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Characteristics of Wastewater from the Pulp · Paper Industry and its Biological Treatment Technologies†

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요 약

본고는 펄프 · 제지산업 폐수에 함유된 오염물질들의 특성과 생물학적 처리기술들에 대해 설명한다. 펄프 · 제지산업 폐수는 고농도의 생화학적 산소요구량 (BOD)과 화학적 산소요구량 (COD)을 포함하고 높은 독성을 보이며 강한 흑갈색을 띠는 것이 특징이다. 특히, 펄프의 표백공정에서 리그닌의 염소화에 의해 다이옥신, 퓨란과 같은 독성의 유기염소화합물이 형성된다는 것이 알려져 있다. 이에 따라 최근 펄프 · 제지산업은 기존의 표백처리를 무염소공정(TCF)으로 대체하고 있다. 펄프 · 제지산업 폐수처리에 사용되는 모든 생물학적 기술들은 폐수와 박테리아의 접촉 메커니즘에 기반을 두고 있는데, 이것은 박테리아가 폐수 내 유기물질을 먹이로 이용하여 세포로 전환함으로써 폐수 내 BOD농도를 감소시키는 것이다. 펄프·제지산업 폐수의 생물학적 처리에서 호기성 처리와 혐기성 처리 모두 효과적인 것으로 밝혀졌다. 뿐만 아니라, 최근 곰팡이류를 이용한 생물학적 처리, 생물-응집-여과기법을 혼용한 처리 등도 폐수처리분야에 새롭게 적용되었다. 이러한 기술들로 처리된 폐수를 펄프 · 제지공정에 재활용함으로써 제조공정의 물소비량을 상당히 감소시킬 수 있다.

주제어 : 펄프 · 제지, 폐수, 생물학적 처리, 생화학적 산소요구량(BOD), 염소표백

Abstract

This paper describes characteristics of pollutants in wastewater from the pulp and paper industry and biological technologies for the wastewater treatment. The wastewater from the pulp and paper industry contains high concentrations of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and shows high toxicity and strong black-brown color. In particular, organic chlorinated compounds such as dioxins and furans may be formed by the chlorination of lignin in wood chips. Thus the pulp and paper industry is recently trending toward total chlorine-free (TCF) bleaching processes. All biological technologies for pulp and paper wastewater treatment are based on the contact between wastewater and bacteria, which feed on organic materials in the wastewater, thus they reduce BOD concentration in it. Both aerobic and anaerobic treatments were found to be effective for the wastewater treatment. Furthermore, advanced technologies such as fungal application and combined biological-filtration process have been also introduced to the wastewater treatment field. These technologies would be useful for water recycling to reduce water consumption throughout pulp and paper making process.

Key words : Pulp and Paper, Wastewater, Biological Treatment, Biochemical Oxygen Demand (BOD), Chlorine Bleaching

1. INTRODUCTION

In recent years, the pulp and paper industry has become one of the most important industries in most of countries along with the increase of paper demand in

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educational and information-oriented society. Especially, the pulp and paper industry ranks the fifth-largest in the USA and leads the country's economy as a major industry in Canada.[1,2] In addition to North America, India and China are emerging as new countries in the pulp and paper industry market, based on both abundant natural and human resources and recent economic development.[3]

The growth of pulp and paper industry has been accompanied with a large amount of wastewater due to the large consumption of freshwater resource throughout its overall manufacture process.[4] Paper manufacture is divided into two processes such as manufacturing pulp from wood and paper from pulp. And the wastewaters are also divided into wastewater produced from pulp making factory and that from paper making factory. Specifically, pulp wastewater is generated from processes of crushing, digesting, washing, bleaching, concentrating and removing ink and fiber, whereas paper wastewater is produced from processes using screens, washers, paper making machines, beaters and adjusting and mixing tanks.

The wastewater contains high concentrations of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in presence of a lot of organic matters and has a high toxicity by toxic matters and strong black-brown color by lignin.[5] The black-brown color effluent may increase water temperature and decrease the concentration of dissolved oxygen. Pulping bleaching operation generates wastewater containing strong toxic materials because of chlorine application for brightening pulp. Therefore, it is needed to treat the contaminants in the wastewater using appropriate water treatment technologies before flowing into receiving water, and to reuse the treated water to reduce water consumption throughout pulp and paper making process.

Since pulp and paper industrial discharges include a variety of contaminants, various treatment technologies have been also applied. For example, total suspended solids (TSS), absorbable organic halides (AOX), total organic carbon (TOC) and color matters can be removed by coagulation and precipitation using conventional coagulants such as aluminum sulfate and new coagulants such as horseradish peroxide, known as chitosan, and polyethylene oxide (PEO).[6,7] Adsorption and ion-exchange using activated charcoal, fuller's earth and coal ash are also effective for removing color, COD, dissolved organic carbon (DOC), AOX, heavy metals and chlorides.[8,9] Several researchers have reported that membrane filtration was suitable for removing heavy metals, AOX, COD and color from pulp and paper wastewater.[10-12] Chemical oxidants such as ozone, ozone plus photocatalysis and ozone plus UV are also efficient for removing COD, TOC and color.[13,14] In addition to the physicochemical treatments, various biological treatments such as aerobic and anaerobic treatments and fungal treatment show high removal efficiencies for BOD, COD, TSS, AOX and chlorinated phenolics.[15-17] Those are considered as an environment-friendly technology which does not generate secondary contaminants in its application to wastewater treatment.

