iJRASET
International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 8 **Issue:** XI **Month of publication:** November 2020

DOI: https://doi.org/10.22214/ijraset.2020.32313

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 8 Issue XI Nov 2020- Available at www.ijraset.com

Chemical treatments of Effluents from Agro-Based Paper Mill in Uttar Pradesh State of India

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Abstract: ***Discharge of large amount of wastewater as effluent from pulp and paper industries in the surrounding streams result in serious health and environmental problems. These large quantities of effluents need to be treated after characterization prior to their disposal. Physicochemical characteristics of effluents from an agro-based paper mills located in Uttar Pradesh state of India were analyzed in terms of pH, colour, TS, TDS, TSS, turbidity, BOD, COD and AOX. The results found markedly higher values of all physicochemical parameters of effluents from various processing units of the paper mill than the permissible limit thus necessitating appropriate treatment prior to their discharge in the environment. In the present paper several types of coagulant viz. Ferric chloride, lime, alum and Ferric chloride with poly acryl amide(PAM) have been examined for their effectiveness of reducing chemical load of the effluent.***

Keywords: Effluents, Physicochemical, effluent, BOD, COD, AOX

I. INTRODUCTION

The pulp and paper industry is one of the major industries utilizing high quantity of water resulting in the generation of large amounts of wastewater [1]. Incessant discharge of toxic effluents to the water bodies and adjoining crop fields are reducing soil fertility and causing severe contamination to rivers, canals, ponds, wells etc. thereby making the water unfit for irrigation and human consumption [2]. It is the sixth largest environment polluting industry discharging a variety of pollutants into the environment [3].

About 60 m^3 of water is required to produce a ton of paper, even with the most modern and efficient operational techniques, resulting in the generation of at least 50 m^3 of wastewater [4]. The wastewater generated from paper making process include large number of degraded organic and inorganic contaminants, depending on types of raw materials, end product and use of chemicals such as sodium carbonate, sodium sulphide bisulfites elemental chlorine dioxide, calcium oxide, hydrochloric acid, etc [5].Among the various processes of paper making, pulping especially chemical pulping and pulp bleaching generate highly contaminated wastewater which contains various toxic substances such as resin acids, unsaturated fatty acids, chlorinated resin acids, diterpene alcohols, juvaniones and others. Major problems of the wastewaters are high organic content, dark brown colour, AOX and other toxic pollutants [6].

Majority of Indian paper and pulp mills discharge their effluents, containing bleach and black liquor, directly into the receiving water bodies, and thus cause serious environmental concern [7, 8]. The paper mill effluent contains high concentrations of recalcitrant dissolved organic matter and in turn inducing high biochemical oxygen demand [9]. The unabatedly discharge of wastewater from the paper industry affect aquatic and land ecosystems [10]. It has been widely reported in many research studies regarding toxic and lethal effects on the aquatic organisms exposed to the wastewater, which includes physiological changes, liver damage, mixed function oxygenase activity, respiratory stress, [11-13]. The sustainability of irrigation agriculture has to face challenges due to industrial effluents discharged in nearby water bodies which tend to produce alkalinity and salinity in irrigation water making it unfit for this purpose [14]. Industrial effluents contaminate the land due to its high salt and metal contents and thereby reducing fertility of the soil. [15].

The extensive studies have been done regarding the extent of pollution due to discharge of wastewater from the pulp and paper mills to the receiving water bodies confirming impregnation of the effluents with several pollutants [16-23]. However, the volume and characteristics of the pollutants varies depending on the type of raw materials, manufacturing processes, amount of water and treatment technologies adopted [24]. Due to the severe toxic effects of pulp and paper mill effluents, reduction and/or removal of pollution load prior to their discharge into the environment is crucial. For efficient treatment of paper mill effluents, assessment of the actual pollution load exerted by each individual processing unit in terms of certain physicochemical parameters is considered essential. The present study therefore was aimed to devise efficient treatment strategy after determining the physicochemical characteristics of wastewater emanating from different processing units of an Indian pulp and paper mill located in Uttar Pradesh state of the country.

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ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429
Volume 8 Issue XI Nov 2020- Available at www.ijraset.com

II. MATERIALS AND METHODS

A. 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 2000C 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 nephlometric turbidity unit (NTU).

B. Selection of Paper Mill

The pulp and paper mill selected for the study is located at 29° 28' 17.0292" N, 77° 41' 48.2352" E in the state of Uttar Pradesh (U.P.), India.

This is a large scale agro-based paper mill primarily using wheat straw, bagasse and other agro- wastes as raw material for manufacturing printing and writing papers with an installed capacity of 300 tpd. The mill adopts soda pulping process for pulp production using 10-12% caustic (NaOH) charge for wheat straw and 14-16% 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 6-8%.

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 30-50 m^3/t and 50-60 m^3/t of paper respectively. For chemical recovery and effluent treatment, the mill uses conventional and activated sludge system.

