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Pollution Prevention in the Pulp and Paper Industries

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1. Introduction

Pulp and paper industry is considered as one of the most polluter industry in the world (Thompson *et al.*, 2001; Sumathi & Hung, 2006). The production process consists two main steps: pulping and bleaching. Pulping is the initial stage and the source of the most pollutant of this industry. In this process, wood chips as raw material are treated to remove lignin and improve fibers for papermaking. Bleaching is the last step of the process, which aims to whiten and brighten the pulp. Whole processes of this industry are very energy and water intensive in terms of the fresh water utilization (Pokhrel & Viraraghavan, 2004). Water consumption changes depending on the production process and it can get as high as 60 m^3/ton paper produced in spite of the most modern and best available technologies (Thompson *et al.*, 2001).

The wastewaters generated from production processes of this industry include high concentration of chemicals such as sodium hydroxide, sodium carbonate, sodium sulfide, bisulfites, elemental chlorine or chlorine dioxide, calcium oxide, hydrochloric acid, etc (Sumathi & Hung, 2006). The major problems of the wastewaters are high organic content (20-110 kg COD/air dried ton paper), dark brown coloration, adsorbable organic halide (AOX), toxic pollutants, etc.

The environmental problems of pulp and paper industry are not limited by the high water consumption. Wastewater generation, solid wastes including sludge generating from wastewater treatment plants and air emissions are other problems and effective disposal and treatment approaches are essential. The significant solid wastes such as lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, wood processing residuals and wastewater treatment sludges are generated from different mills. Disposal of these solid wastes cause environmental problems because of high organic content, partitioning of chlorinated organics, pathogens, ash and trace amount of heavy metal content (Monte *et al.*, 2009).

The major air emissions of the industry come from sulfite mills as recovery gurnaces and burnes, sulfur oxides (SOx), from Kraft operation as reduced sulfur gases and odor problems, from wood-chips digestion, spent liquor evaporation and bleaching as volatile organic carbons (VOCs), and from combustion process as nitrogen oxidies (NOx) and SOx. VOCs also include ketone, alcohol and solvents such as carbon disulfide methanol, acetone and chlorofom (Smook, 1992).

Many kinds of the wastes as summarized above are generated from different processes. The amount, type and characteristics of these wastes are important to provide the best treatment technology. Physicochemical and biological treatment technologies are used extensively for the pulp and paper mills. The lab-scale and full-scale studies about sedimentation/floatation, coagulation and precipitation, adsorption, chemical oxidation and membrane filtration were carried out in the literature to examine physico-chemical approach (Pokhrel & Viraraghavan, 2004). Biological treatment both aerobic and anaerobic technologies are preferred for treatment of pulp and paper mills because of wastewater composition consisting of high organic compounds and economical aspects. Additionally, some fungi species are used to remove color and AOX from the effluents (Taseli and Gokcay, 1999). In some countries, tertiary treatment is applied to obtain discharge limits of regulations (Thompson *et al.*, 2001). Finally, the wide application in the full-scale plants for treatment pulp and paper mills is hybrid systems, which is combined physico-chemical and biological treatment alternatives (Pokhrel & Viraraghavan, 2004).

Disposal strategy of solid wastes generated from pulp and paper industry is varied depends on the country and the regulations obeyed. After sorting and handling, dewatering, thermal application such as combustion and anaerobic digestion to obtain energy and deposit in landfills are general applications. However, the solid wastes should be monitored after landfill deposition because of toxic characteristics of the compounds (Monte *et al.*, 2009).

Also gaseous pollutants are other environmental problems generated from pulp and paper industry. To minimize these pollutants, physico-chemical methods such as adsorption to activated coal filters absorption, thermal oxidation, catalytic oxidation and condensation have been widely used (Eweis *et al.*, 1998). In the last decade, low cost and effective trends have been developed to prevent the limitation of physico-chemical applications such as energy cost and generating secondary pollutants (Sumathi & Hung, 2006).

Waste minimization, recycle, reuse, and innovative approaches developed in last 10 years become more than an issue. In this chapter, waste characterization of this industry in terms of type and source with management approaches was discussed. Exemplary applications were presented. Finally 'state of the art' approaches for the environmental problems of this industry were argued.

2. Waste characterization and source

Pulp and paper industry is one of the most water and energy consuming industry in the world. This industry uses the fifth largest energy consumer processes; approximately 4% of total energy is used worldwide. Also during pulp and paper process, the important amount of waste is produced. It has been estimated that 500 million tons of paper and etc. per year will be produced in 2020. Three different raw materials are used in the pulp and paper industry as nonwood fibers and wood materials; soft and hard woods. Waste and wastewaters are generated from both of pulp and bleaching processes. Additionally, 100 million kg of toxic pollutants are released every year from this industry (Cheremisinoff & Rosenfeld, 2010).

2.1 Manufacturing technologies and process description

Pulping process is the first step of the production. The main steps of this part are debarking, wood chipping, chip washing, chip digestion, pulp screening, thickening, and washing. Mechanical and chemical operation processes in pulping are used in the worldwide. While mechanical processes involve mechanical pressure, disc refiners, heating, and light chemical processes to increase pulping yield; wood chips are cooked in pulping liquors at high temperature and under pressure in the chemical pulping processes. (Sumathi & Hung, 2006). Additionally, mechanical and chemical processes can be combined in some applications. The yield of mechanical processes is higher (90-95%) compared to chemical processes (40-50%). However quality of the pulp obtained from mechanical processes is lower and also the pulp is highly coloured and includes short fibers (Pokhrel & Viraraghavan, 2004). Therefore, chemical pulping carrying out in alkaline or acidic media is mostly preferred. In alkaline media generally referred as Kraft Process, the woodchips are cooked in liquor including sodium hydroxide (NaOH) and sodium sulfide (NaS_2). Mixture of sulphurous acid (H_2SO_3) and bisulfide ions (HSO_3^-) is used in acidic media named as sulfide process.