Due to increasingly deep concern on the environment and public health, the treatment technologies of pulp and paper wastewater have been already reviewed in several papers, but most of them have dealt with the removal of BOD, COD, AOX and color in the wastewater using physical, chemical and biological treatment technologies. In this paper, therefore, we tried to focus on sources and environmental impacts of chlorine among the contaminants in pulp and paper wastewater, and also to review both established and newly advanced biological technologies for pulp and paper wastewater treatment.

2. SOURCES AND CHARACTERSICS OF POLLUTANTS IN PULP AND PAPER WASTEWATER

A pulp and paper making process can be generally divided into five stages: (1) wood preparation, (2) digester house, (3) pulp washing, (4) pulp bleaching, and (5) paper making (Fig. 1). In the process of wood preparation, soil, dirt and bark are removed from the wood, and chips are separated from the bark and water is used to clean the wood. Therefore, the wastewater from this process contains high concentrations of TSS, BOD, dirt, grit and fiber, etc. And the effluent generated from a digester house is called "black liquor." Kraft spent cooking "black liquor" contains cooking chemicals as well as lignin and other extractives from the wood. The wastewater contains resins, fatty acids,

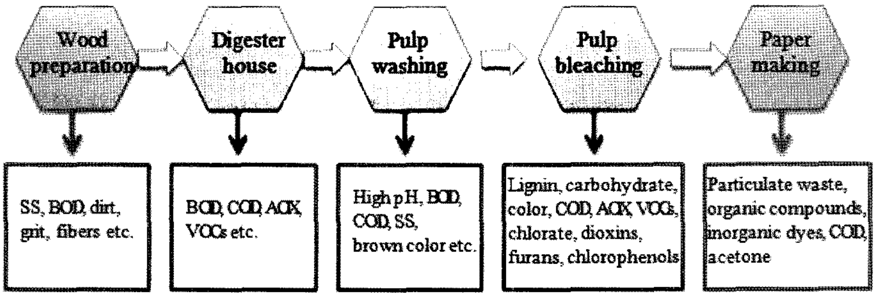

Fig. 1. Pulp and paper making process and pollutants sources.

color, BOD, COD, AOX and volatile organic compounds (VOCs; i.e., terpenes alcohols, phenols, methanol, acetone and chloroform etc.). The effluent from the pulp washing contains high concentrations of BOD, COD, suspended solids (SS) and shows high pH and dark brown in color. The effluent generated from bleaching contains high concentrations of dissolved lignin, carbohydrate, COD, AOX, inorganic chlorine compounds such as chlorate (ClO_3^-) and organo chlorine compounds such as dioxins, furans, chlorophenols and VOCs such as acetone, methylene chloride, carbon disulfide, chloroform, chloromethanes and trichloroethanes, etc. In the last paper making process, the effluent contains high concentrations of particulate waste, organic compounds, inorganic dyes, COD and acetone, etc.[18)]

The characteristics of pulp and paper wastewater are various depending on the type of each process, type of wood materials, process technologies, internal recirculation and water amount. Among the processes, pulping process produces a large volume of wastewater by chemical pulping. The general characteristics of the wastewater generated in various process stages are shown in Table 1.[19)] The concentrations of BOD and COD are mostly high in all of the processes, and it means that the wastewater contains high concentrations of organic substances. Thermo-mechanical pulping (TMP) process is to steam the raw materials under pressure for a short time to separate fibers from raw material, and chemi-thermomechanical pulping (CTMP) is a further modified process of TMP using chemicals. In the process of Kraft bleaching using chorine, the pH of water increases up to 10.1, and the Kraft foul process also increases the pH of effluent due to the use of NaOH or Na_2S, but the pH becomes acidic in the sulfite condensate process.

3. ENVIRONMENTAL IMPACT AND TOXICITY OF CHLORINE

The dioxin family, extremely toxic pollutants, may be formed from the pulp bleaching process using chlorine. Chlorine forms various organic chlorinated compounds by the chlorination, oxidation and degradation of lignin in wood chips. These organic chlorinated compounds include several dioxin members such as dioxins, furans and polychlorinated biphenyls (PCBs). The most toxic member of the dioxin family is 2,3,7,8-TCDD (tetrachlorodibenzo dioxin).[20)] Toxicity degree of dioxins is expressed by the concept of toxicity equivalents (TEQ), which is calculated as Σ(concentration x TEF) where TEF is the toxic equivalency factor and indicates relative toxic degrees of other isomers when the TEF of 2,3,7,8,-TCDD, the most toxic compound among dioxins, is considered as 1.0. The TEF of dioxins is shown in Table 2.[21)] 2,3,7,8-TCDD, often known simply as TCDD, is known to be lethal even at very low concentrations. However, the reasons for its potency are very subtle, and connected with its structural similarity to potent natural hormones. The power of hormones lies in their ability to act in a trace amount as chemical messenger-controlling vital processes in the body. Thus, an accidentally produced contaminant, i.e. TCDD, from the chemical industry can act as a wrong key in the subtle system of trace chemical messengers in the body by mimicking the action of a hormone.[20)]