C. Collection of Sample

Effluent samples were collected from different streams of the paper mill i.e. chlorination (C), extraction (E), combined bleach plant (CBP) and Combined effluent (CE) at an interval of one hour for six hours and then mixed to make it composite for physicochemical analysis.

The effluent samples were collected in pre-cleaned plastic containers in summer (May, 2015) and winter (January, 2016) to observe any change in the characteristics of the effluent but not much variation was observed due to change in temperature (season), since the process conditions in the paper making remains almost consistent.

Furthermore, the samples were acidified with nitric acid and containers with samples were preserved in refrigerator at 4^0C till further analysis. Any change in the characteristics of the effluent mainly depends on the raw material and the chemical used in pulping and bleaching process.

D. Physicochemical Characterization of Effluents

Effluents samples collected from all the four streams of processing units of the paper mill were analyzed for their physicochemical characteristics following prescribed standard protocols [25-27]. 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 dissolved solid (TDS), total suspended solid (TSS), biological oxygen demand (BOD) and chemical oxygen demand (COD) were determined volumetrically/titrimetrically as per standard methods.

The adsorbable organic halide **(**AOX) was measured with AOX analyzer (Analytic Jena- Multi X2000). All tests and measurements were carried out in triplicates to access the repeatability of the results.

E. Physicochemical Characteristics of Effluents

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 units of the mill were subjected to physicochemical characterization for parameters such as pH, colour, TS, TDS, TSS, turbidity, BOD, COD, and AOX as per standard methods. The mean values and standard deviation of studied physicochemical parameters of the paper mill effluents are presented in table- 1.

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III. RESULT AND DISCUSSION

Table 1: Physicochemical values of effluents from different processing stages

Parameter	Processing stages of the paper mill			
	C -Stage	E- Stage	CBE- Stage	CE-Stage
pH	1.82±0.03	9.32±0.04	7.26±0.07	9.84±0.06
COD (ppm)	881.52±3.19	1162.25±5.26	921.52±5.76	2710.12±4.52
BOD (ppm)	404.55±1.65	571.54±3.50	355.65±3.50	1342.22±3.50
TS (ppm)	1718.49±0.65	2435.20±5.18	2084.67±3.15	4252.29±4.46
TSS(ppm)	200.22±2.01	217.54±2.63	380. 35±3.20	1220.15±3.15
TDS (ppm)	1518.27±2.65	2218.66±2.64	1704.32±5.35	3032.14±3.32
Colour (PCU)	481.44±0.58	2230.25±0.98	921.50±0.07	3936.16±5.76
AOX (ppm)	35.84±0.12	38.35±0.21	24.25±1.14	15.75±0.51
Turbidity(NTU)	121.22±2.62	149.22±1.75	113.23±1.46	481.22±2.61

Values are given as Mean ± SE (n=3)

The physicochemical analysis revealed the extent of pollution load in effluent discharge from different processing units of the paper mill. Data presented in table1 pointed towards highest pollution load in the effluents discharged from CE unit as compared to those from C, E and CBE units. Effluent discharge from CE unit contain bleach plant effluent, surplus backwater from paper machine and discharge from entire processing units which are responsible for its darkest colour, higher BOD, COD along with higher TS, 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. Nevertheless, presence of low and high molecular weight chlorinated organic compounds generated during pulping and pulp bleaching may also be responsible for colour of effluents from different processing units of the mill. Effluents from E unit recorded the maximum AOX value followed by those discharged from C and CBE units. The CE unit effluents however showed the lowest AOX value.

The mean value of pH varied from 1.82±0.03 to 9.84±0.06 across the four processing stages which may be due to the use of different process and chemicals at various different processing units. 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 [28]. The effluent from CE unit recorded the pH value of 9.84 which is a little higher than WHO prescribed tolerance limit of pH value i.e. 6 to 9 for the paper industry effluent [29].

Colour of effluents or wastewaters depends 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 [30,31].The colour of the effluent from all the four processing stages measured in PCU showed considerable variation ranging from 481.44±0.58 to 3936.16±5.76 PCU. Data presented in table 1 revealed that CE effluent exhibited highest colour value followed by E and CBP stages. 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 [32].

The mean total solids (TS) concentrations in effluents from C, E, CBE and CE units ranged from 1718.49±0.65 to 4252.29±4.46 ppm (Table 1). Effluent discharge at CE unit showed the highest TS whereas the lowest TS were found in effluent at the C unit. The observed values of TS after the factory effluent discharge were higher than the WHO maximum permissible limit of 500 ppm for disposal into surface water bodies [33]. Total dissolved solid (TDS) is a measure of the combined sum of inorganic and organic substances contained in a liquid which primarily includes minerals, salts, and organic matter which can be a general indicator of water quality. In the present study, the highest TDS was found in effluent samples from CE unit (3032.14±3.32 ppm) followed by E (2218.66±2.64 ppm) and CBE (1704.32±5.35 ppm) units. Effluents from C unit however recorded the lowest (1518.27±2.65 ppm) TDS (Fig.1). It is obvious that TDS values in discharge from all the processing units are higher than the WHO maximum permissible limit of 500 ppm (500 mg/L) for the disposal of wastewater into surface water [33]. Discharge of wastewater with higher TDS 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 [34].