During the pulp processing, approximately 5-10% of the lignin comes from the raw materials cannot be removed and these are responsible from the dark colour of the end product. The production of white paper (pulp bleaching) includes five or optional six treatment steps with sequentially elemental chlorine (C1), alkali (E1), optional hypochlorite (H) stage, chlorine dioxide (D1), alkali (E2), and chlorine dioxide (D2). The general process steps are given in Figure 1.

2.2 Wastewater

Different pulping processes utilize different amount of water and all of these processes are water intensive. The quality of wastewater generated from pulping and bleaching is significantly distinctive because of the process and chemical types (Billings and Dehaas, 1971). Approximately 200 m^3 water are used for per ton of produced pulp and most of them are highly polluted, especially wastewater generated from chemical pulping process (Cecen *et al.*, 1992). Wood preparation, pulping, pulp washing, screening, washing, bleaching, paper machine and coating operations are the most important pollution sources among various process stages. Wastewaters generated from pulping stage include mostly wood debris, soluble wood materials, and also some chemicals from chemical pulping process. Bleaching process wastewater has a different quality. These wastewaters are not higher strength than pulping process wastewater, however they include toxic components.

Process steps and the generated wastewaters from these steps are given in Figure 2.

The wastewater characteristics and their strengths changed depending upon the pulping processing. Kraft process is widely used worldwide approximately 60% within all pulp production includes both mechanical and chemical pulping (Holmberg & Gustavsson, 2007). The regional or geographical distribution of the pulping processes is given in Table 1.

Region	Process Type	Pulp Production (million tons)					
		2004	2005	2006	2007	2008	2009
North America	Chemical wood pulp	59.6	59.1	57.3	55.6	54.8	48.6
	Mechanical wood pulp	16.3	16.2	15.3	14.4	13.6	11.7
	Total Production	75.9	75.3	72.6	70.0	68.4	60.3
Europe	Chemical wood pulp	26.8	25.9	27.5	27.3	32.4	29.5
	Mechanical wood pulp	11.5	11.2	12.4	12.1	14.3	11.9
	Total Production	38.3	37.1	39.9	39.4	46.7	41.4

Table 1. Pulp production in North America and Europe (Food and Agriculture Organization (FAO) Database, 2011)

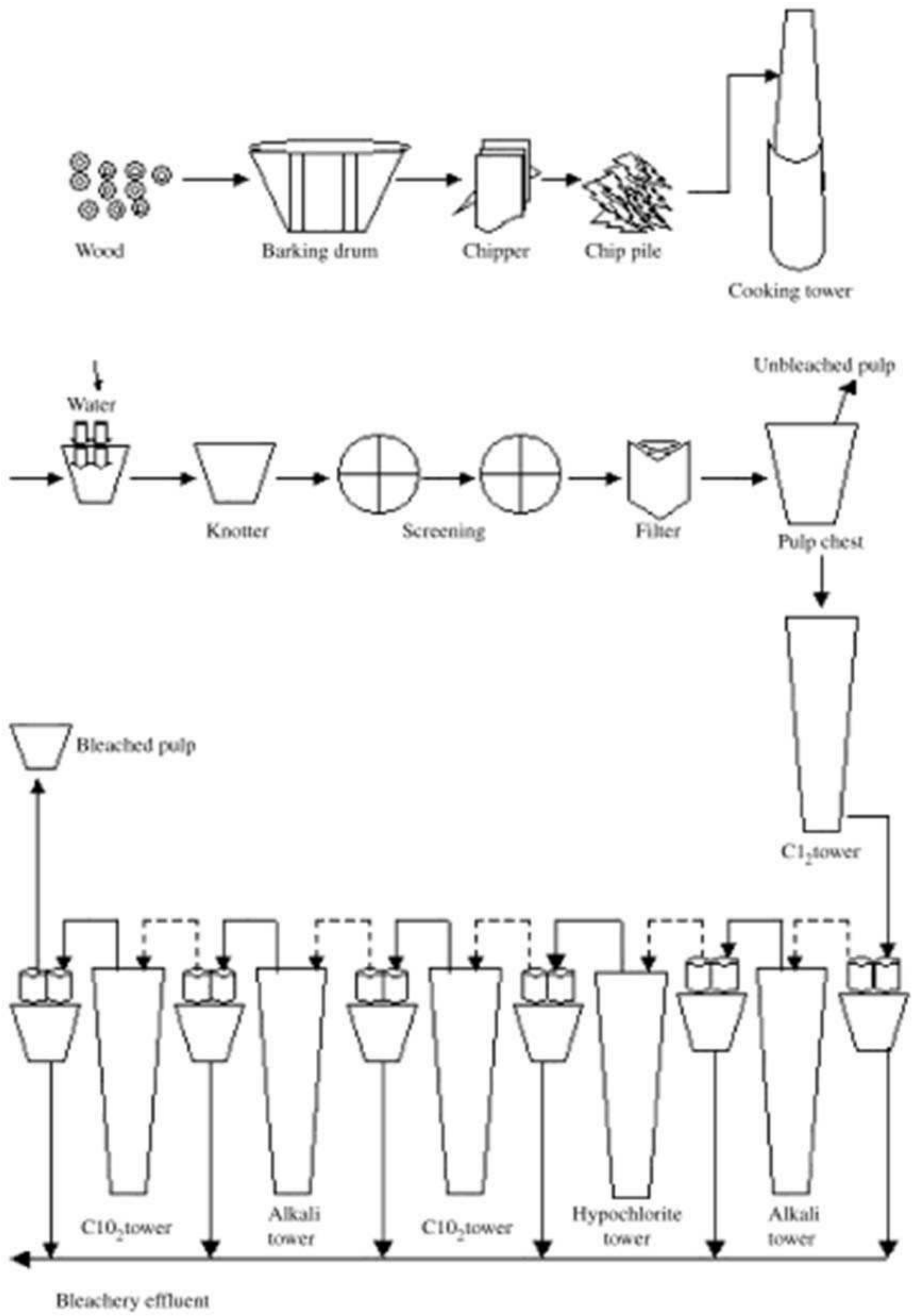

Fig. 1. Process scheme of a conventional pulp and paper industry (Sumathi & Hung, 2006)