In addition, chlorine forms toxic disinfectant by-

Table 1. Typical characteristics of wastewater (mg/L) in different remediation processes[19)]

Process	Parameters									
	pH	SS	BOD_5	COD	Carbohydrate	Acetic acid	Methanol	N	P	S
TMP (1)	-	383	2,800	7,210	2,700	235	25	12	2.3	72
TMP (2)	4.2	810	2,800	5,600	1,230	-	-	-	-	-
CTMP	-	500	3,000-4,000	6,000-9,000	1,000	1,500	-	-		167
Kraft bleaching	10.1	37-74	128-184	1,124-1,738	-	0	40-76	-	-	-
Kraft foul (1)	8.0	16	568	1,202	-	-	421	-	-	5.9
Kraft foul (2)	10.2	0	10,700	16,000	-	-	-	306	1	91
Kraft foul (3)	9.5-10.5	0	5,500-8,500	10,000-13,000	-	-	7,500-8,500	350-600	0.02-1.55	120-375
Sulfite condensate (1)	2.5	-	2,000-4,000	4,000-8,000	-	-	250	-	-	800-850
Sulfite condensate (2)	2.8-5.9	-	3,700-5,110	9,800-27,100	-	-	-	-	-	840-1,270
NSSC pulping:										
Spent liquor	-	253	13,300	39,800	6,210	3,200	90	55	10	868
Chip wash	-	6,095	12,000	20,600	3,210	820	70	86	36	315
Paper mill	-	800	1,600	5,020	610	54	9	11	0.6	97

Table 2. Relative toxic equivalent factor (TEF) of dioxins[21)]

Dioxins	TEF
2,3,7,8-tetrachlorodibenzo dioxin (TCDD)	1.0
2,3,4,7,8-pentachlorodibenzo dioxin (PeCDD)	0.5
1,2,3,4,7,8-hexachlorodibenzo dioxin (HxCDD)	0.1
1,2,3,6,7,8-hexachlorodibenzo dioxin	0.1
1,2,3,7,8,9-hexachlorodibenzo dioxin	0.1
1,2,3,4,6,7,8-heptachlorodibenzo dioxin (HpCDD)	0.01
1,2,3,4,6,7,8,9-octachlorodibenzo dioxin (OCDD)	0.001

products (DBPs) such as trihalomethane (THM) through the reaction with humic compounds or other organic substances.[22)] Humic compounds form as part of the decomposition of organic materials such as leaves, grass, wood or animal wastes. Because THMs are very seldom associated with groundwater, they are primarily a concern where surface water supplies are used. THMs are generally suspected to be carcinogenic, mutagenic and teratogenic.[23)] Representative THM by chlorine is trichloromethane (chloroform; $CHCl_3$) formed by the following reactions:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \quad (1)$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl \quad (2)$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl \quad (3)$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl \quad (4)$$

Lifetime consumption of water supplies with THMs at a level greater than 0.10 mg/L is considered by US Environmental Protection Agency (US EPA) to be a potential cause of cancer. A California study indicates that THMs may be responsible for reproductive problems and miscarriage. The study found a miscarriage rate of 15.7% for women who drank five or more glasses of cold water containing more than 0.075 mg/L THMs, compared to a miscarriage rate of 9.5% for women with low THMs exposure.[24)]

Therefore, current water treatments try to focus on improving the removal efficiency of humic compounds, a precursor of THMs, in raw water using strong oxidants and coagulants, etc. before an oxidation process using chlorine.[23)] US EPA has indicated that the best available technology for THM control at treatment plants is to remove precursors through "enhanced coagulation." Enhanced coagulation refers to the process of optimizing the filtration process to maximize removal of precursors. Removal is improved by decreasing pH (to levels as low as 4 or 5), increasing the feed rate of coagulants, and possibly using ferric coagulants instead of alum.

Nowadays, on the other hand, the pulp and paper making industry is trending toward total chlorine free (TCF) bleaching processes to prevent the formation of toxic compound by the use of chlorine. In these processes, ozone or hydrogen peroxide (H_2O_2) is used instead of chlorine or chlorine dioxide. In both cases, these are stronger oxidants than chlorine so that they can be expected to form a greater amount of low-molecular weight compounds.

4. BIOLOGICAL TREATMENT TECHNOLOGY OF PULP AND PAPER WASTEWATER

All biological technologies of wastewater treatment are based on the contact between wastewater and bacteria, which feed on organic materials in the wastewater, and thus they reduce BOD concentration in it. Through the metabolism of simple bacteria, the organic matters that they eat are transformed into cellular mass, which is no longer in wastewater, but can be precipitated at the bottom of a settling tank or retained as slime on solid surfaces or vegetation in the system. Then, cells need not only organic matter as food but also oxygen to breathe. Thus various treatment methods have been developed according to the use of oxygen such as aerobic and anaerobic treatment and their modified methods.

