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Physicochemical Analysis of Effluents from Agro-Based Paper Mill in Uttarakhand State of India

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Abstract : The pulp and paper industries discharge of large amount of effluent as wastewater in the surrounding streams thereby causing serious health and environmental problems. These large quantities of effluents need to be characterized for evolving proper treatment strategy prior to their disposal. Physicochemical characteristics of effluents from an agro-based paper mills located in Uttarakhand state of India were analyzed in terms of pH, colour, TS, TDS, TSS, turbidity, BOD, COD, and AOX. The effluent samples collected from different processing units of the paper mill varied considerably across the discharge streams. The mean values pH, colour, TS, TDS, TSS, turbidity, BOD, COD, and AOX were found in the range of 2.55–9.8±0.05, 410–2802 PCU, 1980.65–2785.79 ppm, 1650.67–2470.35 ppm, 315.44–401.35 ppm, 73.22–349.37 NTU, 170.32–670.42, 705.52–2000.55 ppm, and 14.98–40.82 respectively. Result shows that all the studied physicochemical parameters of effluents at different processing units of the mill are higher than the permissible standards that need proper treatment for their safe disposal.
Keywords : Effluents, Physicochemical characteristics, Paper mill, BOD, COD.

Introduction

The pulp and paper industry is one of the important industrial sectors on account of its socio-economic importance as it is directly related to the industrial and economic growth of the country. Economic benefits of the pulp and paper industry have led it to be one of the most important industrial sectors in the world. The paper making is a water and energy intensive process and pulp and paper industry is ranked as the third world's largest consumer of water consequently producing high amounts of waste waters [1]. The natural raw material

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used for the processes are wood, cellulose, vegetables, rice husk, fibres and also waste-paper. It is worth mentioning here that the effluent characteristics may vary according to the process applied and chemicals used by industries during different processes [2]. In general, high organic material and suspended solid contents are considered major pollutants of pulp and paper industry effluents [3]. Pollution of groundwater due to disposal of industrial and municipal effluents in water bodies is a major concern in many cities and industrial clusters in India [4]. The paper mill waste water contains high biological oxygen demand (BOD) and chemical oxygen demand (COD) due to organics like, lignin, cellulose, fatty acids, tannins, resin acids, terpenes, phenolic compounds, chlorinated organic compounds and coal. Inorganics like sodium, calcium, silicates, Aluminium oxide (Al_2O_3), muds, grits, ferric oxide (Fe_2O_3), sulphur and its compounds [5]. Deliberate discharge of such type of harmful chemical compounds into the environment has enough potential to disrupt the structure and functioning of the natural ecosystem, some of which are toxic, mutagenic, persistent, bio-accumulating, thus causing numerous harmful disturbance in biological system [6]. Black liquor or spent cooking liquor is one of the major byproducts of pulp and paper manufacturing, which contains10-50% lignin that is the main organic matter found in the liquor. Among the paper making processes, pulping especially by chemical pulping generates waste water which contains wood debris and soluble wood materials. Similarly bleaching generates toxic substance as it utilizes chlorine for brightening the pulp [7].

There are many chemicals in paper mill effluent known to be toxic to animals and humans and proved to be genotoxic and cancer. Tetrachlorodibenzo-dioxin (TCDD) found in paper mill effluent and one of the most toxic chemicals is a very aggressive carcinogen that also impairs reproductive health and may cause sterility. It is most commonly consumed by eating contaminated fish or drinking contaminated water. Some other toxins like nitrite nitrogen, chlorides, transition metals, chelating agents, and dioxins found in paper mill effluent have been shown to cause ailing effect in humans. Drinking contaminated water causes ulceration of internal organ linings, severe diarrhea, and if left untreated can end in death [8]. The colloidal or suspended solids has a deleterious effect on the receiving streams as anaerobic decomposition of these solids consumes dissolved oxygen in the water and thus affects the aquatic life in very adverse way [9]. The high volume of effluent discharge and the economic constraints has made it essential for paper industries to treat the effluent to the extent where the quality of effluent comes within the norms of regulatory bodies. For the pollution abetment and environmental protection it is necessary to assess the quality of effluent in terms of physiochemical parameter so that appropriate treatment measure could be evolved to minimize the pollution load of such industrial water for their use in irrigation, industries and other purposes.

