated to unbleached pulp and black liquor. The black liquor is recycled as white liquor produced by concentrating in multistage evaporators, burning at boiler and treating with lime. The separated pulp is bleached by multi-stage process using different bleaching agents and subsequent washings after every process. Elemental chlorine, alkali extraction, hypochlorite, chlorine dioxide, elemental oxygen and alkali hydrogen peroxide are used in the bleaching operations. The pulp is cleaned with water and made into mat consisting of fibers deposited at various angles but essentially in the plane of sheet wire mesh. The water contents are drained out using press. The chemical requirements are in the range of 135–270 kg NaOH and 80–90 kg of Na_2S and $NaCO_3$ per ton of pulp. Some losses due to leakage and washings are compensated by make up chemicals. During chipping, bleaching and washings large amount of water is used and discharged as wastewater. About 40–45% of raw materials are recovered as cellulose fibers and the remaining parts are discharged into wastewaters. The wastewater generation per ton of products is varying and that too depending upon the water availability and water-recycling techniques followed. In the earlier days, as the black liquor, washing wastewater and paper machine wastewater were discharged into the effluent stream, the water consumption had been 250–300 m^3 per ton of production. Off late, most of the industries have reduced water consumption and wastewater generation up to 130 m^3 t^{-1} by recycling the black liquor from pulp mill for chemical recovery and reusing paper machine wastewater in pulp mill after imparting desired treatment. The wastewater generation is also depending on the quality of raw materials used. The pulp stocking and paper production capacity of India is estimated to be 6.4 million tons per annum from 406 industries out of that only 37% are wood based and 63% are non-wood based such as agro based, waste paper and imported pulps (CPCB 2003a, b). Rice straw is pulped by soda alkali lye and hot stream then bleached using alkali peroxide followed by sulphite bleaching. Waste papers are crushed, de-inked by air floatation and bleached by either using hypo chlorite or hydrogen peroxide/sulphite solutions. The washings waters are discharged as effluents.

Wastewater treatment in the paper industries in India

Wastewaters are generated from pulp mill, bleaching units and paper machines besides utility sections. Paper machine wastewater contains low dissolved organics and more pulp fiber, which could be recycled after settling down the suspended fibers. Pulp mill wastewater with high BOD and TSS is treated by Activated Sludge Process (ASP) either together with paper machine effluent or alone after primary clarification. The sludges generated are in the range of 3–40 t d^{-1}. Degradable organic materials are removed in the biological process and non-degradable colored effluents are discharged. As the final effluents contain high color and considerable quantity of AOX are not allowed for discharge into river and to be used for agricultural purpose. The industries covered under the study are following the treatment explained above except the unit I, which has aerated lagoon instead of ASP. The provided treatments are attaining the standard limits of 100, 30 and 250 mg l^{-1} of TSS, BOD and COD, respectively (CPCB 2000). Moreover for high color and AOX concentration should further be removed before disposal. The schematic diagram of the available effluent treatment plant is presented in Fig. 1. Post treatment with activated carbon (after biological treatment) of wastewater from a paper and paperboard industry was recently investigated to remove refractory

