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## Assessment of physicochemical characteristics of effluents from orient paper mills Amlai dist. Shahdol (M.P.)

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#### Abstract

The release of substantial volumes of wastewater as effluent from the pulp and paper industries into nearby streams leads to significant health and environmental issues. It is crucial to study and understand the properties of these large quantities of effluents in order to develop effective treatment methods before their disposal. The physicochemical characteristics of effluents originating from an agricultural-based Orient paper mill in the Amlai, Shahdol Madhya Pradesh of India were examined, including pH levels, color, turbidity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), and adsorbable organic halogens (AOX). The effluent samples collected from different processing units of the paper mill exhibited substantial variations across the discharge streams. The mean values pH, colour, turbidity, BOD, COD, TS, TDS, TSS and AOX ranged from  $1.84 \pm 0.05$  to  $9.82 \pm 0.08$ ,  $480.46 \pm 0.62$  to  $3935.15 \pm 6.08$  PCU,  $115.26 \pm 2.07$  to  $480.38 \pm 4.11$  NTU,  $356.62 \pm 2.12$  to  $1340.28 \pm 4.62$  ppm,  $882.54 \pm 2.03$  to  $2708.11 \pm 3.26$  ppm,  $1720.45 \pm 0.54$  to  $4255.30 \pm 5.08$  ppm,  $1520.24 \pm 1.37$  to  $3033.16 \pm 4.26$  ppm,  $201.24 \pm 3.16$  to  $1218.28 \pm 4.82$  ppm and  $16.63 \pm 1.19$  to  $40.44 \pm 4.08$  ppm respectively. The findings revealed significantly elevated levels of all physicochemical parameters in the effluents from different processing units of the paper mill, surpassing the allowable limit. Consequently, it is imperative to implement suitable treatment measures before releasing them into the environment.

**Keywords:** Orient paper mill, effluents, physicochemical characteristics, BOD, COD

#### 1. Introductions

The pulp and paper industry faces significant environmental concerns, primarily concerning the excessive use of fresh water and the creation of a substantial amount of toxic wastewater. Even with the most advanced and efficient operational methods, it takes approximately 60 cubic meters of water to produce one ton of paper, resulting in the production of at least 50 cubic meters of wastewater. The wastewater generated during the paper-making process contains a multitude of degraded organic and inorganic pollutants, which vary depending on the raw materials used, the final product, and the utilization of chemicals like sodium carbonate, sodium sulfide bisulfites, elemental chlorine dioxide, calcium oxide, and hydrochloric acid (Zou *et al.* 2016) <sup>[1]</sup>. Pulp and paper mills produce wastewater that contains over 250 different chemicals at various stages. Among the different paper-making processes, pulping, particularly chemical pulping and pulp bleaching, result in highly polluted wastewater containing toxic substances such as resin acids, unsaturated fatty acids, diterpene alcohols, juvaniones, chlorinated resin acids, and others. The primary issues with these wastewaters include their high organic content, dark brown color, presence of AOX, and other hazardous pollutants (Tjandraatmadja, *et al.* 2008) <sup>[2]</sup>.

The nature of pulp and paper mill effluent is intricate and varies from mill to mill, influenced by various factors such as raw materials, manufacturing processes, and treatment methods. Extensive research has been conducted to analyze the pollution caused by the discharge of wastewater from these factories into natural water bodies. The findings have confirmed that the effluents from pulp and paper factories contain numerous pollutants (Onuegbu, *et al.* 2013; Cantinho *et al.* 2016; Sobhanardakani *et al.* 2018; Mojeed *et al.* 2020) <sup>[3-6]</sup>. However, the quantity and characteristics of these pollutants differ depending on factors like raw materials, manufacturing processes, water usage, and treatment technologies (Zhang, *et al.*

2017) [7]. Due to the harmful effects of these effluents, it is crucial to reduce or eliminate the pollution before releasing them into the environment. To achieve efficient treatment of paper mill effluents, it is essential to assess the pollution load exerted by each processing unit using specific physicochemical parameters. Thus, the purpose of this study was to determine the physicochemical properties of wastewater from different processing units in an Orient paper mill located in Shahdol district Madhya Pradesh, with the aim of developing an effective treatment strategy.