The main objective of the physicochemical analysis of water is to determine the status of pollution load in the wastewater discharged from various streams of processing units of industries so as to formulate suitable treatment and disposal strategies. This paper presents the physiochemical characteristics of effluents from the pulp and paper industry located in Uttarakhand state of India which is using agricultural reduces like bagasse, wheat straw, etc. as raw material. The wastewater from the paper industry is characterized for pH, colour, total solid (TS), total dissolved solid (TDS), total suspended solid (TSS), turbidity, biological oxygen demand (BOD), chemical oxygen demand (COD) and adsorbable organic halides (AOX).

Materials and Methods

Chemical and Analytical

All the chemicals used were of analytical grade and referred to Sdfinechem, Ranbaxy,. All the reagents and test solutions were prepared in triple distilled water and preserved in Schott Duran bottle. The laboratory glass used, were washed with detergents and rinsed with distilled water and then oven dried at 200^{0}C prior to use. The pH of the effluent samples was measured by using microprocessor digital pH meter (Remi). The turbidity of effluent samples was measured by using turbidity meter and the readings were recorded as nephlometric turbidity unit (NTU).

Selection of pulp and paper mills

The pulp and paper mill selected for the study is located at 29° 12' 37.5156" N, 78° 57' 42.5880" E in the state of Uttarakhand, India. This is small scale paper mill primarily using agro-based wheat straw, Bagasse, etc. as raw material for manufacturing printing and writing papers with an installed capacity of 100 tpd. The mill adopts soda pulping process for pulp production using 8-10% caustic (NaOH) charge for wheat straw and 12-14% for bagasse during pulping. Oxygen bleaching followed by chemical bleaching is done in four stages following CEHH protocol and the total bleach chemical demand of the mill is 7-9%. Each of the bleaching steps is preceded and followed by counter current washing with fresh water. The mill generates bleach plant effluent and combined effluent to the tune of 32-35 m^3/t and 45-60 m^3/t of paper respectively. For chemical recovery and effluent treatment, the mill uses conventional and activated sludge system.

Collection of effluent samples

Samples from different streams were collected hourly for six hours and then mixed to make it composite for laboratory study from Agro based Mill of U.P (India). Effluent samples from different streams i.e. chlorination (C), extraction (E), combined bleach plant (CBP) and combined effluent (CE), were collected hourly for six hours from the Mill and then mixed to make it composite for laboratory study. The effluent samples were collected during summer (May, 2015) and winter (January, 2016) to observe any change in the characteristics of the effluent. Furthermore, the samples were acidified with nitric acid and gallons containing samples were preserved in refrigerator at 4^0C till further analysis.

Physicochemical Characterization of Effluents

Effluents samples collected from various sections of processing units of the paper mill were subjected to physicochemical analysis according to standard methods [10,11]. The pH of effluent samples was measured at the site of collection using microprocessor based pH meter (Labtronics). Colour of the samples was analyzed by spectrophotometric method. Turbidity of the effluent was measured by using turbidity meter (Hach 2100AN). The remaining effluent characteristics parameter, i.e., total solid (TS), total suspended solid (TSS), total dissolved solid (TDS), BOD and COD were determined volumetrically/titrimetrically as per standard methods. AOX were measured with AOX analyzer (Analytic Jena-Multi X2000). All tests and measurements were carried out in triplicates in order to access the repeatability of the results.

Results and Discussion

Physicochemical analysis

The agro-based paper mill under study produces a variety of writing and printing paper using bagasse, wheat straw and other agricultural residue as a primary raw material. The effluent samples collected from various processing stages of the mill were subjected to physicochemical characterization for parameters such as pH, colour, TS, TSS, TDS, turbidity, COD, BOD and AOX according to standard methods. The mean values and standard deviation of studied physicochemical parameters of the paper mill effluent are summarized in the Table-1.