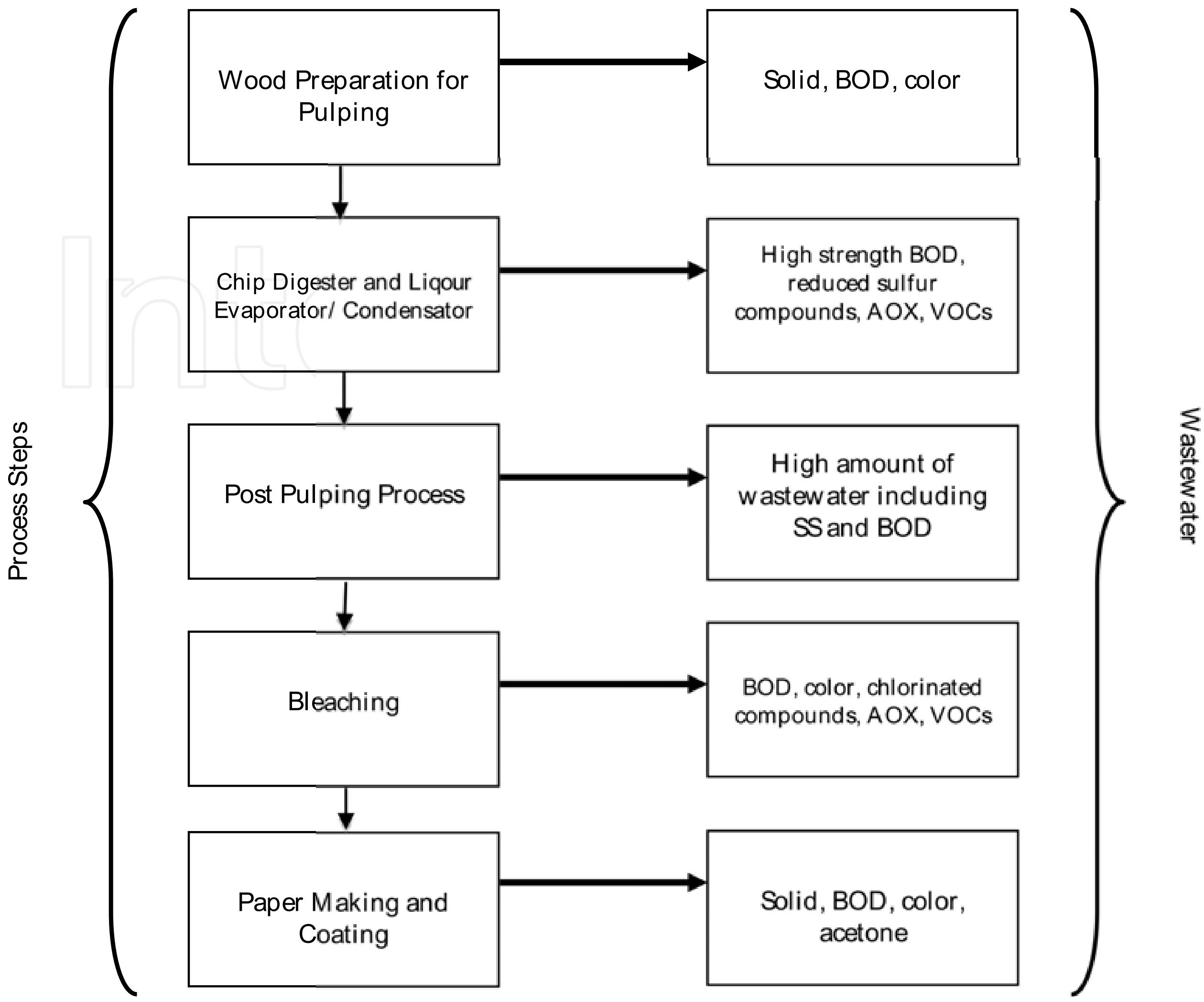

Fig. 2. Wastewater producing steps from pulp and paper mill (Smook, 1992; EPA, 1995)

The wastewaters generated from pulping process consist various wooden compounds such as lignin, carbohydrate and extractives and the treatment of these wastewaters by biologically is difficult. Addition of them, some toxic compounds such as resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, chlorinated resin acids, and others can exist in the wastewaters subjecting to the process (Pokhrel & Viraraghavan, 2004). The most important reaction in the bleaching step is oxidation of chlorine and the main problem about the wastewater content is chlorinated organic compounds or AOX (Sumathi & Hung, 2006).
The toxic effects of these by-products in the wastewaters on environment have been studied. Various studies reported that fish living in pulp and paper industry wastewaters have toxic/lethal effects on the daphnia, fish, planktons and other bioata in the receiving water bodies (Owens *et al.*, 1994; Hickey and Martin, 1995; Yen *et al.*, 1996; Vass *et al.*, 1996; Liss *et al.*, 1997; Lindstrom-Seppa *et al.*, 1998; Leppanen and Oikari, 1999; Johnsen *et al.*, 1998; Erisction and Larsson, 2000; Schnell *et al.*, 2000b; Kovacs *et al.*, 2002).

2.3 Solid and hazardous wastes

Wastewater and consequently solid wastes are the main environmental problem of the pulp and paper mills because this industry has a very water intensive production processes

(Cabral *et al.*, 1998; Thompson *et al.*, 2001). Solid wastes from pulp and paper industries are mainly treatment sludges, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, and wood processing residuals. Wastewater treatment sludges have a significant concern for the environment because of including chlorinated compounds (EPA, 2002). The characteristics of all solid waste generated from the pulp and paper mills are organic exception of boiler and furnace ash. The chemicals of the solid wastes are varied depends on the process type. Solid wastes, sources and qualities are given in Table 2.