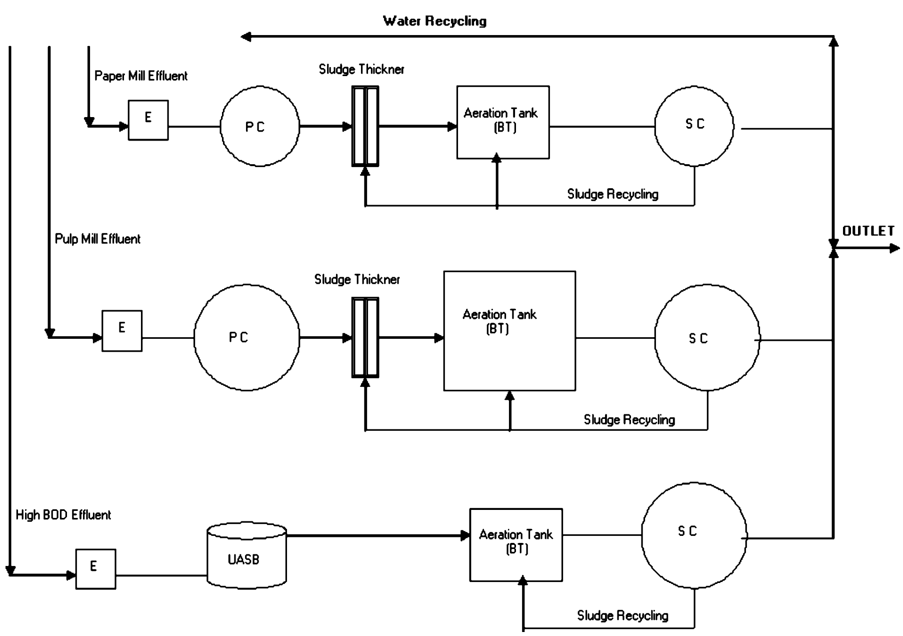

Fig. 1 Schematic diagram of integrated wastewater treatments followed in pulp and paper industries. *E* equalization, *PC* primary clarifier, *BT* biological treatment, *UASB* up-flow anaerobic sludge blanket, *SC* secondary clarifier

Table 2 Characteristics of wastewaters of paper industries using hard woods and C–EP–H–H, C–E–Do–D1 and O–Do–EOP–D1 bleaching sequence

Parameter	Paper industry-I		Paper industry-II		Paper industry-III		Paper industry-IV	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
pH	6.78	7.12	7.3	7.9	6.55	6.87	8.02	7.4
Elect. conductvity, mS cm^{-1}	1.7	1.4	2.1	1.9	1.8	2.1	1.8	1.6
TSS, mg l^{-1}	580	124	520	112	236	64	456	86
TDS, mg l^{-1}	1,574	978	1,538	1,114	1,728	1,268	1,260	840
COD, mg l^{-1}	1,472	456	1,522	371	1,004	400	819	136
BOD, mg l^{-1}	580	60	600	100	280	47	250	30
Hardness as CaCO3, mg l^{-1}	–	2,576	700	550	565	423	164	178
Chloride, mg l^{-1}	–	124	–	356	569	448	199	155
Sulphate, mg l^{-1}	–	143	–	95	124	168	168	190
Phosphate, mg l^{-1}	–	0.05	1.3	0.4	0.34	1.48	3.16	1.29
TKN, mg l^{-1}	–	2.58	2.69	1.60	–	–	–	–
AOX, mg l^{-1}	17.2	8.05	16.90	7.77	10.9	6.1	1.57	0.64

–, not analysed.

organics and color. However, the cost of transportation and regeneration was concluded to be very high (Temmink and Grolle 2005).

Characterization of paper industry effluents before and after treatments

The characteristics of wastewaters of Paper units I and II, which are wood based industries adopting C–EP–H–H bleaching are presented in the Table 2. The water quality of unit-I is slightly exceeding the standard in terms of TSS, COD and COD, as the treatment methods are not adequate. The unit has already started up-gradation of the effluent treatment plant. Another wood based paper industry Unit-II is also exceeding the effluent quality standard values in terms of TSS, BOD and COD. Segregation of high BOD effluent and construction of Up-flow Anaerobic Sludge Blanket (UASB) has already been started in the industry. Characteristics of effluents of the industries unit-III and unit-IV which are using wood, wastepaper and imported pulp are presented in Table 2. Due to application of oxygen de-lignifications and less/free elemental chlorine bleaching, the organic loads generated are comparatively lesser than the other two units (Figs. 2 and 3).

The characteristics of rice straw based and wastepaper based paper industries industries are summarized in the Table 3. Unit-V has no chemical recovery system and the black liquor was also mixed with effluents whereas the other rice straw based units' segregates the black liquor and stored into lagoons. The variations in the COD and BOD load before and after treatment are shown in the Figs. 2 and 3. Unit-VI was producing about 20 t d^{-1} of unbleached paper for making packaging materials. Waste papers were bleached by sulphite bleaching after alkali peroxide treatment and

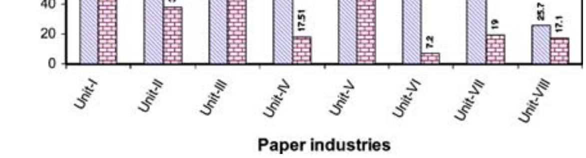

Fig. 2 Reduction of COD loads due to imparting treatments for paper manufacturing industries wastewaters

