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Toxicity Removal of Pulp and Paper Mill Effluent by Employing Chemicals

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ABSTRACT

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. Large amount of toxic effluent is released during process of paper production. Pulp and paper mill spent wash (raw effluent) is highly acidic in nature with high BOD, COD, TDS, TSS, phenol, sulphate, nitrogen, phosphorus, potassium and metals viz. Mn Zn Cu Ni Fe and Na . Effluent was treated with chemicals $FeCl_3$ and $KMnO_4$. pH was found to increase from 7.8 to 8.4 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $KMnO_4$. Similarly colour, COD and BOD were decreasing with increasing concentration of $KMnO_4$. Maximum colour, COD and BOD reduction were recorded 21.25%, 93.79% and 81.48% respectively at 5g l^{-1} concentration of $KMnO_4$. Decrease in pH was recorded from 3.3 to 2.0 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $FeCl_3$ (Ferric chloride). Decrease in colour, COD and BOD were also observed with increasing concentration of $FeCl_3$. Maximum colour, COD and BOD reduction were recorded 99.10%, 54.16% and 85.92% respectively at 5g l^{-1} conc. of $FeCl_3$.

Key words: Pulp and Paper Mill , Chemical Treatment, Lignin

INTRODUCTION

The pulp and paper industry is huge, technically diverse, operating a wide variety of manufacturing process on a range of fibre types from tropical hard woods to straw for pulping and bleaching for paper preparation. The effluent of these industries contains stray wood chips, bits of bark, cellulose fibres, dissolved ligneous material (30-45%), saccharinic acid (25-35%), formic acid and acetic acid (10%) and extractives (3-5%). The residual lignin present in wood fibre is major colouring material, and also reacts with chlorine molecules and forms organochlorine compounds in the effluent. About 20% of the organically bound chlorine found in bleaching effluent corresponds to relatively low molecular mass (m.w 4000) products. [1]

Chlorine released after bleaching cross-reacted with lignosulphonic acid, resins, and related compounds and forms chlorinated hydroquinone, phenols, dibenzo-p-dioxin and dibenzofuran in the effluent.

These chlorinated compounds are highly toxic, mutagenic and ecoestrogens. They are partly responsible for the high oxygen demand (BOD and COD). The toxicity of a chlorinated compound increases with increasing number of chlorine atoms in the organic compound, and it is believed that polychlorinated dibenzo-p-dioxine is probably one of the most toxic compounds with an LD_{50} value of 1 μg/kg body weight is formed in the effluent of pulp and paper mill.[2]

In pulp and paper mill, 273-455 m^3 of water is required per tones of paper produced that consequently generate 300 m^3 as wastewater. Alkali pulp and paper mills provided with soda recovery, discharge about 270-450 liters of water per kg of paper with an average of 305 lt/kg and the amount of lignin discharged being 40-50 g/kg of bleached paper produced. In a small paper mill without soda recovery, all of the black liquor (200-250 g/kg of paper made) is discharged. The pollution load in terms of biological oxygen demand (BOD) from small paper mill is 2-5 times the pollution load from large paper mills with soda recovery. The BOD load discharged per tones of paper by mills varies from 3.45 kg to 6.5 kg.[3]

Effluents released by pulping and bleaching are polluting characterized by parameters unique to these wastes such as colour and organic halides (AOX). The untreated effluents from pulp and paper mills discharged into water bodies, damages the water quality. The brown colour imparted to water due to addition of effluents is detectable over long distances. The effluents have high biological and chemical oxygen demands (BOD and COD), lignin compounds and their derivatives. The dark brown colour is due to the formation of lignin degradation products during the processing of lignocellulosics from paper and pulp manufacture. The undiluted effluents are toxic to aquatic organisms and exhibit a strong mutagenic effect. Further more some compounds in the effluents are resistant to biodegradation and can bioaccumulate in the aquatic food chain.[4]

Earlier variouss physical chemical and biological processes have been done to remove the colour of the pulp and paper mill effluents. Physical and chemical processes are quite expensive to remove only high molecular weight chlorinated lignins, colour, toxicants, suspended solids and COD but BOD and low molecular weight compounds like alcohals, acids appreciably are not removed efficiently. [5]Present aim of study is physico-chemical analysis and identification of colour forming compounds in pulp and paper mill effluent and to assess the colour removal efficiency of pulp and paper by physical treatment using $FeCl_3$, $KMnO_4$,

Materials and Methods

Location

The study was conducted with the effluent released from Pulp and Paper mill, Chattishgarh. The factory uses cane molasses as the raw material. The efflcuent flows out into a 'nala' for about 10 km, which passes through the villages. The villagers use this effluent for the irrigation.

Sampling

The effluent sample from the Pulp and Paper mill were collected at the main outlet point where combined effluents from the factory are being disposed of into mill influent water. Water samples at the point of discharge were collected in clean plastic container from the main outlet. The sample was collected i.e. April 2016 from pulp and paper mill, Chattishgarh. Immediately after collection the water samples were brought to the laboratory and kept in the refrigerator at 4^0C till used for analysis.