Source	Waste Type	Waste Characteristic
Wastewater Treatment Plant	Sludge	Organic fraction consistes wood fibers and biosludge.
		Inorganic fraction consists clay, calcium carbonate, and other materials
		20-60% solid content
		pH≈7
Caustic Process	Dregs, muds	Green liquor dregs consisting of non-reactive metals and insoluble materials; lime mud
Power Boiler	Ash	Inorganic compounds
Paper Mill	Sludge	Colour waste and fibre clay including slowly biodegradable organics such as cellulose, wood fibres and lignin

Table 2. Solid waste types and sources from pulp and paper mills (EPA, 2002; Nurmesniemi *et al.*, 2007)

2.4 Gas emissions

Air pollutants and gas emissions are the other concern about the pulp and paper industry. The most important gas emission is water vapours. Additionally, particulates, nitrogen oxides, volatile organic compounds (VOCs), sulfur oxides and total reduced sulfur compounds (TRS). The gas emissions sources and types are given Table 3.

3. Waste management

During the pulp and paper production, high usage of water and energy results in large amount of waste generation like wastewater, solid waste and air emissions. Different types of waste are produced from different production steps and all these wastes pose important environmental problem. To solve this problem:

- Waste minimization can be done by using new and best available technologies.
- End-of-pipe treatment technologies should be used before the discharge and/or disposal.

Source	Major Pollutants
Chemical Pulping Process	VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone [MEK])
	Reduced sulfur compounds (TRS)
	Organo-chlorine compounds
Bleaching	VOCs (acetone, methylene chloride, chloroform, MEK, chloromethane, trichloroethane)
Wastewater Treatment Plant	VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)
Power Boiler	SO2, Nox, fly ash, coarse particulates
Evaporator	Evaporator noncondensibles (TRS, volatile organic compounds: alcohols, terpenes, phenols)
Recovery Furnace	Fine particulates, TRS, SO2, Nox
Calcining (Lime Kiln)	Fine and coarse particulates

Table 3. Air pollutants types and sources from pulp and paper mills (EPA, 2002)

3.1 Waste minimization

Modern waste minimization approach is by two means. This first way is chemical recovery and recycling. This system especially in chemical pulping process significantly reduces pollutants and additionally economical return is another important aspect. Chemical recovery is necessary because of the basic economic viability of the kraft process. According to EPA, all kraft pulp mills worldwide use chemical recovery systems. However, there is still no recovery system in some sulfite mills. Additionally, scrubber system particulate "baghouses" or electrostatic precipitators (ESPs) are often mill air pollution control components (EPA, 2002).

The second way to minimize waste production from pulp and paper mills is the application of best available techniques (BAT) according to the Integrated Pollution, Prevention and Control (IPPC) Regulation. An effective waste minimization method reduces cost, liability, regulatory burdens of hazardous waste management (Rouleau & Sasseville, 1996; Holland, 1997). Furthermore, hazardous waste generation can be reduced by waste management methods including:

- production, planning and sequencing
- process adjustment and/or modification
- raw material replacement
- housekeepingwaste segregation ans seperation
- recycling

The industries have developed and applied new technologies instead of conventional pulping and bleaching processes. Some examples of these new technologies are given below:

Organic Solvent Pulping: This process is more economical for small and medium scale plants for significant recovery and reuse of chemicals. In this process, organic solvent like ethanol, methanol, etc. are preferred. However, this process is more energy consumer than conventional ones (Sumathi & Hung, 2006).

Acid Pulping: Acetic acid under the high pressure is used for treating of wood chips. The disadvantage of this process is to loss of acid, however recovery is possible (Sumathi & Hung, 2006).

Biopulping: Microorganism or microbial enzymes such as xylanases, pectinases, cellulases, hemicellulases, ligninases, and their combination are used in the pulping process to improve the properties of pulp (Kirk *et al.*, 1996). Biopulping is preferred because:

- To reduce the chemical and energy utilization
- To reduce the pollutants
- To increase the yield and strength properties of pulp.

Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) Bleaching: Elemental chlorine has been used instead of chlorine dioxide and hypochlorite and oxygen, ozone, caustic soda, and hydrogen peroxide have been applied for TCF bleaching of Kraft pulps to reduce the chlorinated organic wastes (Sumathi & Hung, 2006).

Biobleaching: Fungal cells and or their enzymes are used for pretreatment of pulp. A number of studies showed that application of white rod fungi reduces the chemical dosage of bleaching and enhances the brightness of paper (Kirkpatrick *et al.*, 1990; Reid *et al.*, 1990; Daneult *et al.*, 1994).

Extended Delignification: Enhanced removal of lignin before bleaching step is the main concern of this method (Gullichsen, 1991; McDonough, 1992). It may be achieved by extended cooking, oxygenation, ozonation, and addition of chemical catalysts. Extended delignification positively affect on the bleach effluent quality parameters such as COS, BOD, color and AOX.

3.2 Treatment strategies

Although the best approach is to minimize the waste generation from the pulp and paper mills and to recycle, the treatment applications are still necessary. In this section, up-to date treatment technologies are given.

3.2.1 Wastewater treatment

End of the pipe pollution treatment strategies are necessary to provide the discharge limits. The general flow-chart of a typical wastewater treatment plant is given Figure 3.

The main treatment application for wastewater generated from pulp and paper process is primary and secondary treatment. However, tertiary treatment can be an obligation in future due to possible new legislations. The physicochemical step is rare at present.

Primary Treatment

In this step, the aim is to remove suspended solid such as bark particles, fiber, fiber debris, filler and coating materials and consequently organic materials. Primary clarification can also be achieved without sedimentation and flotation. However Thompson *et al.* (2001) mentioned that sedimentation is generally preferred application for the pulp and paper mills in UK and approximately 80% of suspended solid was removed successfully. Also

Rajvaid and Markandey (1998) reported 70-80% of removal in the sedimentation. Dissolved air flotation and filtration are the other option as primary treatment for pulp and paper mills.