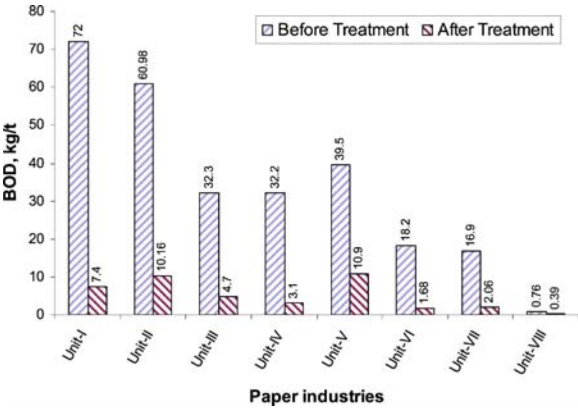

Fig. 3 Reduction of BOD loads due to imparting treatments for paper manufacturing industries wastewaters

thus the sulphate concentration (350 mg l^{-1}) was higher in the effluents and AOX (0.76 kg t^{-1}) was low. The more chloride and sulphate contents in the wastewaters are due to application of their compounds in the pulp manufacturing process. The concentration of heavy metals viz Pb, Cr, Cu, Zn and Co are found low both in the untreated (0.002, 0.02, 0.02, 0.04 and BDL mg l^{-1}) and treated (BDL, BDL, 0.01, 0.13 and BDL mg l^{-1}) effluents of wastepaper recycling units. Significant concentration of Fe (0.69 and 0.25 mg l^{-1}) and Mn (0.13 and 0.11 mg l^{-1}) were found in the wastewaters before and after treatments, respectively, which might have been leaching of the ink and printed materials of waste papers. Cadmium was found to be below detection limit (BDL) in the untreated and treated effluents.

In the earlier days water requirement per ton of paper production was 250–440 m^3 (CPCB 1991) whereas now it has been reduced to 71–161 m^3 by recovering and regeneration of black liquor and waste minimization by reusing paper machine wastewater in pulp mill washings etc. The commonly used raw materials such as bamboo, casuriana, eucalyptus bagasse have different lignin contents. Usage of low lignin content raw material, waste paper and imported pulp in the paper machine had reduced the water consumption thence pollution load. Efficiencies of the available treatments in removal of BOD and COD in the studied paper industries are presented in the Fig. 5. The percentage removal of COD and BOD were in the range of 30–82 and 45–90, respectively, for the studies paper industries.

AOX generation and discharge in paper industries

Bleaching operations are main sources of AOX generation. Three types of bleaching chemical combinations such as chlorine and hypo, chlorine and chlorine dioxide and chlorine dioxide and oxygen are followed for bleaching the pulp in the industries. The AOX concentrations in the bleaching unit's effluents were 63, 18.71 and 11.2 mg l^{-1}, respectively. AOX formation in Unit

Table 3 Characteristics of wastewaters of paper industries using agro-based and waste paper and chlorine bleaching

Parameter	Paper industry-V		Paper industry-VI		Paper industry-VII		Paper industry-VIII	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
pH	9.04	6.40	6.51	7.22	7.36	7.51	6.8	7.0
Elect. conductvity, mS cm^{-1}	1.9	1.5	2.3	2.5	2.4	2.3	2.3	2.3
TSS, mg l^{-1}	1,027	280	600	104	370	24	370	60
TDS, mg l^{-1}	1,750	1,168	1,704	1,710	1,639	1,716	1,822	1,678
COD, mg l^{-1}	1,020	670	780	103	805	303	667	444
BOD, mg l^{-1}	400	110	260	24	270	33	160	89
Total Hardness as CaCO3, mg l^{-1}	788	385	951	894	712	730	1,047	990
Ca– Hardness as CaCO3, mg l^{-1}	663	316	782	811	683	678	1,000	900
Chloride, mg l^{-1}	410	265	325	315	450	440	597	587
Sulphate, mg l^{-1}	120	162	281	593	251	350	34	47
AOX, mg l^{-1}	14.15	6.73	16.65	5.88	12.28	6.35	5.84	4.96

