Reduction of COD of Pulp and paper mill effluent using Sequencing batch reactor

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Abstract --Paper mills generate varieties of pollutants depending upon the type of the pulping process. The wastewaters discharged from these mills have high chemical oxygen demand (COD) and colour, which indicating high concentrations of recalcitrant organics. This study was conducted using a Sequencing Batch Biofilm Reactor of 3.3 L working volume, operated in an aerobic condition and packed with .For the two months, they can be set at 24 hours and later it was adjusted to 12 hours in order to evaluate the performance of the system. The treated wastewater samples for these studies were taken from a recycled pulp and paper mill factory in Moradabad, India with different batch characteristics. The results also indicated that the Biofilm attached can substantially remove these recalcitrant organics in the wastewater, within the range of 10 - 100% COD removal. COD reduction can see easily and the use combination with SBR is one of the best methods for the COD reduction. Thus, COD reduction can observed about 60-80%.

Index Terms— Biofilm, Chemical oxygen demand (COD), COD reduction, Effluent, Paper mill effluent, Recalcitrant organics, Sequencing batch reactor.

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1 INTRODUCTION

THE pulp and paper industry is one of India's oldest and core industrial sector. The socioeconomic importance of paper has its own value to the country's development as it is directly related to the industrial and economic growth of the country. Although paper has many uses, its most important contribution to modern civilization is its use as a medium to record knowledge. The main steps in pulp and paper manufacturing are raw material preparation, such as wood debarking and chip making; pulp manufacturing; pulp bleaching; paper manufacturing; and fibre recycling. Pulp mills and paper mills may exist separately or as integrated operations. Manufactured pulp is used as a source of cellulose for fibre manufacture and for conversion into paper or cardboard. Pulp manufacturing starts with raw material preparation, which includes debarking (when wood is used as raw material), chipping, and other processes such as depithing (for example, when bagasse is used as the raw material). Cellulosic pulp is manufactured from the raw materials, using chemical and mechanical means.

The manufacture of pulp for paper and cardboard employs mechanical (including thermo mechanical), chemimechanical, and chemical methods. Mechanical pulping [1],[2] separates fibres by such methods as disk abrasion and billeting. Chemimechanical processes involve mechanical abrasion and the use of chemicals. Thermo mechanical pulps, which are used for making products such as newsprint, are manufactured from raw materials by the application of heat, in addition to mechanical operations [3],[4],[5]. Chemimechanical pulping and chemithermomechanical pulping (CTMP) [6] are similar but use less mechanical energy, softening the pulp with sodium sulphite, carbonate, or hydroxide. Chemical pulps are made by cooking (digesting) the raw materials, using the Kraft (sulphate) and sulphite processes. Kraft processes produce a variety of pulps used mainly for packaging and high strength papers and board. Wood chips are cooked with caustic soda to produce brownstock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy [7]. Pulp is also manufactured from recycled paper. Mechanical pulp can be used without bleaching to make printing papers for applications in which low brightness is acceptable primarily, newsprint. However, for most printing, for copying, and for some packaging grades, the pulp has to be bleached. For mechanical pulps, most of the original lignin in the raw pulp is retained but is bleached with peroxides and hydrosulphides [8]. In the case of chemical pulps (Kraft and sulphite), the objective of bleaching is to remove the small fraction of the lignin remaining after cooking. Oxygen, hydrogen peroxide, ozone, peracetic acid, sodium hypochlorite, chlorine dioxide, chlorine, and other chemicals are used to transform lignin into an alkali soluble form.

2 WASTE CHARACTERISTICS

The significant environmental impacts of the manufacture of pulp and paper result from the Pulping and bleaching processes. In some processes, sulfur compounds and nitrogen oxides are emitted to the air, and chlorinated and organic compounds, nutrients, and metals are discharged to the wastewaters.

2.1 Air Emissions

In the Kraft pulping process, highly malodorous emissions of reduced sulfur compounds [9], measured as total reduced sulfur (TRS) and including hydrogen sulfide, methyl mercaptan, dimethyl sulfide,

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and dimethyl disulfide, are emitted, typically at a rate of 0.3–3 kilograms per metric ton (kg/t) of air dried pulp (ADP- Airdried pulp is defined as 90% bone-dry fiber and 10% water) [10]. Other typical generation rates are: particulate matter, 75–150 kg/t; sulfur oxides, 0.5–30 kg/t; nitrogen oxides, 1–3 kg/t; and volatile organic compounds (VOCs), 15 kg/t from black liquor oxidation. In the sulfite pulping process, sulfur oxides are emitted at rates ranging from 15 kg/t to over 30 kg/t. Other pulping processes, such as the mechanical and thermo mechanical methods, generate significantly lower quantities of air emissions. Steam and electricity generating units using coal or fuel oil emit fly ash, sulfur oxides, and nitrogen oxides. Coal burning can emit fly ash at the rate of 100 kg/t of ADP.