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The undissolved matters including fibres, inorganic fillers, pigments, etc. in the effluents signify their total suspended solids (TSS). The mean TSS contents of effluents from C, E, CBE and CE units varied from 200.22±2.01 to 1220.15±3.15 ppm. Effluents from CE unit showed the highest value of TSS followed by CBE and E units; C unit effluents however recorded the lowest TSS. The values of TSS in effluents from all the four streams found to be higher than the WHO maximum limit of 100 ppm (100 mg/L) for discharge of waste water to surface water bodies. Suspended solids reduce the rate of photosynthesis by aquatic flora, oppress benthic organism, and retard the efficiency of biological treatment processes [35].

Turbidity of effluent is due to the presence of insoluble matters, soluble coloured compounds, and plankton which is measured either as a reduction in the intensity of transmitted light or as an increase in the intensity of scattered light. Effluents from C, E, CBE and CE units exhibited mean value of turbidity as 121.22±2.62, 149.22±1.75, 113.23±1.46 and 481.22±2.61 NTU respectively. Highest turbidity was observed for effluents from CE unit whereas C unit effluents showed the lowest turbidity (Table 1). The turbidity values of effluents from all the four units are in consonance with respective TS, TDS and TSS values. Higher turbidity retards light penetration in the water thereby reducing photosynthesis and production of dissolved oxygen. Effluent turbidity can be considered as efficiency measure of coagulation-flocculation process of the unit. The results of turbidity measurement evidently suggest much higher turbidity in effluents of all processing units and the values are greater than the WHO prescribed standard limits of 5 NTU (ideally below 1 NTU) [33].

BOD 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 355.65±3.50 to 1342.22±3.50 ppm. Effluent from CE unit recorded the highest value of BOD while CBE unit effluent showed the lowest value. Effluents from the all the units exhibited BOD values much higher than prescribed limit of 100 ppm (100 mg/l) for safe disposal of effluents as per Indian Standard (IS). The high biological oxygen demand and coupled low oxygen content of effluents affect the survival of aquatic animals of receiving water body [36].

The amount of oxygen required to breakdown both organic and inorganic matter is termed as chemical oxygen demand (COD) which is one of important indicators of pollution load in effluents. The mean value of COD for effluents from all the four units recorded in the range of 881.52±3.19 to 2710.12±4.52 ppm. Highest value of COD was found for the effluent from CE unit whereas minimum COD value was recorded for C unit effluents. The COD values of effluents from all the four processing units are higher than 350 mg/l, the acceptable limits [37]. This suggested the toxic nature of effluents which may be due to high chemical concentration along with biologically resistant organic substances [38].

The bleaching sections of paper mills, generally use chlorine-based chemicals which result in release of organically bound chlorine compounds such as dioxins and furans, chlorinated phenolic compounds, etc. in the effluents discharged from these units. The adsorbable organic halide **(**AOX) is the measure of such organically bound chlorine compounds [39]. As per the results (Table 1), the mean values of AOX in effluents from the four processing units ranged from 15.75±0.51 to 38.35±0.21ppm.Discharge of wastewater with high concentration of harmful organically bound chlorine compounds into the environment has enough potential to disrupt the structure and functioning of the natural ecosystem. Some of these chemicals are toxic, mutagenic, persistent, bio-accumulating thus exerting acute toxic effect on aquatic organisms, cause severe ecological threats and numerous harmful disturbances in biological system [40].

The higher level of colour in the bleach effluent of CE unit is indicative of high lignin content extracted out with alkali. Higher COD in CE effluents is due to presence of highly non-biodegradable lignin, phenol compounds and various toxic substances [41, 42]. 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. Effluents from various processing units exhibited physicochemical values higher than permissible limits thus need to be properly treatment for their safe disposal [43, 44].

A. Treatment of Pulp and Paper mill Effluent (Coagulation/Flocculation Study)

In this experiment, the effect of ferric chloride, lime, and alum on COD, BOD, TS, TDS, TSS, Color, AOX and turbidity at each stage of effluent was studied with respect to different amount of chemical doses (100, 300, 500 ppm), pH (~7), revolution (50, 100 and 150 rpm) and retention time intervals (30, 80, and 130 min). A stock solution of 10g/L of ferric chloride, alum and lime was prepared and different doses of 100, 300 and 500 ppm respectively were taken out from this stock solution. For experiment of ferric chloride, alum and lime, total 27 runs were performed for which, 250 ml conical flasks were filled with 100 ml of effluent with different chemical doses.

Treatment with combination of poly acryl amide (PAM) with ferric chloride was done in another set of experiment. In this set of experiment, combination of PAM and ferric chloride was undertaken at the optimum conditions in order to assess the effects of combined treatment on pollution reduction in terms of all the physicochemical parameters.