IV is lower than other, as such applies non-residual chlorine free bleaching and using more imported pulp and waste paper. Application of ClO_2 has an added advantage of higher pulp brightness, improved fiber strength and lower the chemical consumption besides low generation of AOX (Johnston et al. 1996). Figure 4 shows the comparison of AOX loads before and after treatment for different paper manufacturing industries with varying raw materials and bleaching sequences. AOX generation in elemental chlorine bleaching and partial ClO_2 bleaching and elemental chlorine free bleaching processes is 2, 1.25 and 0.13 kg t^{-1}, respectively. Unit I and II are mostly forest based raw materials and using elemental chlorine and in the Units III the raw materials are forest and partially following ClO_2 bleaching unit IV the entire belching operation is residual chlorine free. Units V and VI maximum usage is rice straw and partially waste paper. In Unit VII maximum and purchased pulp/wastepaper less quantity of rice straw are pulped and bleached. Unit VIII uses cent per cent waste paper and hypochlorite bleaching is adopted. Present practice of wastewater treatment (Primary settling followed by ASP and clarification) removes about 13–70% of AOX (Fig. 5) after treatment and similar observation was made in earlier studies also (EPA 2002). Following treatment with a bench scale activated sludge system, approximately 70% of AOX from laundry wash water and 54% of AOX from domestic wastewater have been removed (Say Kee Ong et al. 1995). Currently available treatments are not suitable for quantitative removal of AOX in the effluent and hence various cleaner technologies are adopted. Most of the industries have completely/

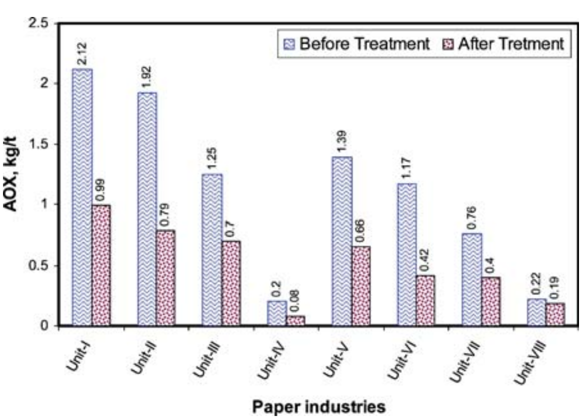

Fig. 4 Reduction of AOX loads due to imparting treatments for paper manufacturing industries wastewaters.

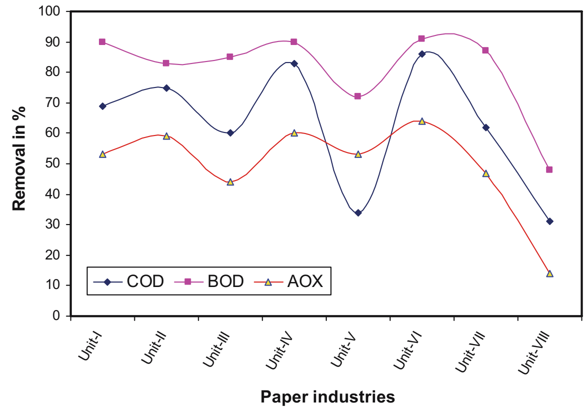

Fig. 5 Removal of COD, BOD and AOX after treatments in paper manufacturing industries wastewaters

partially shifted over to non-elemental chlorine bleaching process to reduce AOX discharge (Table 4).

Process in textile industries wastewater production

Natural (cotton, silk wool etc.,) and man made fibers (polyester and nylon) are the raw materials processed in the textile units by spinning, sizing, desizing, weaving, bleaching and dyeing for manufacturing of cloths/garments. Bleaching and dyeing processes generate voluminous quantity of wastewaters with high TDS, hardness and AOX. Tirupur, one of the most important industrial towns in Tamil Nadu, India has clusters of large, medium and small scale bleaching and dyeing industries. Presently 712 numbers of dyeing and bleaching industries with wastewater generation of about 84,000 m^3 d^{-1} are in operational. Among the small scale units, two following hypochlorite bleaching and one with peroxide bleaching were studied for analysis of AOX, physicochemical parameters and heavy metals in the bleaching and final effluents.

Bleaching is batch process initially the yarn/cloth are made into wet able by mixing with 0.5% of wetting oil to 100 kg of material and 800 l of water and the water is drained out as wastewater. Then bleaching with 10% bleaching solution, followed by washing, neutralization and washings are carried out and 15–16 m^3 of water is used for bleaching of 200–350 kg of cloth. In average 45–80 l of wastewater is generated per kg of cloth for hypo bleaching and the time consumed is about 8–10 h per a batch. In peroxide bleaching the bleaching operations are carried out by wetting of cloth, oxidation with H_2O_2, soda ash and soda at 100°C, cold washing

Table 4 Comparison of bleaching chemicals applied and AOX discharge per ton of paper production