4.1. Aerobic Treatment Processes

4.1.1. Activated sludge process

Activated sludge commonly means the community of active aerobic microbes which can form floc with organic matter. Activated sludge process consists of a set of two basins. In the first basin, air is pumped through perforated pipes at the bottom of the basin, and air rises through wastewater in the form of many small bubbles. These bubbles accomplish two functions: they provide oxygen from the air to the wastewater and create high turbulent conditions that favor intimate contact among cells, organic matters in the wastewater and oxygen. The second basin is a settling tank, where water flow is made to be very quite so that the cellular material may be removed by gravitational settling. Some of the cell material collected at the bottom is captured and fed back into the first basin to seed the process. This process is illustrated in Fig. 2.

Knudsen *et al.* (1994)[25] have reported that the removal efficiency of BOD and soluble COD by a two-stage activated sludge process could be achieved. Hansen *et al.*[26] have suggested upgrading an activated sludge plant by adding flood beds (floating biological bed) in series which increased COD and BOD removal efficiency from 51% to 90% and 70% to 93%, respectively. Chandra (2001)[27] has reported efficient removal of color, BOD, COD, phenolics and sulfide by microorganisms such as *Pseudomonas putida*, *Citrobater* sp., and *Enterobacter* sp. in the activated sludge process. And Mohamed *et al.* (1989)[28] have announced removal of chlorinated phenols, 1,1-dichlorodimethyl sulfone (DDS) and chlorinated acetic acids in an oxygen activated sludge effluent treatment plant. Raghveer and Sastry (1991)[29] have released that a minimum of mixed liquor suspended solids (MLSS) of 2000-2500 mg/L and an aeration time of 6-8 hours were required to remove 83-88% of BOD.

4.1.2. Modified activated sludge processes

- *Step aeration process*

This method has been developed to equally distribute oxygen in wastewater in an aeration tank. Differently from the standard activated sludge process in which all of raw wastewater flows into an inlet of the aeration tank, the wastewater flows equally into more than two inlets in this process. Therefore, this process leads to equalize oxygen demand for wastewater in the aeration tank and to make the size of the aeration tank smaller (Fig. 3).

- *Tapered aeration process*

The purpose of this process is to supplement oxygen deficiency of raw wastewater at the inlet of an aeration tank in the standard activated sludge process. Oxygen demand varies depending on influent and effluent wastewater in the aeration tank. Accordingly, different air amounts can be supplied to the tank. More aeration devices are generally installed at the bottom of the inlet in the tank compared to the outlet of the tank (Fig. 4).

- *Oxidation ditch process*

In this process, raw wastewater is bubbled with a mechanical aeration device in a reactor looking like an

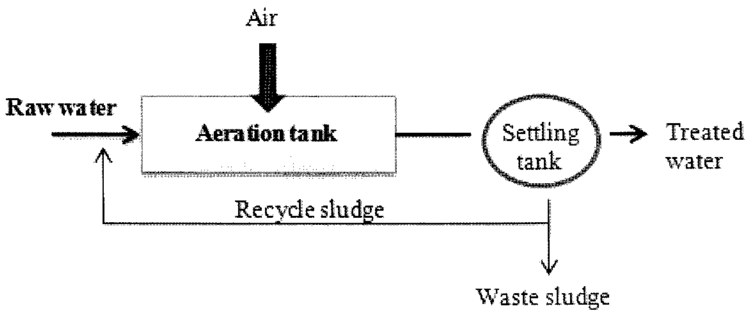

Fig. 2. Schematic of standard activated sludge process.

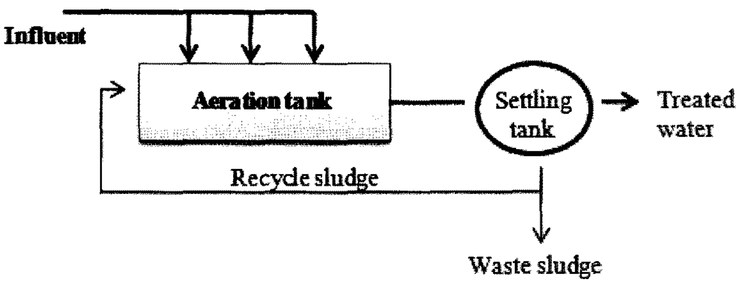

Fig. 3. Schematic of step aeration process.

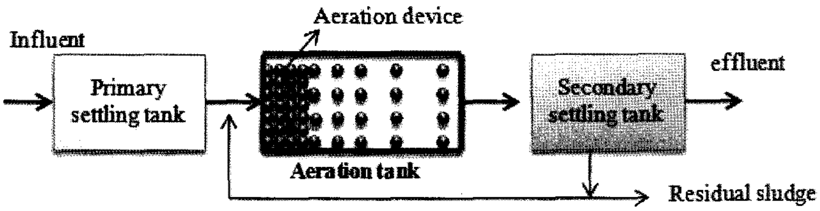

Fig. 4. Schematic of tapered aeration process.