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10ppm dose of PAM with optimized dose of ferric chloride at the optimum condition (rpm, RT) in 250ml conical flasks which were filled with 100ml bleach effluent and combined effluent from different sections of the mill. Here the experiments were conducted in triplicate in order to assess the repeatability of the results. The pH of the samples was then adjusted to 7 with the help of 1 N NaOH and 1 N H_2SO_4. Effluent was then subjected to mixing at different rotation and retention time as mentioned above. The treated samples were filtered and analyzed for COD, Color, AOX and other parameters as per APHA and CPPA standard methods.

B. Ferric Chloride Treatment

It is well known that in aqueous medium, ferric chloride hydrolyzes to form positively charged ions and polymeric ions that have a very large surface area and they tend to absorb onto surface of negatively charged colouring organic matter and forms insoluble precipitates which eventually which eventually settle down as sludge [45]. The chemical treatment with $FeCl_3$ was carried out under optimum condition of 100 ppm dose, 150 rpm and 80 minutes retention time at C-stage, the optimum condition of dose 500ppm, 50 rpm and Rt.30 minutes for E-stage, 300ppm dose, 150 rpm and 80 minutes retention time for CBE-stage and under optimum condition with a dose of 500 ppm at 100 rpm for 130 minutes retention time for CE-stage. The reduction efficiency of the treatment is presented in the following table.

Table 2: Reduction (%) with the $FeCl_3$ treatment

parameters	C -Stage	E-Stage	CBE -Stage	CE-Stage
COD (ppm)	81.92	87.01	76.31	78.96
BOD (ppm)	54.51	52.44	54.60	51.31
TS (ppm)	24.57	19.36	12.36	14.06
TSS(ppm)	13.04	33.04	14.75	26.74
TDS (ppm)	24.90	17.98	17.02	8.97
Colour (PCU)	71.41	71.51	70.55	72.71
AOX (ppm)	15.18	39.63	24.91	47.41
Turbidity(NTU)	56.93	59.75	51.21	59.64

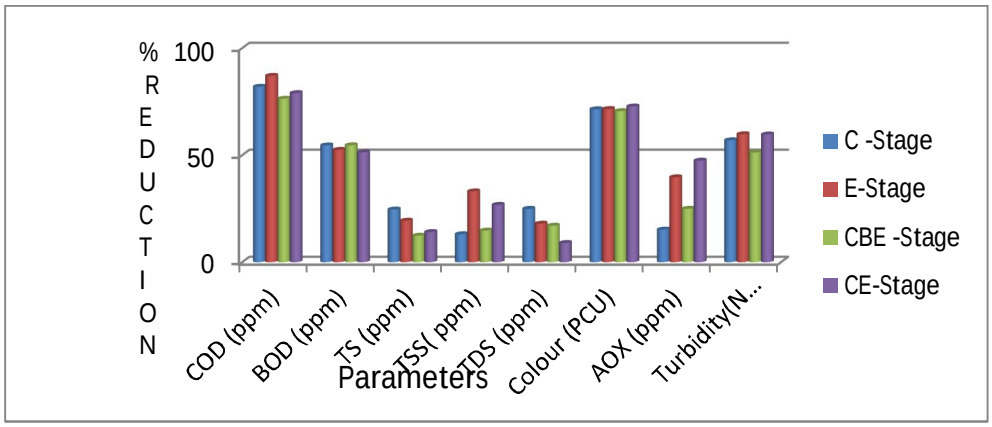


Fig1: Reduction (%) with the $FeCl_3$ treatment

From table 2.0 and fig1, it is amply clear that the reduction in COD (ppm) is 81.92%, 87.01%, 76.31% and 78.96% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in BOD (ppm) is 54.51%, 52.44%, 54.60% and 51.31% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in color (PCU) is 71.41%, 71.51%, 70.55% and 72.71% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in AOX (ppm) is 15.18%, 39.63%, 24.91% and 47.41% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TS (ppm) is 24.57%, 19.36%, 12.36% and 14.06 % for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TSS (ppm) is 13.04%, 33.04%, 14.75% and 26.74% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TDS (ppm) is 24.90%, 17.98%, 17.02% and 8.97% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in Turbidity (NTU) is 56.93%, 59.75%, 51.21% and 59.64% for the all four stages named C-, E- CBE-, and CE- respectively. The results obtained are very much in conformity with the expectation and hence this treatment may be used as pre treatment step for reduction in the mentioned parameters to reduce the inlet pollution load that would lead to overall reduction in chemical and energy consumption along with improvement in efficiency of effluent treatment plant.

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C. Lime Treatment

Lime having great potential as a colour reducing chemical, easy availability and being cost effective is natural selection for the purpose. Lime is considered better decolourising agent due to precipitation of calcium salts of weak organic acid produced by chemical separation and fragmentation of lignin during pulping and bleaching. The treatment of wastewater from pulp and paper mills takes advantage of the fact that large amounts of calcium oxide are routinely combined with water and then converted to calcium carbonate during the process of regeneration of the pulping chemicals that are used for kraft cooking of the fibers which is known as massive lime strategy [46]. The chemical treatment with lime was carried out under optimum condition of dose100ppm, rpm 150, RT 80minutes at C-stage, dose500ppm, rpm50, RT 30minutes at E-stage, dose 300ppm, rpm150, and RT 80minutes for CBE-stage and dose500ppm, rpm100, RT 130min for CE-stage. The reduction efficiency of the treatment is presented in the following table.