Table 1: Physicochemical values of effluents from processing stages of the paper mill

Parameters	Processing stages of the paper mill			
	C	E	CBE	CE
pH	2.55±0.045	9.25±0.02	6.18±0.03	9.8±0.05
Colour (PCU)	410±0.060	1121±0.06	1845±0.40	2802±1.15
TS (ppm)	2172.25±4.01	2785.79±6.56	2387.14±7.20	1980.65±11.55
TDS (ppm)	1771.25±2.01	2470.35±3.29	2005.64±6.65	1650.67±9.97
TSS (ppm)	315.35±5.31	332.44±3.34	381.50±1.01	401.65±2.67
Turbidity (NTU)	73.22±1.32	95.55±1.01	106.23±0.67	349.37±0.68
BOD (ppm)	170.32±4.35	670.42±1.06	625.35±8.80	655.75±2.31
COD (ppm)	935.35±0.060	1125.61±0.06	705.52±0.40	2000.55±1.15
AOX (ppm)	40.82±0.38	26.05±0.39	24.62±0.15	14.98±0.50

Values are given as Mean ± SE (n=3)

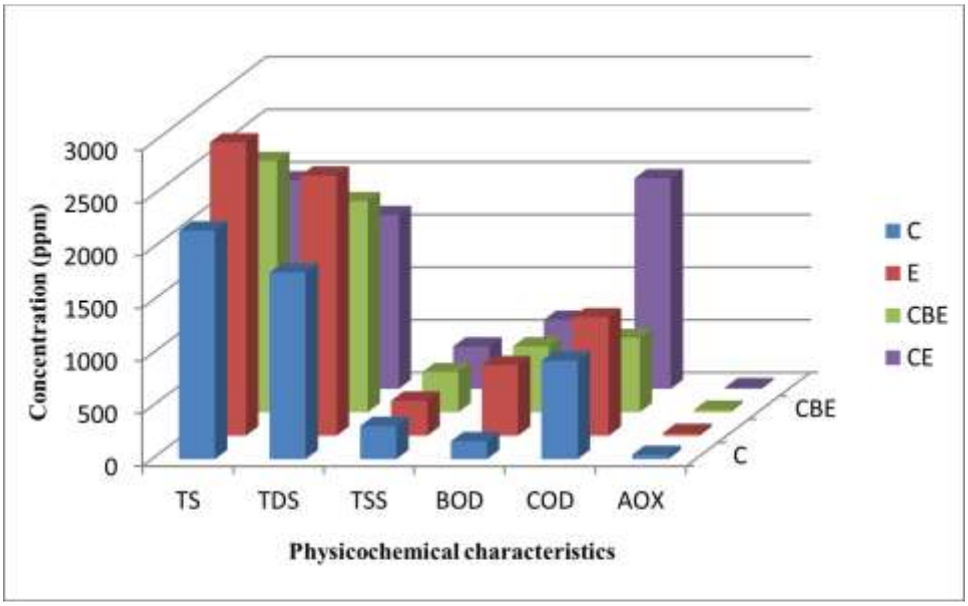
It is evident from the results of physicochemical analysis of effluents from different processing units presented in table 1 that values of all the studied parameters vary to a great extent across the processing stages. The mean value of pH varied from 2.55±0.045 to 9.8±0.05 across the four different stages which may be due to the different process and chemicals used at various stage of processing. The pH value is a measure of acidity and alkalinity of effluents which is useful in designing treatment protocol and determining its efficiency.