## 2. Materials and Methods

### 2.1 Chemical and Analytical

All the chemicals used were of analytical grade and referred to Sd Fine Chem Ltd. and 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 °C prior to use. The pH of the effluent samples was measured by using microprocessor based digital pH meter (Remi). The turbidity of effluent samples was measured by using turbidity meter and the readings were recorded as nephelometric turbidity unit (NTU).

### 2.2 Collection of Sample

Effluent samples were meticulously procured from diverse streams within the paper mill, including chlorination, extraction, combined bleach plant, and combined effluent. These samples were collected at regular intervals over a span of six hours, and subsequently combined to form a composite sample for comprehensive physicochemical analysis. Precautions were taken to ensure the cleanliness of the plastic containers used to store the samples, which were obtained during both summer (May, 2021) and winter (January, 2022) seasons. The purpose of this dual collection was to ascertain whether any alterations in the effluent's characteristics occurred due to changes in temperature. However, it was discovered that the temperature variation had minimal impact, as the process conditions involved in paper production remained remarkably stable. To further preserve the samples, they were acidified with nitric acid

and stored in a refrigerator at a temperature of 4 °C until they could be subjected to additional analysis. It is important to note that any modifications in the effluent's properties are primarily influenced by the raw materials utilized as well as the chemical agents employed in the pulping and bleaching processes.

### 2.3 Physicochemical Characterization of Effluents

Samples of effluents collected from every stream in the paper mill's processing units were meticulously analyzed to determine their physicochemical properties, in accordance with established protocols (Akpoy, 2011; Turek *et al.* 2019 and Tytła, 2019) [8-10]. The pH of the samples was measured on-site using a microprocessor-based pH meter from Labtronics. The color of the samples was assessed using a spectrophotometric method, while the turbidity was determined with a Hach 2100AN turbidity meter. Additionally, the remaining characteristics of the effluent, including total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD) and adsorbable organic halides (AOX), were measured volumetrically or titrimetrically, following standardized procedures. The AOX analysis was performed using an AOX analyzer from Analytic Jena-Multi X2000. To ensure the reliability of the results, all tests and measurements were conducted in triplicate.

## 3. Results and Discussion

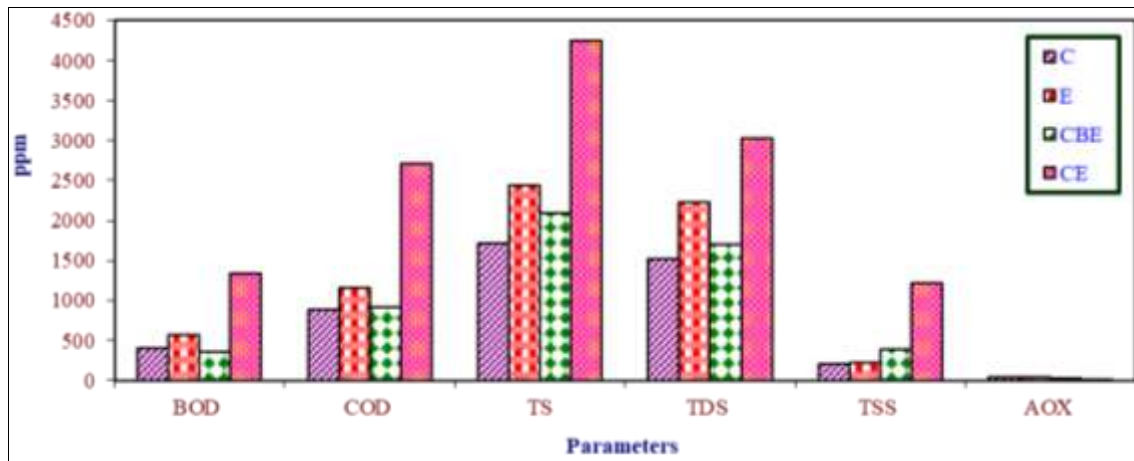
### 3.1 Physicochemical Characteristics of Effluents

The paper mill being examined in this study specializes in producing an assortment of writing and printing paper by utilizing bagasse, wheat straw, and other agricultural waste as its main source material. Effluent samples were gathered from different processing units within the mill and underwent physicochemical analysis to determine various parameters including pH, color, turbidity, BOD, COD, TS, TDS, TSS, and AOX, following established protocols. The average values and standard deviation of these studied physicochemical parameters in the effluents from the paper mill are outlined in Table-1.