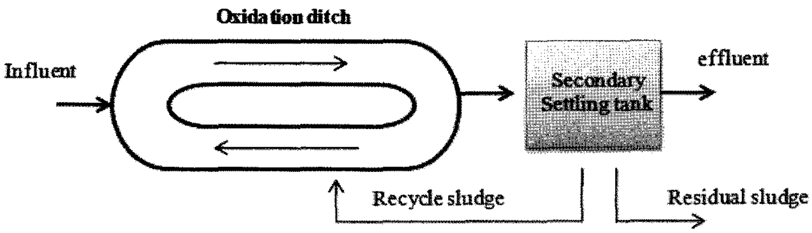

Fig. 5. Schematic of oxidation ditch process.

oval track without passing a primary settling tank, and then water and sludge are separated in a secondary settling tank by gravitation. The mechanical aeration device mixes raw wastewater with activated sludge and makes raw water circulated in the tank to prevent the settlement of the sludge, producing oxygen in the tank to treat raw wastewater (Fig. 5).

- *Sequencing batch reactor (SBR) process*

This process has a reactor which acts as both aeration tank and secondary settling tank without separated secondary settling tank. In one reactor, both nitrification and denitrification can be generated by setting up 'aerobic condition — non-oxygen condition — anaerobic condition' in a reaction cycle. Many researchers have reported that organic pollutants of Kraft mill wastewater could be greatly removed by SBR treatment.[30,31] Reid and Simon (2000)[32] have reported removal efficiencies of 100% for methanol and 90% for COD by SBR. Substantial removal of COD, TOC, BOD, lignin and resin acids of TMP wastewater using high rate compact reactors (HCRs) at a retention time of 1.5 hours had been reported.

4.1.3. Fixed microbial film process

This process is based on the reaction that raw wastewater directly contacts microbial film on the surface of a contactor in a reactor. The advantages of this process are as follows: (1) it does not need to adjust the amount of microbes in a reactor, (2) it does not need recycle sludge and does not have a bulking problem and generates a small amount of sludge, so that its operation is relatively simple compared to activated sludge process. However, it shows some disadvantages as follows: (1) it may discharge particular SS from secondary settling tank, (2) the pH of treated water may decrease, (3) the concentration of BOD may increase due to a possibility of nitrification in the process.

- *Trickling filter process (TFP)*

This process consists of a bed of fist-size rocks over which the wastewater is gently sprayed by a rotating arm (Fig. 6). Slime (fungi and algae) develops on the rock surface, growing by intercepting organic material from the water as it trickles down. Since the water layer passing over the rocks makes thin sheets, there is good contact with air and cells are effectively oxygenated. Worms and insects living in the ecosystem also contribute to the removal of organic material from the water. The slime periodically slides off the rocks and is collected at the bottom of the system, where it is removed.

- *Rotating biological contactor (RBC)*

The basic process is similar to that occurring in a trickling filter. In operation, a media consisting of a series of circular disks mounted side by side on a common shaft is rotated through wastewater flow (Fig. 7). The surface of the disk is covered with biological slime similar to that on the media of a trickling filter.

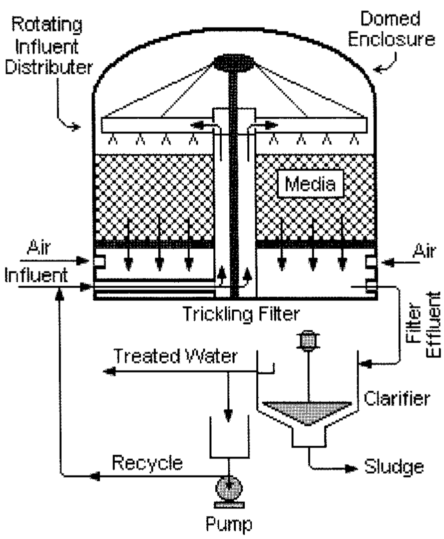

Fig. 6. Typical complete trickling filter system.

RBC units are usually installed in a concrete tank so that the surface of the wastewater passing through the tank almost reaches the shaft. This means that about 40% of the total surface area of the disks is always submerged. The organisms in the slime remove organic matters from the wastewater for aerobic decomposition. The disk continues to rotate, leaving the wastewater and moving through the air. During this time, oxygen is transferred from the air to the slime. As the slime reenters the wastewater, excess solids and waste products are stripped from the media as sloughing.[33)]

4.2. Anaerobic Treatment Processes

Anaerobic microbes are used in anaerobic biodegradation process and they grow well under conditions of high concentration of organic matters and no molecular oxygen (O_2). Anaerobic microbes obtain energy from organic matters and consume it for cell synthesis and metabolism, and then convert into gaseous final products such as methane (CH_4) and carbon dioxide (CO_2) as shown in the following reaction:

Anaerobic microbes + Organic matter + Combined oxygen $\rightarrow$ New cell + Energy + CH_4 + CO_2 + Other products

Where, combined oxygen = CO_3^{2-}, SO_4^{2-}, NO_3^- and PO_4^{3-}
other products = H_2S, H_2 and N_2

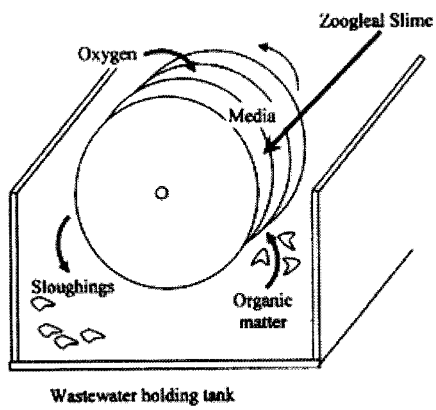

Fig. 7. Schematic cross-section of the contact face of the media used in a rotating biological filter (RBC).