2.2 Liquid Effluents

Wastewaters are discharged at a rate of 20-250 cubic meters per metric ton (m3/t) of ADP. They are high in biochemical oxygen demand (BOD), at 10-40 kg/t of ADP; total suspended solids, 10-50 kg/t of ADP; chemical oxygen demand (COD), 20-200 kg/t of ADP; and chlorinated organic compounds, which may include dioxins, furans, and other absorbable organic halides, AOX, at 0-4 kg/t of ADP. Wastewater from chemical pulping contains 12-20 kg of BOD/t of ADP, with values of up to 350 kg/t. The corresponding values for Mechanical pulping wastewaters are 15-25 kg BOD/t of ADP. For chemimechanical pulping, BOD discharges are 3 to 10 times higher than those for mechanical pulping. Pollution loads for some processes, such as those using nonwood raw materials, could be significantly different. Phosphorus and nitrogen are also released into wastewaters [11]. The main source of nutrients, nitrogen, and phosphorus compounds is raw material such as wood. The use of peroxide, ozone, and other chemicals in bleaching makes it necessary to use a complexion agent for heavy metals such as manganese.

3 MANUFACTURING PROCESS

In general, paper is manufactured by applying a liquid suspension of cellulose fibers to a screen, which allows the water to drain, and leaves the fibrous particles behind in a sheet. The liquid fibrous substrate formed into paper sheets is called pulp.

Processes in the manufacture of paper and paperboard can, in general terms, be split into three steps: pulp making, pulp processing, and paper/paperboard production. Paperboard sheets are thicker than paper sheets; paperboard is normally thicker than 0.3 mm. Generally speaking, however, paper and paperboard production processes are identical [12]. First, a stock pulp mixture is produced by digesting a material into its fibrous constituents via chemical, mechanical, or a combination of both. In the case of wood, the most common pulping material, chemical pulping actions release cellulose fibers by selectively destroying the chemical bonds in the gluelike substance (lignin) that binds the fibers together. After the fibers are separated and impurities have been removed, the pulp may be bleached to improve brightness and processed to a form suitable for papermaking equipment. Currently, onefifth of all pulp and paper mills practice bleaching [13]. At the papermaking stage, the pulp can be combined with dyes, strength building resins, or texture adding filler materials, depending on its intended end product. Afterwards, the mixture is dewatered, leaving the fibrous constituents and pulp additives on a wire or wiremesh conveyor. Additional additives may be applied after the sheet making step. The fibers bond together as they are carried

through a series of presses and heated rollers. The final paper product is usually spooled on large rolls for storage.

4 MATERIALS AND METHODS

4.1 Sample collection

The effluent samples (bleached) were collected from a pulp and paper mill effluent and were stored in plastic containers, kept at 4 °C and transported to our laboratory. The remaining effluent sample was kept in the cold room for later use.

4.2 Inoculums

The inoculums used in this experiment were collected from oxidation pond and procured from a batch anaerobic reactor located in the laboratory, which has been maintained at ambient temperature condition.

4.3 SBBR

A reactor with 3 L working volume was used in this study. It was operated at room temperature. The reactor was earlier operated at hydraulic retention time (HRT) of 36 hours can of the six months and later can adjusted to HRT of 24 hours in order to make the performance comparison of the Biofilm between both the HRTs. The samples were analyzed for COD, AOXs and the amount of biomass washout before being fed into the reactor.

5 EXPERIMENTAL METHOD

The overall methodology of this study is as illustrated the SBBR system was initiated with the characterization of the influent and effluent samples and these were followed by the kinetic studies of the microorganism growth and the optimization of reactor operating parameters [14], [15], [16]. The COD and biomass parameters were analyzed using the standard methods with the respective instruments as listed in Table 2. The Adsorbable organic halides were extracted using the solid phase extraction (SPE).

6 RESULTS AND DISCUSSION

The characteristics of batches of samples from recycled paper mill factory were determined. That the maximum influent concentrations obtained for COD on all samples were 7860 mg/L while the COD values on the effluent were below 300 mgL/1. The removal ranges for COD 24 hours were 50–80% and 50–66%, respectively. As was previously observed by the study of Barr et al. (1996), the removal of COD was found to decrease with the decreasing of the HRT. It was also observed that at the initial stage of the study (approximately within the first 20 days), the COD removal was higher even though the biomass concentration was below 2000 mgL1. This was most probably due to the adsorption of the COD onto the freshly introduced .The concentrations of the compounds as identified in the paper mill effluent with their percentage removals were as shown in the concentrations of phenol were found to be very low and could hardly be detected.

The efficiency of a system is also very dependent on the characteristics of the microbe population in the reactor. Analysis of the growth kinetic parameters in SBBR had deduced that the system is capable to operate a long biomass retention time under anoxic condition (or less oxygen). Anderson et al. (1996) has reported that the consumption of nonbiodegradable substrate would lower the specific growth rate.