Table 3: Reduction (%) with the lime treatment

parameters	C -Stage	E-Stage	CBE -Stage	CE-Stage
COD (ppm)	74.09	80.64	78.76	74.93
BOD (ppm)	58.96	58.83	54.88	63.69
TS (ppm)	9.68	13.96	19.25	27.60
TSS(ppm)	51.37	43.57	15.86	17.93
TDS (ppm)	17.73	19.64	20.00	31.68
Colour (PCU)	50.88	54.90	45.56	82.77
AOX (ppm)	29.54	39.68	14.83	60.63
Turbidity(NTU)	32.17	37.46	34.70	39.25

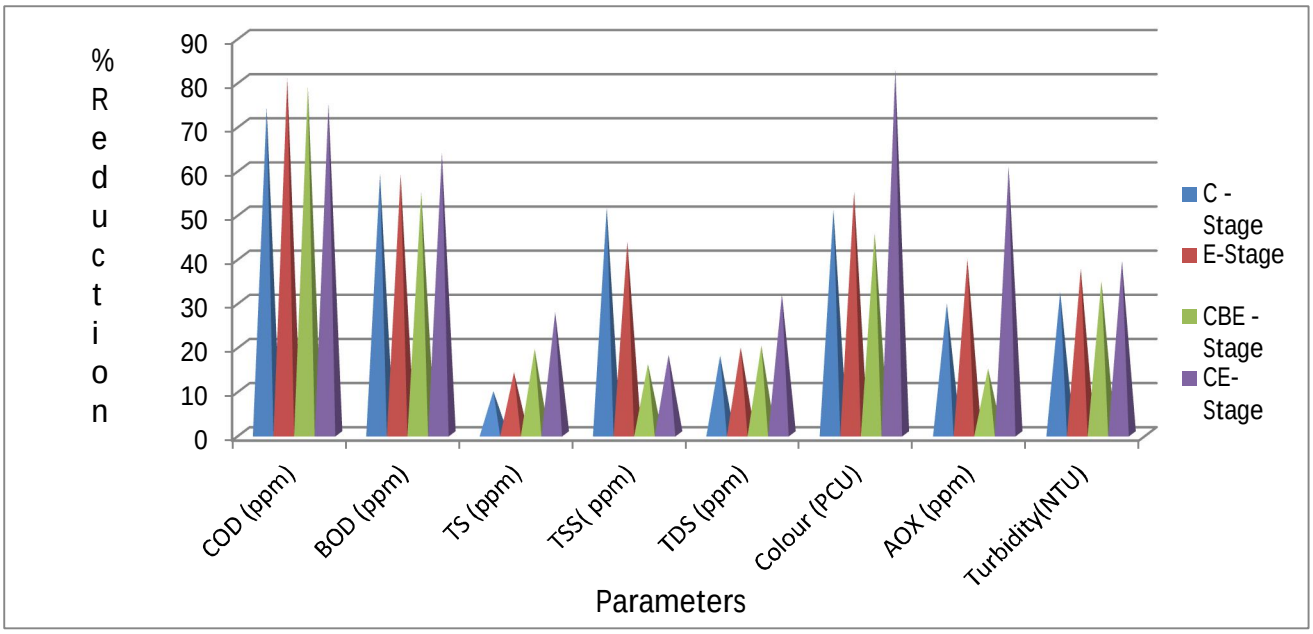


Fig2: Reduction (%) with the lime treatment

Table 3.0 and fig 2, indicates that the reduction in COD (ppm) is 74.09 %, 80.64%, 78.76% and 74.93% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in BOD (ppm) is 58.96%, 58.83%, 54.88% and 63.69% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in color (PCU) is 50.88%, 54.90%, 45.56% and 82.77%for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in AOX (ppm) is 29.54%, 39.68%, 14.83% and 60.63%for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TS(ppm) is 9.68%, 13.96%, 19.25% and 27.60% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TSS (ppm) is 51.37 %, 43.57 %, 15.86 % and 17.93%for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TDS (ppm) is 17.73%, 19.64%, 20.00% and 31.68% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in Turbidity (NTU) is 32.17%, 37.46%, 34.70% and 39.25% for the all four

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stages named C-, E- CBE-, and CE- respectively. Notably, lime is found to be more efficient in terms of colour reduction capacity which validates the fact of being good decolourising agent, similar is the opinion of various researchers regarding its efficacy in terms of pollution load reduction.