Effluent from different processing units may have both acidic and alkaline nature. In this study, effluent from chlorination section showed minimum mean value of pH which is in highly acidic range due to the formation of organic acids while processing. In fact, reactions of chlorine with water at chlorination stage lead to formation of hypochlorous acid and hydrochloric acid. The low pH of C-stage effluents may be due to dissociation of hypochlorous acid into hydrogen ion and hypochlorite ion. The highest pH value of effluents from CE unit may be due to the addition of alkali at this stage for the precipitation of total solids which produces hydroxyl ions in water thereby raising the pH of effluent making it alkaline in nature [12]. The effluent from CE unit recorded the pH value of 9.8 which is slightly higher than WHO prescribed tolerance limit of pH value for the paper industry effluent as 6 to 9 [13]. The discharge of waste water into water bodies may cause a drop or increase in their pH due to the size and activities of microbial population. The pH of water is the important for the biotic compound because most of the plant and animal species can survive between narrow pH from slightly acidic to slightly alkaline.

Colour of effluents or wastewaters depend on concentration of lignin which come up due to the presence of low and high molecular weight chlorinated organic compound produced during different processing stages like pulping, bleaching and alkali extraction as the lignin degradation products [14-16]. The colour of the effluent from all the four processing stages measured in PCU showed considerable variation ranging from 410±0.060 to 2802±1.15 PCU. Visibly, the effluent had a yellowish brown to dark brown appearance at the time of samples collection. Data presented in table 1 revealed that CE effluent exhibited highest colour value followed by E, CBP and C stage. The darkest colour of CE effluent of the paper mill may be due to presence of some amount of black liquor. The colour of effluent has impact on its aesthetics, transparency and gas solubility [17].

The mean total Solids (TS) concentrations in effluents from C, E, CBE and CE units ranged from 1980.65±11.55 to 2785.79±6.56 ppm respectively (Table 1). The lowest TS were found in effluent from the CE unit whereas effluent discharge at E unit showed the highest TS (Fig. 1). Disposal of wastewater with high TS in water bodies may adversely affect the aquatic flora through delaying their photosynthetic process due to lesser clarity and consequent reduction in the passage of light. Furthermore, such effluents get warmed rapidly and hold more heat which is unfavourable for aquatic lives that are adapted to survive at a lower temperature.

Total dissolved solid (TDS) was highest for discharge at E unit (2470.35±3.29 ppm) followed by CBE (2005.64±6.65 ppm) and C (1771.25±2.01 ppm) units. Effluents from CE unit however recorded the lowest (1650.67±9.97 ppm) TDS (Fig.1). The observed values of TDS in discharge from all the processing units were higher than the WHO maximum permissible limit of 500 ppm (500 mg/L) for the discharge of wastewater into surface water. Effluents with higher TDS discharged in water bodies may increase salinity of water thereby making it unfit for irrigation and drinking purposes. Consumption of water with high TDS are reported to cause detrimental impact on alimentary canal, respiratory system, nervous system, coronary system besides, causing miscarriage and cancer [18].



Total suspended solids are usually referred to the undissolved matters including fibres, inorganic fillers, pigments, etc. present in the waste water. The mean TSS contents of effluents from different points C, E, CBE and CE varied from 315.44±3.34 to 401.35±5.31 ppm. The highest TSS was found in effluents from CE unit followed by CBE and E units whereas C unit effluent recorded the lowest TSS (Fig. 1). The TSS values measured at all the four discharge points are higher than the WHO maximum limit of 100 ppm (100 mg/L) for discharge of waste water to surface water bodies. Effluent discharge at E unit recorded the lowest TSS. Suspended solids lead to reduced photosynthesis by aquatic flora, oppress benthic organism, adversely affect the biological treatment and result in clogging of pipes and pumps [19].

Turbidity in wastewater is due to the presence of insoluble matters, soluble coloured compounds, and plankton measured either as a reduction in the intensity of transmitted light or as an increase in the intensity of scattered light, is an important parameter for the assessment of effluent quality [19]. The mean value of turbidity of effluents from C, E, CBE and CE streams has been found as 73.22±1.32, 95.55±1.01, 106.23±0.67 and 349.37±0.68 NTU indicating maximum and minimum turbidity in effluents from CE and C streams respectively (Table 1). This is further supported by the TSS values of effluents from the four streams. Turbidity of effluent from a processing unit also indicates the effectiveness of coagulation-flocculation process of the unit. Turbidity can affect the colour of the water. Higher turbidity reduces the amount of light penetrating the water, which reduces photosynthesis and the production of dissolved oxygen. The results clearly indicated the elevated turbidity in effluents at all processing units and are higher than the WHO standard limits of 5 NTU and should ideally below 1 NTU [20].