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

S. No	Name of the parameter	C	E	CBE	CE
1.	pH	1.84±0.05	9.36±0.03	7.28±0.06	9.82±0.08
2.	Colour (PCU)	480.46±0.62	2229.24±1.07	920.48±3.05	3935.15±6.08
6.	Turbidity (NTU)	121.26±1.55	149.22±1.84	115.26±2.07	480.38±4.11
7.	BOD (PPM)	402.56±2.02	570.55±3.14	356.62±2.12	1340.28±4.62
8.	COD (PPM)	882.54±2.03	1160.14±4.16	920.45±3.85	2708.11±3.26
3.	TS (PPM)	1720.45±0.54	2436.25±2.31	2085.68±4.12	4255.30±5.08
4.	TDS (PPM)	1520.24±1.37	2219.61±3.41	1706.42±6.02	3033.16±4.26
5.	TSS (PPM)	201.24±3.16	218.56±1.84	382.44±6.01	1218.28±4.82
9.	AOX (ppm)	35.86±3.77	40.44±4.08	26.22±5.06	16.63±1.19

Values are given as Mean ± SE (n=3)



**Fig 1:** Physicochemical values of effluents from different processing stages of the Orient paper mill

The diverse processing units of the paper mill exhibit significant variations in the values of the studied parameters, as revealed by the physicochemical analysis results of effluents, as shown in Table 1.

Throughout the four different stages of processing, the pH level ranged from  $1.84 \pm 0.05$  to  $9.82 \pm 0.08$ . This variation can be attributed to the use of different processes and chemicals in each stage. pH is a measure of acidity and alkalinity in effluents, and it is valuable in designing treatment procedures and assessing their effectiveness. Effluent from different processing units can have both acidic and alkaline properties. In this particular study, the effluent from the chlorination section had the lowest pH level, indicating high acidity due to the formation of organic acids during processing. The reactions between chlorine and water in the chlorination stage result in the production of hypochlorous acid and hydrochloric acid. The low pH in the C-stage effluents may be caused by the dissociation of hypochlorous acid into hydrogen ions and hypochlorite ions. On the other hand, the highest pH level in the effluents from the CE unit may be due to the addition of alkali during this stage, which is used for the precipitation of total solids. This process generates hydroxyl ions, ultimately raising the effluent's pH and making it alkaline (Ohoru *et al.* 2019) [11]. The pH value recorded in the effluent from the CE unit was 9.84, slightly higher than the World Health Organization's recommended pH limit of 6 to 9 for paper industry effluents (Samer, 2015) [12]. Discharging wastewater into water bodies can have an impact on their pH, depending on the size and activities of the microbial population. pH is crucial for the survival of various plant and animal species, as they can typically thrive within a narrow pH range, ranging from slightly acidic to slightly alkaline.

The color of wastewater is determined by the concentration of lignin, which is produced during various stages of processing such as pulping, bleaching, and alkali extraction. This degradation of lignin results in the formation of low and high molecular weight chlorinated organic compounds (Suthar, 2008 and Crini and Lichtfouse, 2019) [13-14]. The effluent from these processing stages displayed a significant range of colors, from yellowish brown to dark brown. The highest color value was observed in the effluent from the CE stage, followed by the E and CBP stages. The intense color of the CE effluent may be attributed to the presence of black liquor. The color of the effluent affects its appearance, transparency, and gas solubility (Xing, *et al.* 2011) [15].