Wastewater from pulp and paper industry is one of the serious problems due to the high concentration in COD and color substances.Several treatment systems have been introduced for treating this kind of wastewater on the basis of its high removal efficiency and low operating cost. NAINI pulp and paper Industries Co., Ltd, one of the biggest companies to produce pulp and paper products in India, was used for checking the wastewater quality. The wastewater from this factory had high concentration of COD, BOD₅ and color substances as 1255 mg/l, 449 mg/l and 697 Pt- Co units, respectively. The COD: BOD ratio was 2.8:1. This means that the pulp and paper industry wastewater contains large amounts of organic compounds that are difficult to biodegrade and inorganic reducing substances. However, most of the pulp and paper industry factory still uses the biological treatment system such as the oxidation pond, aerated lagoon or activated sludge. Many factories have problems with the fluctuation in the quality of the effluent, stability of the system and, operating and investment cost. The SBR system has been introduced into several kinds of industries such as seafood and meat processing industries for reduction of investment and operating costs. In this study, we have tried to introduce the SBR system to treat pulp and paper industry wastewater. The results show that the microorganisms in SBR system can remove both organic matters (COD and BOD₅) and color substances from the wastewater. The effluent qualities, except color intensity passed the standard permission .The removal efficiencies of SBR system improved with the increase of HRT, except for color removal efficiency. The COD removal efficiencies of the SBR system were increased from 73.26% to 89.80% while the color removal efficiency was reduced from 56.96% to 48.92Yo when HRT of the system was increased from 1 day to 3 days. It means that when the HRT was increased, the organic loading was decreased then; the removal efficiency was increase.

TABLE 1DIFFERENT VALUES FOR BATCH PROCESS

Date 18 June,2010	MLSS Conc. At starting stage	4340Kg/m3
Date 18 June,2010	VSS Conc. At starting stage	1520mg/l
Date 28 June,2010	MLSS Conc.	3840 Kg/m3
Date 28 June,2010	VSS Conc.	1540 mg/l
Date 12 July,2010	MLSS Conc.	5220 Kg/m3
Date 12July,2010	VSS Conc.	2520 mg/l

 TABLE 2.

 The AOXs were extracted using the solid phase extraction (SPE)

 Technique and later analyzed using the HPLC instrument.

PARAM- ETER	INSTRU- MENTS	METHOD	REFERENCE
Chemical Oxygen	HACH DR 5000 Spec-	Digestion Method	EPA
Demand (COD)	trophotome- ter		
Absorbable organohal- ides (AOX)	(HPLC) with UV detector (Agilent series 1100)	Zorbax-SB C18 Column (150mm×4.6mm×5μm) Mobile phase: 20% Aceton Nitril (ACN)/80%0.01MH3PO4 to 45%CAN in 7.5 min- with gradient of 80% ACN in 2min and UV detection at 254 nm	Agilent technologies (2002)
Biomass	Filtration unit	Mass liquid Suspended solids	APHA (1992)
Kinetic growth	-	Monod Equation	Monod (1949)

7 CONCLUSION

The study can show that selection of suitable processes effect the COD removal. The results of this initial study thus reaffirm the fact that SBBR system treatment of recycled pulp and paper mill effluents could be considered as an alternative option not only for energy cogeneration but also as a means of significantly reducing some of the more important, albeit organic recalcitrant, objectionable parameters. COD reduction can see easily and the use of with combination with SBR is one of the best methods for the COD reduction. The reduction were observed about 60-80% and rest of the parameters analysied as shown in the graph below from fig.1 to fig.5

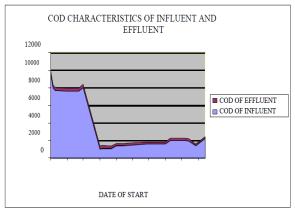


Fig. 1: COD characteristics of influent and effluent observed.

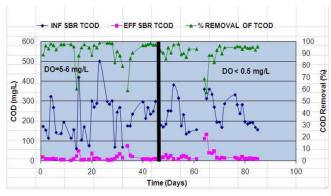


Fig 2: Time Vs COD concentration and their %age removal

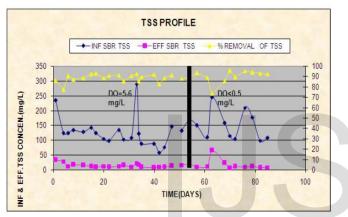


Fig 3: Time Vs Influent & Effluent TSS Concentrations.

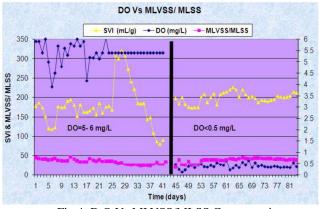


Fig 4: D.O Vs MLVSS/MLSS Concentration

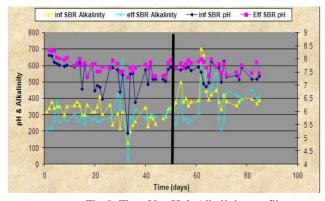


Fig 5: Time Vs pH & Alkalinity profile

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