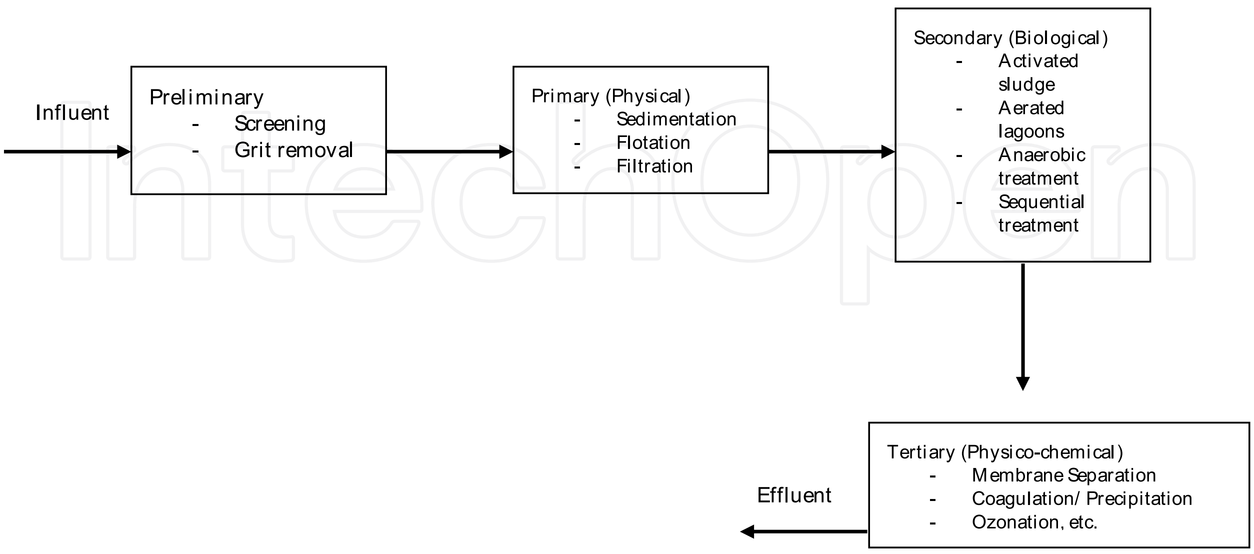

Fig. 3. Flow scheme of general wastewater treatment plant of pulp and paper industry

Secondary Treatment

Aerobic lagoons, activated sludge systems, anaerobic treatment and sequential biological treatment (aerobic-anaerobic or anaerobic-aerobic) are the most common biological treatment application for pulp and paper mills. In this section, the details of these processes are given and they are discussed. Performances of various biological treatment processes are summarized in Tables 4.

Activated Sludge Systems:

This conventional treatment system is used in treatment of several industrial wastewater types in order to remove COD, BOD, SS, and AOX. There are a lot of studies in the literature to show the treatability of pulp and paper mills by activated sludge system. Some of them focused on the BOD, COD, AOX and other specific compound removal under different operation conditions. Schnell *et al.* (1997) showed that 74% of filtered COD, nearly %100 BOD5, resin and fatty acid removal were achieved in the full-scale plant. Saunamaki (1997) reported that 82% and 60% COD removal efficiency at paper mills and pulp mills, respectively in full-scale activated sludge systems of Finland. Knudsen *et al.* (1994) claimed high COD and BOD removal efficiency by two stage activated sludge process. Also Hansen *et al.* (1999) and Chandra (2001) showed similar results.
The other part of these studies focused on the removal of AOX and other specific compounds such as chlorinated phenols, guaiacols, catechols, vanillins, 1,1-dichlorodimethyl sulfone (DSS), and chlorinated acetic acid (Mohamed *et al.*, 1989; Demirbas *et al.*, 1999; Bajpai, 2001; Chandra, 2001). The main operational problems of the pulp and paper mills are macro nutrient (N and P) limitation in the systems and growth of the filamentous microorganisms and bulking problems. The nutrient limitation problem is overcome by addition of nutrient. However, the dosage is important point on this step because the external addition causes adverse environmental effects such as eutrophication.

Cingolani *et al.* (1994) highlighted that the main causes of bulking in the pulp and paper mills treatment are poor oxygenation, low organic loading rates and also nutrient limitations. This problem can also be controlled by installation of a selector or addition of chemicals such as chlorine, ferrous salts, lime or talk powder. Selectors are mostly preferred application for bulking (Forster, 1996; Marten and Daigger, 1997; Prendle and Kroiss, 1998; Andreasen *et al.*, 1999).

Aerated Lagoons (Stabilization Basins):

Aerated lagoons are the simple and economical biological systems and they have been studies very well as lab-scale and full-scale at the pulp and paper mills. These systems have been used for removal of BOD, low-molecular weight AOX and fatty acids at full-scale applications (Bajpai, 2001). Stuthridge and Macfarlane (1994) showed that 70% of AOX could be removed efficiently in a short residence time. Welander *et al.* (1997) reported that COD removal was achieved as 30-40% in a full-scale lagoon and 60-70% in a pilot-scale plant. Lab-scale treatability studies were conducted by Chernysh *et al.* (1992) to monitor the AOX and TOC removal of bleached kraft effluent. Slade *et al.* (1999) also reported three aerated stabilization basins, which treated elemental chlorine free (ECF) integrated bleached Kraft mill effluents.