Paper manufacturing industry	Bleaching chemicals	kg t^{-1} of paper	AOX per ton of paper produced	AOX per ton of bleached pulp	Wastewater per ton of total product
Paper industry unit-I	Chlorine	45	0.99	1.67	124
	Peroxide	14			
	Chlorine dioxide	–			
Paper industry unit-II	Chlorine	10.5	0.79	0.87	102
	Peroxide	5.0			
	Chlorine dioxide	–			
Paper industry unit-III	Chlorine	44	0.70	0.71	115
	Peroxide	–			
	Chlorine dioxide	8			
Paper industry unit-IV	Oxygen	9.0	0.08	0.10	129
	Peroxide	4.0			
	Chlorine dioxide	27.5			
Paper industry unit-V	Chlorine	80	0.66	0.89	99
	Hypochlorite	90			
Paper industry unit-VI	Chlorine	70	0.42	0.63	72
	Hypochlorite	110			
Paper industry unit-VII	Chlorine	80	0.40	0.83	63
	Hypochlorite	120			
Paper industry unit-VIII	Hypochlorite	16	0.19	0.19	39

Table 5 Characteristics of textile bleaching and dyeing industries wastewaters

Parameters	Textile bleaching unit-I		Textile bleaching unit-II		Textile bleaching and dyeing unit-III	
	Bleaching effluent	Treated effluent	Bleaching effluent	Treated effluent	Bleaching effluent	Bleaching & dyeing effluents (After treatment)
pH	2.67	8.05	7.27	7.39	10.28	8.9
EC, mS cm^{-1}	13.3	10.0	11.0	11.2	5.1	7.5
T. residual chlorine, mg l^{-1}	4.2	2.6	21.0	2.8	BDL	BDL
Total suspend solids, mg l^{-1}	10	25	309	10	220	BDL
Total dissolved solids, mg l^{-1}	7,405	6,369	9,324	8,688	4,667	5,573
BOD, mg l^{-1}	173	100	145	90	1,650	195
COD, mg l^{-1}	525	298	455	298	2,318	439
Total hardness, mg l^{-1} as CaCO3	2,670	1,620	5,250	4,400	180	1,350
Ca-hardness, mg l^{-1} as CaCO3	1,900	840	3,400	3,000	28	1,260
Chloride, mg l^{-1}	2,778	2,803	2,779	2,921	332	1,306
Sulphate, mg l^{-1}	1,942	473	2,365	1,866	192	168
T KN, mg l^{-1}	8.2	5.0	27.8	4.7	29.5	7.3
Phosphate, mg l^{-1}	13.97	0.01	0.4	BDL	0.12	BDL
Na, mg l^{-1}	2,670	1,620	1,000	1,100	1,500	1,850
Cu, mg l^{-1}	0.07	0.05	0.06	0.09	0.05	0.06
Ni, mg l^{-1}	0.06	0.07	0.11	0.12	0.03	0.11
Zn, mg l^{-1}	0.02	0.11	0.03	0.01	0.23	0.03
Pb, mg l^{-1}	BDL	BDL	0.01	BDL	0.02	BDL
Cd, mg l^{-1}	BDL	BDL	BDL	BDL	BDL	BDL
Cr, mg l^{-1}	BDL	BDL	BDL	0.12	0.04	0.08
AOX, mg l^{-1}	18.03	13.34	17.14	13.05	BDL	0.40

EC Electrical conductivity, *BDL* Below Detection Limit.

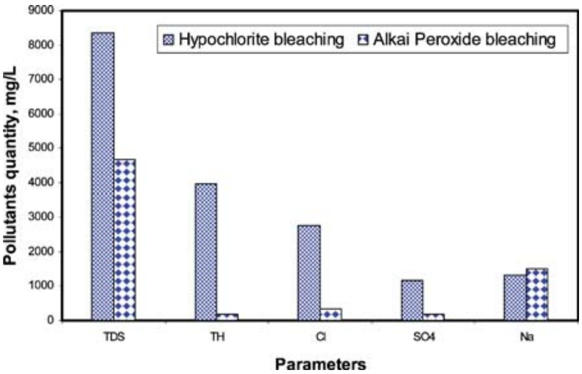

Fig. 6 Comparison of wastewater quality of hypochlorite bleaching and peroxide bleaching operations in textile industries

and acetic acid washing followed by cold washings. Entire process takes only 4–6 h and volume of wastewater generation is also less compare to hypo bleaching. Recently attempt was also made to bleach the colored compounds that chemically bound on cellulosic fabrics by a selective photolysis of the colored compounds by a KrF excimer laser (248) in the presence of $NaBH_4$ with discharge of AOX free wastewater and one min irradiation time (Ouchi et al. 2001).