Pretreatment of the Kraft mill black liquor was investigated by Poggi-Varaldo *et al.* (1996)[34] and they reported that continuous anaerobic treatment of wastewater contaminated with black liquor was feasible at low to medium loading rates, with a total COD removal of 48-80% and biodegradable COD reduction of 87-96%. Jahren *et al.* (1999)[35] has compared anaerobic and aerobic treatment for TMP mill effluent and found that respective 84% and 86% removal of COD from anaerobic and aerobic treatment systems was achieved.

4.3. Anaerobic digestion process

This process can be classified in a few ways: (1) small or large treatment capacity, depending on the concentration of organic matter in wastewater, (2) intermediate (35°C) or high temperature (55°C), depending on operating temperature, and (3) two types of digestion, depending on the function of a digestion tank. Table 3 shows the characteristic of each digestion process.

4.4. Anaerobic contactor process

This process is used to treat wastewater polluted by soluble organics at a high concentration consisting of mainly soluble and colloidal substances. It is similar to anaerobic digestion process, but a different point is to recycle digested sludge such as the case of activated sludge process. Its advantages are as follows: (1) it is good to apply to treat wastewater, containing high concentration of soluble organic matters using a small digestion tank, (2) overall temperature, microbes and pH can be regularly fixed throughout the reactor. On the other hand, disadvantages are as follows: (1) the installation and construction of mixing equipments are difficult, (2) operation may be failed due to low precipitable ability of floc, (3) pretreatment device for degasification of sludge is needed[36].

4.5. Anaerobic filter process

This process is normally used to treat soluble organic matters at high or low concentration and low temperature such as 20°C. It is similar to an aerobic filter process, but a different point is that oxygen is not produced in it. Its advantages are as follows: (1) its structure is simple and sludge recycling is unnecessary, (2) fast start is possible after long idleness, and (3) less sludge is generated. On the other hand, its disad-

Table 3. Characteristics of various anaerobic digestions

	Type I	Type II
	Small Capacity Digestion	**Large Capacity Digestion**
· Organic matter concentration	· 0.64-1.60 kg VS/m^3·day	· 2.4-6.4 kg VS/m^3·day
· Digestion duration	· 30-60 days	· 10-20 days
	Double Digestion Tank I	**Double Digestion tank II**
· First digestion tank	· Digestion of organic matters	· Acid fermentation tank
· Second digestion tank	· Division of liquid, solid and gas, Storage of digested sludge	· Methane fermentation tank
	Single Anaerobic Digestion Tank	**Double Anaerobic Digestion Tank**
· Advantage	· Less construction cost · Simple and easy operation	· Stable treatment at large capacity of contaminants · Efficient treatment at high SS concentration ·Excellent application to the removal of heavy metals
· Disadvantage	· Low stability of process · Sensitive to the change of water capacity · Difficult to keep optimum metabolism of microbe	· Difficult to operate · Need of pH adjustment

vantages are as follows: (1) start-up time is long and filling media is expensive, 2) The quality of treated water may be worse in the case of treating raw wastewater containing high SS concentration, and (3) filter may be blocked due to the accumulation of microbes.

4.6. Upflow anaerobic sludge blanket (UASB)

This process does not have any fixed microbial filter different from those in other anaerobic microbial film processes. Instead, an influent contact sludge blanket by its upward-flow and organic matters in wastewater are removed by metabolism (Fig. 8). This process can keep MLSS up to 10,000 mg/L. Its advantages are as follows: (1) microbial retention time can be adjusted, (2) mechanical mixing or filtering media is unnecessary, (3) no recirculation of effluent is needed. On the other hand, its disadvantages are as follows; (1) effective device for the division of gas and solid is needed, (2) diffusion device of wastewater at the low part of a reactor is needed, and (3) stable operation method has not been established.[37]

4.7. Anaerobic fluidized bed process

This process produces influent as upflow through a reactor filled with media such as sand of 0.2-1.0 mm diameter, activated carbon, glass ball or tire piece, etc. and treats organic matter by the contact between wastewater and fixed-growing microbes on the surfaces of the media (Fig. 9). This process can keep the amount of microbes in the reactor because the surfaces of suspended media are very large. Therefore, it is suitable for the treatment of organic wastewater of low concentration which needs a short HRT.