Anaerobic Treatment Processes:

Anaerobic treatment processes are more suitable for treatment of high strength wastewater such as pulp and paper mills. In the literature, there are a variety of studies on the anaerobic treatability and microbial community of this type of effluents (Poggi-Varaldo *et al.*, 1996; Bajpai, 2000; Ince *et al.*, 2007). Also, anaerobic microorganisms are more efficient than aerobics in order to degrade chlorinated organic compounds. However, the sulphur content in the wastewaters is the main disadvantages for application of anaerobic systems, because one of the end products is hydrogen sulphide in the anaerobic biodegradation in the presence of sulphate (Lettinga *et al.*, 1991). Although Hamm *et al.* (1991) reported that the toxic effect of H_2S is less than high concentration of Ca^{2+} and SO_4^{2-}. The other important issues for the application of anaerobic treatment in pulp and paper mills are toxicity of wastewater, anaerobic biodegradability characteristic of specific waste types such as lignin derivates, resin and fatty acids, loading capacity, response to loading fluctuation, and recovery of energy and chemicals (Sumathi and Hung, 2006). Several hundred tons of inorganic chemicals per day for delignification are used in a conventional pulp and paper mill. So, the recovery and reuse of these chemicals are one of the most economical and environmental concern. Addition of it, the black liquor is rich in lignin and a conventional pulp and paper mill produces 1.7-1.8 tons dry solid of black liquor per ton produced pulp and the potential energy of this liquor from anaerobic digestion is 250-500 MW (Stigsson, 1998; Larson *et al.*, 2000). Anaerobic contact reactor, up-flow anaerobic sludge blanket (UASB) reactor, anaerobic filter, and fluidized bed reactor are mostly employed reactor types in pulp and paper mills. The anaerobic treatment efficiency of different plants from pulp and paper industry is given in Table 5.

Fungal Treatment:

Fungal species have been used to remove colour and COD from pulp and paper mills (Eaton *et al.*, 1980; Livernoche *et al.*, 1983; Wang *et al.*, 1992; Gokcay and Dilek, 1994; Duran *et al.*, 1994; Sakurai *et al.*, 2001). Pencillium sp., P. chrysosporium and white rod fungi are the most widely used species. Choudhury *et al.* (1998) reported that Pleurotus ostreatus was removed 77% of lignin, 76.8% of BOD, 60% of COD, and 80% of colour.

Tertiary Treatment

Coagulation/Precipitation:

Addition of metal salts to generate larger flocs from small particles for removing the pollutants easily is the main principle of this method. There are some studies to find the most effective chemicals such as horseradish peroxide (chitosan), $Al_2(SO_4)_3$, hexamethylene diamine epichlorohydrin polycondensate (HE), polyethyleneimine (PEI) to remove AOX, total organic carbon and colour (Tong *et al.*, 1999; Ganjidoust *et al.*, 1997). The authors reported that chitosan is more effective to remove these pollutants from others. Dilek and Gokcay (1994) stated that alum salts as coagulant were removed 96% of COD from the paper machine, 50% of COD from pulping, and %20 COD from bleaching effluents. The other study showed that polyelectrolytes were more effective than the conventional coagulant on the removal of turbidity, COD, and colour (Rohella *et al.*, 2001).

Adsorption:

This method relies on the addition of an adsorbant such as activated coke, fuller's earth, coal ash, activated carbon, and activated charcoal to the wastewater to remove the pollutants. High removal of colour by activated charcoal, fuller's earth, and coal ash was reported (Murthy *et al.*, 1991). Also Shawwa et al (2001) showed that high removal of colour, COD, DOC, and AOX from bleaching wastewater by activated coke.

Chemical Oxidation:

Advanced oxidation methods such as photocatalysis, photo-oxidation, Fenton type reactions, wet oxidation, ozonation are used to achieve the destruction of chromophoric and nonchromophoric pollutants in pulp and paper mills. The achievement of photocatalytic reaction in the removal of COD is depended on the concentration of COD and chloride, which are below a certain level (Balcioglu and Ferhan, 1999). Fenton and photo-fenton reactions are highly effective for the treatment of bleaching kraft mill effluent (Perez *et al.*, 2002). Verenich *et al.* (2000) showed that wet-oxidation are increased the biodegradability of the pulp and paper mill effluent from 30% to 70%. Also ozonation is one of the most effective methods. Several author showed that the effectiveness of this method (Hostachy *et al.*, 1997; Zhou and Smith, 1997; Yamamoto, 2001; Freire *et al.*, 2000).

Membrane Filtration:

Membrane filtration is a potential method to remove colour, COD, AOX, salts, heavy metals, and total dissolved solids from pulp and paper mills (Zaidi *et al.*, 1992; Afonso and Pinho, 1991; Falth, 2000; Merrill *et al.*, 2001). The effluent of membrane filtration can be used again in production process or discharge directly to the receiving water bodies. Dube *et al.* (2000) showed that 88% and 89% removal of BOD and COD, respectively was achieved by reverse osmosis (RO).
The performance of physico-chemical process at the pulp and paper industry is summarized in Table 6.

Treatment Process			Parameters														References
			TSS		BOD		COD		AOX		Chlorinated Phenolics		Color		Methanol		
			Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (Pt–Co)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	
Activated sludge	Paper mill		1435	90.6	512	94.2	1210	82.4	–	–	–	–	–	–	–	–	Saunamaki (1997)
	Pulp mill		738	76.4	336	93.8*	1192	57.1	11.7	55	–	–	–	–	–	–	Saunamaki (1997)
	Kraft mill	I	–	–	270	>95*	660 (F)	60	22.5	36	0.255	74	–	–	–	–	Schnell et al. (2000a)
		II	–	–	270	>98	660 (F)	70	22.5	40	0.255	83	–	–	–	–	Schnell et al. (2000a)
	Pulp and paper mill		–	–	–	96.63	–	96.8	–	–	–	96.92	–	–	–	–	Chandra (2001)
	Paper mill		–	–	1000	99	1533[a]	85	–	–	–	–	–	–	–	–	Knudsen et al. (1994)
Aerobic stabilization basin	Kraft mill	I	–	–	270	>95	660 (F)	62	22.5	53	0.255	85	–	–	–	–	Schnell et al. (2000a)
		II	–	–	270	>98	660 (F)	73	22.5	55	0.255	86	–	–	–	–	Schnell et al. (2000a)
	Kraft mill		–	–	–	–	–	20–65	–	17–70	–	–	–	–	–	–	Chernysh et al. (1992)
Other Biological Reactor Types	HRC (TMP Mill)		–	–	1150	98	3340	79	–	–	–	–	–	–	–	–	Magnus et al. (2000a)
	Total plant efficiency		–	–	1490	99	5000	86	–	–	–	–	–	–	–	–	Magnus et al. (2000a)
	MBBR (HRT 4.5 hrs)		–	–	–	65– 75	–	85– 95	–	–	–	–	–	–	–	–	Borch-Due et al. (1997)
	SBR		–	–	–	98	–	85– 93	–	–	–	–	–	–	–	–	Franta and Wilderer (1997)
	Anaerobic (GAC)		–	–	–	–	1400	50	–	–	–	–	1300	50	–	–	Jackson-Moss et al. (1992)
	Kraft mill Windsor		–	–	1429	69	2036[b]	59	–	–	–	–	–	–	1095[b]	84	Dufresne et al. (2001)