Characterization of textile effluents (bleaching and dying)

The characteristics of the bleaching and dying processes wastewaters are presented in the Table 5. The wastewaters consist of more TDS would deteriorate the quality of receiving water resources. Addition of calcium and sodium hypochlorite and caustic soda for bleaching action and washings followed by acid neutralization contributes more TDS and high EC in the effluents. Neutralization and flocculation increase in the parameters has occurred due to the dissolution of impurities in the lime and flocculent. Considerable reduction has been achieved in TSS, BOD and COD. As the Electrical Conductivity and TDS are very high, the treated water is not suitable for irrigation. However the heavy metals contents are less than the prescribed limit for effluents discharge. Formation of AOX generation is more in the hypo bleaching process compared to the peroxide bleaching (Fig. 7). AOX generation in the effluents is more compare to the standard prescribed by European countries. In addition to AOX free effluent, the alkali peroxide bleaching generates less TDS and hardness in the effluents (Fig. 6). Higher BOD and COD may be contributed due to the application of acetic acid in the process. The followed physical chemical treatment has less effect on reduction of AOX (Fig. 7). The quantities of AOX discharged from the hypochlorite bleaching textile units are higher than the prescribed limit of 1.0 mg l^{-1}.

Conclusion

Characteristics of wastewaters before and after treatments and AOX formation in wastewaters per ton of paper produced are significantly varying from industry to industry. Application of different raw materials and bleaching agents and use of unbleached/purchased pulp are reasons for reduction in pollution loads. Currently adopted treatments reduce the organics load considerably but the AOX reduction has been recorded to be 10–65%. Quantum of AOX is more when elemental chlorine bleaching is adopted whereas application of chlorine dioxide reduces the AOX generation. Even when similar bleaching processes are followed the AOX concentration is varying, as the quality of raw materials used and treatment efficiency are different in different paper mills. High AOX contents are recorded in the effluents of agro-based paper industries. Peroxide bleaching in textile bleaching industry generates AOX free and low volume effluent with lower bleaching time. The treatment techniques in regard to the hypochlorite bleaching are found insignificant in removal of AOX.

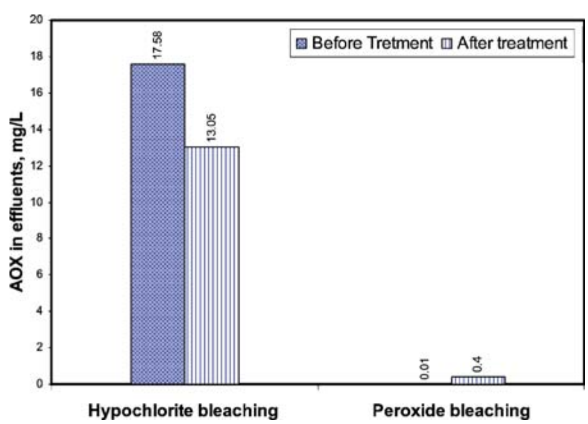

Fig. 7 Comparison of AOX formation and discharge in the effluents of hypochlorite bleaching and peroxide bleaching operations in textile industries

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Appendices

APHA	American Public Health Association
ISO	International Standard Organization
EC	electrical conductivity
TDS	total dissolved solids
TRC	total residual chlorine
TSS	total suspended solids
BOD	biochemical oxygen demand
COD	chemical oxygen demand
TKN	total Kheldhal nitrogen
AOX	adsorable organic halides
AR	analytical grade
ETP	effluent treatment plant
ASP	activated sludge process
UASB	up-flow anaerobic sludge blanket
TCDD	tetra-chloro dibenzo dioxin
TCDF	tetra-chloro di-benzo furan
C–EP–H–H	chlorine bleaching–alkali peroxide extraction–hypo bleaching–hypo bleaching
C–E–H–H	chlorine bleaching–alkali extraction–hypo bleaching–hypo bleaching
C–E–Do–D1	chlorine bleaching–alkali extraction–ClO_2 bleaching–ClO_2 bleaching
O–Do–EOP–D1	oxygen–ClO_2 bleaching–alkali peroxide extraction–ClO_2 bleaching

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