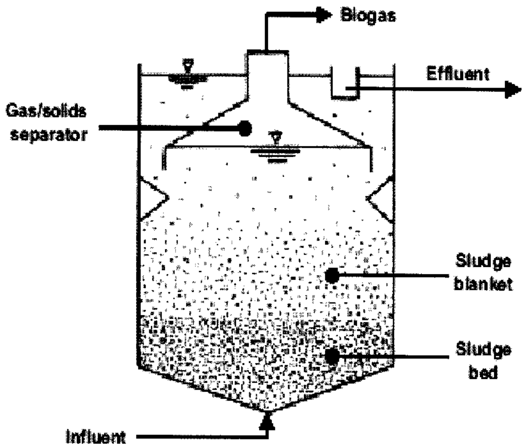

Fig. 8. Schematic of upflow anaerobic sludge blanket (UASB).

5. ADVANCED BIOLOGICAL TECHNOLOGY APPLICATION

5.1. Bioremediation of Pulp and Paper Effluent by White-Rot Fungi (WRF)

Activated sludge process, which is the most widely used biological treatment system, is ineffective in total removal of color and toxicity of pulp and paper wastewater. In order to improve this problem, recent research has been focused on biotechnological approaches using white-rot fungi (WRF) due to their powerful lignin-degrading enzyme system. Malaviya and Rathore (2007)[38] have recently reported the efficiency of WRF for pulp and paper wastewater treatment. In their study, two basidiomycetous fungi (*Merulius aureus* syn. *Phlebia* sp. and an unidentified genus) and a deuteromycetous fungus (*Fusarium sambucinum* Fuckel MTCC 3788) were isolated from soil affected by wastewater of pulp and paper mill over several years. These isolates were immobilized on nylon mesh and the consortium was used for bioremediation of pulp and paper mill wastewater in a continuously aerated bench-top bioreactor. Fig. 10 shows the removal efficiencies of color, lignin and COD in the order of 78.6%, 79.0% and 89.4% in 4 days.

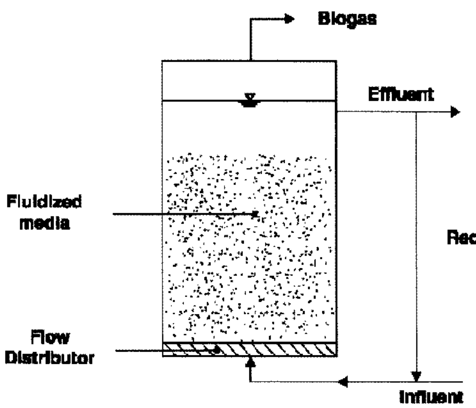

Fig. 9. Schematic of anaerobic fluidized bed process.

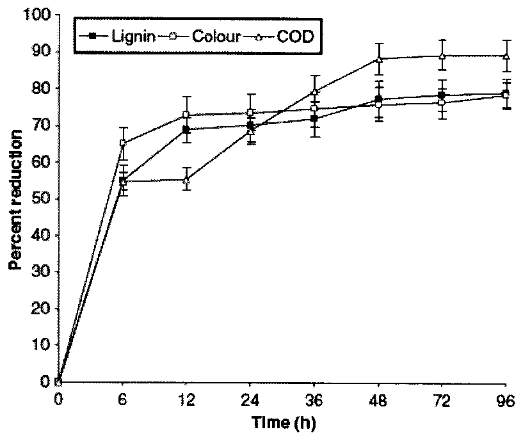

Fig. 10. Changes in pollution parameters of pulp and paper mill effluent during treatment with immobilized fungal consortium in a bench-top bioreactor.[38)]

5.2. Combined biological treatment-membrane filtration-reverse osmosis

The Gippsland water factory (GWF),[39)] located in the Gippsland region of Victoria, Australia, will be the first treatment plant in the world to combine anaerobic pre-treatment with membrane bioreactor processing to effectively treat pulp mill wastewater. The GWF construction started in February 2007. Once the new system is commissioned in 2009, it will be operated by the GWF alliance for a two-year period, prior to commercial handover to GWF.

The treatment process will include three main stages: (1) biological treatment, (2) membrane filtration, (3) reverse osmosis (Fig. 11). Specifically, the GWF includes a biological process called anaerobic treatment. This process uses a different class of microbial organism to pre-treat the wastewater produced from Australian Paper. This process does not use any air and thus does not need the electricity normally used during conventional treatment. Anaerobic treatment also generates a biogas rich in methane which will be captured and used to generate electricity on-site. The energy will be used to help power operational activities at the plant and minimize environmental impacts.

During membrane filtration, the biologically treated water is separated from the sludge through a series of membranes acting as filters. The membranes, which are suspended vertically, are housed in a tank with a pump attached. The pump creates a partial vacuum that draws the biologically treated water through the holes into the membrane, leaving the sludge on the outside. Each membrane periodically cleans itself to remove the sludge from its surface so the filtration process can continue. The filtered and biologically treated water that is to be recycled then progresses to the third stage of the water treatment process, reverse osmosis. When combined with the aerobic biological treatment and sludge separation steps described above, the combined system is called a membrane bioreactor.