Analytical methods

Electrical conductivity (EC) of the effluent was measured using a pocket type digital EC meter (Hanna Instruments Co.) calibrated at 20^0C. The reading was taken in milli siemens (ms m^{-1}). pH of the effluent sample was measured by a pH meter (model PR 8404) using glass electrode.

For total suspend solids 100 ml of the sample was centrifuged at 2000 rpm for 10 minute. The supernatant was removed and the residue was washed three times by resuspending it in distilled water and recollecting by centrifugation. The residue was finally transferred quantitatively to preweighted dish (X1g). The dish was weighed again after drying (X2g) to a constant weight (X1g). The dish was weighed again after drying (X2g) to a constant weight at 105^0C. TSS was calculated by using the following formula.

$$TSS\,(ppm) = \frac{(X_2 - X_1) \times 1000 \times 1000}{ml\ of\ sample}$$

The TDS was calculated as the difference between the total solids (TS) and total suspended solids (TSS), TDS (ppm), TS (ppm)-TSS (ppm).

COD and Colour unit was calculated by according to the standard method [6]. The sample was centrifuged at 1000 rpm for 30 minutes to remove all the suspended matter. The pH was adjusted to 7.6 with 2 M NaOH (CppA standard method) and then used for the measurement of absorbance at 465 mm. The absorbance values were transformed into colour unit (CU) using the following relationship.

$$CU = 500 \times \frac{A_2}{A_2}$$

where

A_1= Absorbance of 500 cu platinum cobalt standard solution (A_{405} = 0.132) and A_2 = Absorbance of the effluent sample [6]

Effects of different chemicals on pulp and paper mill individually and in combination

Three sets of three 100 ml sterilized Erlenmeyer flasks were filled with 50 ml of sample effluent. In one set of flask $Al_2(SO_4)_3$ was added at the rate of each 1 g/l, 2 g/l and 5 g/l whilst in second set $KMnO_4$ was added at the rate of 1 g/l, 2 g/l and 5 g/l. The entire flasks were shaken at 150 rpm and 25^0C for 2 hrs. Thereafter, all the samples were centrifuged at 5000 rpm for 10 min. After that pH, EC, TSS TDS, COD and colour were measured.

Results

Pulp and paper mill Effluent was collected i.e. April 2016 from Pulp and Paper mill, Chattishgarh. The physico chemical analysis of spent wash (raw effluent) was highly acidic in nature with high BOD (32000 ppm), COD (45000 ppm), TDS (9566.66 ppm), TSS (97686.66 ppm), phenol (5.1ppm), sulphate (3800 ppm), nitrogen (299 ppm), phosphorus (767.66 ppm), potassium (481.33 ppm) and low content (Table 1). Raw pulp and paper mill effluent contains metal viz. Mn (3.68 ppm), Zn (3.781 ppm), Cu (0.31ppm), Ni (0.86 ppm) Fe (72.07 ppm) and Na (498 ppm). However, the pH of treated pulp and paper mill effluent was acidic and other parameters including metals were high in comparison of **MINAS** value. Physiochemical characteristics were analyzed and the data are given in Table 1.

The colour of the effluent was dark brown and colour unit was recorded 6287.87CU, whilst pH was in acidic range 5.1, (Table 4.1, Plate No. 1). The biochemical oxygen demand (32000 mg l^{-1}) and chemical oxygen demand (45000 mg l^{-1}) were also recorded.The pulp and paper mill also contained a good amount of N, P and K and chlorine content (Table 1)

From Table 4, pH was found to increase from 7.8 to 8.4 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $KMnO_4$. Similarly colour, COD and BOD were decreasing with increasing concentration of $KMnO_4$. Maximum colour, COD and BOD reduction were recorded 21.25%, 93.79% and 81.48% respectively at 5g l^{-1} concentration of $KMnO_4$ (Table 2, Plate No. 1).

From Table 3, Decrease in pH was recorded from 3.3 to 2.0 on increasing concentration (1 gl^{-1} to 5 gl^{-1}) of $FeCl_3$ (Ferric chloride). Decrease in colour, COD and BOD were also observed with increasing concentration of $FeCl_3$. Maximum colour, COD and BOD reduction were recorded 99.10%, 54.16% and 85.92% respectively at 5g l^{-1} conc. of $FeCl_3$ (Table 3).

Table 1

Physico Chemical Analysis of Pulp and Paper Mill Effluent

Parameters	Mean value
BOD	32000± (577.35)
COD	45000 (±946.48)
Nitrogen	299 (±9.46)
Phenolic compounds	5.1 (±0.06)
Phosphorus	767.66 (±26.26)
Sulphate	3800 (±57.73)
Total suspended solids (TSS)	97686.66 (±566.10)
Total dissolved solids (TDS)	9,566.66 (±88.19)
Chlorine	2800(±26.83)
Colour	6287.87 (± 97.85)
Total organic carbon	2880(±22.30)
K	481.33 (±28.93)
Na	498 (±16.83)
Cu	0.31 (±0.03)
Fe	72.07 (±12.76)
Mn	3.68 (±0.64)
Ni	0.86 (±0.01)
Zn	3.781 (±0.06)

All the values are in ppm means (n=3) ± standard error.