The turbidity of effluent is influenced by various factors, including insoluble substances, colored compounds that can dissolve, and plankton. This turbidity can be measured by either the decrease in transmitted light or the increase in scattered light. When analyzing the turbidity of effluents from different units (C, E, CBE, and CE), it was found that the mean turbidity values were  $121.26 \pm 1.55$ ,  $149.22 \pm 1.84$ ,  $115.26 \pm 2.07$ , and  $480.38 \pm 4.11$  NTU, respectively. Notably, the highest turbidity was observed in the effluents from the CE unit, while the lowest was found in the effluents from the C unit (Table 1). These turbidity values align with the respective levels of total solids (TS), total dissolved solids (TDS), and total suspended solids (TSS). Higher turbidity levels hinder the penetration of light in water, which consequently reduces photosynthesis and the production of dissolved oxygen. Therefore, the turbidity of effluent can serve as an indicator of the efficiency of the coagulation-flocculation process in the unit. The results of turbidity measurement clearly indicate significantly higher turbidity levels in the effluents from all processing units, surpassing the World Health Organization's recommended standard limit of 5 NTU (ideally below 1 NTU) Morand *et al.* (2009) [16].

The term "biological oxygen demand (BOD)" refers to the amount of oxygen needed for the breakdown of organic matter by microorganisms, as well as the water body's ability to purify itself. This measurement is used to determine the levels of dissolved oxygen and the extent of organic pollution in effluents. The BOD values for effluents at different units ranged from  $356.62 \pm 2.12$  to  $1340.28 \pm 4.62$  ppm, with the highest value recorded in the CE unit and the lowest in the CBE unit (see Figure 1). All units' effluents exhibited BOD values significantly exceeding the safe disposal limit of 100 ppm (100 mg/l) according to the Indian Standard (IS). The high BOD and low oxygen content of the effluents have a detrimental impact on the survival of aquatic organisms in the receiving water body (Kumar *et al.* 2015) [17].

The measurement of the amount of oxygen needed to break down both organic and inorganic substances, known as chemical oxygen demand (COD), is a crucial indicator of pollution levels in wastewater. The average COD values for the effluents from all four units ranged from  $882.54 \pm 2.03$  to  $2708.11 \pm 3.26$  ppm. The highest COD value was observed in the effluent from the CE unit, while the lowest was found in the effluent from the C unit (Figure 1). All four processing units had COD values exceeding 350 mg/l, the acceptable



limit (Duan, *et al.* 2020) [18]. This indicates that the effluents are toxic, likely due to high concentrations of chemicals and biologically resistant organic compounds (Marciniak *et al.* 2019) [19].

The levels of total solids (TS) in the wastewater released from various units (C, E, CBE, and CE) ranged from  $1720.45 \pm 0.54$  to  $4255.30 \pm 5.08$  parts per million (ppm) (see Table 1). The CE unit had the highest TS concentration in its effluent, while the C unit had the lowest (refer to Fig. 1). It is worth noting that the measured TDS values exceeded the maximum permissible limit of 500 ppm set by the World Health Organization (WHO) for disposing of wastewater into surface water bodies (Morand, *et al.* 2009) [16]. Such high levels of TS in water bodies can have detrimental effects on aquatic plants by hindering their ability to carry out photosynthesis due to reduced clarity and limited light penetration. Additionally, these effluents warm up quickly and retain more heat, which is unfavorable for aquatic organisms that thrive in cooler environments.

The measurement of total dissolved solids (TDS) encompasses the various inorganic and organic substances present in a liquid, including minerals, salts, and organic matter. This measurement serves as a general indicator of water quality. In our current study, the highest TDS levels were observed in the effluent samples from the CE unit, followed by the E and CBE units. Conversely, the lowest TDS levels were found in the effluents from the C unit. It is worth noting that all processing units had TDS levels exceeding the maximum permissible limit set by the World Health Organization for wastewater disposal into surface water (Morand, *et al.* 2009) [16]. The discharge of high TDS wastewater into water bodies can elevate water salinity, rendering it unsuitable for irrigation and drinking. Consumption of water with elevated TDS has been linked to adverse effects on various bodily systems, including the digestive, respiratory, nervous, and cardiovascular systems. Additionally, it has been associated with increased risks of miscarriage and cancer (Li, *et al.* 2011) [20].