Reverse osmosis is most commonly used to remove salt from water. It can remove more than 90% of the salts contained in wastewater. The reverse osmosis process uses a semi-permeable membrane that has pores about one-ten millionth of a millimeter in diameter. The salty water is placed on one side of the membrane filter and pressure is applied to drive the wastewater through the semi-permeable membrane. This process removes the salts and other particles contained in the filtered and biologically treated

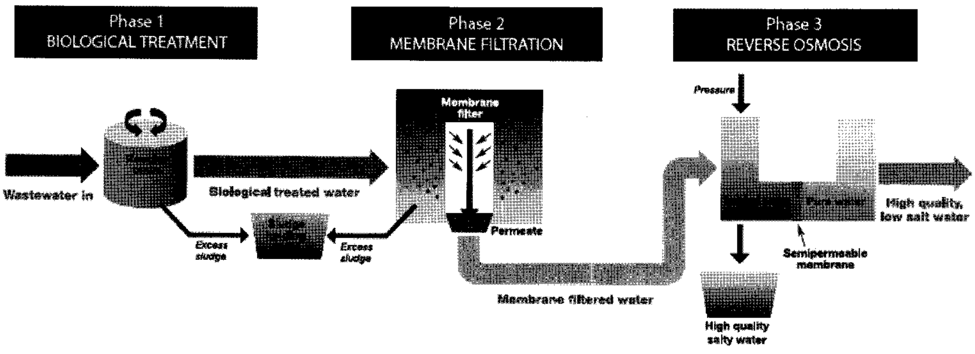

Fig. 11. Schematic of combined biological treatment-membrane filtration-reverse osmosis process.[39)]

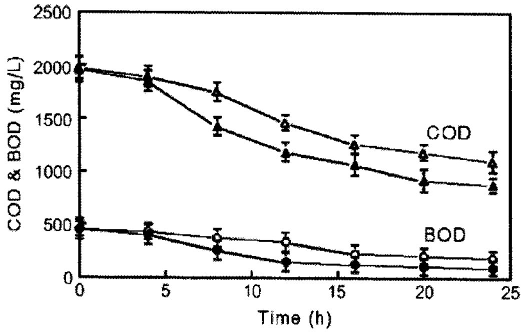

Fig. 12. COD and BOD reduction in PBW by FBR operation on a pilot scale in presence (N, d) and absence (4, s) of additional nitrogen and phosphorous.[40)]

wastewater to create a high quality, low salt water product.

5.3. Combined biological-coagulation-filtration

As aforementioned, sequencing batch reactor (SBR) is a fill-and-draw activated sludge system for wastewater treatment, and in this system, wastewater is added to a single "batch" reactor, treated to remove undesirable components, and then discharged. Fed batch reactor (FBR), however, is relatively a new concept in wastewater treatment technology. It involves the slow addition of highly concentrated wastewater (or nutrient medium) into an aeration tank/reactor with no effluent removal until the tank is full. Afzal and his co-workers (2008)[40)] have carried out an experiment on paper and board mill wastewater treatment using combined biological-coagulation-filtration process. In their research, biological treatment by FBR followed by coagulation and sand filtration (SF) resulted in a total COD and BOD reduction of 93% and 96.5%, respectively. A significant reduction in both COD (90%) and BOD (92%) was also observed by SBR process followed by coagulation and filtration (Fig. 12).

6. CONCLUSIONS

The authors suggest following conclusions based on above reviews on the biological technologies for the treatment of pulp and paper wastewater and further studies to be carried out:

(1) Primary pollutants of pulp and paper wastewater are lignin, fatty acids, color, BOD, COD, AOX and VOCs.

(2) Chlorine may form toxic chlorinated organic compounds by the chlorination, oxidation and degradation of lignin in wood chips. Nowadays the pulp and paper industry is trending toward total chlorine-free (TCF) bleaching processes.

(3) All biological technologies for the wastewater treatment are based on the contact between wastewater and bacteria which transform organic matters they eat into cellular mass. Both aerobic and anaerobic treatments are effective for pulp and paper wastewater.

(4) Activated sludge process is representative of aerobic treatments. Also, there are several modified processes: step aeration, tapered aeration, oxidation ditch and SBR processes, etc. Most of processes achieve high removal of BOD.

(5) Anaerobic microbes utilize combined oxygen in the condition such as CO_3^{2-}, SO_4^{2-}, NO_3^- and PO_4^{3-} (no O_2). They obtain energy from organic matters, consume it for cell synthesis and metabolism, and then convert into CH_4 and CO_2. There are several anaerobic processes such as anaerobic digestion, anaerobic contactor, anaerobic filter and UASB processes.

Advanced technologies for the wastewater treatment have been introduced to achieve more effective treatment by making up disadvantages of currently established technologies. Further studies are needed in the investigation of microbe species to utilize in the pulp and paper wastewater treatment and on the removal of chlorine from pulp and paper bleaching wastewater. It would be also interesting to develop other biological treatment process modified from established processes.

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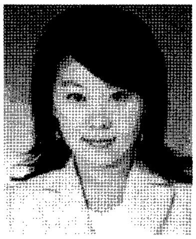

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