D. Alum Treatment

It has been found that most of the reported research work used aluminium, ferrous salts and its polyelectrolyte for the coagulation/ flocculation process, to remove the toxic organic materials from the wastewater in order to make it amenable to secondary treatment, like wet air oxidation (WO) or biological treatment. The treatment was performed under optimum condition of at 100 ppm dose, 50 rpm for 80 minutes retention time at C-stage, 500 ppm dose, 50rpm for 30 minutes retention time at E-stage, 300 ppm dose,150rpm for 80 minutes retention time for CBE-stage and 500 ppm dose, 100rpm for 130 minutes retention time for CE-stage. The reduction efficiency of the treatment is presented in the following table.

Table 4: Reduction (%) with the Alum treatment

parameters	C -Stage	E-Stage	CBE -Stage	CE-Stage
COD (ppm)	84.46	88.72	85.67	81.80
BOD (ppm)	56.99	56.43	58.08	60.46
TS (ppm)	8.99	24.90	28.04	33.89
TSS(ppm)	57.65	43.57	19.27	34.20
TDS (ppm)	17.78	31.65	30.00	16.17
Colour (PCU)	71.75	72.13	71.95	77.65
AOX (ppm)	25.64	45.31	32.74	61.77
Turbidity(NTU)	61.51	71.16	56.43	63.91

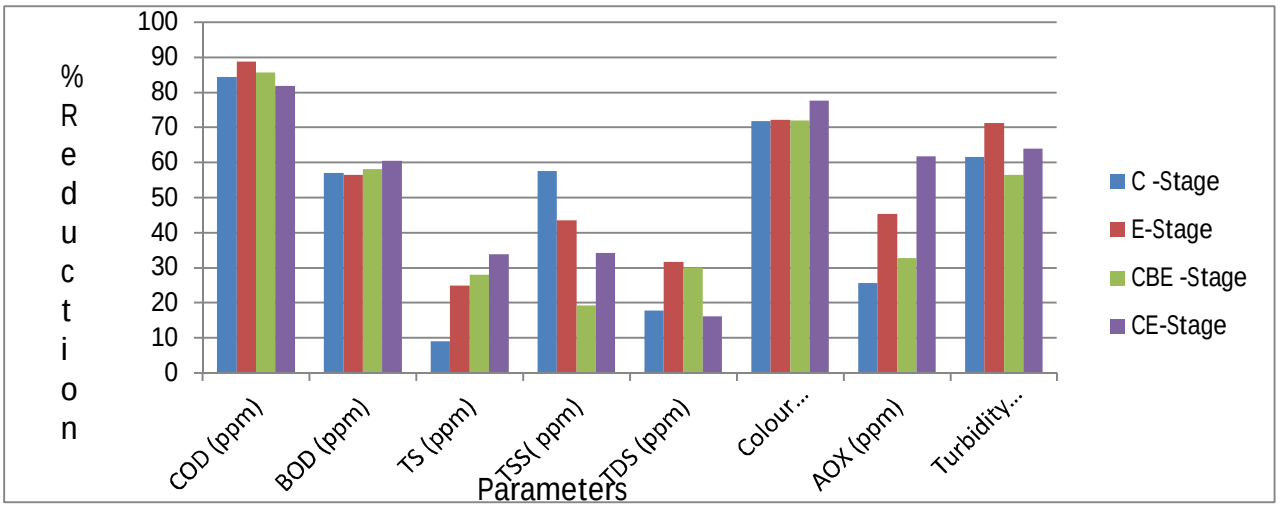


Fig3: Reduction (%) with the Alum treatment

From table 4.0 and fig 3, it is obvious that the reduction in COD (ppm) is 84.46 %, 88.72 %, 85.67% and 81.80% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in BOD (ppm) is 56.99%, 56.43%, 58.08 % and 60.46% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in color (PCU) is 71.75%, 72.13%, 71.95% and 77.65% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in AOX (ppm) is 25.64%, 45.31%, 32.74% and 61.77% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TS (ppm) is 8.99 %, 24.90%, 28.04% and 33.89% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TSS (ppm) is 57.65%, 43.57%, 19.27% and 34.20 %for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TDS (ppm) is 17.78%, 31.65 %, 30.00% and 16.17% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in Turbidity (NTU) is 61.51%, 71.16%, 56.43% and 63.91% for the all four stages named C-, E- CBE-, and CE- respectively. Although economical, in comparison to other methods, the precipitation method has other associated drawbacks like dewatering and disposal of the generated sludge. However, coagulation/flocculation can be used as an effective primary treatment method to remove much of the, COD, BOD, Colour, toxicity and other parameters. This

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treatment will make the secondary treatment cost effective as well as efficient in the removal of residual toxic organic compounds which signifies the role of alum for pre treatment and post treatment for the pollution load reduction and obviously is in consonance with the findings of the previous researchers regarding its pollution load reducibility in the respective stages.