Table 2

Effect of $KMnO_4$ on pH, CU, COD and BOD of the pulp and paper effluent

Conc. Of $KMnO_4$ / Parameters	$1g\ l^{-1}$	$3g\ l^{-1}$	$5gl^{-1}$
pH	7.8±0.34	8.1 ±0.17	8.4 ±0.11
CU	5835.47±1347.57 (7.19%)	5005.44±634.06 (20.39%)	4951.40 ±557.38 (21.25%)
COD (mgl^{-1})	28400±2338.80 (11.25%)	23866.66±2808.51 (25.41%)	1986.66±2313.96 (93.79%)
BOD (mgl^{-1})	17666.66±881.91 (60.74%)	12000±2390.40 (73.33%)	8333.33±1452.96 (81.48%)

Table 3

Effect of $FeCl_3$ on pH, CU, COD and BOD of the pulp and paper effluent

Conc. Of $FeCl_3$ / Parameters	$1g\ l^{-1}$	$3g\ l^{-1}$	$5gl^{-1}$
PH	3.3±0.31	2.3±0.57	2.0±0.15
CU	123.73±34.87 (98.03%)	134.24±15.27 (97.86%)	56.16±4.00 (99.10%)
COD (mgl^{-1})	22666.66±4745.68 (29.16%)	16000±1454.70 (50%)	14666.66±1763.83 (54.16%)
BOD (mgl^{-1})	14000±881.91 (68.88%)	10666.6±2309.40 (76.29%)	6333.33±1452.66 (85.92%)

All the values are in ppm mean (n=3) ± standard error

Significant correlation can be seen between colour unit, COD and BOD of the effluent. The result of the study also supports the findings of this study. Linear relationships amongst these parameters were observed [7, 8, 9]. Most of these parameters are found to exceed beyond permissible limit and warrants treatment. The pattern of colour removal by chloride and sulphate salts of aluminium and iron were more or less similar. Per milli equivalent of metal ion for coagulation is based on percentage colour removal. [10, 11, 12]

It was observed that ferrous sulphate alone was not effective in reducing the colour of effluent as it does not form floe with pulp and paper mill waste water. The other flocculant i.e. alum, ferric chloride, lime were found effective for colour removal. But these chemicals also depend on the pH of the waste water.

Ferrous sulphate in combination with alum was effective to some extent in reducing colour of effluent due to producing of more acidic chemicals. While COD reduction is comparatively lower. [13, 14, 15]

Thus, initial pH, molecular size and electrical charge have profound influence on the efficiency of colour removal and the chemical dosage required. The coagulant dose required to maximum colour removal was 5000-7000 mg/l in case of ferric chloride and almost double (12000 mg/l) in case of alum. In all cases, colour removal decreased beyond coagulant level (optimum coagulant dose). Percentage colour removal was significantly higher in the case of treated pulp and paper mill waste. [16]

Colour causing substances present in pulp and paper mill waste are microcolloids which are hydrophilic in nature like proteins and other biopolymers. Stability of these colloids depends mainly on the hydration shell and high concentrations of colloids naturally required to withdraw the solvent from the hydration shell. [17]

Potassium permanganate, hydrogen peroxide and bleaching powder were screened for removal of calcium from raw and treated pulp and paper mill waste. Only potassium permanganate and bleaching powder yielded good removal. Highest colour removal was attained 78%, the reduction in COD was of the order of 25-30% only. Similar results of 80% colour removal and 36% and 32% COD and BOD reduction from sugar fermentation process waste water by oxidation with chloride gas were reported by Swamy et al. [18.19]

Potassisum permanganate react with a variety of organic substances which results in a net transfer of an oxygen atom from the manganate ion to the organic substrate. It has been reported that oxidation of organic compounds by potassium permangnate rarely results in complete destruction of molecule. It may, therefore, be inferred that chemical oxidation of colour causing substances results in chromophoric group rather than complete degradation of colour causing substances H_2O_2, Alum, other chemicals show similar reaction mechanism as $KMnO_4$.[20]

CONCLUSION

Many process changes have been implemented or are being considered to reduce the formation of AOX and chlorinated phenols from chemical pulp bleaching operations. There are also possibilities for treatment of effluents with microorganisms and enzymes to remove or dechlorinate organic material. Each option discussed has inherent advantages and disadvantages with regard to capital cost, operating cost, ease of profit, fabrication and installation time. Impact on other mill unit operations is also considered in choosing the best options. Many factors have to be considered in choosing an effective and economical bleaching/ treatment process that meets all the environmental guidelines. It appears that the only long-term solution will probably be to develop the technology which will allow mills to operate with zero effluent.

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