Table 4. Typical wastewater quality of pulp and paper industry and biological treatment efficiencies of these wastewaters ([1] ‘‘F’’ means fraction of COD or soluble COD; [2] Period 1: operating conditions for activated sludge-HRT 2 days, SRT 25 days, Temp. 30 jC, VSS 1800 mg/ l.; [3] Period 1: operating conditions for aerated stabilization basin-HRT 15 days, SRT 15 days, Temp. 30 jC, VSS 60 mg/ l.; [4] Period 2: operating conditions for activated sludge-HRT 1 day, SRT 25 days, Temp. 30 jC, VSS 2800 mg/ l.; [5] Period 2: operating conditions for aerated stabilization basin-HRT 15 days, SRT 15 days, Temp. 20 jC, VSS 70 mg/ l; [6] ‘‘a’’ means soluble COD, [7] ‘‘b’’means unit in g/ d; and [8] ‘‘*’’ means BOD7).

Reactor Type	Mill location	Wastewater Source	Loading Rate (kg COD/m3/d)	BOD5 (mg/L)	BOD5 Removal %	COD (mg/L)	COD Removal %	TSS (mg/L)
Anaerobic contact reactor	Hylte Bruk, AB, Sweden	TMP, groundwood, deink	2.5	1300	71	3500	67	520
	SAICA, Zaragoza, Spain	Waste paper alkaline cooked straw	4.8	10,000	94	30,000	66	
	Hannover paper, Alfred, Germany	Sulfite effluent condensate	4.2	3000	97	6000	85	
	Niagara of Wisconsin, USA	CTMP	2.7	2500	96	4800	77	3300
	SCA Ostrand, Ostrand, Sweden	CTMP	6	3700	50	7900	40	
	Alaska Pulp Corporation, Sitka	Sulfite condensate, bleach caustic and pulp whitewater	3	3500	85	10,000	49	
Upflow anaerobic sludge blanket	Celtona, Holland	Tissue	3	600	75	1200	60	
	Southern paper converter, Australia	Wastepaper	10		80	10,000	> 80	
	Davidson, United Kingdom	Linerboard	9	1440	90	2880	75	
	Chimicadel, Friulli, Italy	Sulfite condensate	12.5	12,000	90	15,600	80	
	Quesnel River Pulp, Canada	TMP/CTMP	18	3000	60	7800	50	
	Lake Utopia Paper, Canada	NSSC	20	6000	80	16,000	55	
	EnsoGutzeit, Finland	Bleached, TMP/CTMP	13.5	1800	75	4000	60	
	McMillan Bloedel, Canada	NSSC/CTMP	15	7000	80	17,500	55	
Anaerobic filter	Lanaken, Belgium	CTMP	12.7	4000	85	7900	70	
Anaerobic fluidized bed:	France	Paperboard	35	1500	83.3	3000	72.2	

Table 5. Selected anaerobic process performance at different pulp and paper industries (Bajpai, 2000)

Treatment Process		Parameters												References
		TSS		COD		TOC		AOX		Color		Lignin/ Resin or Fatty acid		
		Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	Influent (Pt–Co)	Removal Efficiency (%)	Influent (mg/ L)	Removal Efficiency (%)	
Coagulation	Polyelectrolyte	3620	100	4112	55.65	–	–	–	–	4667.5	82.58	480	98.91	Rohella et al. (2001)
	Chitosan	–	–	–	–	–	70	–	–	–	90	–	–	Ganjidoust et al. (1997)
	PE/ PEI	–	–	–	–	–	30	–	–	–	80	–	–	Ganjidoust et al. (1997)
	Alum	–	–	–	–	–	40	–	–	–	80	–	–	Ganjidoust et al. (1997)
Adsorption	Charcoal #1	–	–	–	–	–	–	–	–	3.9 mg/ L	98.13	–	–	Murthy et al. (1991)
	Coal ash #2	–	–	–	–	–	–	–	–	3.9 mg/ L	98.5	–	–	Murthy et al. (1991)
	Fuller earth #3	–	–	–	–	–	–	–	–	3.9 mg/ L	99.21	–	–	Murthy et al. (1991)
	Activated coke #4	–	–	2126	>90	–	–	80.2	>90	2300	>90	–	–	Shawwa et al. (2001)
Oxidation	Wet oxidation	–	–	10,000~19,000	80	3500~4100	80	–	–	–	–			Verenich et al. (2000)
	Ozone + Fenton	–	–	–	–	–	–	–	–	–	~100			Hassan and Hawkyard (2002)
Ozonation	Ozone +UV	–	–	~550	82		–	–	–	–	–			Oeller et al. (1997)
	Photocat. + ozone	–	–	515	85	306	88	27.7	92.5	250	100			Torrades et al. (2001)
	Photocat. + ozone	–	–	3700	57.5	1380	38	69.8	50	7030	65			Torrades et al. (2001)
Membrane	Ultrafiltrtion	–	–	–	85– 90	–	–		85– 91		93–98			Zaidi et al. (1992)
	Nanofiltration	–	–	–	–	–	–	–	93– 96		99.2–99.9			Zaidi et al. (1992)
	Dissolved air +UF	397	100	–	–	828	65	–	–	1747	90			De Pinho et al. (2000)
	Microfiltration +UF	397	100	–	–	828	54	–	–	1747	88			De Pinho et al. (2000)

Table 6. Typical wastewater quality of pulp and paper industry and physico-chemical treatment efficiencies of these wastewater (#1) Charcoal dose 0.4 g/ L and pH 2.0; (#2) Coal ash dose 12 g/ L and pH 2.0; (#3) Fuller earth dose 4 g/ L and pH 2.0; (#4) activated coke dose 15,000 mg/ L

3.2.2 Management and disposal of solid wastes
Integrated solid waste management of pulp and paper mills are through anaerobic digestion, composting, land applications, thermal processes such as incineration/combustion, pyrolysis, steam reforming, and wet oxidation.