E. Ferric Chloride and Poly Acryl Amide (PAM)Treatment

The main function of flocculants, which consist of very high mass poly electrolytes, usually having a cationic charge, is to collect small agglomerates into large agglomerates. The agglomerates formed by means of flocculants tend to be stronger and more shear-resistant than agglomerates brought about just by charge neutralization. In flocculation process, destabilized particles produced by various coagulants stiff into heavy particles which can be separated from waste water, that is why flocculent can be used individually as well as in combination with coagulant. Similar studies were carried out by previous researchers [47]. The treatment was carried out with 10 ppm dose of PAM mixed with the optimised doses of 100 ppm $FeCl_3$ at 150rpm and 80 minutes retention time at C-stage, 500 ppm dose, 50rpm for 30 minutes retention time at E-stage, at 300 ppm dose, 150rpm for 80 minutes retention time for CBE-stage and 500 ppm dose, 100rpm for 130 minutes retention time for CE-stage. The reduction efficiency of the treatment is presented in the following table.

Table 5: Reduction (%) with the $FeCl_3$+PAM treatments

parameters	C -Stage	E-Stage	CBE -Stage	CE-Stage
COD (ppm)	76.58	81.47	83.47	78.97
BOD (ppm)	60.73	60.19	59.80	72.14
TS (ppm)	12.84	17.84	22.30	29.49
TSS(ppm)	39.92	44.17	19.55	19.00
TDS (ppm)	20.98	23.96	22.92	33.72
Colour (PCU)	53.02	55.44	48.71	86.78
AOX (ppm)	31.52	38.46	31.13	52.12
Turbidity(NTU)	37.40	40.81	40.74	42.62

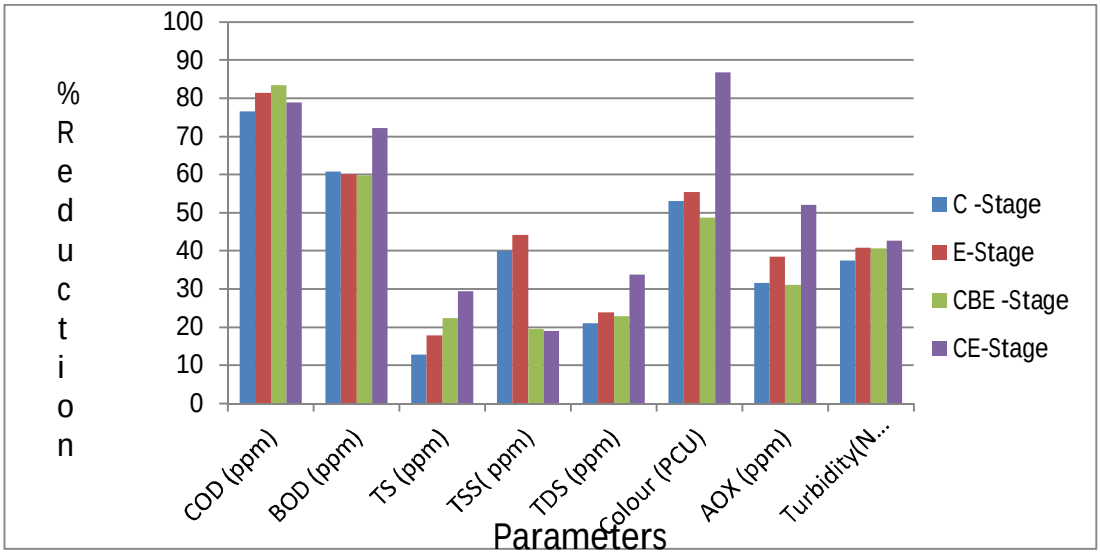


Fig 4: Reduction (%) with the $FeCl_3$+PAM treatments

Table 5.0 and fig 4, it is amply clear that the reduction in COD (ppm) is 76.58%, 81.47%, 83.47% and 78.97% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in BOD (ppm) is 60.73%, 60.19%, 59.80% and 72.14% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in Color (PCU) is 53.02%, 55.44%, 48.71% and 86.78% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in AOX (ppm) is 31.52%, 38.46%, 31.13% and 52.12% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TS (ppm) is 12.84%, 17.84%, 22.30% and 29.49% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TSS (ppm) is 39.92%, 44.17%, 19.55% and 19.00% for the all four stages named C-, E- CBE-, and CE- respectively. Reduction in TDS (ppm) is 20.98%, 23.96%, 22.92% and 33.72% for the all four stages

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named C-, E- CBE-, and CE- respectively. Reduction in Turbidity (NTU) is 37.40%, 40.81%, 40.74% and 42.62% for the all four stages named C-, E- CBE-, and CE- respectively Thus, with combining the poly acryl amide with $FeCl_3$ makes the reducibility even better than chemical used in isolation which again is in conformity with the view of the researchers worked for similar purposes..