Biological oxygen demand (BOD) signifies the amount of oxygen required for microbial degradation of organic matter as well as the self purification capacity of the water body. It is a measure of the organic pollution load of effluents thus quantifies the dissolved oxygen levels. The mean values of BOD for effluents at C, E, CBE and CE units ranged from 170.32±4.35 to 670.42±1.06 ppm. Highest BOD value was found for the effluent from E unit and lowest for that from C unit (Fig. 1). However all the values are higher than IS prescribed limit of 100 ppm (100 mg/l) for safe disposal of effluents. The high BOD and low oxygen content of effluent affect survival of gill breathing animals of the receiving water body [21].

Chemical oxygen demand (COD) is the amount of oxygen required to breakdown both organic and inorganic matter and is one of important parameters for assessing pollution load of effluents. The mean value of BOD for effluents at C, E, CBE and CE units was found as in the range of 705.52±0.40 to 2000.55±1.15 ppm with maximum and minimum values for effluent of CE and CBE units respectively (Fig. 1). The value obtained for effluents of all units are greater than the acceptable limits of 350 mg/l [22] thereby suggesting their toxic nature which may be due to high chemical concentration along with the presence of biologically resistant organic substances [23, 24].

The adsorbable organic halides **(**AOX) is the measure of organically bound chlorine compounds such as dioxins and furans, chlorinated phenolic compounds, etc. present in the effluents discharged from bleaching sections, where chlorine-based chemicals are used [25]. The mean value of BOD for effluents from the four processing units was found as in the range of 14.98±0.50–40.82±0.38 ppm respectively with maximum and minimum values for effluent of C and CE units respectively (Fig. 1). Effluents with high AOX exert acute toxic effect on aquatic organisms and severe ecological threats [19].

The data presented in the Table-1 indicate the extent and degree of pollution at each processing states of the stage. It is evident from the results that the discharge from CE unit is more polluted as compared to that from C, E and CBE units. The CE unit that includes bleach plant effluent, excess backwater from paper machine and the discharge from entire processing units contributes to darkest colour, higher COD along with higher TDS, TSS and turbidity as well. Colour in effluent of CE unit is mainly due to lignin, its derivatives and polymerized tannins which are mostly discharged from the pulping, bleaching and recovery sections. Higher COD in CE effluents is due to presence of highly non-biodegradable lignin, phenol compounds and various toxic substances [26, 27]. Results also indicate that the effluent from E-unit is more polluted than that of from C and CBE units owing to high TS, TDS, BOD and COD. The higher level of colour in the bleach effluent of E unit is indicative of high lignin content extracted out with alkali. Nevertheless, colour of effluents from different processing units of the mill may be due to the presence of low and high molecular weight chlorinated organic compounds generated during pulping and bleaching of pulp. The physicochemical values of effluents from various processing units were found to be higher than permissible limits before discharge [28, 29].

Conclusion

Based on the evaluation of physicochemical characteristics of the effluents from different streams, it can be concluded that the values of most of the studied parameter are very much higher than the prescribed limits set by regulatory bodies for discharge of waste water in agricultural fields and water bodies. The only chemical characteristics i.e. pH is found in acceptable limit whereas values of other parameters were found above the permissible limit of effluent. Therefore, adoption of a combination of physical, chemical, and biological treatment processes with optimization that can provide a long-term solution. In addition to control measures, it is also imperative to minimize the wastewater generation. This can be accomplished by optimizing the use of raw materials, by-product recovery, maximizing the reuse of water, process modification, proper operation and maintenance, local regulation regarding the water use and effluent quality, and superior maintenance.

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Conflict of interest : None declared.

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