The presence of undissolved substances such as fibers, fillers, and pigments in the wastewater indicates the amount of suspended solids. The average suspended solids levels in the wastewater from various units ranged from  $201.24 \pm 3.16$  to  $1218.28 \pm 4.82$  parts per million (ppm). The CE unit had the highest concentration of suspended solids, followed by the CBE and E units. The C unit, on the other hand, had the lowest suspended solids levels (see Figure 1). All four streams had suspended solids levels that exceeded the World Health Organization's maximum limit of 100 ppm (100 mg/L) for discharging wastewater into surface water. The presence of suspended solids can negatively impact photosynthesis in aquatic plants, harm bottom-dwelling organisms, and hinder the efficiency of biological treatment processes (Naef *et al.* 2021) [21].

In the bleaching sections of paper mills, chlorine-based chemicals are commonly used. Unfortunately, this leads to the release of various harmful compounds, such as dioxins and furans, chlorinated phenolic compounds, and more, in the wastewater that is discharged from these facilities. The level of organically bound chlorine compounds can be measured using the adsorbable organic halide (AOX) method (Owalude, & Tella, 2016) [22]. According to the findings presented in Table 1, the average AOX values in the effluents from the four processing units ranged from  $16.63 \pm 1.19$  to  $40.44 \pm 4.08$  ppm. Among these units, the

highest AOX value was observed in the effluents from the E unit, followed by the C and CBE units. Surprisingly, the CE unit had the lowest AOX value, as shown in Figure 1. It is crucial to note that discharging wastewater with high concentrations of these harmful organically bound chlorine compounds into the environment can have significant consequences. These compounds have the potential to disrupt the structure and functioning of natural ecosystems. Furthermore, they are toxic, mutagenic, persistent, and bio-accumulative, posing acute risks to aquatic organisms and causing severe ecological threats. They can also lead to numerous harmful disturbances in the biological system (Ngah & Fatinathan, 2008) [23].

The physicochemical examination disclosed the degree of pollution in the effluent discharge from different processing units of the paper mill. Table 1 clearly indicated that the highest pollution load was found in the effluents released from the CE unit, compared to those from the C, E, and CBE units. The discharge from the CE unit includes bleach plant effluent, excess backwater from the paper machine, and discharge from all processing units, which contribute to its dark color, higher levels of BOD, COD, TS, TDS, TSS, and turbidity. The color of the effluent from the CE unit is primarily caused by lignin, its derivatives, and polymerized tannins, which are mainly discharged during the pulping, bleaching, and recovery processes. However, the presence of low and high molecular weight chlorinated organic compounds, generated during pulping and pulp bleaching, may also contribute to the color of the effluents from various processing units of the mill. The higher color level in the bleach effluent of the CE unit indicates a high lignin content extracted with alkali. The higher COD in CE effluents is due to the presence of highly non-biodegradable lignin, phenol compounds, and various toxic substances (Barakat, 2011 and Upadhyay *et al.* 2021) [24-25]. The results also indicate that the effluent from the E-unit is more polluted than that from the C and CBE units, due to high levels of TS, TDS, BOD, and COD. The physicochemical values of the effluents from various processing units exceed the permissible limits, thus requiring proper treatment for safe disposal (Gautam *et al.* 2016 and Orozco-Corona *et al.* 2021) [26-27].

#### 4. Conclusion

The pollution caused by pulp and paper mills stems from the excessive amount of wastewater generated during the paper manufacturing process. Analysis of the effluents from these mills reveals that many of the measured parameters greatly exceed the established limits for safe discharge into agricultural fields and water bodies. However, the pH levels of the effluents remain within acceptable boundaries, while other factors surpass the permissible limits for disposal. Therefore, it is crucial to employ effective techniques for treating the effluents before releasing them into the environment. A comprehensive approach that combines physical, chemical, and biological treatments, implemented under optimal conditions, offers a sustainable solution. Additionally, optimizing operational practices such as raw material usage, by-product recovery, water reuse, wastewater reduction, and machinery maintenance are equally important, in conjunction with treatment and other pollution control measures.

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