IV. CONCLUSION

Reduction efficiencies of $FeCl_3$, lime, alum, and $FeCl_3$+PAM in reduction of parameters viz. COD, BOD, TS, TDS, TSS, Color, AOX and turbidity were determined for the effluents of all the four stages from the selected mill. Results indicated a significant reduction in COD with all the chemical treatments with an average > 80% reduction. Alum was found to be the most effective followed by ferric chloride considering overall conditions of the mill. In terms of colour reduction, the combined chemical treatment with $FeCl_3$+PAM was found to be the most effective followed by the lime. Furthermore, alum was found to be the most efficient in reducing the chlorinated organic halides (AOX) where reduction was more than 60% followed by lime and $FeCl_3$+PAM.The reductions percentage in other physicochemical parameters with the chemical treatments are found appreciably significant that lies in the range of 10 to 60% varying across the different stages. Thus use of these chemicals as pre treatment steps not only reduce the pollution loads, but will also help paper mills in reducing the operating cost of subsequent activated sludge process widely used for treatment of effluent to meet the discharge standards. Secondly, the optimized treatment conditions as evolved through the study for the agro-based paper mill could successfully be used in prediction of their toxicity and effective management and will also help in formulation of proper strategies to counter the pollution load borne by paper mill effluents prior to their disposal into the environment.

V. ACKNOWLEDGEMENT

Author is grateful to the Director, CPPRI, Saharanpur, UP and the Director, Forest Research Institute Dehradun for providing necessary analytical facilities. Help and cooperation rendered by paper mill personnel towards collection of effluent samples and relevant technical information and production statistics of the mill is thankfully acknowledged.

1) Conflict of Interest: None declared.

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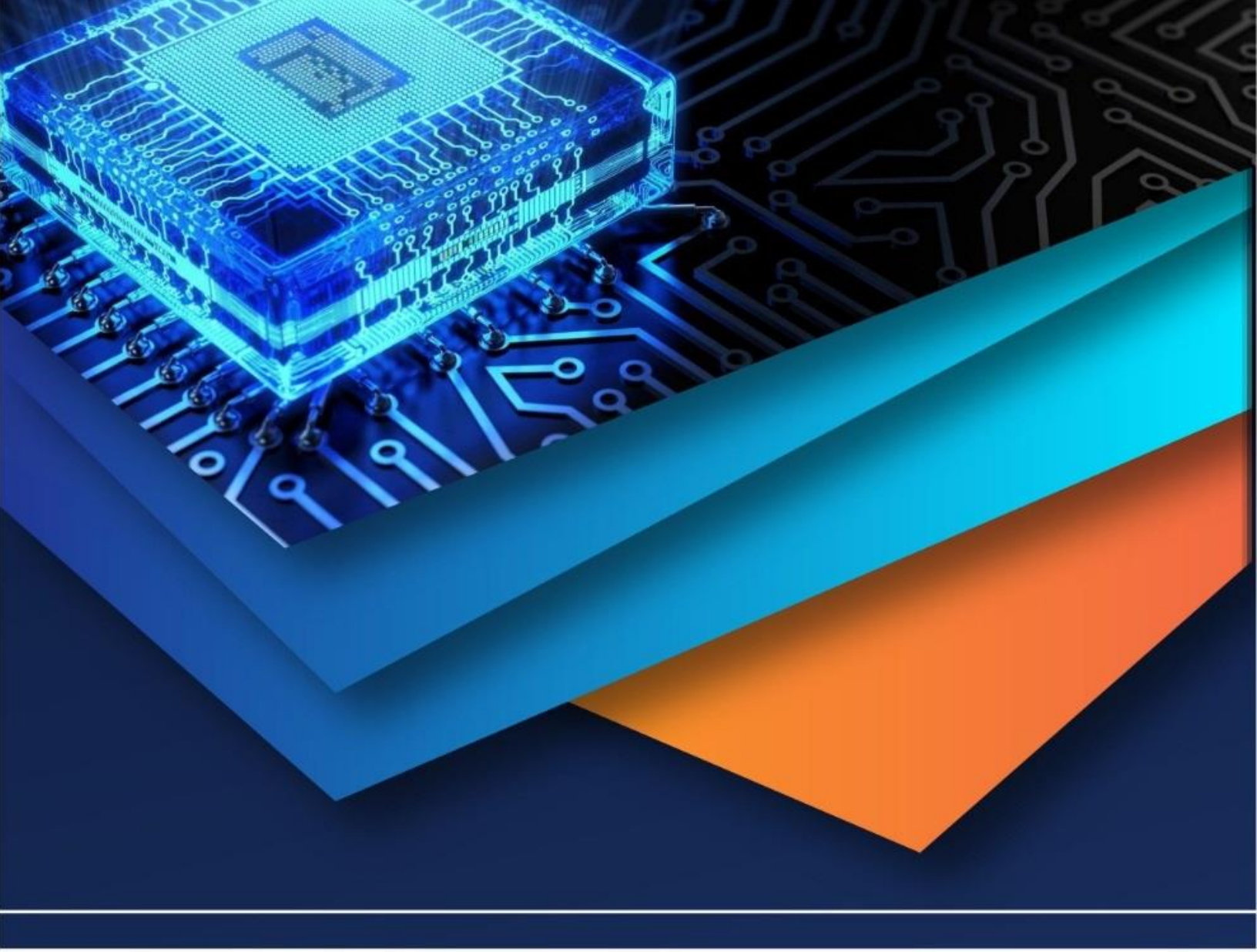
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