Anaerobic Digestion: This process type is a cost effective way due to the high-energy recovery (Verstraete and Vandevivere, 1999; Mata-Alvarez *et al.*, 2000). Industrial wastes, which have high organic content and digestable, are suitable for anaerobic digestion like paper sludge and wastewater treatment plant sludge (Kay, 2003; CANMET, 2005).

Composting: This method is suitable for the wastes and sludge, especially paper fibres and organic materials. The wastes are stabilized via microorganisms with minimal carbon loss. The end product of this process, humus-like material, can be used for houseplants, greenhouse and agriculture (Jokela *et al.*, 1997; Hackett *et al.*, 1999; Christmas, 2002; Gea *et al.*, 2005).

Land Application: This method has been preferred disposal method, especially for the acidic soil due to $CaCO_3$ content of sludge. This application is widely used in the United Kingdom and Northern Europe. Before the application, dewatering and/or incineration treatment are done to the waste/sludge in order to reduce volume (Carr and Gay, 1997; Van Horn, 1997).

Incineration (Combustion): Combination of incineration with power and steam generation is one of the most applied methods in Europe, especially for wastewater treatment plant sludge. However, water and ash content of most sludges cause the energy deficiency. Fluidized bed boiler technology is becoming the one of the best solution for the final disposal of paper mill wastes in order to provide successful thermal oxidation of high ash, high moisture wastes (Busbin, 1995; Fitzpatrick and Seiler, 1995; Davis *et al.*, 1995; Albertson, 1999; Porteous, 2005; Oral *et al.*, 2005).

Pyrolysis: In this process, organic wastes are converted to gaseous and liquid phase under high temperature and in the absence of oxygen. This is an alternative technology to incineration and landfill. This method is suitable for organic content high wastes such as wood, petroleum, plastic waste. However this technology is not sufficient for pulp and paper mill waste. Some investigations have been continue to adapt this technology to pulp and paper mills (Fio Rito, 1995; Frederik *et al.*, 1996; Kay, 2002; Fytili and Zabaniotou, 2008).

Steam Reforming: This technology is used for sludge treatment, however it is still considered as an emerging technology for paper sludges. Steam reforming is a novel combustion technology, which carries out in a steam reforming reaction system (Durai-Swamy *et al.*, 1991; Aghamohammadi and Durai-Swamy, 1995; Demirbas, 2007).

Wet Oxidation: The principle of wet oxidation is that organic compound as solid or liquid form is firstly transferred to water where it contacts with an oxidant under high temperature and pressure. During wet oxidation, waste pulped with water is carbonized and its fuel value increases to the equivalent of medium-grade coal. The waste does not cause any air emission in order to combust without flame or smoke (Kay, 2002). This technology is also considered as an emerging technology like steam reforming.

3.2.3 Treatment of gas emissions
Air pollution control at pulp and paper mills has been important concern in the recent years. Especially VOCs produced form pulp and bleaching steps and steam are conventionally treated by physico-chemical methods such as adsorption to activated coal filters, absorption, thermal oxidation, catalytic oxidation, and condensation (Eweis *et al.*, 1998). I spite of these

pollutants are removed from gaseous phase, they transferred another phase and they are also different pollutants for environment. More innovative approach to solve this problem is biofilters and bioscrubbers that have three steps to remove pollutants from gaseous phase;

- The transfer of pollutants from air to liquid phase,
- The transfer of pollutants from liquid phase to biofilm phase where microorganisms are located, and
- Mineralization of pollutants by microorganisms.

4. Conclusion

The paper demand increases every day as a result of developed population and industrialisation. Water and energy utilization and in particularly waste generation are becoming more important concern ever worldwide. A major goal is to decrease damage to environment by waste minimization, reuse and recycle. To use best available techniques and innovative methods is becoming more an issue. However, end-of-pipe treatment is still the major approach to minimize the risk. To evaluate pollutants and to develop treatment technologies need a holistic approach.

The major pollution load constitutes wastewaters from pulp and paper mills. A variety of wastewater is generated from diverse processes. Different technologies and their combinations have been used for their treatment. The most common applied systems are biological treatment, sequential anaerobic and aerobic systems, followed after primary treatment. Solid waste management and disposal are also another concern. During the final disposal step, the aim should be chemical compound and energy recovery because of environmental and economical aspects. However, the waste minimization has still the first and important approach. Biofilters and bioscrubbers are mostly used for removal of air pollutants and other applications are limited.

The best available treatment technology for all three waste phases depends on the production processes, raw materials and the regulations, which the industries have to obey.

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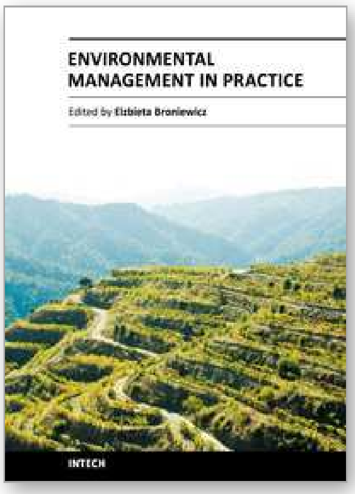

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In recent years the topic of environmental management has become very common. In sustainable development conditions, central and local governments much more often notice the need of acting in ways that diminish negative impact on environment. Environmental management may take place on many different levels - starting from global level, e.g. climate changes, through national and regional level (environmental policy) and ending on micro level. This publication shows many examples of environmental management. The diversity of presented aspects within environmental management and approaching the subject from the perspective of various countries contributes greatly to the development of environmental management field of research.

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